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## EDITORIALS

### ANALYSIS OF THE COAL-TAR DYE INDUSTRY

We are pleased to publish IN THIS ISSUE a lecture on the Coal-Tar Dye Industry which was presented at a meeting of the Board of Directors of the General Chemical Company, on October 23rd, by Dr. Bernhard C. Hesse. This comprehensive analysis of the problem is of peculiar interest at the present time on account of the numerous articles appearing in the daily and magazine press, calling upon the chemical manufacturers of America for the immediate establishment of plants for the production of coal-tar dyes, to prevent a shortage of these products on account of the European war.

It is generally assumed, and often stated, that the United States is not a factor in the coal-tar dye industry because of lack of enterprise or skill on the part of our chemists and chemical manufacturers, but this is far from the truth.

The complexity of this industry is but little understood by the layman. We believe that the careful analysis of the problem which Dr. Hesse has made for the men responsible for the policies of a great chemical manufacturing company will be read with interest and profit, not only by the men charged with the responsibility of developing chemical industry, but by the public who are entitled to know why the hue and cry of the superficial hack-writer is not answered by the immediate erection of great coal tar dye factories. Industrial development, more especially in the case of the coal-tar dye industry, is dependent for its success upon a large number of conditions entirely independent of the financial investment or the technical skill involved in the operation of the processes. An analysis of the charts used to illustrate the lecture shows at a glance the intricate complications of the technical features of coal-tar dye production. These complications do not present insurmountable technical obstacles to the American manufacturer. A more thorough analysis of the lecture and the charts, however, brings out many important points not usually considered. There is the intimate interlocking of processes and products in which an economic balance must be maintained or some phase of the operation will be required to carry prohibitive cost burdens. The slightest change in the value of an intermediate by-product from one of the operations may serve to upset this economic balance, and thereby change the whole process of manufacture. This point is particularly well illustrated in the manufacture of indigo and the influence of the by-products in determining the raw material, process and plant which is used.

The patent situation, which is frequently referred to as being a controlling factor in the German domination of the dye industry, is shown by Dr. Hesse to be deserving of very little consideration, as both the process and product patents have expired in the case of a large number of the important products. On the other hand, the influence of the tariff on the development of

this industry is carefully discussed. The important point is made, which has frequently been suggested in connection with other developments, that the attitude of the consumers of these products in regard to tariff increases is conducive to the development of these industries abroad, rather than in our own country. When consumers prevent proper tariff protection on products which are or could be manufactured at home, it invariably results in fostering the interests of foreign competitors.

America can have a coal-tar dye industry if she pays the price. Dr. Hesse has clearly set forth the conditions which must be met to make possible the development of the industry in the United States. Such an undertaking means that we are attacking the most favorably situated and strongly fortified industrial position in the manufacturing world. In Germany the coal-tar dye production is geographically centralized in relation to the required raw products; it is the most complicated technical and commercial industry known; it is Germany's most prized and profitable industry; the economic balance of by-products which makes their industry possible would not hold in the United States, and years would be required for the upbuilding of a corresponding industry here.

Obviously the development of an American dyestuff industry will require for its establishment every known condition which can favor success. The unlimited support and coöperation of the consumer, the public and the government would be a small price to pay to compensate the manufacturer who has the resources, the courage and the skill to undertake the herculean task of developing a coal-tar dye industry in coöperation or in competition with Germany.

### RECOMMENDATIONS OF THE NEW YORK SECTION OF THE AMERICAN CHEMICAL SOCIETY ON THE ENLARGEMENT OF THE COAL TAR CHEMICAL INDUSTRY IN THE UNITED STATES

The special committee appointed by the New York chemists to investigate and report upon conditions and needs involved in the enlargement of the coal tar dye industry in the United States reported at the regular stated meeting of the New York Section of the American Chemical Society on November 6th. The meeting had been widely advertised and was unusually well attended.

This committee was composed of the following members: J. B. F. Herreshoff, representing the manufacturers of heavy chemicals; I. F. Stone, representing the American coal tar dye producers; J. Merritt Matthews, representing the textile interests; H. A. Metz, representing the importers; David W. Jayne, representing the producers of crude coal tar products; Allen Rogers, Chairman of the New York Section; and Bernhard C. Hesse, chemical expert in coal tar dyes, *Chairman*.

The findings of this committee were considered in

detail and after discussion the report was unanimously adopted by the Section and ordered printed in THIS JOURNAL.

In view of the importance of these recommendations, and the highly representative character of the committee, their conclusions will doubtless be of the greatest value not only to the chemical profession, but also to the layman interested in our industrial possibilities.

The following is the official text of the report:

TO THE NEW YORK SECTION, AMERICAN CHEMICAL SOCIETY:

1—At the meeting on October 9, 1914, the chairman of this Section was authorized to appoint a committee to investigate into the feasibility of expanding the chemical and dyestuff industry in the United States and to report to the Section on November 6, 1914.

2—The undersigned committee was appointed October 15th, and at once proceeded. It addressed letters of invitation to cooperate to those who have been most active in the public prints in urging the expansion of the chemical and particularly the dyestuff industry in the United States; further, an invitation was extended to the maker of the motion which resulted in the appointment of this committee. The assistance from these is *nil*.

3—A request was addressed to trade publications in the City of New York and to some of the metropolitan dailies; in all, nine such publications were requested to publish a suggested notice for the purpose of inviting cooperation; the object of this committee was set forth, and request was made that suggestions be mailed to the chairman of this committee. All but one of these publications have complied with that request. No help has been obtained by this committee from any suggestions mailed to it as a result of this publicity.

4—Your committee has carefully considered all the public suggestions as to methods of improvement and has searched through the governmental regulations of the belligerent nations as to embargo and as to contraband of war in order to construct therefrom a list of chemicals, inclusive of dyestuffs, which have thereby been shut off from the United States, in the hope of thus being placed in a position to make specific recommendations of value.

5—It can be fairly stated that, in general, the chemical industry of this country is efficiently exploited and is making full use of all the opportunities presented to it under the normal conditions existing prior to the state of hostilities. Some of the chemicals which are imported from abroad are made in considerable amounts in this country as well, and the amounts imported under normal conditions depend upon the ordinary normal fluctuations of business conditions both here and abroad. With the stoppage of this foreign supply the domestic production was not at once capable of making up the deficiency, but in a number of instances the American manufacturers have taken steps to increase their capacity, and the strain in the market of those particular things will exist no longer than it will require to expand the manufacturing facilities to the proper extent.

Among these are: ammonia salts, barium chloride, barium nitrate, bleaching powder, sodium cyanide, yellow prussiate, sodium nitrate, sodium hydrosulfite, zinc dust.

6—If, however, it be desired, and if public necessity requires the introduction of the manufacture of explosives and further chemicals and dyestuffs into our home industry, such as coal-tar product explosives, pharmaceuticals, medicinals and other intermediates and finished coal-tar dyes, then alterations of our tariff law are inevitable, and the consumers in the first place and the public in general must share in the burden thus imposed. If conditions of national defense in case of attack by a foreign power require us to manufacture our own explosives and to be, in that regard, independent of all foreign nations at all times,

or if our textile industries or any other of our industries requiring coal-tar chemicals such as dyestuffs shall forever be protected and made independent of foreign nations for the supply of those materials, then the nation as a whole must bear the burden incident to such expansion. Under existing circumstances private enterprise and private capital have gone their limit. They have reached the limit for two reasons:

I—The explosive, dye and similar industries abroad, just referred to, are in a state of high development and of refined organization and are financially the best suited to carry on an offensive campaign against any nation attempting to take business away from them.

II—Domestic manufacturers are prohibited by law from making use of cooperative commercial devices such as pools, trusts, manufacturing and selling agreements and the like, whereas such devices are wholly lawful abroad and are encouraged by the respective governments. In other words, the American chemical industry is expected to cope with the foreign industry while both its own arms are tied behind its back and its opponents have full and free use of their arms.

#### ANTI-DUMPING CLAUSE

7—The remedies required would include an effective anti-dumping clause that would certainly prevent underselling of domestic manufacturers in the United States by unfair methods. What the form of such clause should be is a problem with which your committee is unable to cope; it is strictly a law-making and law-enforcing problem and is allied to the usual problem of determining under-valuation as heretofore carried on by our Treasury Department; it is, however, a much more refined problem than the older problem of proving under-valuation. Nevertheless, your committee believes that with such a mechanism in our law, much would be done toward encouraging our chemical industries.

#### TO CREATE A COAL TAR CHEMICAL INDUSTRY

8—According to the best information that your committee can gather, such an anti-dumping clause alone would not be sufficient, however, to create complete and independent domestic coal-tar explosives, dyestuffs and medicinals industries. It has been conclusively demonstrated during the past thirty years that the present tariff rate of 30 per cent on dyestuffs is not sufficient to induce the domestic dyestuff industry to expand at a rate comparable with the consumption of dyestuffs in this country and that, therefore, all dyestuffs made from coal-tar, whether they be aniline dyes or alizarin, or alizarin dyes, or anthracene dyes or indigo, so long as they are made in whole or in part from products of or obtainable from coal-tar, should all be assessed alike, namely, 30 per cent *ad valorem* plus  $7\frac{1}{2}$  cents per pound specific, and that all manufactured products of or obtainable from coal-tar, themselves not dyes or colors and not medicinal, should be taxed 15 per cent *ad valorem* and  $3\frac{3}{4}$  cents per pound specific.

#### TARIFF TO AID DYE INDUSTRY

9—The best information and judgment your committee can obtain is that the above manufactured products of coal-tar, not dyes and not colors and not medicinal, should carry one-half the duty of the finished coal-tar dye, and that the above rate of 30 per cent *ad valorem* and  $7\frac{1}{2}$  cents specific would probably be sufficient to encourage and enable domestic manufacturers to expand their operations to such an extent as to supply a very material increase in, if not the whole, of these commodities consumed in this country. The reason for a specific duty is to protect the domestic manufacturer in the manufacture of the relatively cheap dyes such as the cheap scarlets, the cheap yellows and the like, whose prices abroad are in the neighborhood of from 12 to 20 cents per pound; with dyes of that type 30 per cent *ad valorem* would not offer so serious an obstacle to importation and underselling thereof as does the  $7\frac{1}{2}$  cents per pound specific;

on the other hand, on dyes whose prices are \$1.00 and upwards per pound the function of the 7½ cents specific more nearly approaches zero; that is, with the cheap dyes the chief function lies in the specific portion of the duty and with the expensive dyes the chief function lies with the *ad valorem* portion of the duty.

This is said to be the price the nation will have to pay to have a complete self-contained and independent coal tar chemical industry. However, it must be remembered that if such an industry be created and importation of coal-tar products inclusive of intermediates and dyes is restricted, its ultimate effect upon the Federal revenues will have to be considered. *It will, therefore, be necessary to determine carefully if the advantages to be gained are equal to the price to be paid.*

#### PATENT LAWS

10—This committee is a unit in the belief that an alteration of our patent laws aiming at compulsory working or compulsory licensing would not be of any substantial benefit to this industry or to the country as a whole. Twenty-nine countries have attempted compulsory licensing clauses and fifty-six countries have attempted compulsory working clauses, and the best information your committee can obtain is that in none of these attempts has there been any appreciable measure of success. While it may be true that under extraordinary conditions, such as now exist, compulsory licensing might have some advantage, yet it is equally true that in normal times the disadvantage due to compulsory licensing or compulsory working would more than overbalance any advantage at all likely to be obtained under stress of unusual conditions.

11—In none of the countries where there have been working or licensing clauses or both, co-extensive with the existence of the coal-tar chemical industry, has there been established any real coal-tar chemical industry and your committee does not feel that an alteration in our present patent laws could be made which would be effective against foreigners and at the same time not be onerous and a hardship to domestic inventors. Your committee believes that in the long run and in the final outcome, our present system with regard to working and licensing is as efficient as that of any other country. In the dyestuff industry, in particular, there are so many non-patented commercial products and so many commercial products once patented, now free from patent restraint, that their production alone would form a basis for a very considerable industry, and your committee feels that the way to encourage that industry, if the establishment of that industry in this country be a national necessity, is through a change in the tariff and the additional anti-dumping feature in the administration of the tariff and not through any change in the patent laws. *Once established, such an industry could develop and ultimately cope with any foreign combination upon fair and equal terms.* Over 90 per cent of the tonnage and of the individual dyes used in the United States will be free from any patent-restraint within the next four years—over 75 per cent of the dyes are now in that condition.

#### AVAILABILITY OF RAW MATERIALS

12—The best information your committee has so far been able to gather is that this country can produce so-called coal-tar raw material in amounts sufficient for the needs of a complete domestic coal-tar chemical industry inclusive of explosives and dyes, *provided* there is a certainty of outlet as to volume and continuity. Those engaged in manufacture here do not want to expand unless the dye-users are willing to make corresponding contracts. In other words, it is a closed circle. If the dye-users will contract sufficiently with the dye-makers, the dye-makers will contract with the coal-tar distillers and the industry will take a start. The initiative rests wholly with the users; if they

cannot afford to contract, the dye-maker and the distillers cannot afford to make their contracts and additional investments.

#### COAL-TAR PRODUCTS

13—BENZOL, TOLUOL AND THE LIKE are produced in sufficient amount in present installations of by-product coke-ovens to provide all of these things that would be needed for a coal-tar chemical industry of a magnitude sufficient to supply the United States market; the separation of these materials from the gas that carries them is dependent upon the market and the demand therefor. There is no inherent defect in our coke-industry with regard to the actual making of these things; the only question involved is whether it be more profitable to burn the benzol, toluol and the like contained in the gas as a fuel than to separate them from the gas and from each other for purposes of sale. Ample supply can be provided before any plant that could use benzol and the like for dyestuff making could be erected in the United States, and thereafter the supply of these materials can readily be kept up to any requirement.

14—The materials of the preceding paragraph are the ones used in the coal-tar explosives industry as well as in the coal-tar medicinals and dyestuffs industries. Each of these three industries coöperates with the others to make full use of those materials; alone, none can fully make use thereof nor succeed; the correct and proper utilization of these materials requires successful co-existence of ALL THREE industries in one and the same country.

15—NAPHTHALENE and ANTHRACENE are contained in the tars produced in the United States in an amount sufficient for the needs of a domestic dyestuff industry and it is merely a question whether it is more profitable to leave them in the creosote oil, where they now occur, or to separate them out of such oil and refine them for purposes of dye manufacture. Ample supply of either of them could be produced and provided at the same time or shortly after any plant could be erected in the United States for the use of these things in the production of dyes.

16—What has been said with regard to the supplies of naphthalene is also true of the supplies of CRESOL.

17—All the CREOSOTE OIL contained in the total amount of coke-oven tar now made is separated from it and used. Increased production of creosote oil requires a greater production of tar, and a greater production of tar is dependent upon increased installation of recovery coke ovens.

18—PHENOL or CARBOLIC ACID supply is primarily dependent upon our deliberately selected method of coal treatment; to change that treatment so as to get more phenol would entail abandonment of other advantages which would not be compensated for by the increased amount of phenol so produced. Under present circumstances freights and haulages play an important part. At isolated plants, separated by considerable distances from each other, small amounts of phenol are produced and the separation of the phenol at such individual places would be economically unprofitable, and in order to concentrate this amount of phenol to or at a point where separation could be conducted profitably would entail freight haulages much in excess of the value of the phenol that would thus be transported.

19—The only source of phenol in sight is that produced synthetically from benzol by means of sulfonation and subsequent melting with caustic soda. This depends, in turn, upon our benzol supply and would be profitable only so long as the United States market is not killed by the dumping of foreign phenol thereon, whether such phenol be synthetic or distilled.

20—SALICYLIC production depends upon availability of phenol and the production of BENZOIC ACID depends upon the availability of toluol which has heretofore been discussed.

21—PHTHALIC ACID made from naphthalene by means of bichromate cannot successfully compete with that made by the mercury and sulfuric acid process which is protected by patents having about three years more to run.

#### MISCELLANEOUS CHEMICALS AND RAW MATERIALS

22—ACETIC ANHYDRIDE can be made without trouble in this country, and will be made in this country so soon as the domestic demand is large enough and steady enough to warrant the installation of a suitable plant.

23—NITRIC ACID: All countries, with the exception of possibly Norway and the countries importing from Norway, are dependent upon Chili for the raw material for making nitric acid. It will not be profitable to make nitric acid from air in the United States until the value of the electric horse power reaches a level of \$3 or \$4 a year, as it is in Norway.

24—AMMONIA and its salts all depend upon recovery coke ovens, and such recovery plants are increasing as fast as circumstances will permit.

25—BARIUM CHLORIDE and other compounds of barium may be made from domestic barytes. A number of attempts have hitherto been made, but with indifferent success. Factories established within the last year promise to be successful.

26—MAGNESIUM CHLORIDE of a sufficient purity to be used in the production of flooring is almost generally made from magnesite found in Greece, which is the only deposit known having sufficiently high purity; there are reports of suitable deposits in California and in lower California so that, with the completion of the Panama Canal, the question of freights, which seems hitherto to have stood in the way of developing these deposits, may be eliminated. Other sources, less remote from centers of consumption, and using other materials, *e. g.*, brine-waste, are about to be successfully operated.

27—MANGANESE in the form of pyrolusite is not known to occur in paying deposits in the United States; these are practically all in the Caucasus.

28—POTASH: In view of the great exertions that have been made for a number of years, both on the part of the federal government through a number of its departments and a great many different groups of capitalists, there is nothing to be said in this report that would be of any value with regard to increased production of potash either as fertilizer or as a chemical.

29—YELLOW PRUSSIAN AND SODIUM CYANIDE can be and have been made from domestic materials in such an amount as to provide practically the entire consumption, or a great portion thereof, in this country so long as there was a sufficient duty on them; the present duty is not enough to protect the American manufacturer, and those who were engaged therein have in large measure withdrawn from the business, but some are reported to be taking up manufacture cautiously and in limited amounts.

30—HYDROSULFITES in solution can be made from domestic materials without interference with any patent rights; the production of solid salts and derivatives are, however, still protected by patents that have a few years more to run.

31—SODIUM NITRITE is produced more cheaply as a by-product in Norway than it can be produced anywhere in the world; unless the price of the electric horse power in this country sinks to a \$3 or \$4 level per year, as in Norway, this product cannot be manufactured in the United States.

32—OXALIC ACID is and has been made to some extent in this country and the information coming to your committee is that suitable efforts are being made to expand the capacity of existing plants.

33—TARTARIC ACID AND CITRIC ACID: To make this country independent of others, with respect to tartaric acid and citric

acid, would call for radical changes on the part of our grape growers and our lemon growers as to the policy of their business.

It is probably true that edible grapes do not produce argols (the crude material for tartaric acid) very largely, and that our domestic lemons do not produce as large yields of juice (the crude material for citric acid) nor as high an acidity as do the Italian lemons; therefore, an independent supply of the raw materials produced in the United States for tartaric and citric acids is in the first instance an agricultural problem, and in the second instance a market problem.

#### GENERAL REMARKS

34—Finally, it should be pointed out that the United States is by no means the only country whose chemical and allied business has been strained or upset by the European war. Each and every other country has felt the strain. British committees have gone into this same subject of expanding British chemical industries and, not only that, but also into the question of making their very basic necessities, and the reports have so far been adverse to any immediate relief by domestic manufacture. The Boston Chamber of Commerce, through its committees, has arrived at the same conclusions for this country.

35—It is further clear that the stability of a complete domestic chemical industry, in so far as it depends upon foreign supplies, is bound up to a successful merchant marine and to an efficient foreign banking condition just as is all our foreign business.

#### FINDINGS

36—Your committee finds as follows, as to the facts:

I—Prior to the hostilities, domestic chemical industry was utilizing and exploiting every reasonable opportunity to its full extent.

II—Since the outbreak of hostilities, domestic industry has increased its output just as fast as physical means could be provided and physical obstacles overcome.

III—Since the outbreak of hostilities, domestic plants that had theretofore been shut down or partly dismantled because of disastrous foreign competition are said to have resumed operation, with caution.

IV—That a 30 per cent duty on some coal-tar dyes for over 30 years has not produced a real coal-tar dye industry in this country.

#### CONCLUSIONS

37—Your committee submits its conclusions as follows:

A—To prevent the unfair underselling alleged to be practised by foreigners in this country, the adoption of an effective anti-dumping clause.

B—The so-called coal-tar "intermediates" which are the basis of the coal-tar chemical industry, inclusive of explosives, medicinals and dyestuffs, should be assessed one-half of whatever the finished dyes are taxed for tariff purposes; *all* coal-tar dyes *without exception* should be taxed alike, namely, 30 per cent *ad valorem* and 7½ cents per pound specific.

C—Changes in the patent laws, such as by compulsory licensing or compulsory working clauses, are *wholly ineffective, do more harm than good and should not be attempted.*

Your committee recommends that this report be submitted to the appropriate committees of Congress. Further, that this report be forwarded to interested organizations.

BERNHARD C. HESSE, *Chairman*

J. B. F. HERRESHOFF

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ALLEN ROGERS

## ORIGINAL PAPERS

## THE CEMENTING VALUE OF BITUMINOUS BINDERS

By LESTER KIRSCHBRAUN

Received August 6, 1914

During the past ten years there has been a great development in the methods of valuating paving bitumens. Early attempts at determining these values were directed towards chemical determinations of properties or constituents which were thought to have an influence upon the quality of materials of this kind. Later developments have indicated that, with few exceptions, the valuable properties of paving materials are included more directly in their physical characteristics. The present status of the determination of paving values includes physical tests as the more important ones, leaving a few chemical tests directed towards determining the permanency of these products, and the care with which they have been prepared.

It will be generally agreed that a most important, if not primary physical property, which paving bitumens must possess is that of cementitiousness. For a long time efforts have been directed towards devising a means of measuring cementitiousness of bituminous binders, but so far nothing has been offered in this direction which has met with general approval. Among the tests commonly employed, that of ductility has been assumed to measure, or to be, in a general way, an indication of cementitiousness. While possibly there is some relationship between ductility and the cementing value of a given type of bitumen, it will be admitted that no mathematically direct relationship, if any, exists at all. So far, then, as our present means of determining cementing values are concerned, this most important feature must be arrived at by indirect interpretation of data which afford no exact means of determining such values.

The writer has for the past four or five years directed his attention to the development of a method for directly and mathematically expressing the cementing value of plastic binders. Various means have been employed in the effort to determine this factor, but all have been discarded as it developed that they fell short of measuring the properties sought for. The writer has, at various times, devised bending or shearing tests; has investigated the tensile strength of briquettes of binders and mixture of same with mineral particles; has investigated the strength of briquettes joined together by films of binder, and has experimented with methods of determining adhesiveness and cohesiveness. These various attempts, while in some cases giving valuable information, have failed, either through the inability to devise a means of obtaining concordant results, or for the reason that the properties actually measured in these efforts did not directly represent the cementing value property sought for. For example, in making tests of briquettes of non-bituminous material stuck together with a film of binder, it is not only difficult, if not impossible, to obtain concordant results on account of variations in

thickness of film, etc., but results obtained do not measure binding value, but measure cohesiveness. When tests of this kind are made, the briquettes fracture with a cleavage, leaving a film or part of a film on either end of the briquette. The property so recorded is *cohesiveness* or the ability of the material to stick to itself. Any method which measures strain endured by the film of asphalt in detaching itself without cleavage or fracture from a foreign surface measures *adhesiveness*. In either case, the operation fails to determine the cementing value or the ability of the material to bind particles together under the conditions of service.

If we analyze the results obtained upon a number of materials through a series of tests for tensile strength (meaning in this case the maximum strain endured in fracturing a briquette of bitumen) we shall find that two different materials may sustain the same maximum stress and indicate the same cohesiveness, but that one material will sustain this strain for but a short time before fracture, while another material will not only sustain the same maximum strain, but will endure it during a longer period or through a much longer distance of elongation. For example, a given type of asphalt cement at a certain penetration will, during application of strain, withstand a maximum of say, three units before fracturing. Another asphalt of certain penetration will withstand the same strain. In the former case, however, after this maximum is reached, an appreciable strain can be sustained for many times the elongation that may be sustained with the latter material. Cohesiveness results in such cases would indicate equality, but as a practical consideration, the latter material might be entirely unfit for paving purposes, and even from superficial observation might not indicate nearly the cementing qualities of the former. Such results, then, not only become misleading and contrary to practical observations, but fail entirely to give us an indication of the property sought for.

The adhesiveness of bituminous binders may be determined by means of a suitable apparatus. While the adhesiveness is a matter of importance in the effectiveness of bituminous application to cold road metal by pouring processes, nevertheless, in considering hot mechanical mixtures, the adhesiveness appears to play little part in holding together the mineral aggregate. When asphalt pavement cracks or fractures or displaces, an examination of the points of fracture discloses that the films of bitumen coating the particles have fractured or cleaved, and not that the bitumen has pulled off the mineral particles through lack of adhesiveness. In other words, the adhesiveness is always greater than the cohesiveness and the binding value. No mechanically measured results of adhesiveness need therefore be considered as a factor in this discussion, although the adhesiveness is a factor in considering pavements built by penetration methods.

What, then, represents the cementing value of a material of this kind? Cementing value must mean the ability of the bitumen to bind or hold together against rupture, particles of mineral matter which it coats or covers. Upon analyzing the conditions applying, it becomes evident that to break apart the bond between any two mineral particles held together by a coating of plastic bitumen, a certain tension must be applied for a certain time or space of action. The application of a tension over a certain distance infers the necessity for the film of binder to elongate at the point of contact of the two particles. The actual amount of elongation may be extremely small, but the relative amount in proportion to the thickness of the coating may be very great. That elongation does necessarily take place must be admitted from practical experience, which has taught us that a certain degree of plasticity or softness of our binders is essential to prevent cracking of pavements. The effect of advancing the softness of the binders is to favor their ability to yield and elongate under strains. Cracking is therefore minimized by superior ability of a soft binder to elongate over a hard binder of the same kind. If this ability to elongate were not essential, and if it actually did not take place in the binder between the particles of aggregate, it is apparent that the hardest binders would be the best, as they would be capable of sustaining greater strains than the softer binders. It will be seen therefore that the ability to elongate is an essential feature, and must operate, otherwise our conclusions would lead us in the direction contrary to actual experience.

Referring again to our consideration of two particles of aggregate bound together, it is necessary, in order to produce fracture or to disrupt the bond, to apply a certain tension over a necessary distance. The product of these factors is work done. The binding value of a plastic binder is then limited to the amount of tension it can sustain over a given distance, or is directly proportionate to the work done in producing fracture or failure of a given unit of material.

An apparatus was accordingly devised for the purpose of recording the factors above mentioned, namely, strain applied over distance. The apparatus in its final form is shown in Figs. 1 and 2. It consists of a rectangular box insulated and lined with galvanized iron or copper. An inclined plane or runway is attached to the box, the lower end of which reaches the bottom of the box, and the other end projects an equal distance outside. This runway carries a carriage through which passes a screw actuated by a set of gears adjustable to the desired speed. Upon the carriage is maintained a dynamometer, to the end of which is connected a flat brass rod, which extends along the runway to within a few centimeters of the end, and of the bottom of the box. This rod is graduated in metric units, and passes under an adjustable bridge at which the readings are recorded during travel of the rod. The runway is edged with guides of sufficient width for the free passage of the briquettes. The arrangement and position of the carriage makes it possible to apply a tension through the rod in a straight line

to briquettes at the lower end of the runway with the box filled with water. At the lower end of the runway is permanently fastened a small boss or projection to which one end of the briquette is attached, the other

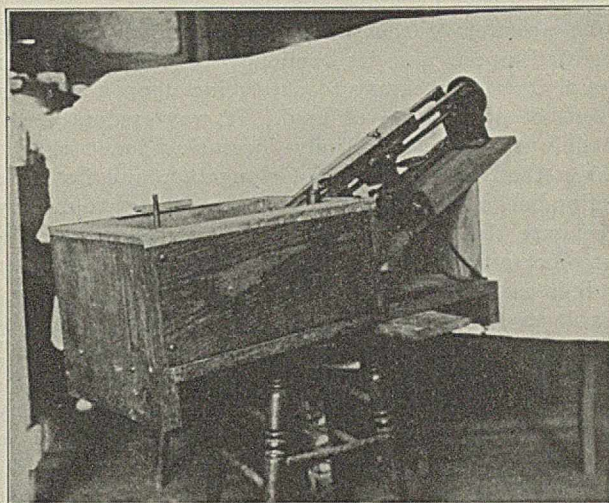


FIG. 1

end being attached to the rod connected with the dynamometer. The position of the bridge gives readings of elongation of the briquette, regardless of the movement of the carriage and dynamometer. The form of briquette adopted is that commonly known as the "Dow" moulds which are used for making ductility tests. These moulds have a minimum cross section of 1 sq. cm.

In working out the method of manipulation, it was of course necessary to determine a constant temperature at which the test should be made. The temperature selected was 5° C. or 41° F. This was selected for several reasons. In the first place it was

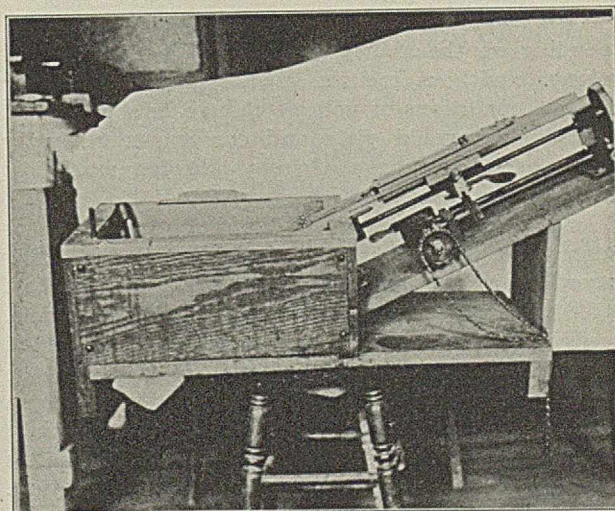


FIG. 2

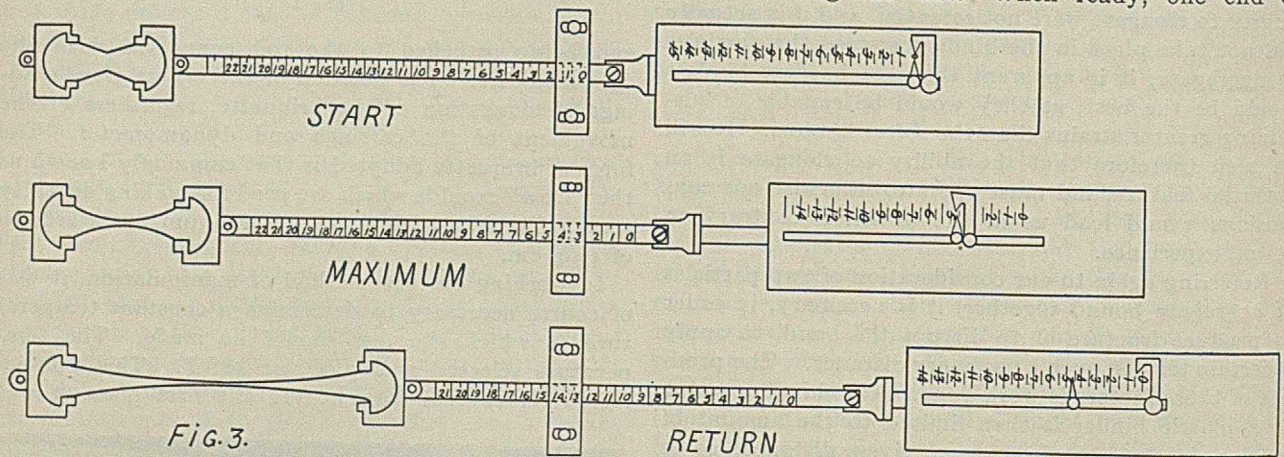
necessary to obtain sufficiently large readings upon the dynamometer. At normal temperatures, bituminous materials of this kind are ordinarily capable of withstanding but very little strain. Secondly, the

strains which produce fracture and cracking in a pavement in actual service are greatest during cold weather. Again, a low temperature being necessary, the temperature of  $5^{\circ}\text{C}$ ., was selected as being easy to maintain constantly with ice and water.

On account of the plastic nature of the material operated upon, and its tendency to elongate under strain, it was necessary to determine upon a uniform means of application of load. It was evidently impossible to set a uniformly increasing load for the reason that, as the material elongated, and its cross section became smaller, it would be necessary to rapidly accelerate the rate of elongation or travel of the dynamometer towards the end of the operation, in order to increase the strain. This would become impracticable as a matter of manipulation, and would be subject to large variation through personal equation and through inability to take the required readings sufficiently rapidly. It was found necessary after many trials to adopt a *uniform rate of travel of carriage and dynamometer*. This is in accord with practical conditions, inasmuch as any strain set up in a pavement would be induced at a variable rate of application,

that in applying strain to the briquette by means of a dynamometer traveling at a uniform speed, the briquette has at first slight tendency to elongate under application of strain, until a maximum is reached, when the rate of elongation of the briquette exceeds the rate of travel of the carriage and dynamometer, at which point the dynamometer begins to register values below the maximum attained, until finally the briquette is either fractured at a reduced cross section through elongation of the material, or the dynamometer returns to zero without fracture of the briquette. An essential difference from the method of determining ductility is that during the entire period of elongation, the material is under substantial strain. Ductility or elongation values that include the distance traveled by an extremely fine thread or filament of bitumen are misleading and immaterial.

In making the test, as finally adopted, the briquettes are prepared in the usual manner as for ductility test, and are placed in the test box at  $5^{\circ}\text{C}$ . They are held for about three-quarters of an hour at this temperature before making the test. When ready, one end of



depending on the ability of various binders to yield or elongate without fracture. It is apparent that under the same conditions of volume change in a pavement a soft binder would yield and conform more easily to the necessary change, thereby allowing much less strain to be set up than with a hard binder.

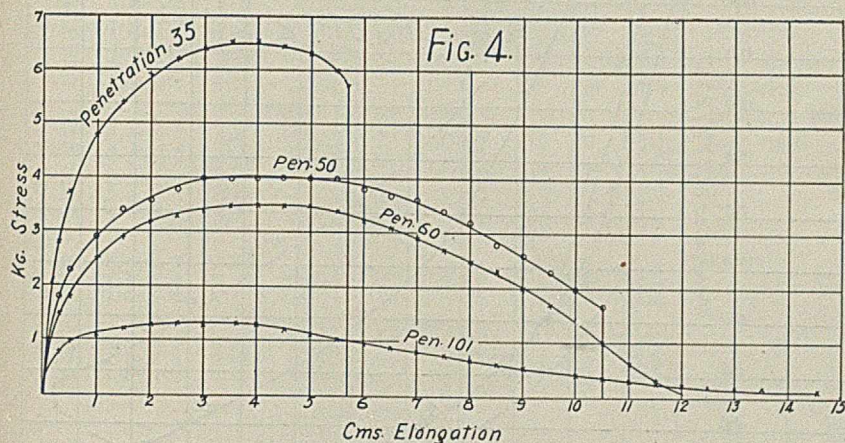
Various trials were made at different speeds in order to determine what speed was most adapted to securing concordant results, and distinguishing to the greatest degree the differences between various materials. Speeds between 1 to 10 cm. per minute were tried upon the same materials. It was found that the higher speeds had a tendency to effect too sudden application of strain, and, with the harder materials, to produce fracture in the corner of the briquettes rather than at the point of minimum cross section. Again, at the faster speeds, it became difficult to take the readings near the time of fracture owing to the rapid travel of the rod and the pointer of the dynamometer. After various trials it was found that a speed of travel of the carriage and dynamometer at the rate of 1 cm. per minute provided to the greatest extent for the factors indicated above. It will be understood

the briquette is hitched to the fixed post at the bottom of the box on the runway, and the dynamometer brought into position so that the end of the rod attached to same may be fastened to the other end of the briquette. The apparatus is driven mechanically, and the carriage is started by closing the split-nut which brings it into contact with the screw. When the end of the dynamometer begins to move over its zero mark, the bridge over the rod is adjusted to the zero mark on the rod. Carriage and dynamometer continue to travel at the rate of 1 cm. per minute, and readings of the dynamometer are taken at every half centimeter of elongation as shown by the rod. This is continued until the briquette fractures or elongates through its maximum back to zero strain. The dynamometer carries a maximum pointer and is graduated in tenths of a kilogram, and the zero mark is taken as one-tenth kilogram, which includes the weight of the briquette and the frictional resistance of parts. The position of the rod and boss are such as to lift the briquette slightly off the runway when the strain is applied, so that no friction results on this account during the application of strain. Fig. 3 illustrates



the position of the briquette and dynamometer at various stages of test.

The results of the data obtained in these determinations may be graphically recorded. The distances elongated are recorded as abscissae, and the strain as ordinates. Fig. 4 gives a typical example of results obtained upon the same material of different consistencies under this method of test. The areas en-



closed by these curves represent the product of the strain applied and the distance of its application, or the work done. The unit of value is expressed as kilogrammeters. This area may be obtained from the graphical plot of the result, or may be secured much more quickly, and sufficiently accurately, by addition of the ordinates. The readings are taken for every 0.5 cm. or 0.005 of a meter. Every unit of ordinate therefore represents 0.005 kilogram meters, and the sum of the ordinates multiplied by this factor gives the area or the work done in kilogram meters. Expressed mathematically, the formula for calculating the result is  $\Sigma Y \times 0.005$ . This is sufficiently accurate for practical purposes. Referring again to Fig. 4, it will be noted that the same material at different consistencies requires widely varying amounts of work for failure. With the harder materials, a comparatively sharp curve is obtained, which reaches a certain maximum, and then becomes less as the material elongates faster than the carriage travels. When the cross section is reduced to a point at which it is unable to withstand the strain induced, it breaks. With the materials of the softer consistency there is a tendency of the curve

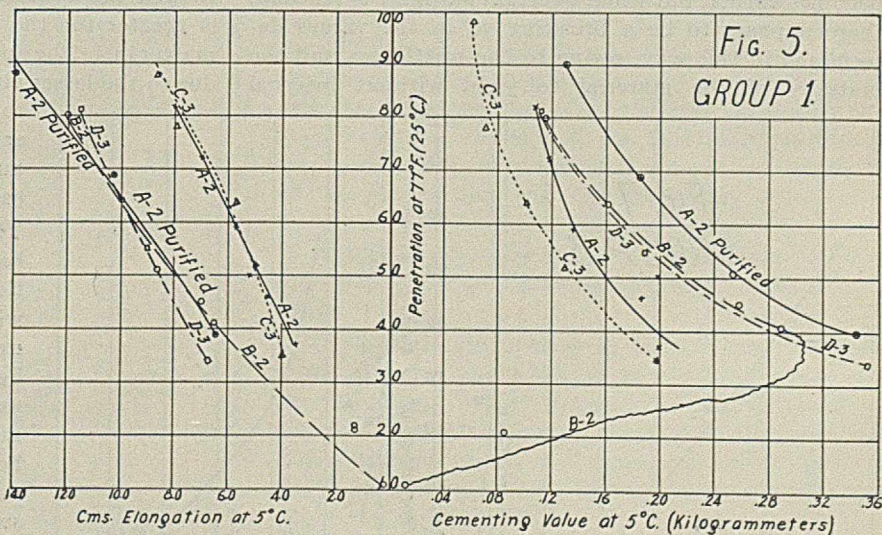
to flatten and to become larger as the material is more plastic. A consistency is finally reached at which the material is able to progress through to its maximum and back to zero (or 0.1 kg.) without fracture. All tests were obtained in duplicate, and the results indicate a limit of accuracy of 0.02 kg. meter from an average, on the highest results, to a much closer agreement upon the lower values. Exception to this accuracy

is noted upon the hard brittle materials, which are unable to elongate uniformly without setting up internal strain, due to the corners of the briquettes.

Having established a satisfactory method of determining the value sought for, it was desired to outline a series of investigations covering the following points:

- 1—Survey of the characteristics of commercial products with special reference to determining the degree of differentiation possible with the various materials.
- 2—The possibility of valuating fluxes by this method.
- 3—Test of the commercial products, the chemical characteristics of which indicate inferior preparation.
- 4—The determination of a possible effect upon cementing value induced by improper preparation upon a series of products made known under known conditions.
- 5—The determination of standards of value necessary for practical application.

In order to take complete information of the characteristics of commercial products, it is necessary to collect such data as would represent a wide range of consistency for each material. The refined asphalt was accordingly used and fluxed with the kind of flux ordinarily used in practice. Determinations were made upon each material at a number of different consistencies, and these cementing values were graphically expressed as abscissae and the consistencies as ordinates. The various materials examined were grouped into three classes according

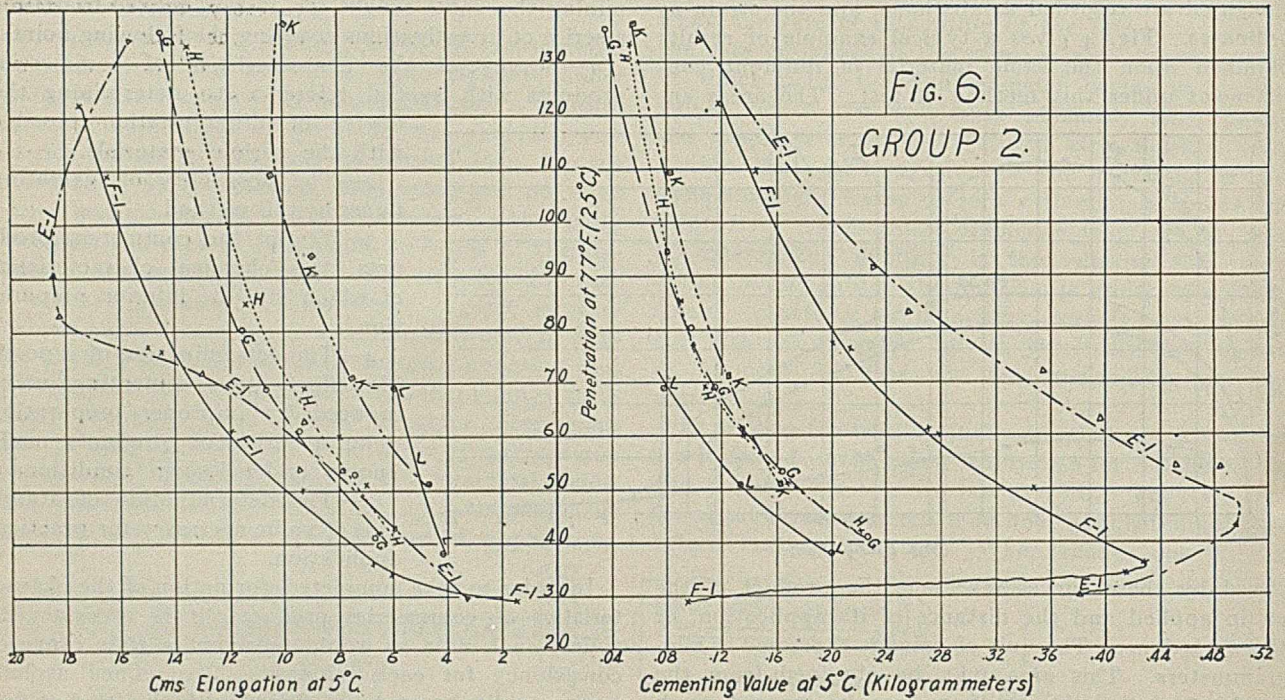


to their origin. Record was made of the cementing value as determined by the data presented before, together with the elongation and the maximum strain sustained. These data are given in Table I (page 981).

Group 1 contains asphalt cements prepared from solid natural bitumens, and Groups 2 and 3 include products made from natural liquid bitumens.

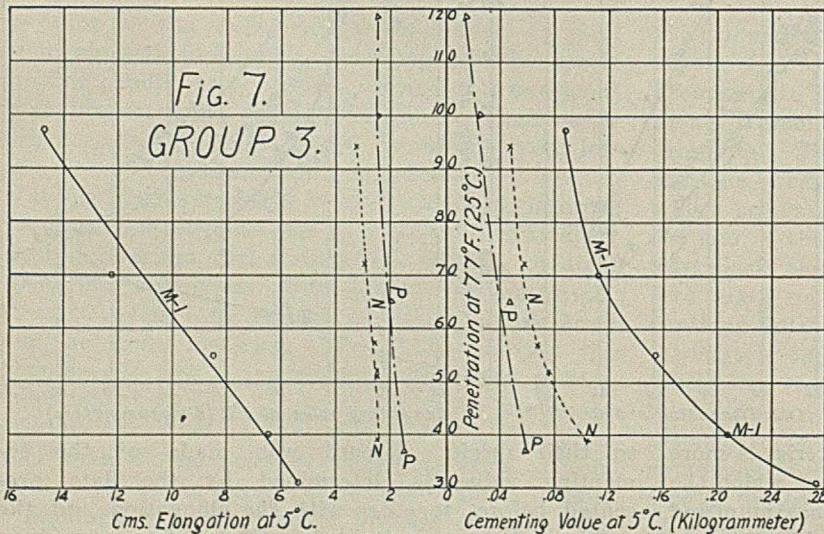
Results obtained are given graphically in Figs. 5, 6 and 7. It was found desirable to plot elongation in order to complete the means of interpretation of the results. The graphical presentation of this data

pull. Such procedure, however, would minimize the differences between these materials at those consistencies at which such differences are of greatest importance.



indicates a relationship between consistency and cementing value on one hand, and consistency and elongation on the other. By referring to plates, it is possible to compare the values of any of the materials at the same penetration. It will be noted that the cementing value increases generally as the consistency becomes harder, but when a certain hardness is reached, there appears to be a breaking off in the values determined in this way, owing to the brittleness and the inability of the material to yield without internal

The effect of the presence of mineral matter upon the binding value and elongation is illustrated in case of material A-2, which was examined with the mineral matter in, and with the mineral matter removed. The presence of mineral matter in these materials lowers the result obtained for cementing value, although the cohesiveness or maximum strain recorded is greater for the same consistency with the mineral matter in. The apparent lowering of cementing value is due to the lesser elongation produced under strain, and to the fact that the bitumen when examined with its contained mineral matter is actually softer than indicated by penetration of the whole.



strains induced by the form of briquettes. This is a factor dependent upon the speed of the pull, and in all likelihood there would be a continuation of the curves beyond the present points at a slower rate of

to resist cracking, than we do under heavy traffic. This is true because, as is well known, heavy traffic tends to knead the pavement and relieve the stresses set up by changes of temperature. It will be

Fig. 6.  
GROUP 2.

Fig. 7.  
GROUP 3.

TABLE I—GROUP 1—FIG. 5  
Asphalt "C" and Flux 3

Pen. at 77° F	Max-imum strain	Average	Cementing Values	Average	Elongation Cms.	Average
35	5.7- 5.7	5.7	0.199-0.198	0.199	4.0- 4.0	4.0
52	3.2- 3.0	3.1	0.134-0.126	0.130	5.0- 5.0	5.0
64	2.3- 2.2	2.25	0.101-0.101	0.101	5.5- 6.0	5.75
78	1.4- 1.1	1.35	0.077-0.063	0.070	7.5- 8.5	8.0
98	1.1- 1.0	1.05	0.060-0.063	0.062	8.5- 9.0	8.75
Asphalt "B" and Flux 2						
41	5.1- 5.0	5.05	0.269-0.308	0.288	6.0- 7.0	6.5
51	3.8- 3.6	3.7	0.278-0.233	0.255	9.5- 8.0	8.75
64	2.6- 2.4	2.5	0.154-0.168	0.161	9.0-11.0	10.0
80	1.6- 1.5	1.55	0.114-0.106	0.111	12.0-12.0	12.0
45	4.3- 4.3	4.33	0.259-0.257	0.258	7.0- 7.2	7.1
11	6.4- 7.2	6.8	.....	0.017	0.2- 0.25	0.22
22	7.3- ...	7.3	0.087-.....	0.087	1.2- 1.2	1.2
Asphalt "A" and Flux 2						
37	6.3- 6.5	6.4	0.194-0.202	0.198	3.5- 3.5	3.5
50	4.2- 4.4	4.3	0.215-0.186	0.201	6.0- 4.5	5.25
59	2.8- 2.9	2.85	0.119-0.152	0.136	5.0- 6.5	5.75
72	2.3- 2.3	2.3	0.111-0.125	0.118	6.5- 7.5	7.0
82	2.0- 2.1	2.05	0.107-0.109	0.108	8.5- 7.5	8.0
46	4.5- 4.5	4.5	0.197-0.172	0.185	4.8- 4.3	4.6
Asphalt "A-2" Purified						
39	6.0- 6.1	6.05	0.338-0.348	0.343	6.5- 6.5	6.5
69	2.4- 2.4	2.4	0.183-0.164	0.174	10.0-10.5	10.25
88	1.6- 1.6	1.6	0.137-0.123	0.130	13.0-15.0	14.0
Asphalt "D" and Flux 3						
34	5.8- 6.5	6.15	0.324-0.379	0.352	6.5- 7.0	6.75
55	2.7- 2.6	2.65	0.191-0.185	0.188	9.0- 9.0	9.0
81	1.3- 1.5	1.4	0.105-0.121	0.113	11.5-12.0	11.75

GROUP 2—FIG. 6

Asphalt "E" and Flux 1						
30	13.7-13.6	13.65	0.369-0.393	0.382	3.2- 3.4	3.3
43	9.9- 9.6	9.75	0.469-0.503	0.486	5.5- 6.4	5.95
54	6.6- 6.5	6.55	0.470-0.430	0.450	8.0- 7.7	7.85
72	4.0- 4.3	4.15	0.343-0.364	0.353	15.0-11.0	13.0
63	5.0- 4.8	4.9	0.401-0.389	0.395	9.0- 9.5	9.25
91	2.75-2.85	2.62	0.224-0.234	0.229	18.0-19.0	18.5
83	2.9- 2.8	2.85	0.251-0.263	0.257	18.0-18.5	18.25
134	1.2- 1.3	1.25	0.099-0.103	0.101	16.0-15.5	15.75
Asphalt "F" and Flux 1						
29	5.9- 7.2	6.8	0.074-0.149	0.097	0.9- 1.7	1.5
34	7.3-7.2-7.8	7.4	0.415-0.382-0.441	0.413	6.5-5.7-6.1	6.1
36	7.5- 6.9	7.2	0.463-0.394	0.428	7.0- 6.5	6.75
50	5.1- ...	5.1	0.354-0.344	0.347	8.0-10.5	9.25
61	3.5- ...	3.5	0.269-.....	0.269	12.0-....	12.0
76	2.8- ...	2.8	0.212-.....	0.212	13.0-....	13.0
77	2.5- 2.4	2.45	0.206-0.195	0.201	14.5-15.5	15.0
109	1.6- 1.6	1.6	0.133-0.155	0.144	16.0-17.0	16.5
122	1.1- 1.4	1.25	0.111-0.123	0.117	17.0-18.0	17.5
Asphalt "H" and Flux "H"						
42	3.9- 4.0	3.95	0.216-0.225	0.220	6.5- 6.5	6.5
51	2.8- 3.05	2.93	0.169-0.163	0.166	6.5- 7.5	7.0
60	2.3- 2.35	2.33	0.138-0.135	0.137	8.0- 8.0	8.0
69	1.7- 1.8	1.75	0.102-0.114	0.108	9.0- 9.5	9.25
77	1.8- 1.8	1.7	0.103-0.095	0.099	9.5- 9.5	9.5
85	1.2- 1.2	1.2	0.0938-0.0878	0.091	11.5-11.5	11.5
133	0.5- 0.5	0.5	0.0517-0.0518	0.052	13.5-14.0	13.75
Asphalt "G" and Flux "G"						
41	3.8- 4.1	3.95	0.221-0.229	0.225	7.0- 6.5	6.75
53	2.8- 2.9	2.85	0.165-0.158	0.162	7.5- 7.2	7.35
61	2.2- 2.1	2.15	0.137-0.134	0.136	9.5- 9.5	9.5
69	1.8- 1.7	1.75	0.124-0.105	0.115	10.5-11.0	10.75
80	1.4- 1.5	1.45	0.093-0.103	0.098	11.0-12.0	11.5
136	0.3- 0.3	0.3	0.036-0.033	0.035	14.0-14.5	14.25
Asphalt "L"						
38	5.5- ...	5.5	0.199-.....	0.199	4.2- ...	4.2
51	3.4- 3.1	3.25	0.146-0.122	0.134	4.5- 5.0	4.75
69	2.0- ...	2.0	0.077-.....	0.077	6.0- ...	6.0
Asphalt "K"						
51	3.8- 4.0	3.9	0.150-0.173	0.162	4.5- 5.0	4.75
71	2.4- 2.4	2.4	0.129-0.121	0.125	7.5- 7.5	7.5
94	1.5- 1.6	1.55	0.077-0.082	0.080	9.0- 9.0	9.0
109	1.3- 1.2	1.25	0.085-0.082	0.084	10.5-10.5	10.5
137	1.0- 0.9	0.95	0.059-0.054	0.057	9.5-10.5	10.0

GROUP 3—FIG. 7

Asphalt "M" and Flux 1						
31	5.5- 6.0	5.75	0.263-0.284	0.273	5.5- 5.3	5.4
40	3.8- 3.9	3.85	0.213-0.202	0.208	6.2- 6.8	6.5
55	2.6- 2.2	2.4	0.167-0.141	0.154	8.5- 8.5	8.5
70	1.3- 1.4	1.35	0.112-0.113	0.112	12.5-13.0	12.25
97	0.9- 0.9	0.9	0.088-0.086	0.087	14.5-15.0	14.75
Asphalt "N" and Flux "N"						
39	4.7- 4.6	4.65	0.105-0.103	0.104	2.5- 2.5	2.5
52	3.3- 3.4	3.35	0.075-0.077	0.076	2.5- 2.5	2.5
57	2.8- 2.8	3.8	0.068-0.062	0.065	2.5- 2.5	2.65
72	2.2- 2.3	2.25	0.058-0.060	0.059	3.0- 3.0	3.0
94	1.8- 1.7	1.75	0.045-0.049	0.047	3.0- 3.5	3.25
Asphalt "P" and Flux "P"						
37	4.3- 4.3	4.3	0.059-0.059	0.059	1.5- 1.5	1.5
100	1.2- 1.2	1.2	0.025-0.023	0.023	2.4- 2.5	2.5
118	0.9- 1.0	0.9	0.015-0.016	0.016	2.5- 2.5	2.5
65	2.5- 2.7	2.6	0.045-0.050	0.047	2.0- 2.0	2.0

noted that the cementing value is not directly proportionate to the elongation, and that in some cases the binding value of two different materials at the same penetration is very similar, whereas their ability to elongate at the same penetration is appreciably different. Likewise, particularly at the lower penetrations, some materials elongate to practically the same extent, yet their cementing values are widely different. It is evident from the study of this graphical data, that it is not only necessary to consider the elongation as a factor in the cementing value, but it is also necessary to consider it apart from the cementing value. If this were not so, our pavements would be less liable to crack when laid at the harder consistencies. It appears, therefore, that while the cementing value indicates the ability of the material to bind aggregate together, a minimum ability to elongate is also necessary to avoid cracking. This is well illustrated with material "N" which, when laid, has sufficient cementing value to bind the mineral particles together for light traffic, but which has a very pronounced tendency to crack. Its binding ability at no consistency would be sufficient for conditions of heavy traffic. It will further be noticed that the general tendency of the elongation curves is to straighten upward beyond a certain consistency, and in some cases, even to retreat. This indicates that beyond a certain amount, fluxing not only results in less binding value, but results in reduced ability to elongate, and that nothing would be gained, so far as plasticity is concerned, by further fluxing. In the case of materials "P" and "N," there would hardly be any consistency at which the material might be handled which would overcome the tendency to crack. This in a practical way has been actually found to be the case. Attention may be called, at this point, to the fact that various materials showing the same maximum strain or cohesiveness possess widely different cementing values. For example, asphalt "G" at 53 penetration shows 2.85 kg. maximum strain. The same value for cohesiveness is shown by asphalt "E" at 83 penetration, yet the cementing value of this latter greatly exceeds that of asphalt "G." This is a typical example which indicates the ability of this test to differentiate beyond any ordinary tension tests.

Table II is given showing the results of investigations made in the effort to determine the possibility of valuating various fluxes. In this series of tests the same asphalt was used throughout, and was fluxed with different fluxes, the cementing values and other data being determined as indicated before. These are given in Table II.

Graphical results are shown in Fig. 8. It will be noted that the cementing values of these materials are progressively greater as the fluxes tend towards asphaltic base, with this exception that the paraffine combination shows slightly better values than the light-semi-asphaltic. This is due to the fact that much less paraffine base flux was used to produce the consistencies noted than in the case of the light semi-asphaltic flux. When, however, the elongation

curves are examined, a progressive increase without exception is noted in ability to elongate as the fluxes used partake more of an asphaltic character. It will

TABLE II—FLUX TESTS—FIG. 8

R. A. and Paraffine Flux						
Pen. at 77° F.	Maximum strain	Average	Cementing Values	Average	Elongation Cms.	Average
45	3.9-4.0	3.95	0.082-0.083	0.083	2.5-2.3	2.4
53	3.0-3.1	3.05	0.115-0.144	0.130	4.6-5.0	5.0
88	1.7-1.7	1.7	0.072-0.075	0.074	5.5-5.5	5.5
76	2.1-2.1	2.1	0.093-0.095	0.094	5.5-5.5	5.5
R. A. and Light Semi-Asphaltic Flux						
39	3.8-3.9	3.85	0.092-0.114	0.103	3.0-3.7	3.35
68	1.5-1.5	1.5	0.096-0.096	0.096	8.2-8.0	8.1
83	1.2-1.1	1.15	0.077-0.067	0.072	8.5-8.5	8.5
44	3.0-3.0	3.0	0.188-0.141	0.165	7.4-5.5	6.45
R. A. and Heavy Semi-Asphaltic Flux						
34	5.8-6.5	6.15	0.325-0.379	0.352	6.5-7.0	6.75
55	2.7-2.6	2.65	0.191-0.185	0.188	9.0-9.0	9.0
81	1.3-1.5	1.4	0.105-0.121	0.113	11.5-12.0	11.75
R. A. and Asphaltic Flux						
130	0.4-...	0.4	0.043-...	0.043	14.0-...	14.0
79	1.4-1.3	1.35	0.119-0.125	0.122	13.0-14.5	13.75
59	2.7-2.6	2.65	0.246-0.198	0.222	13.0-11.0	12.0
45	4.1-4.2	4.15	0.316-0.327	0.322	9.0-8.8	8.9
35	6.0-5.8	5.9	0.282-0.246	0.264	5.0-5.5	5.25
51	3.6-3.6	3.6	0.254-0.249	0.252	8.5-8.5	8.5
33	.....	.....	.....	0.210	.....	4.4

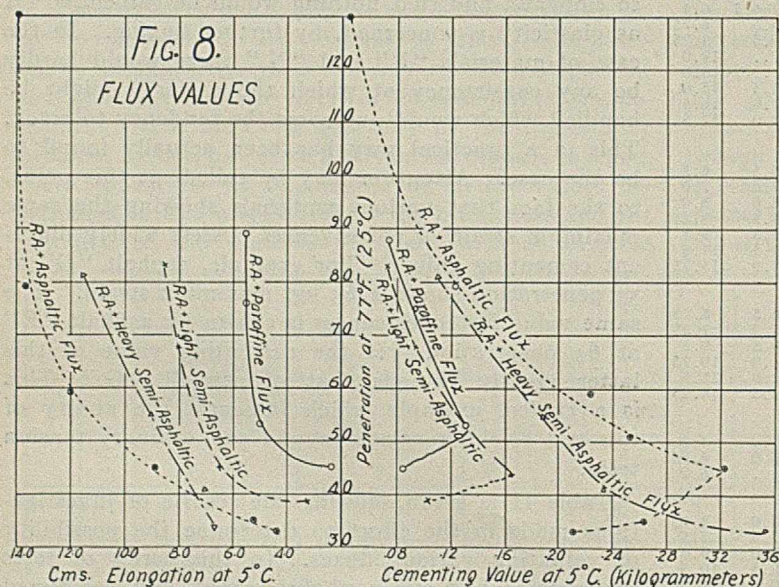
be noted that the ability to elongate would become even a more sensitive indication of the character of the flux itself than the cementing value. The practical necessity for considering this ability to elongate is aptly illustrated here. This refined asphalt used with paraffine fluxes has proven unsatisfactory in practice. Under light traffic, pavements laid with this have shown sufficient binding qualities to hold the mineral particles together, but the tendency to crack is very decided. On the other hand, this refined

materials have been encountered which gave indication, from analysis, of having been poorly prepared—so much as to warrant their rejection for use. A few of these samples were on file, and were available for cementing value tests. These materials were generally refined asphalts of from 30 to 40 penetration, reduced from liquid albumen. They were subjected to the cementing value test at the consistency at which they were obtained, and then fluxed with the same asphaltic flux to a consistency corresponding to paving penetration, in order to afford comparison with normal products of the same type. The determination of cementing value and elongation are given in Table III, together with the principal analytical characteristics.

These results are graphically shown in Fig. 9, and are given in connection with a curve showing the quality of an average acceptable commercial sample of material prepared from similar crude. It is evident from the study of these results that the chemical indications of inferior preparation shown by the high fixed carbon and per cent insoluble in carbon tetrachloride are confirmed by actual lowering of the cementing qualities, and elongation values.

In order to confirm the indications of lowering of cementing qualities with accompanying evidences of poor preparation, products were made in the laboratory from the same asphaltic base crude oil under known conditions. These were made in a small still, and were prepared at temperatures of 525°, 700° and 825° to 850° F. at the end of the distillation. Four runs were made, two of which were conducted at the last named temperature. In the first three runs, the materials were not pushed to a hard penetration, but of the last two runs at 850° F., one was pushed to a very hard consistency. In order to obtain an indication as to the comparative extent of cracking which took place, composite samples of the distillate were tested for gravity. In the first two runs, samples were taken from the still at various points of consistency indicated hereafter. In the fourth run, the material, as stated, was pushed to a very hard penetration and fluxed back with well prepared asphaltic base flux from the same crude. All of these samples were tested for cementing value, and those

samples most nearly corresponding in consistency or penetration were examined for their main chemical characteristics. These results are given in Table IV (page 984) and are shown graphically on Fig. 10. On account of the insufficient number of points of elongation secured, no attempt was made to draw a smooth curve covering these points. Inspection of the above tabulated results shows that very little change or decomposition has occurred under 700° F., in running down to the consistencies noted. The material prepared at 850° F. gives evidences of substantial decomposition. This is indicated by a lighter



asphalt with light semi-asphaltic flux has shown, in a practical way, that the cracking tendency is greatly reduced in laying at a sufficiently high penetration, and it has been much more satisfactory than the previous combination, even though its cementing value is not greater. The material with the asphaltic flux and the heavy semi-asphaltic flux have been eminently successful under service conditions. It is evident from the above that the method described furnishes a means of determining the value of various fluxes and their suitability in asphalt combinations.

During the course of commercial practice, various

gravity of distillate and falling off in solubility in carbon disulfide. The gravity of distillate in runs T-3 and T-4 hard are, of course, not strictly comparable owing to the different consistencies to which these were pushed. As a consequence of the decomposition that has occurred, there follows a substantial increase of fixed carbon *over normal*, and the conversion of part of the bitumen to a form insoluble in carbon tetrachloride. The differences between products obtained in the two T-4 runs show that not only is temperature a factor in decomposition, but also the degree to which the operation is pushed, or the degree of "concentration" resulting. This latter

to note the persistency with which material prepared from this crude retains its cementing value even when badly decomposed; and although showing evidences in this direction which would cause its rejection under standard specifications, its cementing value has not been reduced below an acceptable minimum. As to whether or not materials so prepared, and possessing the characteristics of the last named product would *retain* the cementing value indicated, is a matter requiring investigation before any conclusion can be drawn as to the effect of the features noted. It will be seen, in referring to commercial products prepared from crude of this character, that the loss of cementing

TABLE III—Fig. 9

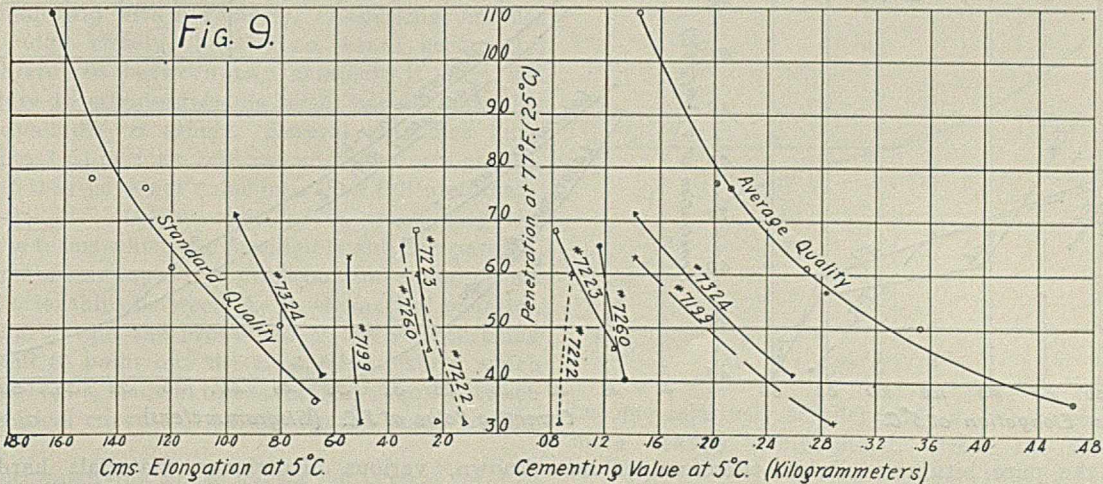
No.	7199	fluxd.	7222	fluxd.	7223	fluxd.	7260	fluxd.	7324	fluxd.
Pent. at 77° F.....	32	63	32	60	46	68	40	65	41	71
Duct. at 77° F.....	60 cm.		4.5 cm.		7.5 cm.		7.0 cm.		1.2 per cent	
5 hr. loss.....	0.4 %		0.6 %		0.8 %				65 cm.	
Per cent hardening.....	25.0		25.0		36.9				43.9	
CS <sub>2</sub> soluble.....	99.7		98.9		99.0		99.0 %		99.7	
Mineral.....	0.2		0.2		0.2				0.2	
Difference.....	0.1		0.9		0.8				0.1	
CCl <sub>4</sub> soluble.....	97.0		90.0		94.4		95.9		97.9	
Fixed carbon.....	16.6		18.6		17.7				16.9	
Cementing value at 5° C.....	0.289	0.141	0.085	0.096	0.126	0.082	0.136	0.117	0.258	0.141
Elongation at 5° C.....	5.0	5.5	1.2	2.9	2.5	3.0	2.5	3.75	6.5	9.75

is in confirmation of the investigations made by the writer some time ago.<sup>1</sup>

It will be observed from the inspection of the graphical data that the most cementitious materials were produced at the lower temperatures, and that the cementing values decrease as the conditions of preparation become more severe. While the differences in cementing value between materials produced at 525° and 700° F. are slight, there is a substantial difference between these results and those obtained with the materials produced at 850° F., and between these latter, prepared at substantially the same temperature, but pushed to a varying degree of hardness.

value is much greater with slighter evidences of decomposition than is obtained from the products prepared in the laboratory. No explanation of these variations is offered, aside from the indications given by these commercial products of having been prepared by other methods, than those involving straight distillation.

It is evident that this method of determining cementing values is capable of distinguishing between products prepared with more or less care, and that a reduction in cementing properties follows as a consequence of decomposition occurring during preparation.



There is marked loss in cementing value in the material pushed to hard penetration and fluxed back, and the evidences of decomposition are very decided. In fluxing this hard material (T-4) back with well prepared flux, approximately equal quantities of flux were required to bring it back to 62 penetration. The effect of the introduction of so large a quantity of well prepared flux has, of course, minimized the loss of cementing value. Nevertheless, it is astonishing

In the previous discussion, various commercial asphalts which have been used in paving work have been examined, together with their appropriate and inappropriate fluxes. There has also been observed the effect on asphalt derived from liquid bitumen, of improper conditions of preparation. It remains, therefore, to analyze the data obtained, in connection with practical results, and to determine, if possible, what cementing characteristics appear to be necessary for the successful binder. Discussion of this

<sup>1</sup> Municipal Engineering, 35, 349.

phase of the matter will be confined to only one form of construction, namely, sheet asphalt pavements.

From long experience with various materials observed in this discussion, and in segregating those binders which, in the writer's observations, have been successful and unsuccessful, certain tentative values may be set which should differentiate the successful or acceptable cement from the non-acceptable. Carefully considering this matter in connection with practical results, the lowest cementing value which is considered acceptable under conditions of light traffic is

materials laid under traffic, calling for a penetration of 35 to 40, with materials of the first group, the writer would prescribe for such traffic a minimum cementing value for the bitumen used of about 0.24 kilogrammeters, and elongation limits between four and six centimeters. Maximum limits of elongation are set as well as minimum limits for the reason that above the maximum limits of elongation, is the accompanying higher consistency, which results in too soft a cement under conditions of hot weather. These limits are, of course, suggestive, and will be modified according

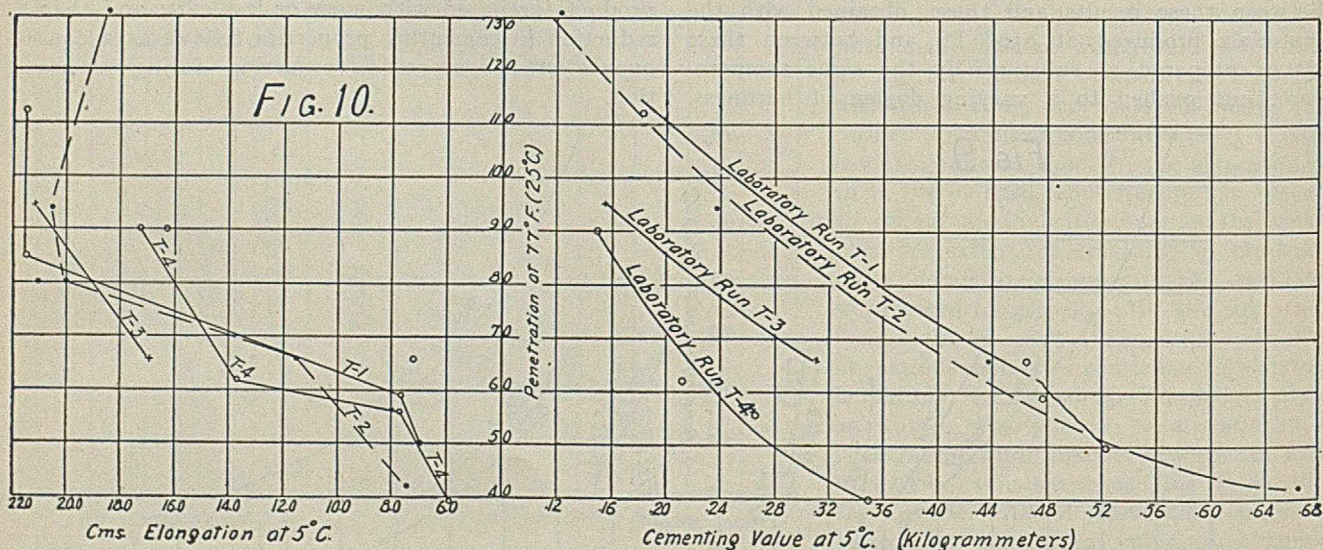
TABLE IV—FIG. 10

	T-1	T-2	T-3	T-4 hard	T-4 fluxed
Temperature still.....	522° F.	700° F.	850° F.	850° F.	.....
Gravity of distillate at 60° F.....	21.2	21.2	26.2	25.6	.....
Pushed to penetration.....	50	42	66	2	.....
Fluxed to penetration at 77° F.....	59	66	.....	.....	62
Ductility at 77° F.....	115 + cm.	115 + cm.	102 cm.	.....	57.0 cm.
Fixed carbon.....	5.5 per cent	7.0 per cent	13.1 per cent	26.4 per cent	15.2 per cent
Soluble in CS <sub>2</sub> .....	99.6	99.7	98.9	85.3	93.3
Soluble in CCl <sub>4</sub> .....	99.6	99.7	97.5	67.9	87.3
Cementing value at 5° C.....	0.478	0.439	0.311	.....	0.212
Elongation at 5° C.....	7.7 cm.	11.5 cm.	17.0 cm.	.....	13.75
Melting point.....	.....	.....	.....	217° F.	.....

set at 0.08 kilogrammeters. This value, if taken alone, will include some materials which, although able under light traffic to bind the mineral particles in a sheet asphalt pavement together, are prone to develop cracking. As stated previously, it is necessary not only to consider the cementing value alone, but also to consider the ability of the binder to elongate, in order to prescribe those which have the property of holding together mineral aggregate without undue tendency to cracking. For light traffic, this elongation value is set between the limits of 8 cm. and 14

to the individual experience and ideas of those who might employ these tests. It is probable that an empirical formula may be devised giving the relationship between traffic units and cementing-elongation values in such a way as to indicate the necessary characteristics applicable for any intensity of traffic.

There remains another factor which may influence the valuating of materials in accordance with these characteristics, and that is, the possible rate of loss of cementing value which will be shown upon tests carried out over a prolonged period of time. As is well



cm. for the pure bitumen. Below these values are found, in the writer's experience, unsuccessful materials for the class of construction referred to, and corresponding to these values are found those which have demonstrated satisfactory use under light traffic.

As previously indicated, pavements under heavy traffic require stronger and more cementitious binders with less need of these binders to elongate. It is difficult to describe accurately conditions which would be understood by all to be designated as heavy traffic. Keeping in mind, however, service records of ma-

known, various bituminous materials harden with age and suffer marked loss of ductility upon standing, sometimes for comparatively short periods of time. It is likely that the materials here examined would likewise show variable rate of loss of cementing value and elongation with age, particularly those materials showing the effects of severe treatment in preparation. Data of this kind covering a period of time or indicating the same effect of accelerated tests will be of considerable importance in fully determining the relative values of various types of binders.

It is the intention of the writer to take up these phases of the subject, but owing to the time necessary to compile complete data, it is considered advisable to present the foregoing in the expectation that the methods employed may be improved upon by others interested, and that the features indicated may be simultaneously investigated by independent observers.

It is suggested that this test not only covers all of the data heretofore furnished by the ductility test, but in addition furnishes direct information as to the cementing values of the materials examined. The elongation values determined during the cementing value tests afford a more accurate and truly representative indication of ductility than the test usually employed. The elongation values determined by this method have an advantage of being taken at a temperature at which such properties come into play most effectively in pavements, and are recorded only while the binder is capable of withstanding an appreciable strain. These values are not clouded by the fine hair-like filaments into which bitumen is drawn at normal temperatures, and which have no significance in determining any valuable property. In addition, it is difficult, if not impossible, by the usual method, to differentiate between materials having a ductility in excess of certain limits fixed by the devices usually employed, which cannot be extended much beyond 100 centimeters with any significant results.

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HYSTERESIS TESTS FOR RUBBER

By EARL H. DAVIES

Received September 25, 1914

The expert usually judges a piece of rubber by means of a crude hysteresis test which he performs by stretching a small strip with his fingers. Experience enables him to judge closely, but by no means accurately, small differences between two samples; it does not enable him to standardize his tests, nor to make his results available to others. Several machines have been devised to perform and record these tests graphically, but they have not come into their full usefulness, due to the difficulty encountered in translating the graph into terms which are intelligible and comparable. The object of this paper is to point out and explain some of the relationships between the mathematical equation for the curve and the properties of the rubber being tested, and to point out the close relationships which some of the tests, made in this laboratory, show between the theoretical curve and actual curves made by the machine.

The accompanying figure shows the typical form of curve produced by the machine. The ordinates represent tension and the abscissae, stretch. Cheneveau and Heim<sup>1</sup> have shown that this curve has the equation:

$$x = cy + a \sin^2 by \tag{1}$$

and that when OB is drawn tan. to the curve OD at O,

$$c = \tan. \angle YO B.$$

From (1)

$$a \sin^2 by_1 = x_1 - cy_1$$

<sup>1</sup> "Sur l' extensibilité du caoutchouc vulcanisé," *Compt. rend.*, p. 320, Feb. 6, 1911; also, "The Rubber Industry," (1911).

Since  $c = \frac{m_1}{y_1}$  and  $z_1 = x_1 - m_1$

then  $z_1 = x_1 - cy_1$

or  $z_1 = a \sin^2 by_1$  (2)

In like manner it may be shown that  $z_2 = a \sin^2 2by_1$  (3)

From (2)  $\sin^2 by_1 = \frac{z_1}{a}$

Since  $2 \sin^2 A = 1 - \cos 2A$

then  $\frac{2z_1}{a} = 1 - \cos 2by_1$

or  $\cos 2by_1 = \frac{a - 2z_1}{a}$  (4)

From (3)  $\sin^2 2by_1 = \frac{z_2}{a}$  (5)

Since  $\cos 2A = 1 - \sin^2 A$

then  $\cos^2 2by_1 = 1 - \sin^2 2by_1$

and from (4) and (5)  $\left(\frac{a - 2z_1}{a}\right)^2 = 1 - \frac{z_2}{a}$

Whence  $a = \frac{4z_1^2}{4z_1 - z_2}$  (6)

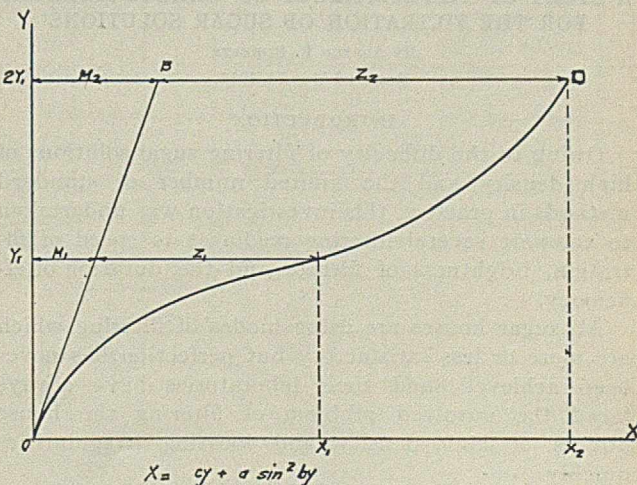
Since  $\cos^2 A = 1 - \sin^2 A$

From (2)  $\cos^2 by_1 = 1 - \frac{z_1}{a}$  (7)

From (6) and (7)  $\cos^2 by_1 = \frac{z_2}{4z_1}$  (8)

Whence  $by_1 = \cos^{-1} \sqrt{\frac{z_2}{4z_1}}$  (9)

That these terms are not so mysterious as they appear, becomes evident after an analysis of the above proof. Thus we find the constant "c" is dependent solely upon the initial resistance of the rubber to stretching; it will be largest for a pure gum stock and



become relatively smaller and smaller as the stock is more heavily compounded. From the relationship in Equation 6 we can readily see that in the case of a pure gum stock where the stretch is long and uniform, ( $m_1$ ) and ( $m_2$ ) having been large "a" will be relatively large, in comparison with a "tread" stock which will be strong and cause the entire curve to be fairly steep, but will be small in comparison with a "whiting stock," which is characterized by an initial stiffness after which it offers comparatively little resistance to stretching. Equation 9 shows that for pure gum or tread stocks  $\cos b$  will be small and "b" consequently large.

The ease with which these values could be standard-

ized in specifications for a given stock is apparent, and the value of such standards both from the point of the manufacturer and the buyer is obvious.

We have done some work in this laboratory to find how closely the curve computed from the equation agrees with the actual curve, of which the following example is typical: For our work we used the "Schwartz Rubber Testing Machine." Test specimens were cut from a "Goodyear" auto inner tube, and from curves drawn in testing these specimens we obtained constants which gave the equation:

$$x = 1.17y + 2.06 \sin^2 34.6y$$

Another tube made by the same formula was selected at random and a curve drawn from a sample of this tube. Assuming various values for  $y$ , the  $x$  to correspond was computed from the equation and compared with the same values as measured on the curve. The results were as follows:

$y$ Inches	$o$	$by$	$n$	$x$ (computed) Inches	$x$ (from curve) Inches	Diff. Inches
0.2	6	55		0.26	0.26	0.00
0.5	17	18		0.77	0.78	-0.01
1.0	34	36		1.84	1.86	-0.02
1.5	51	54		3.04	3.05	-0.01
2.0	69	12		4.14	4.08	+0.06
2.5	86	30		4.78	4.70	+0.08
3.0	76	12		5.26	5.17	+0.09
3.5	58	48		5.61	5.60	+0.01
4.0	41	36		5.71	..	....

These are actual measurements from the curve representing only arbitrary values for  $x$  and  $y$ .

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## A STUDY OF THE EFFICIENCY OF VARIOUS METHODS FOR THE FILTRATION OF SUGAR SOLUTIONS<sup>1</sup>

By ALFRED E. ROBERTS  
Received May 13, 1914

### INTRODUCTION

Owing to the difficulty of filtering sugar solutions of high density and the limited number of standard methods in practice, this investigation was undertaken to compare several filtering media as to speed of filtration, brightness of filtrate and the duration of efficiency.

All sugar houses are using modes of filtering which are more or less satisfactory but perfection has never been achieved, and their laboratories have always faced the unsolved problem of filtering the house liquors of high density and locating irregularities quickly.

The purpose of this work has been primarily to perfect a rapid filtration process for sugar laboratories and secondarily to improve house practice.

There is scarcely any literature on the subject, though some reference to different filtering media to be used on a large scale can be found.<sup>2</sup>

### EXPERIMENTAL

The materials used in this research were the three different grades of cloth commonly employed in sugar refineries which will be designated in this paper as

<sup>1</sup> A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science to the Faculty of the Graduate School of New York University.

<sup>2</sup> Noel Doerr, "Cane Sugar," p. 281.

thin bag, thick bag, close bag; alundum, white filter paper No. 597 Schleicher and Schull, Eimer and Amend's Best gray filter paper, 40-mesh sand, asbestos, Fuller's earth, infusorial earth and sawdust.

Suction and different hydrostatic pressures were considered and many modifications of apparatus were tried. The majority of the experiments, however, were conducted with a cylindrical tube  $1\frac{1}{2}$  inches in diameter, having a barrel 6 in. in length and a stem of 3 in. This special tube is represented in Fig. 1.

In nearly every case the tube was used in an upright position and at all times it was surrounded with a jacket of hair felt in order to maintain a comparatively constant temperature. That the temperature did not drop very low during short filtrations may be seen by referring to Fig. 2. In general, the solutions of sugar were about  $30^\circ$  Bé density, and before filtering the temperature was raised to  $180^\circ$  F. The cold apparatus caused the solutions to drop about  $20^\circ$  during the first 10 min. but after that time the temperature decreased very slowly. A more elaborate and efficient device could have been arranged, but complicated apparatus is undesirable for rapid work in a sugar laboratory.

During the preliminary experiments with the bag filters, it was found that greater speed of filtration could be procured by using a circular piece of wire gauze instead of a perforated porcelain plate to support the cloth; hence the apparatus adopted for the first series of filtrations was the cylindrical tube mentioned above with the wire gauze support in the bottom; resting on this was a cloth cut to fit the tube and this was held in position by a tight-fitting rubber gasket.

Each bag filter was tested as to rate of filtration of an undefecated solution, clearness being disregarded, and the typical results are herein recorded in Fig. 3. As would be expected from the weave and general

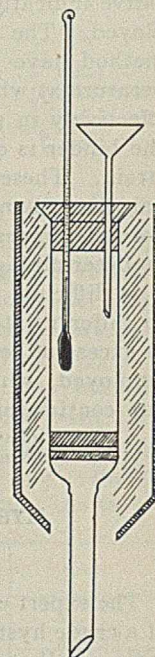


FIG. 1—SPECIAL TUBE FOR FILTRATION OF SUGAR SOLUTIONS OF HIGH DENSITY

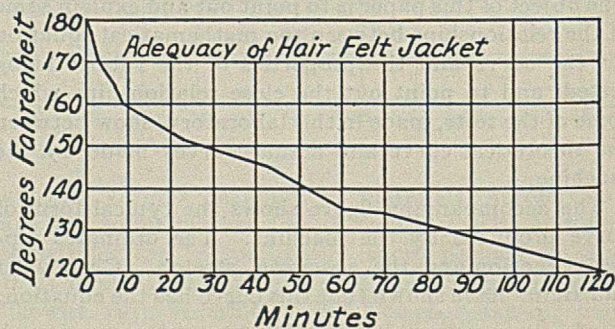


FIG. 2

texture of the cloth, the thin bag gave the highest rate of filtration, the thick bag second and the close bag third; the fact that the thin bag allowed 100 cc. to pass through in 7 min. suggested its adoption, while the



thick cloth permitted only about one-fifth and the close cloth one-tenth that amount to pass through in the same time.

These conditions were then modified in one respect. A thin bag filter attached to a wire was placed on the

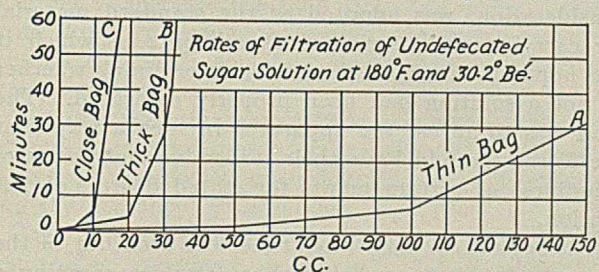


FIG. 3

fixed thin bag and as soon as the filtration became slow the upper cloth was removed. This modification hastened the process in a marked degree (Fig. 4) with the thin and thick cloth, but the action of the close bag was not sufficiently rapid to make it a competitor.

Tests with each of the filtering media proved that perfect clearness could not be obtained without defecation; hence, all solutions in subsequent experiments were defecated either with Horne's dry subacetate of lead or with bone-black paste neutralized with lime.

In determining the relative values of cloth, alundum, sand, asbestos, Fuller's earth, infusorial earth and sawdust, numerous filtrations were found necessary in order to perfect manipulation. The regular tube was used and the solutions were kept at a constant head of six inches while ascertaining the rates of filtration, the amounts possible to pass through the respective filters,

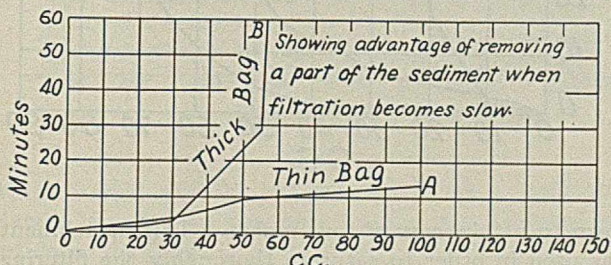


FIG. 4

and the clearness of filtration. Fuller's earth and infusorial earth could not be arranged in this form of apparatus to produce satisfactory results.

It is evident from the following table and Fig. 5 that the material used for defecation influences both the rate and duration of filtration. The time of 30 min. was chosen arbitrarily for the sake of uniformity in making comparisons.

RELATIVE RATES OF FILTRATION AND LIVES OF FILTERS			RELATIVE RATES OF FILTRATION AND LIVES OF FILTERS		
BONE-BLACK DEFECTION			LEAD SUBACETATE DEFECTION		
FILTER	Cc. in 30 min.	Relative life	FILTER	Cc. in 30 min.	Relative life
Sawdust.....	150	...	Thin bag.....	32.5	2.0
Asbestos.....	35	3.0	Asbestos.....	23	1.75
Thin bag.....	23	2.1	Thick bag.....	23	1.5
Sand.....	22.5	4.3	Close bag.....	20	1.5
Close bag.....	16	3.3	Sand.....	19	1.25
Thick bag.....	14	2.1	White paper.....	10.5	1.0
White paper.....	13	1.0	Alundum.....	10.5	1.0
Gray paper.....	11	1.7	Gray paper.....	9.5	1.0
Alundum.....	8	1.2			

As the solutions ceased to filter after prolonged intervals the mode of determining the relative lives of

the filters was to allow them to stand overnight and note the numbers of cc. which had passed through during that time. The numbers were simplified so that the least efficient filter is represented by unity.

A great deal of difficulty was experienced in determining the exact time of filtrates becoming clear. The only satisfactory device used was made by attaching to the stem of the filter tube a straight calcium chloride tube, the end of which was bent in such a way that the bulb was kept constantly full of liquor (see Fig. 6). By holding a magnifier over this bulb its contents could be examined for clearness. Time was counted from the instant solutions were poured upon the respective filters and the results were as follows:

	Min.		Min.
Thin bag, one thickness.....	17	Gray paper.....	6
Thin bag, two thicknesses(a).....	4	Asbestos.....	2
Thick bag.....	7	Sand.....	2
Close bag.....	4	Sawdust.....	3
Alundum.....	2	Fuller's earth.....	Never
White paper.....	3	Infusorial earth.....	Never

(a) Filtration was very slow, only 15 cc. passing through in 26 min.

In filtering with alundum a special disc was made to fit the standard tube and the same rubber gasket as

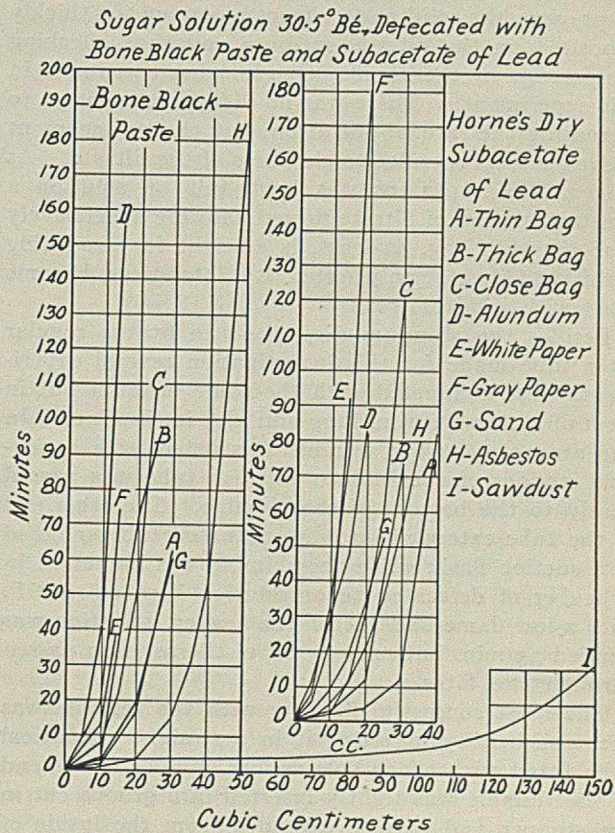


FIG. 5

was used with the cloth and paper filters was placed in close contact with it to prevent the solution from passing over the edge of the disc. The asbestos filter was prepared by first placing in the tube a porcelain filter plate; then a layer of washed asbestos of fine fiber was poured upon the plate to the thickness of one-eighth of an inch. The sand used was 40-mesh and the depth most satisfactory was 3 in. The sawdust filter was prepared by filling the tube loosely with the material and then packing tightly until the

depth was 4 in. The sawdust thus measured weighed 27 g. A small wad of glass wool was used in the stem of the tube to prevent sawdust from passing into the filtrate.

In order to hasten filtration, suction was employed with the different media, but in each case it was a failure because clearness was always destroyed by suction.

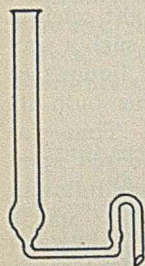


FIG. 6  
DEVICE FOR  
DETERMINING  
CLEARNESS OF  
FILTRATES

Favorable results, however, were obtained by increasing the height of the column of liquor. A marked increase in efficiency was demonstrated in the case of the thin bag by using 3 ft. hydrostatic pressure. Fig. 7 compares this medium with a head of six in. and 3 ft. and also in a Büchner funnel having a diam. of 5 in. It is evident at once that it is better to increase pressure than surface.

An attempt was made to hasten filtration through the thin bag by inverting the whole apparatus and operating it like the Danek filter. The object of this style of filtering is to prevent the solid matter from becoming too thickly deposited on the filtering medium and thus checking the passage of the liquid. One foot head was used in this experiment. There was no disappointment as to increasing the rate of filtration, but the arrangement proved a total sacrifice to clearness of the filtrate. As long as the apparatus was kept full of solution a constant stream of filtrate flowed showing conclusively that the thin bag, at least, is efficient for producing a bright filtrate only after its interstices become filled with solid matter.

Besides the alundum disc made to fit the regular filter tube made for this investigation several experiments were conducted with the same medium but in form of a thimble 4 in. long and 1 $\frac{1}{4}$  in. in diam. In one arrangement the thimble was fitted with a one-hole stopper of rubber into which a tube was passed nearly to the bottom of the thimble. The other end of the tube extended into a graduated tube enclosed in a suction flask, while the thimble was immersed in a beaker of defecated sugar solution kept at 180° F. with a low flame underneath the beaker. Suction was applied 35 min. but only 25 cc. of the solution passed through the filter.

The most successful filtering with the thimble was accomplished by inverting it in a straight cylindrical tube fitted with a one-hole rubber stopper. The end of the thimble was tightly inserted in a groove cut in the stopper and a tube extended from the inside of the thimble through the stopper and into a suction flask. Hair felt was used as a jacket to prevent too great a decrease in temperature. With this arrangement the following results were obtained:

SOLUTION 31° BAUMÉ, DEFEATED WITH LEAD 6 IN. HEAD					
Cc.	Min.	Cc.	Min.	Cc.	Min.
5	1	30	14	50	40
10	2	35	24	55	40
20	5	40	27	60	51
25	9	45	29	65	67

The filtrate was clear in 3 min. and, as nothing could be drawn through after 65 cc. were filtered, this amount represents the life of this size thimble under

these conditions. Owing to the fact that suction had been unsuccessful in previous experiments in producing a clear filtrate, the pump was not started until the solution began to come clear at the end of three min.

Sawdust, having surpassed all other media under consideration, was adopted as the standard material for carrying on a series of experiments in which it was hoped to arrange a device for determining whether or not a solution had been properly defecated. The plan was to adjust the apparatus in such a way that the filtrates would have their respective end-points of cloudiness at certain points for stated degrees of defecation.

The regular six-inch filter tube was used but in the top was fitted a one-hole rubber stopper carrying a funnel six inches in length, making a head of eight inches, and a tube was attached to the stem of the filter tube and bent upward to a level with the top surface of the sawdust which weighed 27 g. and was packed

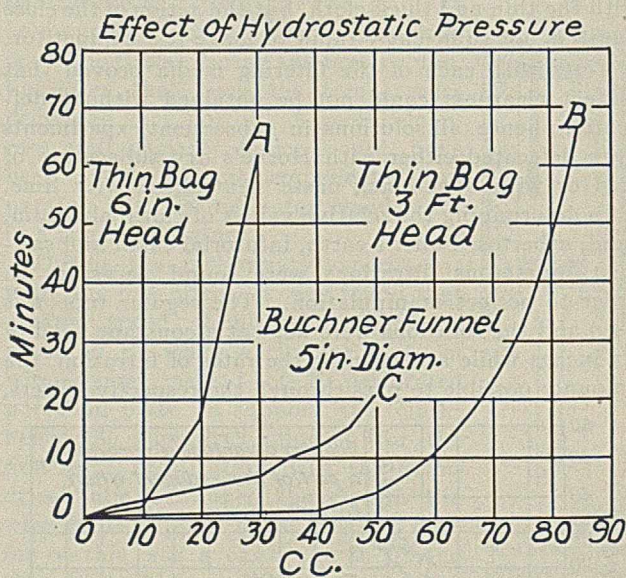


FIG. 7

down to a thickness of four inches. This attachment was used in order to saturate thoroughly the filtering medium and prevent channels before the drip commenced.

Perfectly defecated wash sugar liquor at 33° Baumé was poured into the apparatus and time was counted from the instant of the filtrate reaching the highest point in the outlet tube. A beautiful filtration ensued and would have been satisfactory for any purpose but the one in question. The filtrate being clear, from the first did not furnish a definite point of becoming clear, so the amount of sawdust was decreased one-half. Numerous filtrations were conducted on this basis and in each case the cloudiness disappeared after the first 15 cc. A 50 per cent defecated solution was prepared by mixing equal parts of a fully defecated wash sugar liquor at 32° Baumé and an undefecated wash sugar liquor at 34° Baumé. All filtrates with this solution became clear after 30 cc.

In filtering a 25 per cent defecated solution all filtrates with one exception became clear after 40 cc.; the irregular one cleared after 45 cc.

At this stage the apparatus was modified again. The filtering medium was cut down to six grams and the one-hole stopper was replaced by a two-hole stopper to provide for a tube provided with a pinchcock to be closed as soon as the air was expelled with solution. In order to increase the head and thus secure a more rapid rate of filtration the outlet tube was lowered as soon as the filtrate reached the highest point in the bend.

The first filtration under these conditions was with an undefecated solution. It was allowed to run over night and the filtrate never became clear, demonstrating the necessity of defecation.

Then a fully defecated solution was tried and the first 100 cc., requiring 15 min., was cloudy; after this, it ran clear. This result indicated that there was not a sufficient layer of sawdust, so the amount was increased to 10 g. and the outlet tube was left in place for the rate of filtration was too rapid with one foot head. With this arrangement a rapid and satisfactory filtration was secured, 40 cc. dropping in three minutes and after this the filtrate was clear. Several duplicates were run with the same results except for time,

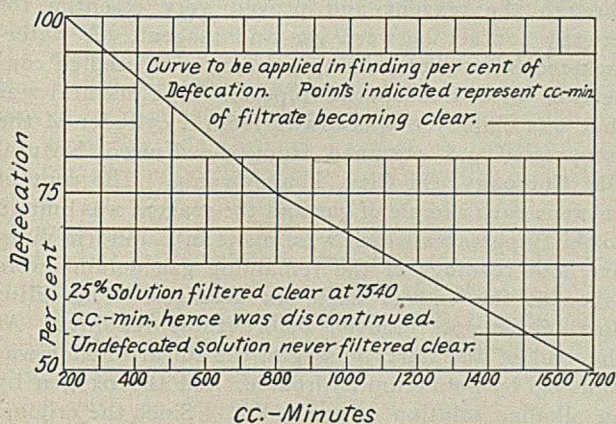


FIG. 8

which varied slightly but not much, as a Hofmann clamp attached to the outlet tube was adjusted to regulate the flow.

A 50 per cent defecated solution was filtered and the point of becoming clear varied from 60 to 100 cc. according to rate of filtration. A 75 per cent defecated solution behaved in the same way except that usually it became clear at about 60 cc. The 25 per cent defecated solution never filtered clear as long as observed. On careful consideration of both volume and time it was evident that clearness depended on a combination of the two, and hence in the concluding experiments the point of the filtrate becoming clear was expressed in "cc.-min." In all fully defecated solutions the filtrate ceased to be cloudy at about 200 cc.-min., the 75 per cent defecated at about 300 cc.-min., the 50 per cent defecated at about 1700 cc.-min., while the 25 per cent defecated solutions never produced a bright filtrate.

The liquors passing through the bag filters in the refinery required about 20 min. to become clear after defecation, while the same solutions became clear in the adopted laboratory filtering device in 3 min. This

relation of house to laboratory could be applied with advantage.

Fig. 8, plotted for this particular apparatus, indicates that the preconceived theory works out in practice, and thus the device can be applied in sugar laboratories to determine at once whether the house liquors are properly defecated.

The results of this investigation seem to prove that sugar refineries should adopt as the universal filtering medium sawdust or some closely allied material. This is confirmed by A. Aulard<sup>1</sup> in his paper on the "Use of Cellulose as a Filtering Substance in Sugar and Other Industries." Sawdust can be easily washed; it is very simple to use, needing no complicated presses, etc.; it is available and cheap; rapid filtration is assured and clear, bright liquors can be secured in a minimum time. The main problem would be in concentrating the increased volume of sweet water which would necessarily be produced in washing the sawdust.

## SUMMARY

- 1—Defecation is necessary with all filtering media.
- 2—Sawdust or some form of wood waste is the most satisfactory for obtaining rapid and clear filtration both for refineries and laboratories.
- 3—To hasten rate of filtration it is better to increase hydrostatic pressure than resort to suction, increased surface of filtering medium, or to invert the filter to keep it free from a deposit of solid matter.

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## THE ABSORPTION OF GASOLINE VAPOR IN NATURAL GAS BY FUMING SULFURIC ACID

By R. P. ANDERSON AND C. J. ENGELDER

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Orndorff and Young<sup>2</sup> apparently were the first to discover that propane is attacked by fuming sulfuric acid. Worstall<sup>3</sup> has investigated the sulfonation of hexane, heptane, and octane by fuming sulfuric acid and found that the reaction takes place readily at the boiling point of the hydrocarbon that was being used, but that cold fuming sulfuric acid is without apparent action on the liquid hydrocarbon. He found<sup>4</sup> also that methane and ethane are slowly absorbed by fuming sulfuric acid, the absorption being more rapid in the case of ethane than in the case of methane.

During the analysis in this laboratory of a sample of natural gas which carried a small amount of gasoline vapor, there was obtained a small decrease in volume (0.1 to 0.2 cc.) during the usual treatment with fuming sulfuric acid. Aside from this indication of the presence of olefines the gas appeared to contain only members of the paraffin group and a small amount of nitrogen. Combustions were made on gas which had been treated with fuming sulfuric acid and on untreated gas. The results of the combustions were figured as methane and ethane, the predominating hydrocarbons, and the untreated gas appeared to

<sup>1</sup> See original communication in *Eighth International Congress of Appl. Chem. (Appendix)* 21, 489-491.

<sup>2</sup> *Am. Chem. J.*, 15 (1893), 249.

<sup>3</sup> *Ibid.*, 20 (1898), 664.

<sup>4</sup> *J. Am. Chem. Soc.*, 21 (1899), 245.

contain more ethane and less methane than the treated gas. This could be explained by the assumption that the fuming sulfuric acid had absorbed some of the gasoline vapors, since the removal of a small amount of these vapors would lessen the apparent percentage of ethane as calculated from the results of a combustion. If this assumption is correct, longer treatment with the fuming sulfuric acid should result in a larger decrease in volume and a greater difference in the apparent amounts of methane and ethane before and after the treatment. Accordingly, a sample of gas was passed back and forth for fifteen minutes over fuming sulfuric acid that was contained in the customary pipette for this reagent. A decrease in volume of 2 cc. was obtained. The approximate results of the combustions that were made are shown below:

	Per cent CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	N <sub>2</sub>	Total
Before treatment with H <sub>2</sub> S <sub>2</sub> O <sub>7</sub> .....	72	27	1	100
After treatment with H <sub>2</sub> S <sub>2</sub> O <sub>7</sub> .....	75	21	2	98

The decrease of 2 cc. that was obtained after a more lengthy treatment with the reagent than is usually given indicates the absorption of gases or vapors other than those of the olefine group since the absorption under the customary conditions amounted to but 0.1 to 0.2 cc. The change in the relative amounts of methane and ethane as calculated from the results of the combustion indicates that the portion that was absorbed contained more gases or vapors of high molecular weight than the portion that remained. The average number of carbon atoms per molecule of hydrocarbon in the portion absorbed by the fuming sulfuric acid may be computed from the data at hand. For example:

Let  $m$  represent the number of molecules in 1 cc. of the gas, and  $x$  the average number of carbon atoms per molecule of hydrocarbon in the portion absorbed by the fuming sulfuric acid;

then  $72 m + 2 \times 27 m =$  the number of carbon atoms in 100 cc. of the original gas,

and  $75 m + 2 \times 21 m =$  the number of carbon atoms in the unabsorbed gas.

$72 m + 2 \times 27 m - 75 m - 2 \times 21 m = 9 m =$  the number of carbon atoms in the absorbed gas,

$$\text{and } x = \frac{9 m}{2 m} = 4.5.$$

The average number of hydrogen atoms per molecule of hydrocarbon may be computed in similar fashion and thus it appears that the gases removed by the fuming sulfuric acid had an average composition of C<sub>4.5</sub>H<sub>11</sub> while the untreated gas averaged C<sub>1.26</sub>H<sub>4.52</sub>.

To determine whether this behavior of the paraffin hydrocarbons toward fuming sulfuric acid might be made the basis of a method for the examination of natural gas for the presence of the higher hydrocarbons, gasoline vapors<sup>1</sup> in particular, the following experiments were performed.

#### BEHAVIOR OF REAGENT WITH REPEATED USE

The absorbing power of the reagent should remain practically constant when treated successively with

<sup>1</sup> For a discussion of the methods in use at the present time, see Burrell and Seibert, THIS JOURNAL, 5 (1913), 895; also Merriam and Birchby, *Ibid.*, 5 (1913), 824.

different portions of the same natural gas for the same time in order that reliable comparisons might easily be made between the amounts of gasoline vapors in different samples of natural gas. If the reagent should deteriorate rapidly on being used, comparable results could be obtained only with fresh reagent and the inconvenience and expense of its frequent renewal would be a serious drawback to its use.

The fuming sulfuric acid that was used in studying the behavior of the reagent with repeated use contained 30 per cent SO<sub>3</sub>, and was placed in an absorption pipette such as is used in the Dennis modification of the Orsat apparatus,<sup>1</sup> in order to effect as rapid an absorption as possible. The upper end of the reservoir chamber of the pipette was connected by means of a rubber stopper and glass tubing with a trap similar to the one used in the same modification of the Orsat apparatus to protect the reagents from the air. In this case, the trap was filled with sulfuric acid and the space between the reagent in the pipette and the sulfuric acid in the trap was filled with natural gas at the beginning of the experiments. This arrangement decreased considerably the interchange of gas and air through the reagent and proved very essential for lengthy contact between gas and reagent. A water-jacketed burette containing mercury was used in connection with this special pipette. The natural gas that was employed was drawn from a cylinder of the compressed gas obtained from the United Natural Gas Company, Oil City, Pennsylvania. The contact between each sample of gas and the reagent was limited to thirty passages which were made in a uniform manner, and readings of the remaining gas volume were taken at the end of each six passages. The sulfur dioxide was not removed before these readings. At the end of the thirty passages, the sulfur dioxide was removed by potassium hydroxide, and the oxygen by an alkaline solution of pyrogallol. Since the original gas contained practically no oxygen the decrease that was obtained on the last absorption served as a measure of the interchange of natural gas and air through the reagent in the pipette and the sulfuric acid in the trap during the absorption. Combustions were performed on two separate portions of each residue and the results were computed as methane, ethane and nitrogen. The results obtained are shown in Table I.

Number of sample	1	2	3	4	5	6-10
Volume after 6 passages.....	3.5	1.9	1.4	1.3	1.0	0.9
Volume after 12 passages.....	5.8	3.6	2.8	2.4	1.9	1.8
Volume after 18 passages.....	7.5	5.0	3.8	3.5	2.9	2.7
Volume after 24 passages.....	9.1	6.3	4.8	4.5	3.7	3.6
Volume after 30 passages.....	10.5	7.1	5.7	5.7	4.6	4.5
Volume after KOH.....	10.8	7.5	6.1	6.2	5.5	5.5
Volume after Pyro.....	12.0	8.1	7.5	6.8	6.1	5.8
Per cent CH <sub>4</sub> .....	72.7	79.1	76.4	79.3	76.7	78.1
Per cent C <sub>2</sub> H <sub>6</sub> .....	11.8	11.8	12.3	12.4	15.3	14.7
Per cent N <sub>2</sub> .....	3.5	1.0	3.8	1.5	1.9	1.4
Carbon atoms per molecule in portion absorbed.....	2.70	3.04	4.01	3.45	3.31	3.30

The first five columns of figures in the above table contain the readings that were made during the absorptions on the first five samples, as the numbers at the top indicate. In general, the amount absorbed at the end of each six passages and after the removal of SO<sub>2</sub> decreased with each successive sample

<sup>1</sup> See Dennis, "Gas Analysis," p. 86.

up to the fifth. From the fifth sample to the tenth the reagent gave approximately uniform results and the average of the various corresponding readings from runs six to ten inclusive is given in the last column. The lack of uniformity in the readings that were obtained from the first four samples may, no doubt, be largely accounted for by the solubility in the reagent of the various constituents of the natural gas. After proper preliminary treatment, however, there seems to be no reason why this reagent should not be used for making reliable absorptions for the comparison of different samples of natural gas.

The average number of carbon atoms per molecule in the portion absorbed from each gas sample was computed from the composition of the residue and that of the original gas, which was found to be  $\text{CH}_4$ —74.1 per cent,  $\text{C}_2\text{H}_6$ —25.7 per cent, and  $\text{N}_2$ —0.2 per cent.

#### BEHAVIOR OF REAGENT TOWARD INDIVIDUAL PARAFFIN HYDROCARBONS

The assumption that gasoline vapors are more easily attacked by fuming sulfuric acid than the lower members of the paraffin series, such as methane and propane, seems to have been substantiated by the experiments that have just been described. It was found also that gasoline vapor was rapidly removed by fuming sulfuric acid from samples prepared by aspirating air through gasoline, a mixture containing 18.6 cc. of gasoline vapor showing a decrease of 10.6 cc. after 6 passages, 13.1 cc. after 12, 14.4 cc. after 18, and 15.6 cc. after 30 passages. These readings were made without the removal of fumes of sulfur dioxide. After 30 passages the gas was passed into a pipette containing potassium hydroxide and a further decrease of 1.9 cc. was obtained, giving a total absorption of 17.5 cc. for 30 passages. Thirty passages with nearly pure methane resulted in a decrease of about 2.0 cc. and with nearly pure ethane, a decrease of about 8.0 cc. was obtained for the same number of passages.

It is not possible, however, to obtain an accurate idea of the relative ease of attack of the different hydrocarbons by fuming sulfuric acid from the previous experiments since the various gases have not been dealt with in the pure condition, and the effect of the partial pressure of each constituent of a mixture upon the speed of its absorption must be taken into account. To obtain comparable data concerning the behavior of the reagent toward the individual paraffin hydrocarbons up to and including heptane in the paraffin series, an apparatus was devised in which all of the necessary operations might be effected at a temperature above the boiling point of heptane, 98.4° C.

A two-way stopcock was joined to the top of an old-style Orsat pipette and this modified pipette was connected to the tip of a jacketed Hempel burette by means of a twice bent capillary tube with a horizontal portion about 10 cm. long. A capillary side-arm carrying a stopcock was blown into the upright portion of the capillary tube a short distance above the top of the burette. The jacket of the burette was filled

with paraffin oil. The burette and the capillary tube that connected it with the pipette were heated to the desired temperature by passing an electric current through a resistance wire that was wound around the jacket and around the capillary tube over to the stopcock above the pipette. The pipette was housed in an asbestos oven with a sheet iron bottom and was heated by a Bunsen flame. The handle of the stopcock was passed through a small opening in the side wall of the oven so that it could be turned without disturbing the heating of the pipette.

In using the apparatus with liquid hydrocarbons, a small volume of a strong solution of potassium hydroxide was drawn in over the mercury which was employed in the burette, to effect the absorption of  $\text{SO}_2$  and  $\text{SO}_3$  which form a part of the gas mixture when it is drawn back into the burette. A small amount of the liquid hydrocarbon was next drawn in over the alkali and the temperature of the entire apparatus was then raised to about 120° C. The volume of gas that was formed by the complete conversion of the liquid hydrocarbon to the gaseous state was next read, the atmospheric pressure and the temperature of the paraffin oil in the jacket being noted at the same time, and the absorption was effected in the usual fashion by passing the gas back and forth from burette to pipette. Sufficient time must be allowed to elapse for the complete absorption of the  $\text{SO}_2$  and  $\text{SO}_3$  before the reading of the remaining volume is made, especially in the case of  $\text{SO}_3$  which is evolved in large quantities by the heating of the fuming sulfuric acid.

**ABSORPTION OF HEPTANE**—Two passages of a sample of heptane gas with a three-minute contact for each passage sufficed for the practically complete absorption of this hydrocarbon by fuming sulfuric acid. The small amount of residual gas did not disappear on cooling to room temperature and was probably air that had diffused through the reagent.

**ABSORPTION OF HEXANE, PENTANE AND ETHANE**—Thirty passages of a sample of hexane gas with an additional three-minute contact every six passages resulted in a decrease in volume of approximately 50 per cent. For pentane, the absorption under the same conditions amounted to approximately 35 per cent and for ethane, approximately 10 per cent.

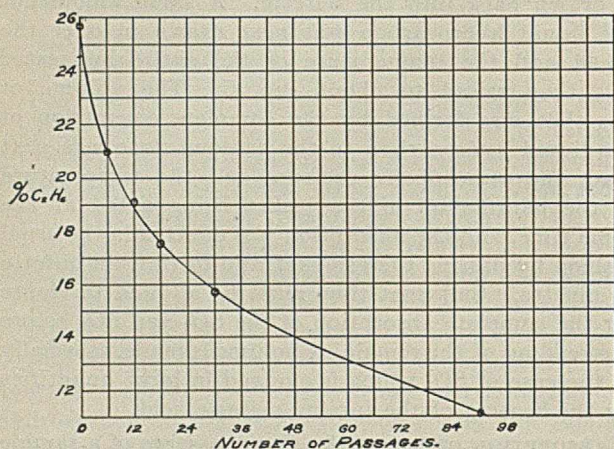
#### EFFECT OF TIME OF ABSORPTION UPON COMPOSITION OF RESIDUE

To determine the effect of the time of absorption upon the composition of the unabsorbed portion, different samples of the same natural gas were treated with fuming sulfuric acid for 6, 12, 18, and 90 times, respectively. Combustions were made on the residues and the results were computed to give apparent percentages of methane and ethane on the basis of the volume of the residue as the total volume. The percentages of ethane that were thus obtained were plotted against the number of passages as shown in the accompanying curve. The value used for 30 passages is the average of runs 4–10 from Table I.

The change in the composition of a sample of natural gas bearing gasoline vapors upon treatment with

fuming sulfuric acid is not proportional to the time of contact. This is to be expected when one considers the relatively small amount of gasoline vapors ordinarily present in samples of natural gas. In the case of the natural gas from which the data for the preceding curve were obtained, the change in composition obtained by 30 passages represents more than two-thirds that produced by 90 passages, and while this particular natural gas is not especially productive of gasoline, undoubtedly 30 passages of any sample of natural gas into fuming sulfuric acid would be sufficient to give data for the amount of gasoline vapor it carries.

COMPARISON OF RESIDUES AFTER TREATMENT WITH  $H_2S_2O_7$  AND AFTER REMOVAL OF GASOLINE ON A COMMERCIAL SCALE—In order to determine the usefulness



of the treatment of a sample of natural gas with fuming sulfuric acid as regards its availability for the production of gasoline, samples of natural gas were obtained from before and after the compressor at points where gasoline is being extracted from natural gas. These samples were analyzed and a portion of the sample from which the gasoline vapor had not been removed was treated with fuming sulfuric acid for 30 passages in the manner previously described, and then analyzed. The results that were obtained are shown in the following table:

Per cent	Natural gas I				Natural gas II				
	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	O <sub>2</sub>	N <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	O <sub>2</sub>	N <sub>2</sub>
Before compressor.....	58.9	40.0	0.0	1.1	41.5	21.8	7.6	29.1	
After compressor.....	71.3	27.2	0.0	1.5	27.7	29.1	..	..	43.2
After treatment with $H_2S_2O_7$ .....	78.0	18.3	0.9	2.8	25.4	23.4	..	11.0	40.2

Thirty passages through fuming sulfuric acid caused a decrease in volume of 9.8 per cent in natural gas I, and 30.0 per cent in natural gas II; the yield of gasoline was about 1 gallon 90° B. per 1000 cu. ft. from natural gas I, and about 5 gallons 97° B. per 1000 cu. ft. from natural gas II. In spite of the pronounced dissimilarity of the two samples, there seems to be a rather close agreement in the composition of the residues obtained by the commercial treatment of natural gas for the production of gasoline and by treatment of the natural gas with fuming sulfuric acid for thirty passages.

## SUMMARY

1—Fuming sulfuric acid exerts an appreciable absorbing action on certain samples of natural gas, the absorption increasing with the amount of gasoline vapors which the natural gas carries.

2—The average number of carbon and hydrogen atoms per molecule of hydrocarbon absorbed by fuming sulfuric acid (and thus the average molecular weight of the hydrocarbons) may be computed from the composition of the gas before and after absorption and from the decrease in volume that is obtained.

3—Application of this reagent to the study of natural gases for the production of gasoline may be made by determining the absorption under certain uniform conditions. It is desirable, however, to determine also the composition of the portion that is absorbed as a check upon the indications obtained by the decrease in volume.

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## THE DETERMINATION OF HYDROGEN IN GAS MIXTURES BY MEANS OF COLLOIDAL PALLADIUM

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In this paper are reported results obtained by the authors, having to do with the use of a solution of sodium picrate and colloidal palladium for determining hydrogen in gas mixtures. Paal and Hartman<sup>1</sup> originated the method. Brunck<sup>2</sup> made an examination of it and recommended it.

In some of the authors' experiments the solution was prepared according to the direction of Paal and Hartman, as follows: 2 g. of sodium picrate and 2 g. of colloidal palladium were dissolved in 100 cc. of water. In other experiments the solution was prepared according to Brunck. He first makes a normal solution of sodium carbonate and neutralizes 5 g. of picric acid with 22 cc. of the solution, thereby producing about 5.6 g. of sodium picrate. He then dilutes the solution to 100 cc. with water and adds 2 g. of colloidal palladium. The life of the solution depends upon the presence of the unchanged reducible substance, the sodium picrate; hence by Brunck's method there is obtained a solution containing more sodium picrate and therefore of longer life. Colloidal palladium itself absorbs large volumes of hydrogen, but if used in the concentrated form it is costly. In the presence of an easily reducible substance, like sodium picrate, it acts only as a catalyst.

The solution is regenerated, after it has lost its absorbing power, as follows: The reagent is transferred from the gas pipette to a flask and much diluted sulfuric acid is added drop by drop to the solution so long as a precipitate results. A large excess of sulfuric acid is avoided because it might cause the colloidal palladium to change to the sulfate through the action of atmospheric oxygen. The precipitate is washed with water, which, although it may dissolve in some of the acid, carries no palladium into solution. The precipitate is then suspended in a small quantity of water and is

<sup>1</sup> Paal, C., and Hartman, W., "Gas Volumetric Determination of Hydrogen by Catalytic Absorption," *Ber. deutsch. chem. Gesell.*, **43** (1910), 243.

<sup>2</sup> Brunck, O., "Estimation of Hydrogen in Gas Mixtures," *Chem. Zeit.*, **1910**, No. 34, pp. 1313-1314, 1331-1332.

dissolved by adding sodium hydroxide drop by drop. Fresh sodium picrate is then added and the solution diluted with water to its original volume of about 100 cc. It is then again ready for use.

For use the authors place the reagent in an ordinary Orsat pipette filled with glass tubes and bring the gas mixture in contact with it by passing it back and forth between the pipette and gas burette until absorption is complete. The following table shows the results obtained when prepared mixtures of hydrogen and air were analyzed for their hydrogen content by means of the palladium solution:

RESULTS OF ANALYSES OF HYDROGEN-AIR MIXTURES

Sample No.	PER CENT HYDROGEN BY	
	Combustion in oxygen	Absorption in Pd solution
1	0.8	0.8
	0.8	0.8
		0.8
2	3.8	3.9
	3.9	3.9
3	28.2	28.3
	28.2	28.3
		28.2
4	28.5	28.2
	28.6	28.6
		28.6

The following analyses show the results obtained in analyzing the coal gas in Pittsburgh: By one method the carbon dioxide, illuminants, oxygen and carbon monoxide were removed by means of the usual absorbents, and the methane and hydrogen burned with oxygen in the slow-combustion pipette. By another method the carbon dioxide, illuminants, oxygen, and carbon monoxide were removed and then the hydrogen absorbed by the colloidal-palladium solution; the residual gas, methane and ethane were next burned in the slow-combustion pipette. In both cases nitrogen was estimated by difference. The second column shows the results obtained by the first method; the third column shows the results obtained by the second method; and the fourth column shows the results of the second column recalculated so as to make allowance for the ethane as determined by the second method. The third and fourth columns should correspond.

ANALYSES OF THE COAL GAS OF PITTSBURGH (a)

CONSTITUENTS	Without hydrogen absorption	With hydrogen absorption	Recalculated from Column 1 to include the ethane
CO <sub>2</sub> .....	2.4	2.3	2.4
Illuminants.....	8.7	8.7	8.7
O <sub>2</sub> .....	0.5	0.5	0.5
CO.....	11.8	11.4	11.8
CH <sub>4</sub> .....	37.5	35.0	35.3
C <sub>2</sub> H <sub>6</sub> .....		1.1	1.1
H <sub>2</sub> .....	35.3	35.8	36.4
N <sub>2</sub> .....	3.8	5.2	3.8
Total.....	100.0	100.0	100.0

(a) The analysis was made over one year ago and is slightly different from some analyses of the Pittsburg gas made recently.

Although the hydrogen results should correspond in Columns 2 and 3, the agreement is only fair.

There are given below other analyses made by the Bureau of Mines. In one column are shown analyses in which the hydrogen and methane were determined together by burning them with oxygen (indicated by *a*). In another column are shown the results obtained by absorbing the hydrogen with colloidal-palladium solution and then burning the methane in oxygen (indicated by *b*).

ANALYSES OF GAS MIXTURES BY TWO DIFFERENT METHODS

No.	Method	CO <sub>2</sub>	Ill.	O <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	N <sub>2</sub>
5118	<i>a</i>	10.3	0.3	3.4	5.6	3.0	1.4	0.0	By difference
	<i>b</i>	10.6	0.2	3.5	5.6	3.0	1.5	0.0	
5093	<i>a</i>	7.5	0.1	7.4	5.2	2.9	1.2	0.0	
	<i>b</i>	7.4	0.3	7.7	5.6	3.0	1.1	0.0	
5052	<i>a</i>	9.6	0.5	1.0	9.7	5.3	2.3	0.0	
	<i>b</i>	9.6	0.6	1.1	9.5	5.6	2.4	0.0	
4862	<i>a</i>	9.0	0.2	6.4	5.1	2.2	1.2	0.0	
	<i>b</i>	9.0	0.2	6.6	5.2	2.4	1.3	0.0	
4837	<i>a</i>	8.2	0.6	6.6	5.2	3.0	1.0	0.0	
	<i>b</i>	8.1	0.6	6.4	5.4	3.3	1.2	0.0	
4725	<i>a</i>	5.3	0.0	12.1	3.6	1.5	0.8	0.0	
	<i>b</i>	5.5	0.0	12.0	3.3	1.7	0.7	0.0	

The above samples were collected in the experimental mine of the Bureau at Bruceton, Pa. They were automatically trapped in a special sampling device as the flame of an explosion traversed the entries of the mine.

The following sample was taken from the exhaust of a gasoline mine locomotive: A large number of these samples were gathered to study the composition of the exhaust gases under different conditions of usage of the motor. It should be added that this sample was collected under particularly bad conditions of motor usage. The analysis marked *a* was made by absorbing the carbon dioxide in caustic-potash solution, the illuminants in bromine water, the oxygen in alkaline pyrogallate solution, and the carbon monoxide in ammoniacal cuprous-chloride solution; the methane and hydrogen were then determined by burning in oxygen and the nitrogen estimated by difference. The analysis marked *b* was made in the same manner except that after the other absorbable gases had been removed the hydrogen was absorbed by colloidal palladium and the methane burned in oxygen.

ANALYSES OF EXHAUST GASES OF A GASOLINE MINE LOCOMOTIVE

No.	Method	CO <sub>2</sub>	Ill.	O <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	N <sub>2</sub>
4280	<i>a</i>	5.9	0.3	1.0	13.3	8.7	0.8	0.0	70.0
	<i>b</i>	5.9	0.2	0.8	13.1	8.6	0.8	0.0	70.6

In the analysis of complex mixtures Paal and Hartman recommend that carbon dioxide, unsaturated hydrocarbons, oxygen and carbon monoxide be first removed before absorbing the hydrogen by the palladium solution. They state that carbon monoxide seems to retard the catalytic effect in that it slows the reaction. They say that oxygen must be removed because oxygen and hydrogen combine in the presence of the palladium and they found that ethylene and hydrogen form ethane in the presence of the palladium solution, and that even if unsaturated hydrocarbons be absent, or present only in negligible quantities, the gas mixture must be treated with bromine water, as such treatment frees the mixture of possible traces of sulfur, phosphorus and arsenic compounds, which, even in traces, retard the catalytic effect.

A solution which the authors of this paper prepared removed 11.3 cc. of hydrogen per cc. of solution before it became too sluggish to use. Theoretically, 1 cc. of the solution should absorb about 40 cc. of hydrogen. Long before this theoretical quantity is obtained, however, the solution becomes sluggish in its action. In analyzing mixtures of hydrogen and air prepared in the laboratory it was found that from 6 to 25 minutes were required to remove the hydrogen from mixtures containing from 0.8 to 30 per cent. To remove the hydrogen from coal gas, exhaust gases from gasoline locomotives, and from

gases collected during explosions in mines, a maximum of 30 minutes was required. All determinations were made by simply passing the gas mixture back and forth into an Orsat pipette containing the solution and provided with glass tubes. The removal of the hydrogen probably should be performed faster if the latter were shaken with the reagent as in a Hempel pipette. The colloidal palladium was obtained by the Bureau from Kalle & Company, Germany: 6 g. cost \$15.84.

In the authors' opinion the advantage of the method over the use of palladium asbestos or palladium sponge is in the fact that it never fails in the authors' experience to work satisfactorily—something that, in the authors' experience, cannot be said regarding the use of the former substances.<sup>1</sup> In addition, it can be placed in an ordinary pipette of a gas-analysis apparatus and does not have to be heated in order to excite it to action. Its disadvantage lies in its slowness of action and the somewhat troublesome method of regeneration of the used material.

Hempel<sup>2</sup> states that the solution slowly loses its absorbing power even in the dark. He recommends that for each analysis small quantities of the freshly prepared liquid be used over mercury. The authors, however, have in satisfactory use at the present time one solution that was prepared in January of this year. The pipette has been surrounded with black paper.

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## IODINE NUMBER OF LINSEED AND PETROLEUM OILS<sup>3</sup>

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The linseed oil used in the manufacture of printing ink is of the so-called "burnt" type. There are two general processes for its manufacture—one in which the oil is heated until the vapors take fire and continue to burn, the oil being allowed to burn until it attains the desired viscosity; and a second in which the oil is heated without permitting it to take fire.

Burnt oil is prepared in several grades, all differing from the raw oil in an increase of viscosity, specific gravity, and acid number, and a decrease in the iodine number. The longer the oil is heated the greater these differences become.

In the determination of the iodine value of some burnt linseed oils difficulty was experienced in obtaining concordant results. Leeds<sup>4</sup> has published some figures for iodine absorption of lithographic oils. Kitt<sup>5</sup> has also published a series of results which show decrease in iodine absorption with increasing viscosity, but the figures do not agree with those given by Leeds; their determinations were made according to the Hübl method.<sup>6</sup> In recent years this method has been so generally replaced by the rapid and more convenient

<sup>1</sup> G. B. Taylor states, however, that the colloidal palladium solution does not work satisfactorily on gases obtained by distilling coal at low temperatures. See THIS JOURNAL, Oct., 1914, p. 845.

<sup>2</sup> Hempel, Walther, "Contribution to the Determination of Hydrogen and Methane in Gas Mixtures," *Z. angew. Chem.*, **25** (1912), 1841.

<sup>3</sup> Published by permission of the Director of the Bureau of Standards.

<sup>4</sup> *J. Soc. Chem. Ind.*, **13** (1894), 203.

<sup>5</sup> *Chem. Rev. Fett. u. Harz Ind.*, **8** (1901), 40; *J. Soc. Chem. Ind.*, **20** (1901), 40.

<sup>6</sup> *Dingler's Poly. J.*, **253**, p. 281; *J. Soc. Chem. Ind.*, **3** (1884), 641.

Hanus<sup>1</sup> method that it was considered desirable to learn the values afforded by this method. Preliminary work showed that small variations in the method employed produced varying results. It has been well established that iodine absorption includes not only the halogen taken up by unsaturated compounds, but that the substitution of halogen for hydrogen with the formation of halogen acid occurs simultaneously. Various methods for determining the amount of substitution have been suggested, with the view of obtaining a corrected value which would represent the addition only, but very little use has been made of them. It has been generally recognized that an excess of iodine is necessary, and it has been assumed that all oils are alike in the amount of excess required. The appended results obtained by us show that this is far from being true. Various quantities of iodine have been suggested as the proper excess which should be present, but practically all of these are given in connection with discussions of the Hübl method, and may not hold true for the Hanus method. Furthermore, there has been a lack of uniformity in the use of the term "excess of iodine." In the following tables this expression is used to mean that percentage of the total amount added which remains unchanged at the expiration of the time allowed for absorption.

### PROCEDURE

The method employed was essentially the modification of the Hanus method suggested by Hunt.<sup>2</sup> Thirteen and two-tenths grams of iodine were dissolved in 1 liter of glacial acetic acid (99.9 per cent), and 3 cc. of bromine added. This solution was always allowed to stand for some days before being used. The thio-sulfate solution employed was approximately tenth normal, and was standardized by means of potassium bichromate. Standardization was repeated at frequent intervals. A freshly prepared starch solution was used; also a 10 per cent solution of potassium iodide, prepared in small amounts and kept in a brown bottle. The temperature of the room was maintained at 25° C. to prevent variations caused by change of temperature. The reagents were of standard quality and errors caused by impurities were eliminated by running blanks with each series of determinations. When it was desired to use like amounts of an oil in a series of tests, 4 g. of the oil were dissolved in chloroform in a 200 cc. graduated flask and the solution allowed to reach room temperature. Ten cc. portions of this solution, representing 0.2 g. of oil, were measured from a burette. The general procedure was as follows: The exact weight of oil was transferred to 250 to 300 cc. glass-stoppered Jena bottles; the required amount of Hanus solution was added from a burette. The mixture was allowed to stand for exactly 30 minutes in a dark closet; 25 cc. of the 10 per cent potassium iodide solution and 100 cc. of water<sup>3</sup> were added,<sup>4</sup> and the excess of iodine was immediately titrated with thio-sulfate.

<sup>1</sup> *Z. Untersuch. Nahr. Genussm.*, **20** (1901), 913; *J. Soc. Chem. Ind.*, **20** (1901), 1246.

<sup>2</sup> *J. Soc. Chem. Ind.*, **21** (1902), 454.

<sup>3</sup> Tolman and Munson, *J. Am. Chem. Soc.*, **25** (1903), 244.

<sup>4</sup> Gill, "Oil Analysis," 6th ed., p. 62, footnote.



The factors known to influence the iodine number are the temperature, the time of absorption, the weight of oil taken, and the excess of iodine present obtained by increasing the amount of iodine solution. The exact effect of each factor was studied by varying one at a time, this procedure being followed with a series of oils.

#### SAMPLES

The samples employed were as follows:

I—A raw linseed oil, Sample No. 3, of the four linseed oils tested by the American Society for Testing Materials<sup>1</sup> in 1909. This sample had been hermetically sealed, immediately upon completion of the tests in 1909, and had been kept in a cool, dark closet.

II—A boiled oil of the so-called "bung-hole" variety.

III—Four burnt linseed oils, Nos. 00, 1, 3, and 5. These oils were obtained from northwestern seed and, after refining, were heated in copper kettles at a temperature of 560 to 600° F., until the desired consistency was attained.

IV—Three petroleum oils. Two of these, marked Light Oil No. 1 and No. 2, were automobile cylinder oils, and the third was an engine oil. Upon analysis these oils gave the following figures:

	B. S. eng.	Light No. 1	Light No. 2
Flash.....	175°	220°	230°
Fire.....	210	265	280
Sp. gr. 20°/4°.....	0.9260	0.8738	0.9265
Carbonization (3 hrs. at 250°), per cent.....	1.01	0.11	0.23
Oxygen absorp. 144½ hrs., per cent.....	1.60	1.91	1.90
Original acidity (mg. KOH, per g.).....	0.70	0.08	0.17
Acidity after exposure.....	13.52	14.39	13.83
Increase in acidity.....	12.82	14.31	13.66

The other constants of the samples were not determined, as they have no bearing on the present problem.

#### DISCUSSION OF RESULTS

Table I, the results of which are plotted in Figs. 1 and 2, shows the difference in behavior of the various linseed oils when the amount of iodine solution added is kept constant and the weight of oil is varied. Fig. 1 shows the change in iodine number with increasing amounts of oil. The curves in Fig. 2 have been calculated from the data given in Table I to represent the change in iodine number with a decrease in the excess of iodine present. It will be of interest to compare these curves with those in Fig. 3. The striking point in this connection is the range in weight of oil over which the iodine number is constant in the raw and boiled oils, as compared with that of the burnt oils. It will be seen that, contrary to the general opinion, the oil with the highest iodine number does not require the largest excess of iodine to reach a maximum absorption value. It is not desirable to work with less than 0.1 g. of oil, because of the difficulty in obtaining constant values. Between 0.1 and 0.2 g. small variations in weight are negligible in raw and boiled oils, but are important in the burnt oils.

It is apparent that substitution plays an important part in the reaction, and we shall refer to this point later on.

<sup>1</sup> See report of Committee E on Preservative Coatings for Structural Materials, Proceedings of the A. S. T. M., 9 (1909), 184; analyses by J. B. Tuttle. Another sample of this same oil was also tested in 1911, results of which are given in report of Subcommittee E of Committee D-1, Proceedings of the A. S. T. M., 11 (1911), 23-30.

TABLE I—LINSEED OIL—WEIGHT OF OIL VARIED  
Temperature—25° C.; Time—30 minutes; Hanus solution—25 cc.

Grams oil	Grams Ad-ded	Iodine Ab-sorbed	Iodine No.	Average	Grams oil	Grams Ad-ded	Iodine Ab-sorbed	Iodine No.	Average
A—RAW OIL					B—BOILED OIL				
0.0522	0.6669	0.0962	184.3	...	0.0600	0.6902	0.1066	177.6	...
0.0522	0.6669	0.0970	185.8	...	0.1181	0.6902	0.2102	178.0	...
0.0522	0.6669	0.0967	185.3	185.1	0.1322	0.6902	0.2355	178.3	...
0.1044	0.6669	0.1940	185.8	...	0.1673	0.6902	0.2984	178.3	...
0.1044	0.6669	0.1935	187.3	...	0.2061	0.6902	0.3682	178.5	...
0.1044	0.6669	0.1949	186.7	186.6	0.2220	0.6902	0.3962	178.4	...
0.1566	0.6669	0.2912	186.0	...	0.2523	0.6902	0.4438	175.7	...
0.1566	0.6669	0.2906	185.6	...	0.2783	0.6902	0.4837	173.7	...
0.1514	0.6669	0.2844	187.8	186.5	0.2920	0.6902	0.4976	170.4	...
0.2004	0.6669	0.3735	186.4	...	0.3217	0.6902	0.5250	163.2	...
0.2004	0.6669	0.3746	186.4	186.4	0.3328	0.6902	0.5346	160.6	...
0.2504	0.6669	0.4543	181.5	...	0.3583	0.6902	0.5518	154.0	...
0.2504	0.6669	0.4572	182.6	182.1	0.3874	0.6902	0.5744	148.2	...
0.3027	0.6669	0.5098	168.4	...	0.3969	0.6902	0.5848	147.4	...
0.3027	0.6669	0.5098	168.4	168.4	0.5550	0.6902	0.6344	114.0	...
0.4542	0.6669	0.5869	129.2	...	D—BURNT LINSEED OIL NO. 1				
0.4542	0.6669	0.5888	129.6	129.4	0.0880	0.6787	0.1220	138.6	138.6
0.5008	0.6669	0.6071	121.2	...	0.1891	0.6787	0.2480	131.1	...
0.5008	0.6669	0.6103	121.9	121.5	0.1917	0.6787	0.2512	131.0	131.0
0.6054	0.6669	0.6091	100.6	100.6	0.2856	0.6787	0.3310	115.9	115.9
0.8013	0.6669	0.6191	77.3	77.3	0.3577	0.6787	0.3788	105.9	...
C—BURNT LINSEED OIL NO. 00					0.3595	0.6787	0.3796	105.6	105.8
0.1235	0.6811	0.1827	148.0	...	0.4377	0.6787	0.4195	95.8	95.8
0.1268	0.6811	0.1882	148.4	148.2	0.5853	0.6787	0.4753	81.2	81.2
0.1465	0.6811	0.2154	147.0	...	F—BURNT LINSEED OIL NO. 5				
0.1842	0.6811	0.2616	142.0	...	0.0517	0.5874	0.0671	130.0	...
0.1863	0.6811	0.2632	141.3	141.7	0.0517	0.5874	0.0668	129.2	...
0.2539	0.6779	0.3401	133.0	...	0.0517	0.5874	0.0682	131.9	130.4
0.2506	0.6779	0.3297	131.6	132.3	0.1034	0.5874	0.1336	129.2	...
0.3489	0.6779	0.4128	118.3	...	0.1034	0.5874	0.1329	128.5	...
0.3562	0.6779	0.4171	117.1	117.7	0.1034	0.5874	0.1325	128.1	128.6
0.4490	0.6779	0.4658	103.7	...	0.1551	0.5874	0.1858	119.8	...
0.4497	0.6779	0.4658	103.6	103.6	0.1551	0.5874	0.1858	119.8	119.8
0.6058	0.6779	0.5216	86.1	86.1	0.2054	0.5860	0.2213	107.7	...
0.7831	0.6779	0.5583	71.3	71.3	0.2054	0.5860	0.2234	108.8	108.3
E—BURNT LINSEED OIL NO. 3					0.2423	0.5870	0.2468	101.9	...
0.1085	0.5846	0.1412	130.1	...	0.2423	0.5870	0.2464	101.7	101.8
0.1085	0.5846	0.1406	129.6	129.9	0.2826	0.5870	0.2671	94.5	...
0.1632	0.5846	0.1962	120.2	...	0.2826	0.5870	0.2680	94.8	94.6
0.1632	0.5846	0.1948	119.4	119.8	0.3634	0.5870	0.3016	83.0	83.0
0.2376	0.5846	0.2463	103.7	...	0.4108	0.5860	0.3163	77.2	...
0.2376	0.5846	0.2463	103.7	103.7	0.4108	0.5860	0.3187	77.6	77.4
0.3264	0.5846	0.2937	90.0	...	0.5249	0.5870	0.2883	66.8	66.8
0.3264	0.5846	0.2944	90.2	90.1	0.6162	0.5860	0.3711	60.2	...
0.4158	0.5846	0.3313	79.7	79.7	0.6162	0.5860	0.3688	59.9	60.0
0.5346	0.5846	0.3612	67.6	67.6	0.7268	0.5870	0.3810	52.4	52.4
0.6534	0.5846	0.3883	59.4	59.4					

Table II, in which the amount of Hanus solution is varied, is plotted in Fig. 3. Even more clearly than Fig. 2 does this show that burnt linseed oils do not readily reach a maximum.

TABLE II—LINSEED OIL—AMOUNT OF HANUS SOLUTION VARIED  
Temperature—25° C.; Oil—0.2 gram; Time—30 minutes

Cc. Hanus sol.	Grams Ad-ded	Iodine Ab-sorbed	Iodine No.	Average	Cc. Hanus sol.	Grams Ad-ded	Iodine Ab-sorbed	Iodine No.	Average
A—RAW OIL					B—BOILED OIL				
20	0.4737	0.3258	162.9	...	20	0.5522	0.3490	174.5	...
20	0.4737	0.3271	163.6	...	20	0.5522	0.3472	173.9	174.2
20	0.4737	0.3266	163.3	163.6	25	0.6902	0.3580	179.0	...
25	0.5928	0.3619	181.0	...	25	0.6902	0.3574	178.7	...
25	0.5928	0.3615	180.8	...	25	0.6902	0.3560	178.0	178.6
25	0.5928	0.3609	180.5	180.8	30	0.8282	0.3606	180.3	...
30	0.7114	0.3747	187.4	...	30	0.8282	0.3606	180.3	...
30	0.7114	0.3754	187.7	187.6	30	0.8282	0.3596	179.8	180.1
35	0.8300	0.3822	191.1	...	35	0.9662	0.3617	180.8	...
35	0.8300	0.3820	191.0	...	35	0.9662	0.3617	180.8	...
35	0.8300	0.3816	190.8	191.0	35	0.9662	0.3617	180.8	180.8
40	0.9486	0.3831	191.6	...	40	1.1044	0.3614	180.7	...
40	0.9486	0.3806	190.3	191.0	40	1.1044	0.3619	180.9	...
50	1.1862	0.3832	191.6	191.6	40	1.1044	0.3634	181.7	181.1
60	1.4235	0.3840	192.0	...	50	1.3759	0.3639	181.9	181.9
60	1.4235	0.3824	191.2	191.6	60	1.6510	0.3625	181.2	...
75	1.7793	0.3846	192.3	...	60	1.6510	0.3630	181.5	181.3
75	1.7793	0.3828	191.4	191.8	D—BURNT OIL NO. 3				
C—BURNT OIL NO. 00					20	0.4622	0.1940	97.0	...
20	0.5408	0.2640	132.0	...	20	0.4622	0.1932	96.6	96.8
20	0.5408	0.2622	131.0	131.6	25	0.5778	0.2128	106.4	...
25	0.6760	0.2820	141.0	...	25	0.5778	0.2152	107.6	...
25	0.6760	0.2812	140.6	140.8	25	0.5778	0.2152	107.6	107.2
30	0.8112	0.2902	149.6	...	30	0.6933	0.2284	114.2	...
30	0.8112	0.2940	147.0	148.3	30	0.6933	0.2282	114.1	114.1
40	1.0816	0.2906	149.8	...	40	0.9244	0.2444	122.2	...
40	1.0816	0.2980	149.0	149.4	40	0.9244	0.2438	121.9	...
50	1.3520	0.3054	152.7	...	40	0.9244	0.2432	121.6	121.9
50	1.3520	0.3044	152.2	152.4	50	1.1556	0.2488	124.4	...
60	1.6224	0.3052	152.6	152.6	50	1.1556	0.2488	124.4	124.4
70	2.0280	0.3066	153.3	...	60	1.3866	0.2518	125.9	...
70	2.0280	0.3060	153.0	153.1	60	1.3866	0.2506	125.3	125.6
E—BURNT OIL NO. 5					75	1.7334	0.2514	125.7	...
20	0.4688	0.1966	98.3	...	75	1.7334	0.2506	125.3	125.5
20	0.4688	0.1950	97.5	97.9	F—BURNT OIL NO. 5(a)				
25	0.5860	0.2148	107.4	...	20	0.4688	0.1804	90.2	...
25	0.5860	0.2140	107.0	107.2	20	0.4688	0.1800	90.0	90.1
35	0.8204	0.2440	122.0	...	25	0.5860	0.1962	98.1	...
35	0.8204	0.2424	121.2	121.6	25	0.5860	0.1946	97.3	97.7
50	1.1720	0.2602	130.1	...	35	0.8204	0.2148	107.4	...
50	1.1720	0.2602	130.1	131.1	35	0.8204	0.2094	104.7	106.0
50	1.1720	0.2584	129.2	129.6	50	1.1720	0.2218	110.9	...
					50	1.1720	0.2186	109.3	110.1

The factor "excess of iodine" may be varied by changing the weight of oil or the amount of Hanus solution. In either case the effect upon the iodine number is about the same.

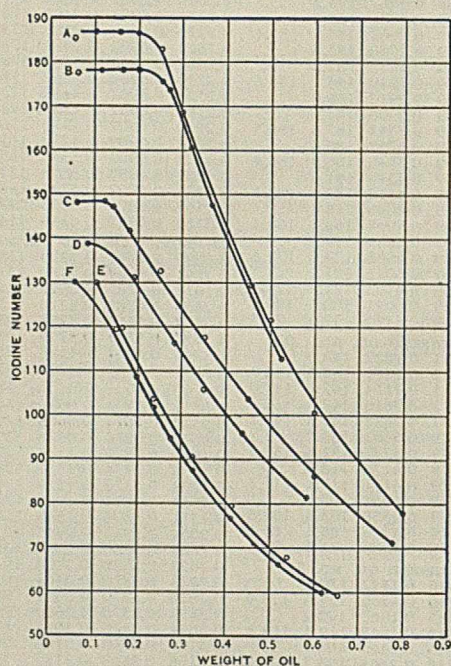


FIG. 1—WIEGHT OF OIL VARIED

It is not sufficient, however, merely to specify the percentage excess of iodine, as the following iodine values, taken from Tables I and II, will show:

Oil	Average iodine numbers	
	on 0.1 g. oil and 25 cc. Hanus sol.	on 0.2 g. oil and 50 cc. Hanus sol.
Raw	186.4	191.6
Boiled	178.5	181.9
No. 00	139.5	152.4
No. 3	111.0	124.4
No. 5	109.0	129.6

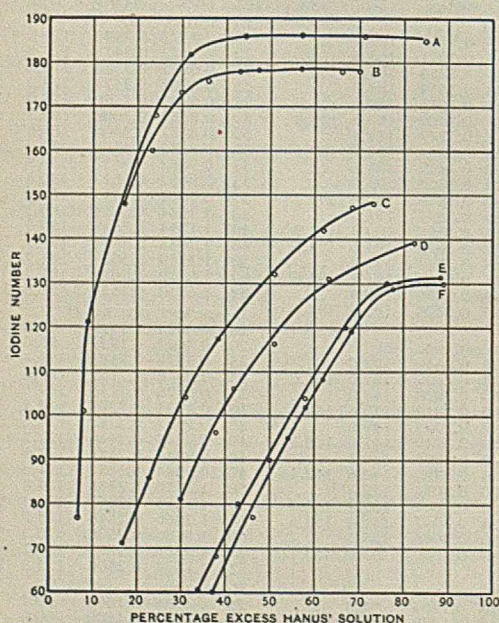


FIG. 2—WIEGHT OF OIL VARIED

These figures, together with the results shown in Tables I and II, demonstrate clearly that in these oils,

at least, an iodine number should always be accompanied by full data as to the conditions under which it is determined, in order that it may be used for comparison.

When dealing with unknown oils it will probably be found satisfactory to determine the iodine value for several weights of oil, other conditions being held constant. For convenience we would recommend the use of 25 cc. of Hanus solution and 30 minutes' absorption. When testing for the purity of a sample of oil any sample of unknown purity could be used as a standard, when by determining the iodine number on both samples under identical conditions adulteration or inferior quality should be readily detected.

The curve for Table II—F will be found on Fig. 6, and will be referred to later. It is placed there so as to contrast it with the results given in Table II—E.

TABLE III—LINSEED OIL—TIME OF ABSORPTION VARIED  
Temperature—25° C.; 0.2 g. oil; Hanus solution—25 cc.

Time Min.	Grams Ad-ded	Iodine Ab-sorbed	Iodine No.	Average	Time Min.	Grams Ad-ded	Iodine Ab-sorbed	Iodine No.	Average
<b>A—RAW OIL</b>					<b>E—BURNT LINSEED OIL NO. 1</b>				
5	0.5972	0.3284	164.2	...	5	0.5746	0.2310	115.5	115.5
5	0.5972	0.3281	164.1	164.2	5	0.5746	0.2310	115.5	115.5
15	0.5972	0.3497	174.9	...	15	0.5746	0.2405	120.3	...
15	0.5972	0.3495	174.8	...	15	0.5746	0.2436	121.8	...
15	0.5972	0.3493	174.7	174.8	15	0.5746	0.2405	120.3	...
30	0.5972	0.3629	181.5	...	15	0.5746	0.2440	122.0	...
30	0.5972	0.3625	181.3	...	15	0.5746	0.2426	121.3	121.1
30	0.5972	0.3616	180.8	181.2	30	0.5746	0.2500	125.0	...
45	0.5972	0.3677	183.9	...	30	0.5746	0.2497	124.9	...
45	0.5972	0.3680	184.0	184.0	30	0.5745	0.2493	124.7	...
60	0.5972	0.3737	186.9	...	30	0.5746	0.2496	124.8	124.9
60	0.5972	0.3736	186.8	...	45	0.5746	0.2540	127.0	...
60	0.5972	0.3733	186.7	186.8	45	0.5746	0.2519	126.0	...
<b>B—BOILED OIL</b>					<b>F—BURNT LINSEED OIL NO. 3</b>				
5	0.6811	0.3380	169.0	...	5	0.6691	0.2252	112.6	...
5	0.6811	0.3342	167.1	168.0	5	0.6691	0.2252	112.6	112.6
15	0.6811	0.3518	175.9	...	15	0.6691	0.2394	119.7	...
15	0.6811	0.3510	175.5	...	15	0.6691	0.2374	118.7	...
15	0.6811	0.3508	175.4	175.6	15	0.6691	0.2402	120.1	...
20	0.6811	0.3548	177.4	177.4	15	0.6691	0.2367	118.4	119.2
30	0.6811	0.3556	177.8	177.8	30	0.6691	0.2472	123.6	...
45	0.6811	0.3600	180.0	...	30	0.6691	0.2483	124.2	...
45	0.6811	0.3602	180.1	180.0	30	0.6691	0.2480	124.0	123.9
60	0.6811	0.3602	180.1	...	45	0.6691	0.2532	126.6	...
60	0.6811	0.3592	179.6	179.9	45	0.6691	0.2532	126.6	...
<b>C—BOILED OIL(a)</b>					<b>G—BURNT LINSEED OIL NO. 5</b>				
5	0.6760	0.3282	164.1	...	5	0.6689	0.2145	107.3	...
5	0.6760	0.3266	163.3	163.7	5	0.6689	0.2118	105.9	...
10	0.6760	0.3422	171.1	...	5	0.6689	0.2120	106.0	...
10	0.6760	0.3402	170.1	170.6	5	0.6689	0.2136	106.8	106.5
15	0.6760	0.3466	173.3	...	15	0.6689	0.2309	116.9	...
15	0.6760	0.3462	173.1	173.2	15	0.6689	0.2271	115.0	...
30	0.6760	0.3490	174.5	...	15	0.6689	0.2271	115.0	...
30	0.6760	0.3506	175.3	174.9	15	0.6689	0.2271	115.0	115.5
45	0.6760	0.3528	176.4	176.4	30	0.6689	0.2390	119.5	...
60	0.6760	0.3528	176.4	...	30	0.6689	0.2390	119.5	119.5
60	0.6760	0.3518	175.9	176.2	45	0.6689	0.2411	120.6	...
<b>D—BURNT LINSEED OIL NO. 00</b>					<b>(a) Temperature 0°.</b>				
5	0.5606	0.2405	120.3	...	5	0.5606	0.2405	120.3	...
5	0.5606	0.2406	120.3	120.3	15	0.5606	0.2509	125.5	...
15	0.5606	0.2509	125.5	...	15	0.5606	0.2495	124.8	...
15	0.5606	0.2495	124.8	...	15	0.5606	0.2486	124.3	...
15	0.5606	0.2486	124.3	...	15	0.5606	0.2501	125.1	124.9
30	0.5606	0.2584	129.2	...	30	0.5606	0.2584	129.2	...
30	0.5606	0.2579	129.0	129.1	30	0.5606	0.2579	129.0	129.1
45	0.5606	0.2607	130.4	...	45	0.5606	0.2607	130.4	...
45	0.5606	0.2593	129.7	...	45	0.5606	0.2593	129.7	...
45	0.5606	0.2586	129.3	129.8	45	0.5606	0.2586	129.3	129.8
60	0.5606	0.2635	131.8	...	60	0.5606	0.2635	131.8	...
60	0.5606	0.2614	130.7	...	60	0.5606	0.2614	130.7	...
60	0.5606	0.2642	132.1	...	60	0.5606	0.2642	132.1	...
60	0.5606	0.2628	131.4	131.5	60	0.5606	0.2628	131.4	131.5

Table III (omitting C) is plotted in Fig. 4. The curves show that after the first five minutes the absorption is slow, and the difference of a few minutes one way or the other after 15 minutes, will have little effect on the iodine value; 30 minutes should prove a very satisfactory time and is now generally adopted.

Figs. 5 and 6 contain two sets of curves showing the effect of temperature. Table III—B and C show that, other conditions being equal, small differences in tem-

perature at which an iodine value is obtained are negligible, so far as boiled oils are concerned, and presumably raw oils also, since their behavior is very much like that of the former. This is not, however, true of the burnt linseed oils, as inspection of the curves for Table II—E and F will readily show. Using the largest practical excess of iodine, the difference between the results obtained at the two temperatures is too great to be considered negligible. Moreover, the fact that the curves are not even approximately parallel makes it difficult to allow for differences in temperature.

It will be seen that about 90 per cent of the absorption occurs in the first 5 minutes. If we assume that the addition of iodine is nearly instantaneous, and the substitution that part of the reaction which continues over a wide range of time, it is evident that any lessening of the time of absorption, which will at best

employed for the determination, with 25 cc. of the iodine solution.

TABLE IV—PETROLEUM OILS—TIME VARIED  
Temperature—25° C.; Hanus solution—25 cc.

TIME—30 MINUTES						TIME—3 HOURS					
Grams oil	Grams I absorbed	Iodine No.	Grams oil	Grams I absorbed	Iodine No.	Grams oil	Grams I absorbed	Iodine No.	Grams oil	Grams I absorbed	Iodine No.
A—LIGHT OIL NO. 1			C—ENGINE OIL			D—ENGINE OIL					
0.2313	0.0683	29.5	0.0202	0.0167	77.9	0.2608	0.1328	50.9			
0.5896	0.1454	24.7	0.0418	0.0307	69.4	0.4382	0.1766	40.3			
0.7542	0.1756	23.3	0.0644	0.0448	65.7	0.8298	0.2391	28.8			
0.9222	0.2006	21.8	0.1312	0.0735	52.9	1.139	0.2854	25.0			
1.0322	0.2105	20.4	0.1683	0.0870	48.8	1.169	0.2873	24.6			
1.5037	0.2621	17.4	0.1932	0.0953	46.6	1.839	0.3474	13.5			
2.3203	0.3288	14.2	1.009	0.2202	21.9						
B—LIGHT OIL NO. 2											
			1.059	0.2235	21.1						
0.2381	0.0807	33.9	1.167	0.2371	20.3						
0.5144	0.1363	26.5	1.203	0.2423	20.1						
0.6800	0.1678	24.6	1.305	0.2516	19.3						
1.0288	0.2145	20.9	2.069	0.3058	14.8						
1.6731	0.2819	16.9									
2.5151	0.3429	13.6									

It is interesting to contrast the behavior of linseed oils with that of mineral oils. The former tend to

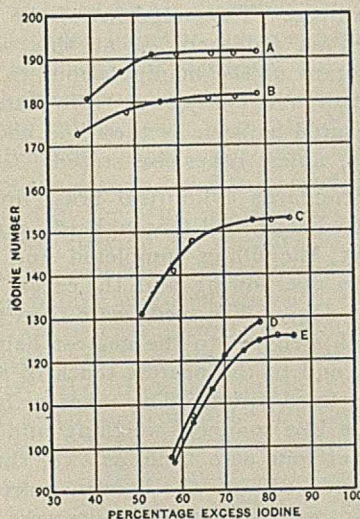


FIG. 3—AMOUNT OF HANUS' SOLUTION VARIED

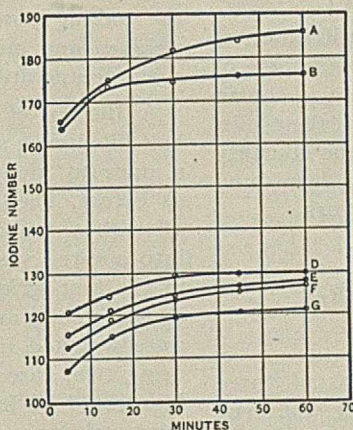


FIG. 4—TIME OF ABSORPTION VARIED

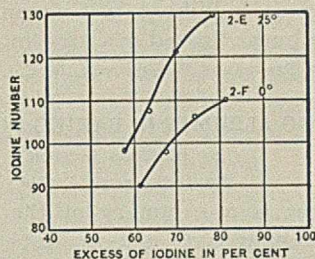
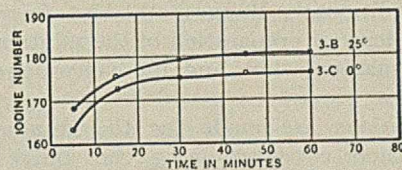


FIG. 5 (above)—TIME AND TEMPERATURE VARIED  
FIG. 6—TEMPERATURE AND EXCESS IODINE VARIED

eliminate only a small part of the total substitution, may give low values which properly belong on the portion of the curve which is rapidly changing its slope.

A study of the effect of temperature on substitution is a more promising field than that of the time factor. Table II—E and F, as plotted in Fig. 6, show that at the lower temperature the effect of increasing the excess of iodine is less than at the higher one. The difference in the iodine values between 15 and 30 minutes is about 5 units (see Fig. 4), whereas the difference between 25° C. and 0° C. at the maximum percentage excess of iodine employed, is 20 units (see Fig. 6).

Table IV (Fig. 7) shows clearly the futility of attempting to reach a constant value for mineral oils by increasing the excess of iodine. For the smaller quantities of oil used in the determination slight changes in the amount of oil taken cause large differences in the iodine number. Undoubtedly the lower values are more nearly correct than the higher ones, and therefore increasing the excess of iodine increases materially the error involved. To obtain concordant results the weight of oil and amount of iodine solution must be defined within very narrow limits. Our results indicate that not less than 1 g. of oil should be em-

approach a constant value with a decreasing weight of oil, or increasing excess of iodine, while, on the contrary, the latter tend to approach a constant value with increasing weight of oil.

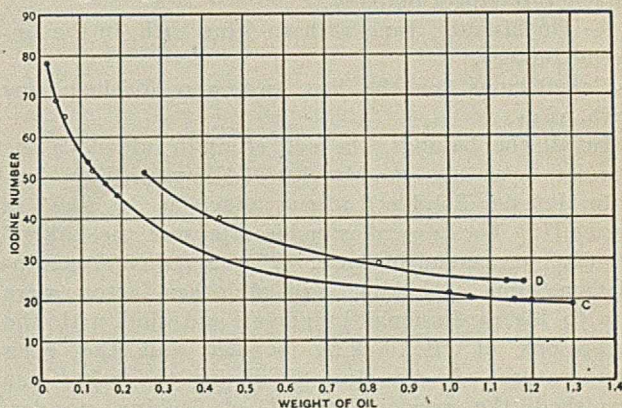


FIG. 7—WEIGHT OF ENGINE OIL VARIED

#### SUMMARY

The iodine values of raw, boiled, and burnt linseed oils were determined by the Hanus method, varying widely the amounts of oil and iodine used and the time of absorption.

It is shown that in order to obtain concordant results for iodine absorption a prescribed procedure must be followed exactly.

To obtain comparable results a standard procedure should be adopted in which the limits are more exactly defined than is true at present. This is particularly necessary in the case of burnt linseed oils. With raw linseed oil a constant value is reached within comparatively wide limits of weight of oil and excess of iodine.

A study was made of the effect of temperature on the iodine absorption, from which it would appear that it may be feasible to improve the Hanus method by working at lower temperatures than those which have been used, and thus eliminate part of the substitution which occurs simultaneously with the addition.

The results obtained show that when used under exact conditions the Hanus method is to be recommended for simplicity of preparation of the solutions employed, ease of manipulation, and for concordance of results obtained.

Suggestions are made for the standardization of the method of determining the iodine number of mineral oils. The necessity for such action is shown by the results on several samples of lubricating oils.

We wish to express our appreciation of the courtesy of Messrs. Ault & Wiborg, of Cincinnati, in furnishing us with the burnt linseed oils used in this work.

BUREAU OF STANDARDS, WASHINGTON, D. C.

### EGG ALBUMIN IN BAKING POWDER

By H. LOUIS JACKSON

Received August 3, 1914

This paper is a summary of the results of three series of comparative baking tests, using different baking powders with and without egg albumin.

They were carried out in the following bakeries in the city of Boise, Idaho:

1—On cup cakes, during July and August, in the Home Bakery, and completed Sept. 4th, 1913.

2—On biscuits, April 23rd to May 15th, by the Shaeffer Baking Company.

3—On biscuits, June 18th to June 24th, in the Imperial Bakery.

Calculations for the last two were finished June 27th, 1914.

In all the bakings, the egg albumin added to the powders was always Merck's "Albumin, Egg, Impalp. Powder Soluble;" it was added as described in Series II. The cup cakes or biscuits were the bakers' regular commercial mixture. The ingredients, manipulation, time of baking, and all other factors were left to his professional judgment and skill with the exceptions of the baking powder and the oven temperature. At the time of mixing the baker was furnished the proper amount of baking powder, weighed to a tenth of a gram. Further details as to the powders are given under each series. The temperature was that regularly used in each bakery, except in the third series, when progressively lower temperatures were employed in order to study the effects of unfavorable conditions.

High and low temperatures are defined as follows by A. J. Stephan, of the Imperial Bakery, the largest in the city: bread requires the highest temperature, baking best at about 500° F. (260° C.); 425° F. (218 $\frac{1}{3}$ ° C.) is the lowest possible for bread, as at this temperature it dries out too much. The highest temperature that can be used is 520° F. (271.1° C.). Pies are baked at 450° to 500° F. (232.2°–260° C.). Cakes, according to kind, at 350° to 450° F. (176.7–232.2° C.). Biscuits require for best results about 490–500° F. (254.4–260° C.); 425° F. (218.3° C.) is considered the lowest that should be used for biscuits, though they will bake poorly at 400° F. (204.4° C.).

The temperature in the first series was not known, as the oven contained no thermometer. All products were judged by the bakers as soon as expedient after removal from the oven. The judgment of the bakers must be regarded as unbiased as, at this writing, they are still ignorant of the manipulations to which the baking powders were subjected. Products were weighed and measured as soon as they had cooled to room temperature, unless otherwise stated.

A Bureau of Standards cylindrical brass liter was half filled with sifted rape seed (through 16), jarred in a uniform manner, the filling completed and jarred as before, filled to overflowing and the excess struck off with a straight edge. The seeds were then poured into a tared vessel, weighed to the nearest half gram in the first series, and to the nearest tenth of a gram in the second and third series. The cakes or biscuits were weighed in a like manner, weighing and measuring two, three, or four at a time, as two, three, or four could be introduced into the liter measure without touching each other. Cakes or biscuits were placed in the liter, one at a time, entirely surrounded by seed, and so on, until the vessel was filled, jarring it in the same manner as before, every care being taken to make this a very uniform procedure. The difference between the first and second weights of seed is that displaced by the biscuits. The intent was to make all measurements so numerous that the unavoidable errors in measurement would be averaged out in the final result. The average weight of 1,000 cc. of seed was found for each baking and is usually the average of ten weighings, though in the first series, three, five, six, eight and nine weighings were averaged together for different bakings.

#### SERIES I

Cup cakes were chosen because in the estimation of the bakers they were best adapted to experiment. The bakers knew this product so thoroughly that they were confident they could detect any change in its appearance. A cream of tartar powder (Cleveland's) was used because it was the only one used in this bakery, and it was not desired to change the nature of their cake in any way, as part of each baking was to supply the regular trade.

Objection may be made that fresh eggs were used as an ingredient in the cakes of the first series, but it

must be remembered that most products baked contain eggs, except in baking powder biscuits.

The method of calculation follows:

Av. wt. of 1,000 cc. seed.....	687.2 g.
Seed weighed with cakes 1 and 2.....	517.8 g.
Seed displaced by cakes 1 and 2.....	169.4 g.
1 gram seed = $\frac{1,000}{687.2}$ cc.....	1.455 cc.
169.4 g. seed $\times$ 1.455.....	246.5 cc.
Wt. cakes 1 and 2.....	82.2 g.
$\frac{246.5}{82.2}$ .....	3.0

Av. specific volume of cakes 1 and 2 is 3.

The cakes were weighed and measured two at a time, constituting a group, and thus the average specific volume for that group were obtained. All groups for a baking were then averaged together in one figure and this alone is given.

The mix in Series I consists of sugar, butter compound, eggs, milk, flour and lemon extract, all measured or weighed by the baker as usual, except that he took particular pains to do everything as accurately and as uniformly as possible. Two ounces of Cleveland's baking powder went into each batch of five dozen cup cakes, which were baked in five tins, holding twelve cakes each. The first batch was baked by the time the second batch was ready, and the second was baked in the same place in the oven as the first, the bakers striving for uniformity throughout. In these large ovens the temperature changes very slowly, the oven baking uniformly for hours at a time.

The two batches were thus contained in ten tins of a dozen each, and the cakes selected for measurement were taken from each pan in an arbitrary manner, so as to avoid any conscious selection. About 30 per cent of the cakes baked were measured.

TABLE I—AVERAGE SPECIFIC VOLUME OF CUP CAKES—SERIES I

Baking No.	No. of cakes averaged	With egg albumin % albumin in parentheses	Without egg albumin
1.....	12	..	3.02
2.....	6	..	2.99
3.....	17	..	3.22—Batch A
3.....	17	..	3.10—Batch B
4.....	18	2.99 (0.5)	3.00
5.....	18	3.10 (1.0)	3.13
6.....	18	3.21 (2.0)	3.17
7.....	20	2.99 (5.0)	3.06
8.....	20	3.20 (20.0)	3.18
Average.....		3.097	3.108
(Weighted mean)		3.10	3.11

The 94 cup cakes made with albuminized powder have an av. sp. vol. of 3.10; 146 cup cakes made with non-albuminized powder have an av. sp. vol. of 3.11. This advantage in favor of non-albuminized powder is scarcely significant in view of the following facts: In Baking 3, two batches designated A and B were baked, neither of which contained egg albumin in the powder used. This was to ascertain what variation might occur when the two batches were identical in every way, although the bakers thought that different powders were being used.

Batch A averaged 3.22 for 17 cakes.

Batch B averaged 3.10 for 17 cakes.

This is a variation of 0.12 in 3.22 and the largest in any one baking. 2.99 was the minimum sp. vol. and occurs three times, twice with egg albumin and once without; 3.22 is the maximum and occurs in the series without the albumin; 3.21 and 3.20 occur with albumin. If the first three bakings are excluded

from the average because only the last five were baked, both with and without albumin, the average for those without egg albumin is still 3.11. Egg albumin was twice in the second batch baked, three times in the first baked.

Bakings 1 and 2 were bought over the counter, before the firm knew they were to be tested. They serve as controls as do the two batches in Baking 3.

#### JUDGMENTS—SERIES I

Bakings 3 and 4 were lost.

Baking 5—In breaking three cakes of each batch, the texture of cakes A (without egg albumin) was a little, though a very little, better than B (with 1 per cent added albumin).

Baking 6—B. cakes (without egg) judged the better mix. B. cakes thought to be slightly larger in volume. (This was not the case when measured.)

Baking 7—B. cakes (without egg) a shade lighter in color than A. cakes. No other differences noticed between A and B cakes.

Baking 8—Judgment lost.

After studying the two batches in every way possible, the final conclusion of the two bakers was about as follows: "Well, it's pretty hard to say which is the better; they are just about as nearly alike as they could be."

As to the variables entering into the work, the average weight of 1,000 cc. of rape seed was determined for each baking and these averages had a maximum variation of 1.7 per cent. This is the smallest variable. The weights of cakes varied greatly. Commonly this was 10 to 15 per cent between the heaviest two and the lightest two in any bake. The weight of rape seed displaced by cakes varied in about the same manner and indicated that no large or constant error of measurement entered into the series. These variations are best shown in Table II.

TABLE II

Number of baking	% difference between max. and min. weights of cakes		Number of baking	% difference between max. and min. weights of cakes	
1.....	10	14	6 A...	3	7
2.....	2	12 (6)	B...	17	8
3 A.....	13	12	7 A...	28	23
B.....	14	17	B...	11	9
4 A.....	10	13	8 A...	12	13
B.....	15	13	B...	13	15
5 A.....	15	17			
B.....	17	15	AVERAGE	12.6	13.4

The most striking difference between Columns 2 and 3, in the same baking, is in the second baking. In the original data there is one weight of "Rape seed displaced by cakes," that looks quite suspicious. Casting out this weight, the final average in this baking is changed from 2.99 to 2.96 and the "percentage difference" to 6. Introducing the figure 2.96 into the final results changes the grand average for cakes without albumin from 3.1084 to 3.1072. In other words, it does not change the final average at all, for, when reported to the correct number of places, we still have 3.11.

This discussion of the errors gives an idea of their magnitude and also shows that the number of measurements has been large enough to make even that value which is most probably in error; without effect on the final average.

## CONCLUSION—SERIES I

The addition of egg albumin to the baking powder used in baking cup cakes was entirely without any measurable result, and without any observable effect that could be seen by two experienced bakers.

## SERIES II

In the second series, another bakery did the work, biscuits were used, and temperatures and times of baking recorded. All biscuits in this series contained:

Flour.....	2 lbs.
Baking powder.....	2 oz.
Compound (melted).....	3 level tablespoonfuls
Salt.....	1 level tablespoonful
Milk.....	$\frac{3}{4}$ quart

The compound was added last. The poorest flour of which the baker knew was used in the first three bakings, because it has been claimed that an albuminized powder shows to greatest advantage with very weak flour. In the fourth baking a strong flour was used. The baker controlled everything in this series except the baking powder which was K. C. Baking Powder. The two ounces were weighed to a tenth of a gram and then to one portion was added the per cent of egg albumin shown in brackets in Table III. The albumin was mixed into the powder by rolling two hundred times on a rubber sheet in the manner used by assayers in mixing powdered ores. The non-albuminized powder was rolled to the same extent, to expose it to the air in like manner. The dough was rolled out between thin strips of wood upon which the rolling pin rested, to secure an even thickness of dough before the biscuits were cut out. Dough left from the first cutting was discarded.

The first batch was baked while the second was being prepared, the second then went into the same place in the oven that the first had occupied. Twice the egg albumin was in the first or A batch, twice in the second or B batch. Four biscuits were usually weighed and measured at the same time, giving a specific volume for the group, and the specific volumes for the groups were averaged together (weighted if less than four in a group) to give the av. sp. vol. for that baking. Table III shows the results:

TABLE III—AVERAGE SPECIFIC VOLUME OF BISCUITS—SERIES II

Baking No.	No. biscuits in average	Time baked Minutes	Temp. of baking ° F.	Average sp. vol. % egg albumin in brackets
1 A.....	29	11	498-500	2.64 (0.1)
B.....	31	13	500- 3	2.78
2 A.....	24	11	494- 5	2.67 (0.2)
B.....	21	11	495- 8	2.52
3 A.....	13	12	485- 7	2.62
B.....	13	12	487	2.52 (0.5)
4 A.....	17	12	489- 90	2.11
B.....	19	12	490- 7	2.28 (1.0)
Average (weighted mean)	of 85 biscuits with egg albumin .....			2.548
	of 82 biscuits without egg albumin .....			2.550

Bakings 2, 3 and 4 set in the pans ten minutes before going into the oven, as certain companies making an albuminized powder claim this to be advantageous. Retaining three places in the final result, the non-albuminized powder gave biscuits with the same sp. vol. as the albuminized powder, namely, 2.55. The lightest biscuits (2.78) were without egg, the next lightest (2.67) with 0.2 per cent egg, the next lightest (2.64) with 0.1 per cent egg, the next lightest

(2.62) without egg. The lightest biscuit was baked two minutes longer than it should have been.

## JUDGMENTS—SERIES II

Baking 1—Batch B slightly better than A (0.1 per cent) but very hard to decide.

Baking 2—Batch B is a little better than A (0.2 per cent) but both very nearly alike.

[Assistant Baker: A (0.2 per cent) biscuits a little better than B.]

Baking 3—Batch A slightly lighter by texture. B (0.5 per cent) raised a little higher (external appearance).

Baking 4—Batch B (1.0 per cent) quite a bit better than A.

These results are rather indecisive, for only in the fourth baking was any decided advantage recorded by the baker's judgment.

In Baking 2, the head baker and his assistant differed, thus showing no real difference between the two batches.

In Baking 3, Batch B was allowed to stand  $13\frac{1}{2}$  minutes, before going into oven, instead of 10, as for A, through a mistake in watching the time.

It was intended to continue this series, but work had to be stopped on account of other duties.

## SERIES III

The third bakery (Imperial Bakery) did the baking and controlled all factors except baking powder, shortening and salt, which were weighed to a tenth of a gram and supplied to the baker at time of mixing. A weak flour was used throughout.

Mix used:

Flour.....	3 lbs.
Baking powder.....	3 oz.
Cottolene (cold).....	3 oz.
Salt.....	$\frac{1}{2}$ oz.
Milk.....	1 qt.

The flour, baking powder and salt were first mixed by hand, then the cottolene worked in by hand, and last the milk added. The baking powders used were Crescent, manufactured with egg albumin and designated C; K. C. powder, manufactured without egg; Atlas, manufactured without egg and designated A; Giant, manufactured without egg and designated G; Interstate, manufactured without egg and designated I. All these powders are alum phosphate powders. Egg albumin was added to part of the non-egg powders in certain bakings in the same manner as in Series II. Bakings 4, 5 and 6 were divided into two portions, designated 1st and 2nd half. The 1st half was rolled out and baked about 9 A.M. The 2nd half stood in the proof closet until about 2 P.M. and was then rolled out and baked. This was to test the claim that dough made with albuminized powder could stand several hours, or over night, and still make good biscuits. The baker could not arrange any other time for the two bakings than 8.30 A.M. and 2.00 P.M. The order of baking batches was that given in Table III. All dough was rolled to a uniform thickness between narrow strips of wood, and that left from the first cutting was discarded.

The difference of 34 in 2627 is 1.3 per cent, and is in favor of biscuits baked with albuminized powder. The greatest gains for powder with albumin are found in the early part of Series III, when one brand of

powder, albuminized as it comes on the market, is directly compared with a non-egg powder as manufactured. This is really unfair, as the two powders used may differ in their effects, aside from the egg albumin in one of them. The most striking failure of egg albumin to improve a given powder is shown

TABLE IV—AVERAGE SPECIFIC VOLUME OF BISCUITS—SERIES III

Baking No.	No. averaged	Time baked Min.	Temp. baking ° F.	Av. sp. vol. bk. pdr.	Kind of egg alb.	Per cent
1 A.....	31	10	495	2.79	C.	0.17
B.....	28	10	495	2.54	K. C.	0.0
2 A.....	28	10	470-1	2.60	K. C.	0.0
B.....	28	11	471-4	2.75	C.	0.17
3 A.....	28	10	465	2.71	A.	0.0
B.....	32	10	465	2.63	C.	0.17
C.....	32	10	465	2.53	G.	0.0
4 C 1st half.....	18	10	450-5	2.66	G.	0.0
B 1st half.....	18	10	455-60	2.63	C.	0.17
A 1st half.....	17	10	460	2.70	A.	0.0
4 C 2nd half.....	14	10	458-60	Lost	G.	0.0
B 2nd half.....	14	10	458-60	2.20	C.	0.17
A 2nd half.....	13	10	458-60	2.15	A.	0.0
5 A 1st half.....	20	12	430-5	2.96	I.	0.0
B 1st half.....	20	12	430-5	2.96	I.	0.2
C 1st half.....	20	12	430-5	2.90	I.	0.5
5 A 2nd half.....	18	12	443-5	2.56	I.	0.0
B 2nd half.....	18	12	443-5	2.54	I.	0.2
C 2nd half.....	18	12	443-5	2.57	I.	0.5
6 A 1st half.....	20	10	455	2.65	G.	0.0
B 1st half.....	20	10	455	2.65	G.	0.2
C 1st half.....	20	10	455	2.59	G.	1.0
6 A 2nd half.....	16	10	460	2.27	G.	0.0
B 2nd half.....	16	10	460	2.25	G.	0.2
C 2nd half.....	16	10	460	2.26	G.	1.0

Average (weighted mean) of 271 biscuits with egg..... 2.627 2.63  
Average (weighted mean) of 238 biscuits without egg... 2.593 2.59

Difference..... 0.034

in Bakings 5 and 6, where the same powder was used first without egg, second with 0.2 per cent added egg, and third 0.5 per cent added egg in Baking 5. In the first half, which was baked at once, the sp. vol. fell from 2.96 with no egg and with 0.2 per cent egg, to 2.90 with 0.5 per cent egg. In Baking 6, 0.0 per cent, 0.2 per cent, and 1.0 per cent egg were present in a second can of Giant powder. The sp. vol. fell from 2.65 with no egg, and 0.2 per cent to 2.59 with 1.0 per cent egg, and in both Bakings 5 and 6, these figures are the averages of 20 biscuits.

SUMMARY OF RESULTS OF BAKING TESTS ON BISCUITS—SERIES III

Baking No.	Temp. baking	Batch	Bk. pdr.	% alb.	REMARKS
(1).....	495	B	K. C.	0.0	Better in looks, taste, odor (judgment of four persons)
(2).....	470-74	B	C.	0.17	Looks better than A. (K. C. 0.00%) no difference in smell or taste
(3).....	465	C	G.	0.0	Best
		B	C.	0.17	2nd
		A	A.	0.0	Poorest
(4) 1st half...	450-60	C	G.	0.0	Best
		B	C.	0.17	2nd
		A	A.	0.0	Poorest
(4) 2nd half..	458-60	B	C.	0.17	Best
		C	G.	0.0	2nd
		A	A.	0.0	Very poor
(5) 1st half...	430-35	C	I.	0.5	Quite good
		B	I.	0.2	2nd
		A	I.	0.0	Very poor
(5) 2nd half..	443-45	C	I.	0.5	Best
		B	I.	0.2	Poorest
		A	I.	0.0	2nd
(6) 1st half...	455	C	G.	1.0	Best
		B	G.	0.2	2nd
		A	G.	0.0	Not bad
(6) 2nd half..	460	C	G.	1.0	Best
		B	G.	0.2	2nd
		A	G.	0.0	Poorest

## JUDGMENT

When biscuits are judged by looks much greater differences are noted than by measurement. It appears that a fine looking, large biscuit may have no greater sp. vol. than a smaller and poorer looking biscuit. This is due to the fact that the larger biscuit is heavier, and the sp. vol. works out about the

same as for smaller biscuits. Just why this is so has not been determined.

This difference in judging by looks and measurement is strikingly shown in Baking 1, when batch B (0.0 per cent) was given the preference in looks, taste and odor, by four bakers, separately, although A (C. 0.17 per cent) proved to be larger in sp. vol. by 0.25 in 2.79.

In Bakings 4, 5 and 6 the bakers awarded the honors very uniformly to the biscuits baked with albuminized powder. The differences were so marked that anyone could not fail to see them, yet, these differences do not show in the sp. vol. These were all baked at too low a temperature, and the 2nd half of a bake was always carried out after the dough had stood about five hours.

## CONCLUSION

It is the opinion of the writer that when bakings are carried out under normal conditions his work has not demonstrated the usefulness of egg albumin in baking powder, and especially in the very small quantity usually present, *i. e.*, from 0.1 to 0.2 of one per cent.

When the temperature of the oven is too low for baking biscuits properly, egg albumin seems to aid in producing a better biscuit.

When the dough is allowed to stand several hours before baking, a much better biscuit is produced by the powder to which egg albumin has been added.

OFFICE OF THE STATE CHEMIST  
BOISE, IDAHO

## IRON IN TOMATOES

By C. A. BRAUTLECHT AND G. CRAWFORD  
Received September 5, 1914

Tomatoes have become of much importance as a garden vegetable during the last decade and present evidence indicates that they will become of greater importance. From the view-point of the food, physiological and agricultural chemist more knowledge of their chemical composition is therefore desirable.

Tomatoes are used as a food in many ways. While fresh, they are eaten raw or cooked; tremendous quantities are canned; they form the basis of many soups; large quantities of tomatoes, or their products, are used as sauces for meat or fish foods; in desert regions, or where good drinking water is scarce, canned tomatoes are used largely because of the water and vegetable acid they contain.

Considering the exchange in soil elements, there seems to be a general agreement that the tomato plant uses relatively little phosphoric acid, but more potash and nitrogen. Much of the potash remains in the vines and roots. In comparison with the amount of crop produced, the tomato does not remove much plant food from the soil.

The acidity of the tomato is supposed to be due to citric acid. A small amount of an alkaloid is also supposed to be present in the juice and this decreases as the fruit ripens. During ripening there is a progressive increase in the organic acids, sugars, starch and non-

protein nitrogen and a decrease in protein nitrogen and cellulose. The proportion of other constituents remains practically unchanged. The amount of sucrose in fresh and dehydrated tomatoes differs, due probably, to inversion resulting from ferments and organic acids. About 0.5 per cent of ether extract is obtainable from the dry matter of the tomato, this amount being reduced, however, by previous alcohol extraction:

Passerini<sup>1</sup> states that the pulp of the tomato contains two coloring matters, a yellow amorphous and a red crystalline substance. These are insoluble in water, soluble in amyl alcohol and very soluble in ether. Both are decolorized by chlorine and bromine water, while hydrochloric acid has no action on them. The yellow substance is much more soluble in alcohol than the red. R. Willstätter and H. H. Echer<sup>2</sup> state that lycopin, the coloring matter of the tomato, differs in several respects from carotin.

E. H. Jenkins and W. E. Britton<sup>3</sup> reporting results on two varieties of tomatoes found no difference between them in water and potash content, percentage limits for water and potash on eight samples being respectively 93.41 to 94.81 and 0.287 to 0.356. H. Snyder<sup>4</sup> found no chemical difference between three varieties. He reports analytical results on three samples: Water, 93.6 to 93.9; protein, 0.80 to 0.86; carbohydrates, 3.79 to 3.85; and ash, 0.54 to 0.69 per cent. W. B. Alwood and W. Bowman<sup>5</sup> found in four samples of one variety: Water, 91.2 to 94.0 per cent; protein, 0.78 to 1.25; carbohydrates, 3.60 to 4.07; fat, 0.33 to 0.47; and ash, 0.34 to 0.73 per cent. W. O. Atwater and A. P. Bryant<sup>6</sup> report on analysis of two samples of canned tomatoes: Water, 94.0 and 94.3 per cent; protein, 0.9 and 1.2; carbohydrates, 3.9 and 4.0; fat, 0.2 and 0.4; and ash, 0.5 and 0.6 per cent. One sample of ash contained 5.8 per cent lime, 8.7 per cent phosphoric pentoxide, 68.1 per cent potash and 3.7 per cent magnesium oxide. A number of other investigators—Ricciardelli, A. F. Bacon and P. B. Dunbar, and Albanarg—report similar results of a few analyses of tomatoes.

It is our intention to report the quantity of water, ash and iron in eleven samples of Florida canned tomatoes from different parts of the state. In the literature available we have found no figures showing the amount of iron in tomatoes.

The tomatoes were cut up and canned without appreciable loss of pulp or juice. When received at the laboratory they were cut up in a meat chopper without loss of juice and the water was determined by loss on evaporation of 150 g. samples at 110° to constant weight. The residue or total solids was ashed in thick porcelain dishes in a muffle furnace, at the lowest possible temperature, yielding a fine gray, white or buff colored ash. This was weighed, pulverized and iron determined in duplicate samples of about 0.2 g. The ash was then digested in hydrochloric acid and

again in sulfuric acid. The solution, free from hydrochloric acid, was reduced with hydrogen sulfide, the excess of hydrogen sulfide removed, the solution cooled and the iron titrated with standard potassium permanganate solution.

PERCENTAGE OF WATER, ASH AND IRON IN FLORIDA TOMATOES

Sample No.	Location		Iron as Fe <sub>2</sub> O <sub>3</sub> (a)				
	Town	County	Water	Ash	ash	whole tomatoes	soil
1	Lake City,	Columbia	94.0	0.39	11.53	0.046	3.03
2	Ponce de Leon,	Holmes	93.0	0.58	4.38	0.026	3.29
3	Live Oak,	Suwanee	91.3	0.58	8.09	0.046	3.83
4	Dover,	Hillsboro	92.6	0.53	20.68	0.106	..
5	Greensboro,	Gadsden	94.6	0.53	18.62	0.100	..
6	Pensacola,	Escambia	94.6	0.55	22.25	0.123	..
7	Paxton,	Walton	92.6	0.56	6.09	0.034	..
8	Tallahassee,	Leon	95.0	0.49	7.75	0.037	..
9	Summerfield,	Marion	95.3	0.38	21.45	0.083	..
10	Green Cove Springs,	Clay	95.3	0.63	12.21	0.077	3.12
11	Tallahassee,	Leon	89.3	0.64	8.47	0.054	..

Average..... 93.4 0.53 12.87 0.066 3.32

(a) Average of closely agreeing duplicates.

## SUMMARY OF RESULTS

I—The tomatoes from ten counties in Florida contained from 89.3 to 95.3 per cent of water. Geographical location of plot on which the tomatoes were grown did not affect the water content. The average amount of water was 93.4 per cent.

II—The ash varied from 0.38 to 0.64 per cent, averaging 0.53 per cent. There was no fixed ratio between the water and ash or iron and ash.

III—The iron in the ash varied greatly from 1.53 to 7.78, average 4.50 per cent. Calculated to ferric oxide this would represent 4.38, 22.25 and 12.87 per cent, respectively. Iron was present in about the same amount in widely separated counties.

IV—Iron in tomatoes, calculated from the iron in the ash, ranged from 0.012 to 0.037 per cent, averaging 0.023 per cent. Calculated to ferric oxide, this would represent 0.034, 0.123 and 0.066 per cent, respectively.

V—In soil on which these tomatoes were grown (four samples), there was from 1.06 to 1.3 per cent iron, equivalent to 3.03 and 3.72, or an average of 3.32 per cent ferric oxide.

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### BLOOD-CHARCOAL AS A PURIFYING AGENT FOR ARSENIC SOLUTIONS PREVIOUS TO TITRATION<sup>1</sup>

By ROBERT M. CHAPIN

Received September 3, 1914

Whenever possible, arsenic is estimated by the highly accurate and convenient method of titration with iodine. As necessary conditions, the solution must be free from other substances capable of absorbing iodine during the titration and from coloring matter to obscure the end points.

This laboratory has been required to examine very many samples of the arsenical dipping baths<sup>2</sup> now so largely used for ridding cattle of Texas-fever ticks. The important insecticidal ingredient of these baths is an alkaline arsenite, and it is in this form that the arsenic is introduced when the baths are prepared.

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> Compare *Farmers' Bulletin* 603, U. S. Dept. of Agric.

<sup>1</sup> *Slag. Sper. Agrar.*, 18, 545.

<sup>2</sup> *Ztschr. physiol. Chem.*, 64, 47.

<sup>3</sup> *Conn. Agr. Expt. Sta., Ann. Rpt.*, 1895.

<sup>4</sup> *Minn. State Bull.*, 63.

<sup>5</sup> *Va. State Expt. Sta., Bull.* 4.

<sup>6</sup> *U. S. Dept. Agr., Bull.* 28.



But with accumulation of dirt and excrement from the cattle during months of use in dipping vats, the baths become culture media for microorganisms which may either oxidize the arsenic, or reduce it again, depending upon prevalent conditions.<sup>1</sup> In a sample of used bath, therefore, it is necessary to determine both actual arsenious oxide and total arsenic.

The organic matter present in used arsenical dipping baths interferes with titration by iodine in both the undesirable ways; it absorbs iodine under the conditions of the titration, thus rendering the end points inaccurate and fugitive, and it imparts color to the solution. An obvious first step is to acidify and filter the bath, adding also a clarifying agent. Purified kaolin or kieselguhr are only moderately beneficial, but in blood-charcoal was found an agent which, used in small amount and with brief digestion, produced water-white filtrates wherein the end points with iodine came out sharply and permanently. Before the substance could be employed in routine analytical work, it was necessary to ascertain if its well-known adsorptive and oxidative powers<sup>2</sup> would affect the arsenic present.

The simple plan of investigation involved treatment of measured portions of a standard arsenious acid in parallel, with and without charcoal, followed by titration with standard iodine. Approximately twentieth-normal solutions were employed and to each 25 cc. of arsenious acid solution was added 5 cc. of 10 per cent (by weight) sulfuric acid, and 0.25 g. blood-charcoal (if any used), previous experiments having shown this quantity to be ample for the purification of 25 cc. of very filthy dipping baths. All filtrations followed by washing were carried to a total volume of 125 cc. Arsenious oxide was titrated in presence of sodium bicarbonate. For total arsenic the 125 cc. of filtrate and washings were boiled down to 50 cc. after addition of 3.5 cc. concentrated sulfuric acid and 2 g. potassium iodide. From the cooled solution, diluted to 250 cc., excess iodine was cautiously removed in presence of starch by a dilute solution of sodium sulfite (0.5 per cent of anhydrous salt), then acid was neutralized with sodium carbonate and bicarbonate, and after further dilution the titration was completed in the usual way.

chased as "acid-washed," was exhaustively purified with hydrochloric acid to free it from iron, consequently there is no reason to believe that the evident oxidative properties it displayed can be attributed to anything else than oxygen of the air likewise adsorbed by it, the power of charcoal to adsorb gases being sufficiently well known.

Other similar experiments, which in view of their simplicity are not detailed, showed that: (1) the amount of arsenious acid oxidized is dependent upon the amount of charcoal used as well as upon the length of heating but not at all upon the concentration of arsenious acid (at any rate between 5 cc. and 25 cc. of twentieth-normal solution in an original volume of 30 cc.); (2) arsenic acid is likewise slightly adsorbed, and likewise quantitatively returned to thorough washing.

As to the practical application of the above observations, it is believed that they may be of considerable assistance in the estimation of both arsenious and arsenic acids in a variety of substances. As a test of the decolorizing power of the charcoal, two grams of a sample<sup>1</sup> of London purple were digested with 100 cc. dilute hydrochloric acid according to the method of the A. O. A. C.,<sup>2</sup> and were then treated for five minutes at 60 to 70° C. with 2 g. blood-charcoal, being stirred most of the time. To obtain the most trying conditions, the solution was then at once filtered with suction, washing continued to a total volume of 250 cc., and the filtrate finally made to 300 cc. A 50 cc. aliquot, which is the quantity officially prescribed for each estimation—corresponding to 0.333 g. charcoal—developed no trace of purple color when treated with excess of either sodium carbonate or bicarbonate.

If actual arsenious oxide is to be determined it is of course necessary to obtain a "correction for oxidation" on the sample of charcoal to be employed, under the precise set of conditions which will prevail in the analysis.

The writer has previously recommended<sup>3</sup> the use of blood-charcoal in the assay of arsenical dips, noting the necessity for a correction, but at that time had reason to believe—and so implied—that it was chiefly attributable to adsorption. The precise cause of the

No.	PROCEDURE	Cc. N/20 I per 25 cc. As <sub>2</sub> O <sub>3</sub> sol.		Apparent loss; cc. N/20 I
		Without charcoal	With charcoal	
1	Direct titration for actual As <sub>2</sub> O <sub>3</sub> .....	25.14	..	..
2	50 cc. As <sub>2</sub> O <sub>3</sub> , 10 cc. H <sub>2</sub> SO <sub>4</sub> , 0.50 g. charcoal; made to 100 cc. in stoppered flask mixed, and filtered after 40 minutes, discarding first runnings. Titrated 50 cc. for actual As <sub>2</sub> O <sub>3</sub> .....	..	24.47	0.67
3	In a 100 cc. beaker, low form, 25 cc. As <sub>2</sub> O <sub>3</sub> , 5 cc. H <sub>2</sub> SO <sub>4</sub> , 0.25 g. charcoal; stirred cold 5 minutes, filtered(a), washed, and titrated for actual As <sub>2</sub> O <sub>3</sub> .....	..	24.97	0.17
4	Similar to No. 3 except heated 5 min. on steam bath. Titrated for actual As <sub>2</sub> O <sub>3</sub> .....	..	24.91	0.23
5	Similar to No. 4 except heated for 40 minutes with occasional stirring. Titrated for actual As <sub>2</sub> O <sub>3</sub> .....	25.15	24.74	0.40
6	Similar to No. 5 except titrated for total arsenic.....	25.14	25.13	Nil

(a) The tests without charcoal were not filtered but were made directly to the desired volume.

In the above table each figure for an iodine titration represents the average result from at least two closely agreeing and wholly independent tests.

From the results it is evident that blood-charcoal, though slightly adsorbing arsenious oxide from acid solution, quantitatively returns it to thorough washing, not, however, in its original state, but more or less oxidized to arsenic acid. The charcoal used, pur-

phenomenon was not of prime importance in a purely technical paper, but in the interests of scientific accuracy the matter has since received this special study.

BIOCHEMICAL DIVISION, BUREAU OF ANIMAL INDUSTRY  
U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON

<sup>1</sup> Obtained through the courtesy of C. C. McDonnell, of the Bureau of Chemistry and stated to contain approximately 25 per cent of dyestuff.

<sup>2</sup> Bureau of Chemistry, *Bull.* 107, Revised.

<sup>3</sup> U. S. Dept. Agric., *Bull.* 76.

<sup>1</sup> Compare U. S. Dept. Agric., *Bull.* 76.

<sup>2</sup> Compare Rosenthaler & Türk, *Archiv. der Pharmacie*, 244 (1906), 517.

THE STRENGTH OF NITRIC ACID, PERIOD OF EXTRACTION, AND IGNITION AS AFFECTING THE GRAVIMETRIC DETERMINATION OF PHOSPHORIC ACID IN SOILS

By O. L. BRAUER

Received September 1, 1914

The question of a good measure of the available phosphorus in soils has long confronted chemists. The earlier investigators thought that by taking a solution of approximately the same strength as the plant acids they ought to get a correct estimate of the available phosphoric acid. In Europe, Dyer's<sup>1</sup> method of 1 per cent citric acid was extensively used, while the American chemists used  $N/200$  HCl. Veitch<sup>2</sup> extracted soil first with water and then with citric acid. Maxwell<sup>3</sup> used 1 per cent aspartic acid. As was pointed out by Hall<sup>4</sup> other factors entered into the determination, giving discordant results. Dargast<sup>5</sup> had already shown that the amount of phosphoric acid varied very much with the solvent. For a given soil he got the following results, in percentages: Aqua regia, 0.108; ammonium oxalate, 0.056; ammonium citrate, 0.042; acetic acid, 0.018; saturated  $\text{CO}_2$ , 0.015; and distilled water, 0.012. Moreover, it was shown that a given method might show low  $\text{P}_2\text{O}_5$  in a soil which would still show a good crop yield. This led to the conclusion that a weak acid does not get all of the soluble phosphates. Wood<sup>6</sup> showed that strong  $\text{HNO}_3$  removed much more  $\text{P}_2\text{O}_5$  than the weaker acids; for example, strong  $\text{HNO}_3$  extracted from the soil 0.23 per cent; 1 per cent citric, 0.08 per cent; 1 per cent citric in excess of enough to neutralize the lime, 0.085 per cent  $\text{P}_2\text{O}_5$ . Other things being equal, the crop yield showed general agreement with the amount of  $\text{P}_2\text{O}_5$  determined by analysis, when the strong acids were used.

Still there is considerable diversity in the strengths of acids used for extraction. Passernini<sup>7</sup> used concentrated  $\text{HNO}_3$ , Williams<sup>8</sup> used HCl (sp. gr. 1.115), and Fraps<sup>9</sup> used  $N/5$  HCl. In 1880 Professor Karl Schmidt showed that the amount of  $\text{P}_2\text{O}_5$  extracted varied with the strength of HCl employed. With 10 per cent hot HCl he got 0.562; with 5 per cent cold HCl 0.09; with 1 per cent cold HCl 0.084, in a soil containing 1.97 per cent total  $\text{P}_2\text{O}_5$ . The first part of the present investigation is to determine the strength of  $\text{HNO}_3$  necessary to obtain all the soluble phosphoric acid, or that included by Hilgard under the term "reserve" material.

Not only in the case of strength of acid used in the extraction is there great diversity of practice among chemists, but also in the length of time used in extraction. Williams<sup>10</sup> used concentrated HCl at the temperature of boiling water for ten hours. Sigmon<sup>11</sup> reported for one-half hour and allowed to stand for 16

hours, then rotated one half hour again. Pagnoult digested for two hours. The official method of the U. S. Dept. of Agriculture<sup>2</sup> is to add the  $\text{HNO}_3$  and evaporate to dryness. Passernini<sup>3</sup> boiled on the sand bath for 1 hour.

The second part of this investigation is to determine the minimum time for the extraction of the soluble phosphates. Fraps<sup>4</sup> found that ignition increased the phosphate soluble in  $N/5$  HCl in both soils and phosphate materials. Lipman,<sup>5</sup> however, found that ignition decreased the phosphoric acid in soils which are soluble in nitric acid.

The third part of this investigation includes a study of the effect of ignition on the amount of  $\text{P}_2\text{O}_5$  set free by extraction with  $\text{HNO}_3$ .

SOILS USED—The soil was powdered up and passed through a 0.5 mm. sieve, and thoroughly mixed. Three soils of quite different  $\text{P}_2\text{O}_5$  content were selected.

1—A very rich, black, fine, silty loam, rich in phosphoric acid and humus from Arroyo Grande, San Luis Obispo County, California.

2—A light, sandy loam, of fairly good humus and  $\text{P}_2\text{O}_5$  content, from Anaheim, Orange County, California.

3—Heavy black adobe soil, low in humus and phosphoric acid, from Porterville, California.

METHOD—Weigh out 3 g. of air-dry soil and extract with  $\text{HNO}_3$  on the steam bath. Filter and wash until washings give no acid reaction. Evaporate to dryness and heat residue at  $130^\circ\text{C}$ . for 2 hours. Extract with 20 cc.  $\text{HNO}_3$  (sp. gr. 1.2). Filter and wash with warm water until the washings give no test for  $\text{Ca}_3(\text{PO}_4)_2$ . Add  $\text{NH}_4\text{OH}$  until a precipitate remains and dissolve in a couple of drops of  $\text{HNO}_3$ . Warm and add ammonium molybdate and stand at  $50-60^\circ$  for 12 hours. Filter and wash with solution of  $\text{NH}_4\text{NO}_3$  in  $\text{HNO}_3$ . Dissolve in  $\text{NH}_4\text{OH}$  and slowly add magnesia mixture to slight excess and stand over night. Filter and wash free from chlorides with a solution of 1 vol.  $\text{NH}_4\text{OH}$ , 1 vol. alcohol and 3 vol.  $\text{H}_2\text{O}$ . Dry in air bath and carefully ignite to constant weight.

STRENGTH OF NITRIC ACID—Samples of No. 1 were extracted with 50 cc.  $\text{HNO}_3$  and the rest with 20 cc.

TABLE I—STRENGTHS OF ACID VARIED  
Per cent  $\text{P}_2\text{O}_5$  found in soil

Strength of acid	No. 1	No. 2	No. 3
15 N.....	0.517	.....	0.067
8 N.....	0.518	.....	.....
4 N.....	0.501	0.177	0.065
2 N.....	0.517	0.187	0.074
N.....	0.516	0.154	0.059
5.....	0.488	0.155	None

$\text{HNO}_3$ . They were all heated for two days on the steam bath, with a watch glass over the soil cup to prevent evaporation of the liquid. The percentages given are computed to the air-dry basis and are averages of three checks on sample No. 1, and two in the other cases, which, with the exception of three instances, did not differ by more than 0.01 per cent.

From Table I it appears that 2N  $\text{HNO}_3$  will give

<sup>1</sup> Ann. Agron., 25, 554.

<sup>2</sup> Div. of Chem., Bull. 43, 387.

<sup>3</sup> Chem. Abs. [2], 1911, p. 535.

<sup>4</sup> Fraps, THIS JOURNAL, 5, 416.

<sup>5</sup> C. B. Lipman, Ibid., 4, 663.

<sup>1</sup> Trans. Lond. Chem. Soc., 65 (1894), 115.

<sup>2</sup> J. Am. Chem. Soc., 21, 1090.

<sup>3</sup> Ibid., 21, 415.

<sup>4</sup> Trans. J. Chem. Soc., 39, 205.

<sup>5</sup> Ann. Agron., 9, 470.

<sup>6</sup> J. Chem. Soc., 69, 291.

<sup>7</sup> J. Chem. Soc. Abs., 1911, p. 535.

<sup>8</sup> U. S. Dept. Agr., Bull. 43, 387.

<sup>9</sup> THIS JOURNAL, 5, 416.

<sup>10</sup> J. Am. Chem. Soc., 17, 925.

<sup>11</sup> Ibid., 29, 929.

as much soluble phosphoric acid as any stronger solution. The normal acid shows a slight decrease in yield in the second and third soils, and the  $N/5$  acid shows a decrease in every case. This agrees with the experience of Wood in that a certain strength of acid is necessary to get all the  $P_2O_5$ . However, it is not necessary to use the concentrated acid as did Passernini. The stronger nitric acids indeed are objectionable because they introduce certain difficulties by bringing down larger quantities of iron and aluminum.

**PERIOD OF EXTRACTION**—In each case 20 cc. of normal acid were used, and the per cent of  $P_2O_5$  given is an average of two closely agreeing checks.

TABLE II—PERIOD OF EXTRACTION VARIED.  
Per cent  $P_2O_5$  found in soil

Period of extraction	No. 1	No. 2	No. 3
1 hr. ....	0.499	0.166	0.053
2 hr. ....	0.513	0.173	0.054
4 hr. ....	0.501	0.166	0.068
8 hr. ....	0.517	0.154	0.059

In one hour practically all the soluble  $P_2O_5$  is obtained. Two hours would be a liberal allowance and sufficient for all cases. Passernini boiled for 1 hour, which is about enough, but Williams boiled on the water bath for 10 hours, which was much longer than necessary. Pagnoul digested for two hours, which was about the right length of time. Hilgard employed the two-day period for digestion with concentrated  $HNO_3$ .

**IGNITION**—Each sample was extracted for 2 hrs. with 20 cc.  $N HNO_3$ .

TABLE III—TIME OF IGNITION VARIED  
Per cent  $P_2O_5$  found in soil

Ignition at red heat	No. 1	No. 2	No. 3
0 .....	0.513	0.18	0.054
1/2 hr. ....	0.499	0.199	0.046
1 hr. ....	0.487	0.195	0.041

In these cases the effect of ignition would seem to be similar to that obtained by Lipman, *i. e.*, to decrease the amount of  $P_2O_5$  soluble in  $HNO_3$ . Sample No. 2 shows practically no change, but the other two show appreciable decreases in the amounts of  $P_2O_5$  extracted, as the period of ignition lengthens and as between ignition and no ignition.

#### SUMMARY

I—Acid weaker than  $1N$  to  $2N HNO_3$  will not extract all the soluble phosphoric acid from a soil.

II—It is needless to extract with the acid for a longer period than 2 hours on the steam bath.

III—Ignition decreases the  $HNO_3$  soluble phosphoric acid in the soils.

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### COMPARISON OF SILICATES AND CARBONATES AS SOURCES OF LIME AND MAGNESIA FOR PLANTS

By W. H. MACINTIRE AND L. G. WILLIS  
Received September 21, 1914

The amount of calcium carbonate in soils has long been considered a very important consideration in their chemical examination; but calcium silicate has not been accorded universal recognition as an important source of lime for growing plants. The same may be said of the corresponding forms of magnesia.

In determining soil carbonates by the present official method of the Association of Official Agricul-

tural Chemists, we find that practically every soil has an *apparent* occurrence of carbonates, but at the same time possessing, in most cases of humid soils, a *lime requirement* by the Veitch method.<sup>1</sup> These two conditions—presence of appreciable amounts of carbonates and lime requirements, which indicate need of carbonates—are diametrically opposite, and were a soil to contain carbonates under laboratory conditions it would have no lime requirement. It is hard to conceive of a soil having 0.27 per cent calcium carbonate and yet having a lime requirement of 3812 lbs. of  $CaCO_3$  per acre (3,500,000 lbs. of soil); however, such results were obtained by the A. O. A. C. method for  $CO_2$  and the Veitch lime requirement method, respectively, upon the loam soil of the farm at this Station. This is strongly indicative of erroneous results from either one or possibly both of the methods cited.

The work of Marr<sup>2</sup> and the results reported by the writers<sup>3</sup> have shown that some soils absolutely free of carbonates, through elimination by dilute acid digestion, will produce heavy evolution of  $CO_2$  from the action of boiling acid upon carbonaceous matter. Marr concluded from his work that the use of 1:50  $HCl$ , and boiling with greatly reduced pressure, gave correct results. Until recently, practically all of the methods advanced for the determination of soil carbonates were based upon the supposed necessity of boiling the soil with acid to completely decompose carbonates and to expel from solution the liberated  $CO_2$ . The more recent work of the writers<sup>3</sup> has demonstrated that phosphoric acid is less active than hydrochloric acid upon soil organic matter and that 1:15  $H_3PO_4$  will liberate and expel from solution all carbonate  $CO_2$  at room temperature with about a 4-inch vacuum. In recent unpublished work the writers are making determinations upon treatments of about 400,000 pounds of limestone per 2,000,000 lbs. of soil and the carbonates from this treatment are entirely liberated by 1:15  $H_3PO_4$  with suction and without heat.

The Association of Official Agricultural Chemists has recognized the incorrectness of its method and is now studying the two methods above cited.

It will thus be seen that in many cases all of the  $CO_2$  found by analyses of soils when boiling with acid has been erroneously considered as in combination with lime, while the lime has occurred largely in the form of silicates and not as carbonates.

#### CORRELATION BETWEEN ACIDITY AND ABSENCE OF CARBONATES

Gaither,<sup>4</sup> in a comprehensive study of a large number of Ohio soils, found that almost invariably there was a close correlation between acidity, as indicated by the litmus-paper test, and absence of carbonates by his modification of the Marr method. We should probably note, however, that the authors have found that soils rich in silicates of calcium and magnesium,

<sup>1</sup> *Jour. Am. Chem. Soc.*, **24** (1902), 1120.

<sup>2</sup> *Jour. Agr. Sci.*, Vol. III, Part 2, 155-160.

<sup>3</sup> *Tenn. Sta. Bull.*, **100**.

<sup>4</sup> *THIS JOURNAL*, **5** (1913), 138.

but devoid of carbonates, will react alkaline toward litmus paper. The litmus-paper test, then, will show acidity in the absence of carbonates, except when there is a considerable amount of the alkali-earth silicates.

#### NATIVE OCCURRENCE OF SILICATES AND THEIR FORMATION IN SOILS

It has been the observation of the senior author that it is a rare exception to find in the Eastern States a cultivated soil which will react alkaline to litmus, unless it has been limed. It would seem, then, that the crops of many of our soils are *compelled* to secure much of their lime from the carbonate of lime formed by the hydrolysis of calcium silicate in carbonated water.

While the occurrence of native lime silicates has received but scant consideration, there has been even less attention paid to the formation of silicates from lime treatments. Total lime, determinations by one of the writers,<sup>1</sup> upon the lime-treated plots of the Pennsylvania Station has shown that the reaction between lime and silicates continues long after attaining alkaline conditions by the satisfying of the *immediate lime requirement*. It was shown that of the total increase of lime over the check plots as a result of the lime treatments, nearly 35 per cent was accumulated as silicates. Investigations recently reported from the Tennessee Station<sup>1</sup> have shown that amounts of CaO, Ca(OH)<sub>2</sub> and precipitated CaCO<sub>3</sub>, in excess of requirements of acidity, have very quickly united with soil silicates. It was found that the burnt and hydrated forms, in amounts equivalent to lime requirements, acted directly with silicates and without carbonation, as in the Veitch procedure, when the treatments were mixed throughout the soil. The precipitated carbonate seemed to combine with siliceous materials as quickly as the oxide and hydrate. The same experiments have shown decidedly quicker reaction between siliceous soil compounds and the oxide, hydrate and precipitated carbonate than between silicates and ground limestone, in excessive amounts of equal basicity. It was also shown that though lime reacts extensively with siliceous materials the silicates formed function in the same manner as does the carbonate but to a lesser degree, which means that *there is conservation of lime in soils when it is present as silicate*.

#### BENEFICIAL EFFECTS OF CALCIUM SILICATE

In extensive plot work at the Tennessee Station marked effects are noticeable from liming over a nine-year period, during which nine crops of cow-peas and nine of wheat have been grown, though only 1800 lbs. per acre were applied—an amount just sufficient to neutralize the acidity requirements indicated by the Veitch method. It is very probable that the present favorable results from liming nine years ago are due to residues of lime in the form of calcium silicate and not to calcium carbonate.

It has probably not been sufficiently emphasized, if emphasized at all, that the average amounts of lime applied are required to neutralize "acidity" or to

satisfy lime requirement; and that the lime of caustic or carbonate formed shortly combines with acid silicates, preventing any accumulation of carbonates as the result of treatments. Gardner and Brown<sup>1</sup> found that applications of burnt lime and ground limestone, in amounts indicated by the Veitch method, reduced the average requirements of a large number of plots by 71 and 72 per cent, respectively. The analyses for residual lime requirements were made about eight months after treatments. This strongly indicates that the continued beneficial effects of moderate liming must necessarily have come from the carbonate of lime, which is derived from the silicates by action of carbonated water.

#### LITERATURE

Although the literature upon the beneficial effects of CaSiO<sub>3</sub>, *under such designation*, is exceedingly scant, a great many data, offered as showing the continued good effects from field treatments of moderate amounts of burnt or carbonated lime, have been attributed directly to the original oxide or carbonate, whereas the beneficial results have been due indirectly to the original treatment, and directly to the continuation of the lime as silicate in the soil. Mieth<sup>2</sup> advanced the query, "Can the lime of calcium silicate serve as plant food?" and he studied the question by water-culture experiments with oats. He concluded that the CO<sub>2</sub> exuded by root activities served to produce carbonated water, which decomposed the calcium silicate and formed free silicic acid and calcium bicarbonate. He further concluded that the easily decomposable calcium silicate should receive consideration as a source of lime for growing plants. Gregorie<sup>3</sup> found, in water cultures of rye, that calcium zeolite "stimulated both root and aerial development," both of which were retarded by an excess of CaCO<sub>3</sub>. Immendorf<sup>4</sup> regarded liming with lime containing soluble silica as beneficial in connection with the formation of zeolites. Pfeiffer,<sup>5</sup> in reviewing literature and discussing the work of Immendorf, concluded that the preponderance of evidence indicated beneficial effects from the use of siliceous lime. Von Feilitzen<sup>6</sup> secured better results with the finest lime, which reacts most extensively with silicates as shown by results published by this Station.<sup>7</sup>

#### SILICATES AS SOURCES OF CARBONATES IN SOIL SOLUTIONS

The data presented in Table I show the comparative amounts of lime and magnesia conveyable in solution as bicarbonates to plants, from carbonates and silicates as the sources of the bases.

These results were secured by placing each charge, in the amounts designated, in 500 cc. of distilled water in glass cylinders and passing a current of CO<sub>2</sub> through the water for 4 hours continuously. The CO<sub>2</sub> entered at the bottom of the cylinders and at such a rate as to

<sup>1</sup> Pa. Sta. Annual Report, 1910-11, 76.

<sup>2</sup> Landw. Vers. Sta., 74 (1910), No. 1, 81; No. 2, 120.

<sup>3</sup> Exp. Sta. Rec., 23, 527.

<sup>4</sup> Ibid., 26, 34.

<sup>5</sup> Ibid., 29, 520, and 30, 127.

<sup>6</sup> Ibid., 23, 426.

<sup>7</sup> Loc. cit.

keep the substances in suspension. At the end of the 4-hour period, the suspended matter was quickly removed by filtration through Buchner filters with suction and the solutions titrated with  $N/20$  acid, methyl orange being used as an indicator. It will be noted that

TABLE I—COMPARISONS OF SOLUBILITIES OF FINELY GROUND MINERAL CARBONATES AND SILICATES OF CALCIUM AND MAGNESIUM IN CARBONATED WATER—PERIOD OF CONTACT, 4 HOURS

SUBSTANCE	Cc. $N/10$ acid to neutralize	Alkalinity in filtrate of g. $CaCO_3$ per liter	G. $SiO_2$ per l. carbonated. $H_2O$
Wollastonite ( $CaSiO_3$ )—10 g.	54.2	0.542	0.0566
Limestone ( $CaCO_3$ )—10 g.	90.0	0.900	..
Serpentine ( $MgSiO_3$ )—10 g.	21.6	0.216	0.0162
Magnesite ( $MgCO_3$ )—10 g.	28.0	0.280	..
Wollastonite and serpentine—10 g. each.	69.35	0.6935	0.0840
Precipitated chalk ( $CaCO_3$ )—10 g.	117.3	1.173	0.0020
Pptd. chalk and serpentine—10 g. each.	121.2	1.212	0.0254
Wollastonite—20 g.	92.2	0.922	..

the silica found in solution would account for but a small part of the  $CaO$  and the  $MgO$  as dissolved silicates, even assuming that the bases were combined as silicates with the  $SiO_2$  found, instead of its occurring as hydrate  $SiO_2$ . The same has been found to be true of the drainage waters from soils devoid of carbonates.

#### PLAN OF EXPERIMENTS WITH CALCIUM AND MAGNESIUM SILICATES

These observations, together with the fact that not only silicates but pure  $SiO_2$  will decompose calcium and magnesium carbonates and that the affinity of  $MgO$  for  $SiO_2$  and  $TiO_2$  is so great as to prevent the occurrence of magnesium carbonate as a solid in soils,<sup>1</sup> suggested a comparison between the silicates of calcium and magnesium, and the carbonates of the two elements. The two soils used in the work were a silty loam of "rotten" limestone origin and a sandy clay loam. Both soils were low in total lime and devoid of carbonates; and each had a lime requirement of about 1 ton of calcium carbonate per 3,500,000 lbs. of soil. The sandy loam contains a considerable quantity of red clay and was apparently benefited physically to a much greater extent than the silty soil, which had a decided tendency to bake. In other basket work upon the same soils the Veitch method had been used as a basis of  $CaO$  and  $MgO$  treatments without cropping. In one set of treatments in this previous work,  $CaO$  and  $MgO$  were applied separately, in amounts chemically equivalent to 16070 lbs. of  $CaCO_3$  per 3,500,000 lbs. of soil in excess of the indication of the Veitch method, both  $CaO$  and  $MgO$  being supplied as c. p. precipitated carbonates. It was found, however, that prior to the seeding of clover, the  $MgCO_3$  had been entirely decomposed with dissipation of the  $CO_2$ , hence the treatments in the magnesium carbonate pots were equivalent to finely divided magnesium silicate. In the silicate treatments the  $CaO$  and  $MgO$  treatments were duplicated as to amounts of  $CaO$  and  $MgO$ , but analyzed 100 mesh native mineral silicates, wollastonite and serpentine, were used as sources of calcium and magnesium. The treatments were thoroughly mixed throughout the entire soil mass. Eight-inch clay pots, painted inside and out with black asphaltum paint, were used as containers, two pots being used for each treatment and as a check on each

soil. No treatments other than lime and magnesia were given. Red clover was used as a measure of plant growth. The seeding was made in the middle of April and the pots were exposed, but protected from unfavorable weather. Distilled water was supplied almost daily.

#### GROWTH OF CLOVER RESULTING FROM TREATMENTS

From repeated seedings upon the two soils, we were unable to obtain any growth in the check pots.

The comparison between the crops of treatments A, Table II, and those of F is very striking for both soils. It should be emphasized that the amount of  $MgO$  applied

TABLE II—TREATMENTS

Each substance (or mixture) listed below was added in the amount equivalent to 16070 lbs. per acre in excess of the Veitch method indication.

A— $MgSiO_3$	D— $CaSiO_3$
B— $MgSiO_3$ and $CaSiO_3$	E— $CaCO_3$
C— $MgSiO_3$ and $CaCO_3$	F— $MgCO_3$
Checks received no treatment.	

was the same in each case, and as before stated the magnesium carbonate had been entirely converted to silicates prior to seeding. Hence the treatments of A and F were identical in the amounts of  $MgO$ , but the magnesia was in one case (A) derived from 100-mesh serpentine, and in the other case (F) from silicates formed from precipitated magnesium carbonate.

In both soils the addition of each silicate alone gave decidedly increased yields. In one soil, the mixture of the two silicates increased the growth above that

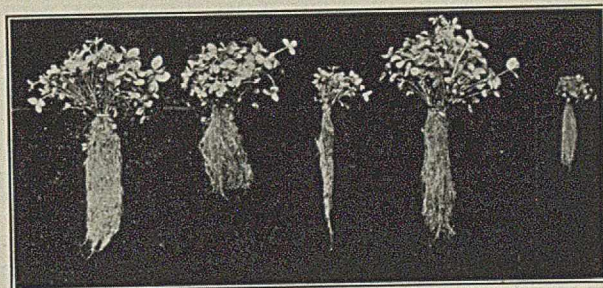


FIG. 1—RED CLOVER IN SANDY CLAY LOAM SOIL. CHECK AND TREATMENT F—NO GROWTH

obtained from either silicate alone, while in the other soil the two-silicate treatments combined gave about the average of the growth secured from the two single silicate treatments.

In both soils the yields obtained from the silicates alone were decidedly better than the results secured from corresponding carbonates applied singly. The applications of the two silicates together were decidedly favorable in both soils, but the substitution of  $CaCO_3$  for  $CaSiO_3$  as supplementary to  $MgSiO_3$  proved decidedly disadvantageous. Experience from practice has, in a number of instances, shown unfavorable results from excessive liming, notably upon the heavily limed plots of the Pennsylvania Station.<sup>1</sup> Gardner and Brown<sup>2</sup> found, from pot work upon the above mentioned limed plots, that additional liming still further reduced the yield of clover. Densch,<sup>3</sup> in noting harmful effects of excessive liming, attributes

<sup>1</sup> Pa. Sta. Bull., 90.

<sup>2</sup> Loc. cit.

<sup>3</sup> Abs. Centbl. Bakt. 2 Abst., 39, (1913), No. 4, 159; 7, 160.

<sup>1</sup> Loc. cit.

the unfavorable results to reduction of nitrates to ammonia, and to the persistent occurrence of nitrites as well as to formation of nitro and nitroso compounds. Ritter<sup>1</sup> attributes injurious results of excessive liming on peaty soils to the poisonous oxidation products

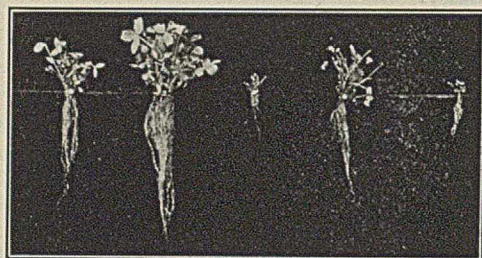


FIG. II—RED CLOVER IN SILTY LOAM SOIL. CHECK AND TREATMENT F—NO GROWTH

of humus. It is evident from the results shown in Table III and Fig. 1 that while harmful results may be expected from excessive amounts of CaO as finely

TABLE III—GROWTH OF RED CLOVER, GRAMS AIR-DRY TOTAL OF 2 POTS FOR EACH TREATMENT OF EACH SOIL

Treatment	Check	A	B	C	D	E	F
		MgSiO <sub>3</sub> (serpentine)	MgSiO <sub>3</sub> and CaSiO <sub>3</sub>	MgSiO <sub>3</sub> and CaCO <sub>3</sub>	CaSiO <sub>3</sub> (wollastonite)	CaCO <sub>3</sub> (precipitated)	MgCO <sub>3</sub> (precipitated)
ON SANDY CLAY LOAM							
No. of plants	0	27	47	26	20	21	1
Wt. of plants	0	11.4813	12.2757	1.8889	13.8557	4.8917	0.0165
ON SILTY LOAM							
No. of plants	0	14	30	30	9	5	0
Wt. of plants	0	1.3427	4.1743	0.1361	0.5892	0.0642	0.0000

divided carbonates, the same may not be said of CaO in the silicate form.

#### SUMMARY AND CONCLUSIONS

Fallacious methods for the determination of carbonates have given data showing occurrences of soil carbonates in many cases where none existed.

The long continued effects of liming in small or moderate amounts is to be attributed not to a continuation of carbonates resulting from treatments, but to the conservation of lime as silicates.

Through hydrolysis, calcium silicate functions in the same manner as calcium carbonate, furnishing lime as bicarbonate to the soil solution.

Excepting phosphates, the occurrence of calcium in soils is very often almost entirely as silicates, while magnesia seldom exists as the carbonate, but is generally to be found as the silicate.

Magnesium silicate formed by MgCO<sub>3</sub>, equivalent to 16070 lbs. of CaCO<sub>3</sub>, per 3,500,000 lbs. of soil in excess of the Veitch method, was decidedly toxic, while the same amount of MgO applied as 100-mesh serpentine was very beneficial.

Calcium and magnesium mineral silicates, wollastonite and serpentine, were very beneficial when applied either singly or jointly.

Calcium silicate, in the quantities used, was decidedly superior to calcium carbonate, when the amounts of CaO were identical.

The addition of CaCO<sub>3</sub> alone effected some increase, but it reduced the beneficial effects of serpentine when added thereto.

The data indicate that CaSiO<sub>3</sub> is decidedly superior to CaCO<sub>3</sub>, both in its effect upon plant growth and as a form tending to conserve lime in soils.

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#### A SIMPLE METHOD FOR DETERMINING THE CRITICAL MOISTURE CONTENT OF SOILS

By R. O. E. DAVIS

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##### SIGNIFICANCE OF THE CRITICAL MOISTURE CONTENT

The critical moisture content of a soil has been described by Cameron and Gallagher<sup>1</sup> as the moisture content at which the physical properties of the soil attain either a maximum or minimum value. This moisture content corresponds to that physical condition of the soil when it is most suited for cultivation and for plant growth. This condition is known to the practical greenhouse man as the optimum condition. It depends upon the moisture content, the aeration, the temperature, mechanical composition and structure of the soil, and the physical condition. The physical condition is the summation of the other factors, and since it is dependent on physical factors, the measurement of the factors has assisted in determining the best physical condition as the optimum condition for plant growth. The critical moisture content then has reference to the condition of the soil in regard to its physical properties and at the same time designates that condition of soil moisture suitable for the growth of plants. This means that the critical moisture content is the most important point to determine in the study of the physical condition of the soil. It is the only measurement that shows a definite correlation between the physical properties and the condition for the plant growth.

The importance of the critical moisture content has been pointed out by Cameron and Gallagher<sup>2</sup> and more recently by Free.<sup>3</sup> Free says, "It is a constant which means something. It may be determined in a dozen different ways and neither the condition of the determination, the history of the sample, nor the personality of the experimenter will affect its value. Unfortunately, it has one serious disadvantage—its determination is exceedingly tedious, laborious and costly."

The critical moisture content is the content at which the soil can be put in the best condition for plant growth, or it determines the best time for tillage operations. The plant can then best obtain the necessary water from the soil because all the other factors encouraging plant growth are at their best.

##### PREVIOUS METHODS OF DETERMINATION

The methods previously employed for obtaining the critical values of the soil were by the determination of the volume-moisture relation or the penetration-moisture relation. The penetration values, measured by the weight required to force a pointed instru-

<sup>1</sup> Bull. 50 (1908), Bureau of Soils, U. S. Dept. of Agric.

<sup>2</sup> Loc. cit.

<sup>3</sup> E. E. Free, "Studies in Soil Physics," *Plant World*, 14 (1912), 36.

ment a given distance into the soil, were determined at different moisture contents. When these values were plotted, using per cent of moisture and penetration as the coordinates, the resulting curve showed the minimum penetration values at the critical moisture content. In a similar way the critical moisture content may be determined by plotting the apparent specific gravity or the apparent specific volume at different water contents. All of these methods are exceedingly laborious requiring special apparatus and consuming much time. In addition, the penetration method is far from accurate, and the other methods are not all that could be desired in this respect.

A still further difficulty is that in securing uniform packing of the soil for the penetration or volume methods, the screening becomes increasingly difficult with increase in water content. With sandy soils this is not serious, but on soils of a silty or clayey character it may be very serious; in many cases screening is entirely impracticable, and in all cases it is accomplished with the expenditure of much patience and labor. The soil collects in little balls that will not pass through the screen, but with shaking become more compact and increase in size. These can be forced through the screen only by rubbing with the hand.

#### THE NEW METHOD

The method adopted as most simple after many experiments with various devices was that of following the capillary movement of water. In some experiments on capillary movement it was noted that after the removal of the soil column from water the movement of water took place for a time, and then ceased. This occurred even though the two layers of soil in contact with each other were very different in their water content. A soil comparatively wet would remain in contact with a soil that was dry for days without any appreciable change in the moisture relations. Experiments were carried out to determine, if possible, the relation of the water in the moist layer of soil to the critical moisture content.

Water, as it advances into a soil by capillary action, moves as a thin sheet covering the soil grains with a thin film of moisture. The thickness of this continuous film of water increases with the nearness of approach to the source of water supply. Between the source of supply and the advance film are all degrees of thickness of water film, from the condition in which the interstitial spaces are filled with free water to that in which the film is extremely thin. The critical moisture content is that in which the water is all in the form of films on the soil grains. Thus, when water is moving through a soil by capillary forces, the water content of the soil just where the water film has advanced farthest is the critical or optimum water content.

In practice it is not possible to measure the exact moisture content where the film is most advanced, but it is possible to break the capillary connection and allow a distribution of the soil moisture until the water is present mostly in the form of film moisture. The determination of the moisture in the first inch of the moist soil column has given values corresponding to

the critical moisture content as determined in the ordinary way.

The apparatus used was a tube of over an inch in diameter. Glass tubes were tried, but the most satisfactory ones were made of brass. Brass tubing, one and a half inches in diameter, was cut into one-foot lengths. The pieces were split lengthwise and in one of the halves was cut a slit half an inch wide extending to within one inch of each end. The slit was covered with a strip of celluloid held in place by drops of solder stuck to the inside of the tube. This affords a window through which the movement of water may be observed. To the edges of one-half of the brass tube at each end were soldered short pieces of copper wire. When the two halves of the tube were placed together the copper wires were bent over and held them together. By wrapping a rubber band around the tube, the halves may be held in position more firmly. The end that is placed in the water is closed by a piece of cotton cloth secured by a rubber band.

The advantages of this type of tube are several. The window affords a means of watching the course of the water as it advances in the soil column. However, the most important advantage is that the tube may be opened up and the soil column removed in its entirety. This can then be divided up and the moisture content of any section determined.

In making the determination of the critical moisture content the tube is filled with soil and one end placed in water. When the water has advanced several inches in the tube it is removed from the water and placed in a horizontal position until capillary movement practically stops. The tube is then opened and a moisture determination made of the moist column of soil in the inch at the extreme end to which the water has advanced.

Experiments to determine the value of this method for determining the critical moisture content of soils were made on seven samples of soils of varying character. They were: Cecil sandy loam, Volusia silt loam, Marshall clay loam, Arlington Farm garden clay, Colbert silty clay loam, Memphis silt loam and Lexington silt loam. The first four were used to obtain comparative results on packing, size of particle aggregates, and length of time necessary to obtain equilibrium in the soil column.

The results on the differences in packing are given in Table I.

TABLE I—EFFECT OF PACKING ON MOISTURE CONTENT PER CENT MOISTURE IN SOIL

PACKING OF SOIL	Volusia silt loam	Garden soil	Cecil sandy loam	Marshall silt loam
Loose.....	15.9	16.0	8.0	15.2
Moderate.....	16.2	16.5	8.5	16.1
Tight (air-free).....	16.8	17.3	8.7	17.3

This shows that the packing does exert an influence, but not so great as was at first expected. When more closely packed, the moisture content is somewhat higher than when loosely packed.

Table II shows the results of different size soil aggregates. The movement is irregular with the large aggregates and the amount of moisture is slightly less than with the smaller ones.

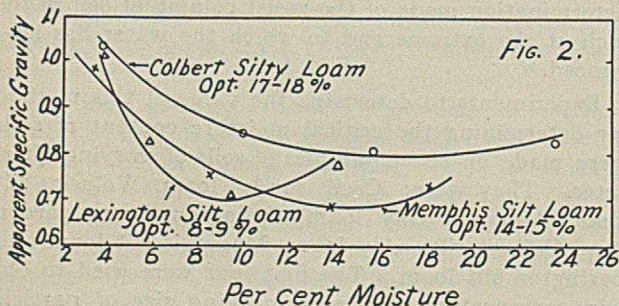
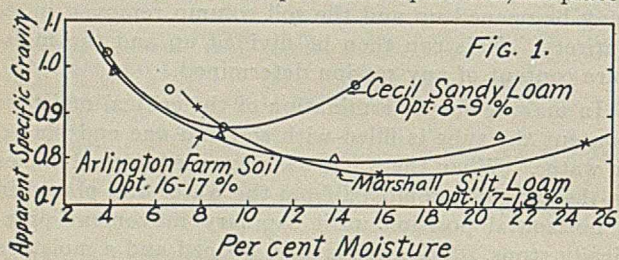
Table III demonstrates the influence of time on the moisture content. It may be seen that after removal from the water the tubes should be left for about 18 hours. Any movement of water after that length of time is very slight; in fact, is almost inappreciable. Leaving the tubes for a much longer time results in the loss of moisture by evaporation.

As a result of these experiments the method adopted was as follows: The air-dried soil is rubbed in a porcelain mortar just sufficiently to break up any lumps of soil. The soil is filled into the brass or glass tube closed at the lower end by cotton cloth. The end of

TABLE II—EFFECT OF SIZE OF SOIL AGGREGATES ON MOISTURE CONTENT  
PER CENT MOISTURE IN SOIL

SIZE OF SOIL	Volusia silt loam	Garden soil	Cecil sandy loam	Marshall silt loam
Coarse.....	16.1	15.3	6.5	15.2
Fine.....	16.6	16.8	10.8	17.0

the tube is tapped on the table until the soil column becomes so solid that the top does not break when the tube is placed in a horizontal position. The tube is then placed in water until the soil column becomes wet an inch or more above the water level. The tube is then removed from the water, the wet end covered with a piece of sheet rubber to prevent evaporation, and placed



in a horizontal position for about eighteen hours. The length of the soil column should be such that the

dry soil beyond the point to which the moisture has advanced is at least two inches.

The tube is opened and the moisture determined in

TABLE III—EFFECT OF TIME ON MOISTURE CONTENT  
PER CENT MOISTURE IN SOIL

Time after taking out of water Hrs.	PER CENT MOISTURE IN SOIL		
	Cecil sandy loam	Marshall silt loam	Volusia silt loam
12	10.8	17.7	17.4
12	7.7	21.0	19.9
24	7.7	16.6	16.6
24	7.6	16.6	16.0
24	..	17.0	16.7
24	..	17.3	..
48	6.4	16.5	..
72	..	..	16.1

a sample taken from the first inch of moist soil next to the dry portion. This moisture content represents the critical moisture content of the soil.

Experiments made to determine the critical moisture content, as compared with that obtained from the moisture-apparent specific gravity curve, were made

TABLE IV—COMPARATIVE RESULTS ON SEVERAL SAMPLES OF SOIL

SOIL	Per cent moisture by capillarity	Critical moisture content by apparent sp. gr.
Cecil sandy loam.....	8.7	8-9.0
Marshall silt loam.....	17.3	17-18
	17.0	
	16.5	
Garden soil.....	16.6	16-17
Volusia silt loam.....	16.7	16-17
	17.0	
Colbert silty loam.....	17.4	17-18
	17.0	
Memphis silt loam.....	14.5	14-15
	14.9	
Lexington silt loam.....	8.5	8-9
	8.7	

on several samples of soil. The curves of moisture-apparent specific gravity are shown in Figs. 1 and 2, and the results from the capillarity method are given in Table IV, which shows that there is a close agreement between the two methods.

#### CONCLUSIONS

It is probable that the critical moisture content of a soil is its most important property in determining the physical condition of the soil.

Previous methods of determining the critical moisture content are tedious and laborious, requiring skill and special apparatus, and are only fairly accurate.

The capillary method of determining the critical moisture content is more accurate than the older methods, is simply and quickly carried out and requires little and inexpensive apparatus.

BUREAU OF SOILS

U. S. DEPARTMENT OF AGRICULTURE  
WASHINGTON

## LABORATORY AND PLANT

### A NEW AND IMPROVED FORM OF KJELDAHL DISTILLATION APPARATUS

By ARTHUR D. HOLMES<sup>1</sup>  
Received August 8, 1914

There are so many forms of distillation apparatus for Kjeldahl determinations in use at present that a chemist contemplating making nitrogen determinations is immediately confronted with the problem of choosing that type which seems best suited to his needs. The factors to be considered primarily are simplicity

<sup>1</sup> Scientific assistant, nutrition investigations.

in design, low cost of construction, facility with which defective or broken parts may be replaced, durability, and ease and efficiency of operation. However, in spite of the fact that there may have been many types of apparatus devised, and many modifications of these types have been made, in almost any apparatus one or more of these essential features are omitted. Probably the most widely used apparatus for this purpose is one in which a metal tank containing several coiled block-tin tubes serves as a condenser. This has some serious disadvantages; one is, that if



the tank or any of the condenser tubes should leak, it becomes necessary to interrupt the use of the entire system while repairs are being made; another is that when it is desirable, at the end of the distilling process, to steam out the entire length of the condenser tube in order that none of the ammonia may be left in it, that can be done only when all the Kjeldahl flasks are ready for steaming at the same instant. In practice, however, the rate of distillation varies in the different flasks, and when a tank type of condenser is used one is obliged either to allow some of the flasks to distill until there is danger of bumping or else to steam out some of the others sooner than is desired. To avoid the difficulties involved in the use of this type of apparatus, which was formerly employed in this laboratory, the apparatus described hereafter (Fig. I), was designed, with the intention of incorporating to as great an extent as possible the features enumerated above. Since it has proven so satisfactory, and is so simple in construction that it may be made by the

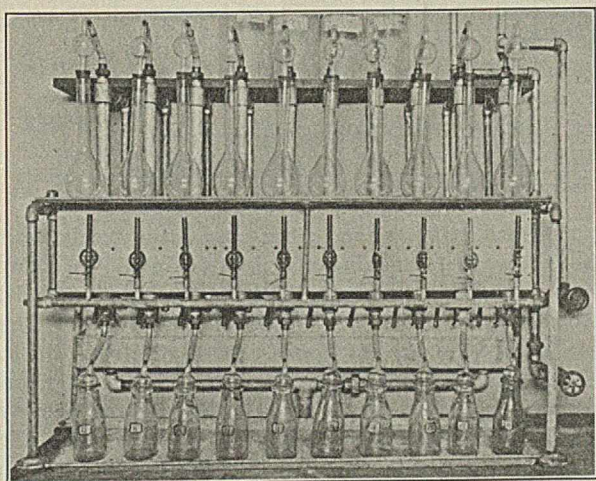


FIG. I

average plumber, a detailed description should prove of value to anyone wishing to construct a similar distillation apparatus. The specifications and accompanying figures (which show details of construction of the complete apparatus set up in readiness for distillation) will convey a definite idea of its construction.

The bank of condensers, which may be composed of any desired number of units, is so constructed that each condenser is entirely separate in every way, even to having an individual water circuit, which may be regulated independently of the remainder of the system. As shown in Fig. II, each condenser jacket, A, is made of 1 1/4 in. galvanized iron pipe 18 in. in length, which terminate at each end, BB, in a 1 1/4 x 3/4 x 3/4 in. galvanized iron T. The inlet end of each condenser jacket is connected directly to the water supply pipe that is common to all by means of a 3/4 in. pipe, C, which carries a 3/4 in. brass union, D, and a "stop and waste" cock, E. The "stop and waste" cock is placed between the brass union and the water main, so that it is possible to shut off the water from any one of the condensers and remove it without interrupting the use of the other units of the system.

In Fig. III it will be noticed that a section of the supporting frame has been removed so as to show clearly the position and function of the "stop and waste" cock. It will also be noticed that the ends of water and gas pipes are fitted with plugs in order to prevent water and gas passing beyond the last condenser inlet and Bunsen burner, respectively. When the handle of the cock is in the position shown, the water circuit is shut off and the waste "pipe" is open, making it possible to drain the condenser jacket and to steam out the condenser tube from the distilling flask to the container in which the ammonia is caught and neutralized. To the outlet end of each condenser jacket is connected a 3/4 in. iron pipe, FF, that discharges into an overflow tank, G, which is common to the entire system.

The condenser tube HH, which is made of 3/4 in. block-tin type, may be easily removed, as it is slipped through the 3/4 in. brass union, II, on each end of the condenser jacket. Each brass union has a male thread on one end which is screwed directly into the T that forms each end of the condenser jacket. The other end of the union fits loosely over the block-tin pipe, and "lamp wicking," such as is commonly used for packing, is placed between the two portions of the unions, after which they are screwed tightly together, forming a water-tight joint. Thus, in case of injury the block-tin tubing may be removed by simply unscrewing the two parts of each brass union on the ends of the condenser.

The ordinary 500 cc. Kjeldahl flask J, used in connection with this apparatus, is connected by means of a rubber stopper, L, to the trap K, the tubing of which is bent at about a 30° angle and connected by means of rubber tubing, M, to the condenser tube. The modified adapter, O, used in connection with the apparatus, is connected by means of rubber tubing, P, to the lower end of the block-tin condenser tube and leads into an ordinary pint milk bottle, Q, which is used as a container for the acid into which the ammonia is distilled. The flasks are heated by Bunsen burners, R, screwed into a 1/2 in. piece of common iron pipe,

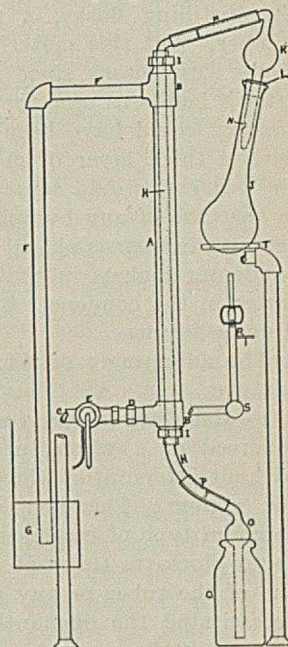


FIG. II

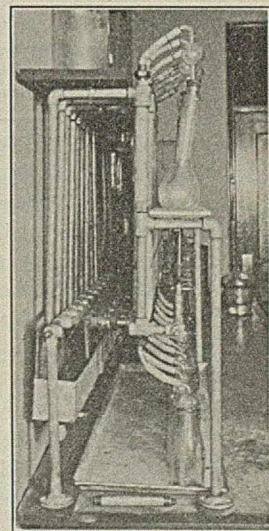


FIG. III

S, which is connected, as shown in Fig. 1, directly through a shut-off valve to the gas main. Gas may be admitted or shut off from the entire system by turning the main valve, or the individual burners may be regulated separately. The plate T, which supports the distilling flasks, is made of so-called "asbestos lumber," but this material was not found to be entirely satisfactory since it had a tendency to break after it had been used for a time. A more satisfactory support could have been made of sheet iron covered with a thick layer of ordinary asbestos board, since the asbestos would serve as a sort of shock absorber in the case of any bumping of the flasks. A piece of asbestos lumber is placed in front of and bolted to the condenser jackets in order to prevent heating of the water in the condenser by radiation of heat from the Bunsen burners.

The advantages of this type of distillation apparatus are:

1—Each condenser is entirely separate and may be removed as a whole, or in part, in case of injury, without interrupting the working of the remainder of the system. This is a decided advantage over the common type of condenser where a tank contains the spiral block-tin tubes of all the flasks in use, since, if one of the tubes or any portion of the tank leaked, it necessitated the dismantling of the whole system in order to make necessary repairs.

2—It is possible by means of the "stop and waste" cock not only to use any desired number of the units of the system, but also to regulate the flow of water through the different units.

3—The apparatus is simple in construction and made entirely of inexpensive materials such as a plumber would ordinarily have on hand.

The author wishes to express his appreciation to Mr. R. D. Milner for his interest and kind suggestions in connection with the construction of this apparatus.

LABORATORY OF NUTRITION INVESTIGATIONS  
OFFICE OF EXPERIMENT STATIONS  
U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON

### A CONVENIENT COLOR CAMERA

By C. M. CLARK

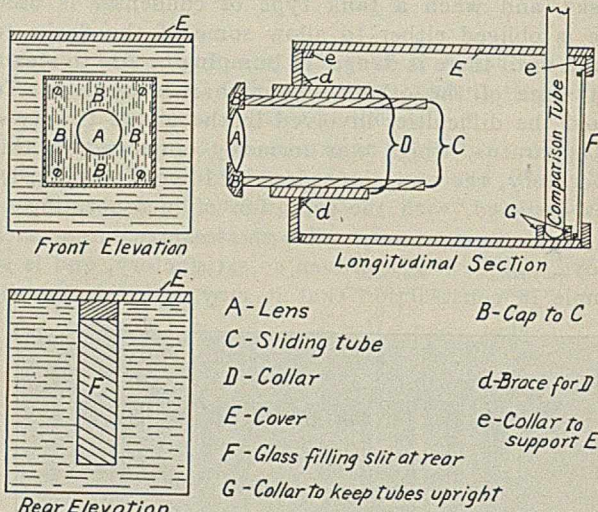
Received June 3, 1914

This camera may easily be made by any one with a little skill in carpentry and a few moments leisure, or it can be cheaply had of any cabinet maker. It has been in use in this laboratory for some time and has given satisfaction. The lens cost about 50 cents.

The box is best made of white pine. It is 160 mm. long, 100 mm. wide, and 100 mm. high, inside measure. In one end is cut a slit 20 mm. wide, extending to within 10 mm. of the inside top and bottom of the box; this slit is closed with a piece of either ground or milk glass, as preferred, but if milk glass be used it must not be over 2 mm. thick. A piece of light blue glass may be set inside the other to neutralize the yellow rays where artificial light is used. The slit must be exactly centered. In the other end, and exactly centered, is cut a hole 60 × 60 mm., and in this is set a collar made of about 6 mm. material and about 50 mm. long, with about 10 mm. projecting outside the box. In this collar

slides a tube made of the same material and about 100 mm. long, carrying at its outer end a 60 mm. sq. cap in which is set a crown glass lens of approximately 160 mm. focus. The lens should be about 35 mm. in diameter and stopped down to about 25 mm.

The cover of the box is loose, and has a collar fitting inside the box to hold it in place. In this cover, exactly opposite the glass closed slit, and about 20 mm. from the edge, is cut an aperture large enough to per-



mit the two comparison tubes to enter freely, yet without play; this opening may be felt lined. A collar having a like aperture may be placed underneath it, on the floor of the box, to steady the tubes. The inside of the box is, of course, painted dead black.

The advantages of this camera are that, as the comparison tubes set exactly in front of the slit and occupy its entire width, all light passes through them, while the lens enables one to bring the tubes into exact focus; and, as only one eye is used, there is less chance of the left hand tube looking the darkest.

The sliding tube should be rubbed with graphite.

CHATTANOOGA CHEMICAL LABORATORY  
CHATTANOOGA, TENN.

### IMPROVED METHOD FOR THE DETERMINATION OF NITROGEN IN STEEL

By L. E. BARTON

Received July 7, 1914

The method usually employed for the determination of nitrogen in steel is the one first published by A. H. Allen and modified by Prof. J. W. Langley.

When operating this method as described by Blair, "Chemical Analysis of Iron," it was observed that the sample and standard for comparison, when treated with Nessler reagent, developed colors differing in quality or tone—the sample developed an orange-yellow and the standard a brownish yellow color—which renders comparison difficult and results inaccurate.

Another difficulty sometimes encountered, which makes comparison impossible, is the clouding of solutions after addition of Nessler reagent upon standing for the specified ten minutes, and is particularly noticeable with the first 50 cc. distillate, in which the ammonia

is comparatively concentrated. However, with properly prepared Nessler reagent, this latter trouble should not occur.

Experimental work was undertaken with the object of developing a more accurate method of determination as a result of which a modification of the above mentioned method was adopted. By this modification of the method, the sample and standard distillates are prepared under similar conditions, and when treated with Nessler reagent develop colors identical in quality or tone, but proportional in intensity to the ammonia present.

If the Nessler reagent is carefully prepared and works properly, the color in sample and standard will develop almost instantly and is fully developed in less than one minute. The solutions treated with such Nessler reagent remain clear or do not cloud appreciably on standing for ten minutes; however, the comparison is best made after standing one minute and all possible difficulty due to clouding avoided.

The determination is also rendered more accurate by taking a larger sample for analysis and using an aliquot part of the total distillate for comparison.

The reagents are prepared exactly as described in Blair's "Chemical Analysis of Iron," seventh edition.

[NOTE—The ammonia-free hydrochloric acid may also be prepared thus: Dilute concentrated hydrochloric acid to specific gravity 1.10 and, without addition of sulfuric acid, distil it. Hydrochloric acid of this strength distills without change in concentration. The first 100 cc. distillate from one liter of acid will usually contain all the ammonia and is rejected; the portions distilled thereafter are collected for use but must, of course, be tested as usual to make sure they are free from ammonia.]

#### METHOD OF DETERMINATION

**DISTILLATION OF SAMPLE**—In a distilling flask of 1000 to 1500 cc. capacity, fitted with separatory funnel and connected with condenser, place 40 cc. prepared caustic soda solution; add 500 cc. distilled water, and distil until the distillate gives no reaction with Nessler reagent.

Dissolve a 5 g. sample of the steel in 40 cc. of ammonia-free hydrochloric acid, and by means of the separatory funnel add the solution slowly to the contents of the distilling flask, washing in finally with ammonia-free water. Distil and collect 150 cc. of the distillate in a graduated flask. Cork the flask and set aside. Experience has shown that 150 cc. of distillate will contain all the nitrogen in the sample.

**PREPARATION OF STANDARD**—After distilling the sample—the apparatus then being free from ammonia, but containing the residue of sample and reagents—25 cc. of standard ammonium chloride solution and 150 cc. of ammonia-free water are added to the contents of the flask, and distillation continued until a *standard* distillate of 150 cc. is collected in a graduated flask. As before, the single distillate will be found to contain all the ammonia from 25 cc. of standard solution.

To the standard distillate is added 6 cc. of Nessler reagent; and since the standard ammonium chloride solution is equivalent to 0.00001 g. nitrogen per cc., 1 cc. prepared standard distillate is equivalent to  $\frac{25 \times 0.00001}{156} = 0.000016$  g. nitrogen per cc. = 0.00016 per cent nitrogen on a one gram sample.

It should be noted that the preparation of a single standard distillate is sufficient for determination of nitrogen in several samples if the comparisons are being made at the same time.

**COMPARISON AND DETERMINATION**—To make the determination, 30 cc. of *sample distillate* (equal to one gram of sample) are placed in one of a pair of Nessler jars and the color developed by addition of 1 cc. Nessler reagent. The standard and sample are allowed to stand one minute to fully develop the color.

Into the other jar the standard distillate is run from a burette until the colors in standard and sample jars are of the same intensity; the final comparison is made after bringing the contents of the jars to the same volume by addition of ammonia-free water to one or the other.

The number of cc. standard distillate multiplied by 0.00016 gives the percentage of nitrogen in the steel.

PERCENTAGES OF NITROGEN FOUND							
No.	N	No.	N	No.	N	No.	N
1.....	0.0038	4.....	0.0032	7.....	0.0038	10.....	0.0035
	0.0037		0.0032		0.0043		0.0035
	0.0037	5.....	0.0043	8.....	0.0037	11.....	0.0033
2.....	0.0035		0.0043		0.0040		0.0038
	0.0035	6.....	0.0040	9.....	0.0038		0.0037
3.....	0.0037		0.0040		0.0043		0.0037
	0.0037		.....		.....		.....

The results shown in the above table indicate the accuracy of the method thus modified.

TITANIUM ALLOY MANUFACTURING Co.  
NIAGARA FALLS, N. Y.

## ADDRESSES

### THE INDUSTRY OF THE COAL-TAR DYES<sup>1</sup> AN OUTLINE SKETCH

By BERNHARD C. HESSE

Received October 29, 1914

At the very beginning, it should be pointed out that the world's market in coal-tar dyes as it stands today comprises, in round numbers, 900 distinct and different chemical substances which are made by the aid of 300 products of transformation, themselves not dyes, of 10 products obtained or obtainable from coal-tar by distillation, refrigeration, expression or the like. Therefore, actually and in reality, the present coal-tar dye industry comprises no fewer than 1,200 different products and as

<sup>1</sup> Address delivered before the Board of Directors of the General Chemical Company, in New York, October 23, 1914.

many or more different processes of manufacture and requires many hundred different sets of apparatus of varying capacities and of differing kinds for many hundred different operations. A manufacturing problem comprising so many independent and yet interlaced units of manufacture and production has, therefore, varied elements of complexity; to what extent this is true will appear later on.

#### THE NATURE OF COAL-TAR

In the production of coal-tar, suitable for use in the coal-tar dye industry, there is made on the average from 100 parts of coal: 72 parts COKE 6 parts TAR (liquid and solid distillate) 22 parts GAS

The gas and coke are not considered here; the distillate, amounting to 6 per cent of the weight of the coal, is the portion of these products with which we are here concerned.

Chemists have ascertained the presence of 155 distinct chemical substances in this liquid and solid distillate or tar; these classify broadly, as follows:

SERIES	No.	SERIES	No.
Marsh gas.....	45	Anthracene.....	5
Benzol.....	73	Phenanthrene.....	5
Naphthalene.....	14	Miscellaneous.....	13

For dyestuff production the first is negligible and the last almost so. The number of chemical elements entering into the composition of the above substances is relatively small, being five only:

CARBON    HYDROGEN    OXYGEN    NITROGEN    SULFUR

According to the combinations of these elements, we have the 5 following classes of compounds:

Carbon and hydrogen.....	76
Carbon, hydrogen and nitrogen.....	37
Carbon, hydrogen and oxygen.....	23
Carbon, hydrogen and sulfur.....	3
Carbon, hydrogen, nitrogen and sulfur.....	3

Rearranging these under the three relevant general series we have:

	Ben- zol	Naph- thalene	Anthra- cene	TOTAL
Carbon and hydrogen.....	25	6	3	34
Carbon, hydrogen and nitrogen.....	32	..	2	34
Carbon, hydrogen and oxygen.....	11	8	..	19
Carbon, hydrogen and sulfur.....	3	..	..	3
Carbon, hydrogen, nitrogen, and sulfur.....	2	..	..	2
TOTAL.....	73	14	5	92

Out of these 92 compounds the coal-tar dye industry uses only 9, namely:

Benzol	Phenol	Methyl anthracene
Toluol	Naphthalene	Phenanthrene
Xylol	Anthracene	Carbazol

These nine make up about from 6 to 12 per cent of the liquid and solid distillate, or from 0.38 per cent to 0.75 per cent of the coal taken, divided approximately as shown in the following chart (Fig. 1) from Dammer, "Chemische Technologie der Neuzeit," Vol. 2, p. 906. The percentages there given are as follows:

	On tar	On coal
Benzol, toluol, etc.....	1.75	0.105
Phenol.....	0.25	0.015
Naphthalene.....	5.95	0.375
Anthracene, etc.....	0.20	0.012

These figures are average and, therefore, illustrative only and not strictly accurate in all cases.

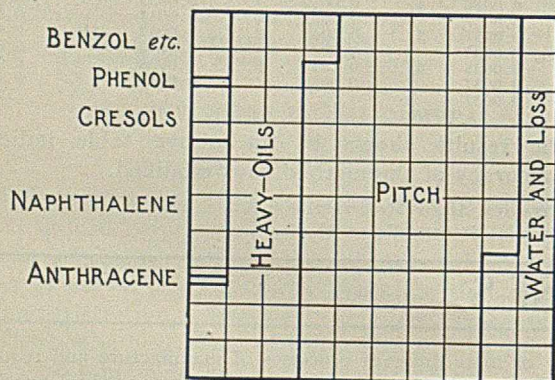


FIG. I.—MAIN CONSTITUENTS OF COAL TAR

Fig. II is a graphic representation of the above relations between the products obtained by the destructive distillation of coal and the coal itself.

None of these solids and liquids are themselves dyes; in fact, most, if not all of them, are substantially colorless and cannot impart color.

The entire coal-tar dye industry is based upon these 9 coal-tar compounds, or crudes; these 9 crudes are converted into about 300 intermediates, themselves not dyes, and these 300 intermediates are turned into 900 and more dyes.

#### THE SCOPE OF THE INDUSTRY

World's figures are not available. The most dependable and most recent figures are those dealing with Germany. In

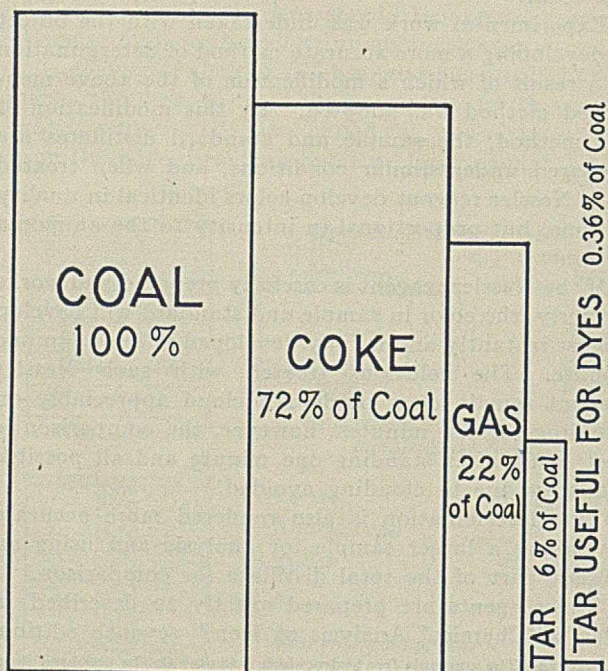


FIG. II.—COMPARISON OF COAL AND ITS DISTILLATION PRODUCTS

the year 1913 the total export value of Germany's coal-tar industry, including dyes and products of chemical transformation of the above 9 crudes themselves not dyes, *i. e.*, intermediates, amounted to \$55,264,522, distributed over 33 countries and shared in by 22 factories. On June 30, 1912, 21 of these factories had a combined capitalization of \$36,700,000 and declared and paid dividends of \$11,600,000, or 21.74 per cent of the capitalization.

Of the 5369 active corporations in Germany on June 30, 1912, 1004, or 18.69 per cent, are divided into 19 groups of the chemical and allied industries. Arranged in the order of their income-producing effects these 19 groups are, in part, as follows:

	Per cent dividends	No. of corporations
Coal-tar dyes.....	21.74	21
Metallurgy.....	11.78	61
Soaps and candles.....	11.65	21
Glass.....	11.61	38
Heavy chemicals.....	11.51	104
Explosives.....	11.22	28

The remainder range between 5 and 10 per cent except mining which is at the foot of the list with 0.51 per cent return.

Therefore, any attempt to take away coal-tar dye business from Germany means attacking the best equipped and the most profitable of Germany's industries.

**PLANT VALUE**—The actual cost of construction of the various plants engaged in coal-tar dye manufacture cannot be determined with any accuracy. All sorts of estimates and guesses have been made ranging from \$50,000,000 to \$1,000,000,000 with the majority in the neighborhood of \$400,000,000.

**ANNUAL TURNOVER**—The annual turnover cannot be determined exactly, but assuming that Germany consumes twice as much as the United States imports, we have a putative turnover of about \$80,000,000 or 2.1 times the capital stock.

The supervision and control of making this \$80,000,000 worth of product, requires at the utmost 1000 works or factory chemists, *i. e.*, on the average, one works or factory chemist for each \$80,000 of annual output.

The gross of \$55,264,552 export value is distributed over more than 900 finished dyes, each chemically different from the other and each requiring a separate though allied manufacture. This amounts to an annual average of \$61,405 for each dye all over the world outside of Germany.

However, we must subtract \$18,534,964 from the \$55,264,552 for the indigo, alizarin, anilin oil and various things, not dyes, to obtain the value of the 900 dyes which is \$36,729,588; or, an average annual world's gross, outside of Germany, of \$40,811 for each of the 900 dyes.

LARGE ITEMS OF MANUFACTURE—The large items of these 900 dyes as nearly as can be ascertained from official sources of exports are:

	Value	Per cent of total	Per cent of total exports to U. S.
Indigo.....	\$12,690,874	23.01	10.38
Alizarin.....	2,219,588	3.99	8.05
Anilin oil.....	1,408,722	2.54	33.42
Anthracene dyes.....	2,914,786	5.22	44.08
Anilin dyes.....	33,814,802	61.24	21.56
Anthracene and benzol compounds not dyes.....	1,492,736	2.72	16.22
Naphthalene compounds, not dyes.....	723,044	1.27	20.53

The dyes, including indigo, alizarin, anthracene dyes and anilin dyes, are sold to 33 countries distributed as shown in Table I.

TABLE I—GEOGRAPHICAL DISTRIBUTION OF GERMANY'S EXPORT DYE-TRADE (PERCENTAGES)

	Anilin dyes	Alizarin	Anthracene dyes	Indigo	Average participation
<b>EUROPE (19)</b>					
Great Britain.....	17.14	24.34	23.72	3.54	
France.....	2.15	1.59	2.52	0.97	
Portugal.....	0.65	...	...	...	
Spain.....	1.02	...	...	0.20	
Italy.....	6.38	...	3.23	1.98	
Austria.....	8.99	3.38	6.80	4.08	
Turkey.....	0.68	...	...	0.33	
Roumania.....	0.35	...	...	...	
Servia.....	0.15	...	...	...	
Bulgaria.....	0.20	...	...	...	
Greece.....	0.10	...	...	...	
Switzerland.....	1.22	4.23	...	...	
Russia.....	1.71	2.83	3.17	1.30	
Finland.....	0.37	...	...	...	
Norway.....	0.42	...	...	...	
Sweden.....	1.40	...	0.73	...	
Denmark.....	0.37	...	...	0.03	
Netherlands.....	2.12	3.09	2.76	1.83	
Belgium.....	3.90	...	1.96	0.94	
<b>Asia (6)</b>					
Japan.....	5.45	...	1.63	2.46	
China.....	13.17	...	...	64.03	
British India.....	5.35	39.89	4.44	0.97	
British Malacca.....	0.22	...	...	0.36	
Dutch East Indies.....	0.38	8.41	1.49	2.86	
Persia.....	...	...	...	0.18	
<b>SOUTH AMERICA (3)</b>					
Argentina.....	0.25	...	...	...	
Brazil.....	0.98	...	...	...	
Chili.....	0.09	...	...	...	
<b>NORTH AMERICA (3)</b>					
Canada.....	0.69	...	...	0.25	
United States.....	21.55	8.03	44.10	10.38	
Mexico.....	0.85	...	...	0.05	
<b>AFRICA</b>					
Egypt.....	0.34	...	...	1.33	
<b>AUSTRALIA</b>					
Australian colonies.....	0.16	...	...	0.47	
<b>RECAPITULATION</b>					
Europe.....	49.32	39.46	44.89	15.20	37.22
Asia.....	24.57	48.30	7.56	70.86	37.82
South America.....	1.32	...	...	...	0.33
North America.....	23.09	8.03	44.10	10.68	21.47
Africa.....	0.34	...	...	1.33	0.42
Australia.....	0.16	...	...	0.47	0.16
Totals.....	98.80	95.79	96.55	98.54	97.42

Germany buys small quantities of dyestuffs from six countries (probably as the United States buys eggs and butter from Canada) as shown below:

GERMANY'S 1913 IMPORTS OF INTERMEDIATES AND FINISHED DYES

	Value	Per cent of total exports
Anilin oil and salt.....	\$ 31,654	2.25
Naphthol and naphthylamine.....	30,940	4.28
Anthraquinone nitrobenzol, toluidin, resorcin, phthalic acid and other coal-tar products.....	116,620	7.81
Anilin dyes.....	1,415,388	4.17
Alizarin red and all other anthracene dyes.....	179,452	3.49
Indigo.....	92,582	0.73
TOTAL.....	\$1,866,636	3.79

#### THE WORLD'S PRODUCTION OF COAL-TAR DYES

In 1896 the world's *anilin* (*i. e.*, only a part of the coal-tar dyes) dye production was estimated at \$25,000,000 distributed as follows:

		Per cent
Germany.....	\$18,000,000	72
Switzerland.....	3,200,000	12.8
France.....	1,600,000 to 2,000,000	8.0
Great Britain.....	1,600,000 to 1,800,000	7.2

This is *exclusive* of alizarin, anthracene dyes and of indigo.

For 1912, value figures are available only for Germany, Switzerland and Great Britain; tonnage figures for Austria. They show the following trade balance in *all* branches; crudes, intermediates and finished dyes, inclusive of anilin dyes, alizarin, anthracene dyes and indigo.

FINAL BALANCES, 1912		
	Imports	Exports
Germany.....	.....	\$51,545,326
Switzerland.....	.....	3,794,898
Great Britain.....	\$6,275,775	.....

The distribution of these balances over the various items is shown in Table II.

#### AVERAGE UNIT PRICES OF CRUDES, INTERMEDIATES AND FINISHED DYES

If the following 1912 tables for Germany, Switzerland and Great Britain are recalculated to cents per pound for each subdivision, in the case of benzol the prices per U. S. gallon are:

British export values =	16.75 cents
German import values =	24.20 cents
German export values =	19.11 cents

The average German import and export values of crudes, intermediates and finished dyes in 1913 was as follows:

	IMPORTS		EXPORTS	
	Cents per lb.	On basis of crudes	Cents per lb.	On basis of crudes
Crudes.....	2.06	1.00	2.83	1.00
Intermediates.....	12.08	5.85	10.07	3.56
Finished dyes.....	23.57	11.42	21.53	7.61

These average figures, unfortunately, give no direct insight into the true enhancement of crudes to intermediates, to finished dyes. While these crudes are as a rule of quite uniform percentage purity, yet the intermediates and the finished dyes are not; some of the intermediates contain only 60 per cent of the theoretical of the corresponding crudes, some of the finished dyes, *e. g.*, indigo, being in the form of 20 per cent pastes with water. This foregoing relationship is, therefore, directive only and *not* quantitative, *i. e.*, it does not represent the actual enhancement per pound of crude or of absolute intermediate to absolute finished dye. A nearer approach to true enhancement of crudes to intermediates is made further on in the case of anilin, naphthol and naphthylamine.

#### ENHANCEMENT OF CRUDES TO INTERMEDIATES

As a matter of mere calculation and making no allowance for losses, etc., 889 lbs. of naphthalene make 1000 lbs. of naphthol or of naphthylamine, and 839 lbs. benzol make 1000 lbs. of anilin oil.

Based on the averages of the corresponding German figures of Table III there is a margin of 10.40 cents per lb. of naphthylamin or of naphthol over the naphthalene cost, to take up the cost of the nitric acid, sulfuric acid, iron, muriatic acid, and caustic soda and other expenses, which amount is practically 7.6 times the naphthalene item. For anilin oil there is a corresponding margin of 6.15 cents per lb. to take up the nitric acid, iron and muriatic costs and other expenses, which amount is only 2.7 times the benzol item.

Enhancement in the anthracene series cannot be deduced from these figures.

TABLE II—DYE PRODUCTIONS IN 1912

GERMANY		Imports	Exports
<b>CRUDES</b>			
Benzol and light oils.....		\$ 508,844	\$ 1,630,538
Naphthalene.....		184,450	211,106
Anthracene.....		66,402	12,138
Phenol.....		536,928	851,802
Cresol.....		7,616	72,352
TOTALS.....		1,304,240	2,777,936
<b>INTERMEDIATES</b>			
Anilin oil and salt.....		4,284	1,558,662
Naphthol and naphthalene.....		41,412	681,870
Anthraquinone, nitrobenzol, resorcin, phthalic acid, etc.....		106,624	1,432,998
TOTALS.....		152,320	3,673,530
<b>FINISHED DYES</b>			
Anilin dyes.....		1,424,192	31,835,832
Alizarin.....			2,197,216
Anthracene dyes.....		127,330	3,428,866
Indigo.....		120,904	10,760,932
TOTALS.....		1,672,426	48,222,846
<b>EXCESS</b>			
Crudes.....			\$ 1,473,696
Intermediates.....			3,521,210
Finished dyes.....			46,550,420
BALANCE.....			\$51,545,326

Enhancement of intermediates to dyes cannot be stated from these figures with any approach to utility and is, therefore, not attempted.

TABLE III—AVERAGE UNIT PRICES (CENTS PER LB.) OF CRUDES, INTERMEDIATES AND FINISHED DYES

	GERMANY		SWITZERLAND		GREAT BRITAIN	
	Imp.	Exp.	Imp.	Exp.	Imp.	Exp.
<b>CRUDES</b>						
Benzol, toluol, etc.....	3.28	2.59	No classification			2.27
Carbolic, crude and refined...	3.48	8.63	Average is			6.19
Naphthalene.....	1.40	1.14	5.51	5.70		2.03
Anthracene.....	1.29	0.78				1.29
<b>INTERMEDIATES</b>						
Anilin oil and salts.....	9.19	8.80				
Anilin oil.....			8.89	7.96		
Anilin and toluidin.....						10.29
Naphthol and naphthylamin.....	12.93	10.55				
Anilin compounds.....			22.68	32.10		
Benzyl, chlorid, nitrobenzol, naphthol, etc.....			12.95	31.33		
Phthalic acid and resorcin.....			25.84	54.41		
Anthraquinone, nitrobenzol, toluidine, resorcin, phthalic acid, etc.....	12.96	11.38				
<b>FINISHED DYES</b>						
Anilin dyes.....	24.82	23.86	29.93	31.87	24.75	
Alizarin.....		16.42	12.70			
Anthracene dyes.....	13.50	26.93				
Alizarin and anthracene dyes.....	(a)	(a)			21.02	
Indigo.....	72.14	17.26			15.41	
Indigo and carmine.....			18.14	18.82		
All other synthetic dyes.....					9.25	

(a) Import is vegetable and dry; export is 20 per cent paste.

GREAT BRITAIN		Imports		Exports	
<b>CRUDES</b>					
Benzol and toluol, gals.....		4,579,667	\$ 918,568		
Carbolic acid, cwt.....		162,459	1,006,008		
Naphthalene, cwt.....		54,312	110,203		
Anthracene, lbs.....		2,938,098	37,872		
TOTALS.....			\$2,072,651		
<b>INTERMEDIATES</b>					
Anilin and toluidine, lbs.....		1,429,130	\$ 155,702		
TOTALS.....			\$ 155,702		
Total imports of crudes and intermediates 145,805 cwt. of a value of \$757,579 (not distributed as to classification)					
		Imports		Exports	
<b>FINISHED DYES</b>					
Anilin and naphthalene dyes.....		283,876	7,025,619		
Alizarin and anthracene dyes.....		61,178	1,285,870	56,728	982,675
Indigo.....		28,302	436,138		
All other synthetic dyes.....		190	1,757		
TOTALS.....			\$ 8,729,224		982,675
<b>EXCESS</b>					
Crudes and intermediates.....					\$1,470,774
Finished dyes.....			\$7,746,549		
BALANCE.....			\$6,275,775		
<b>SWITZERLAND</b>					
		Imports		Exports	
<b>CRUDES</b>					
Of all kinds.....		26,478	321,600	100 kg. 519	Dollars 6,517
TOTALS.....			321,600		6,517
<b>INTERMEDIATES</b>					
Anilin oil.....		12,330	241,668	73	1,281
Anilin compounds.....		7,980	399,000	1,284	90,879
Benzyl chlorid, nitrobenzol, naphthol, etc.....		10,341	295,281	648	44,774
Phthalic acid and resorcin.....		880	48,996	14	1,679
TOTALS.....			984,945		138,613
<b>FINISHED DYES</b>					
Alizarin.....		2,167	60,676		
Anilin, etc., dyes.....		6,167	407,022	73,295	5,150,751
Indigo and carmine.....		716	28,640	7,287	301,900
TOTALS.....			496,338		5,452,651
<b>EXCESS</b>					
Crudes.....			\$315,083		
Intermediates.....			\$846,332		
Finished dyes.....					\$4,956,313
BALANCE.....					\$3,794,898

GERMANY'S 1913 FOREIGN TONNAGE MOVEMENT

The 1913 metric tonnages of Germany of crudes, intermediates and finished dyes are:

Metric tons	IMPORTS	EXPORTS
Crudes.....	17,400	51,318
Intermediates.....	673	16,321
Finished dyes.....	3,238	108,680
TOTALS.....	21,311	176,319

The total tonnage movement is, therefore, 197,630. For every ton imported, Germany exports 8.27 tons; for every dollar Germany imports, she exports \$20.46.

ESTIMATED WORLD'S TOTAL COAL-TAR DYE PRODUCTION, 1912

The export values of coal-tar dyes for 1912 at hand are:

Germany.....	\$48,222,846
Switzerland.....	5,452,651
Great Britain.....	982,675
TOTAL.....	\$54,658,172

A very liberal estimate of the production of the principal countries is about as follows:

United States.....	\$ 3,750,000
France.....	5,000,000
Great Britain (over exports).....	5,000,000
Switzerland (over exports).....	1,000,000
Germany (over exports).....	20,000,000
TOTAL.....	\$34,750,000

This makes ample allowance for all items and gives a grand total of \$89,408,172, or practically \$90,000,000, as the very

maximum of all coal-tar dyes, anilin dyes, alizarin, anthracene dyes and the like and indigo produced by the five leading countries in 1912.

Thus the following is the estimated distribution of total production:

Germany.....	\$68,222,846
Great Britain.....	5,982,675
Switzerland.....	6,452,651
France.....	5,000,000
United States.....	3,750,000

with Russia, Holland, Austria and Belgium to be added. Allowing \$10,000,000 for these, which is clearly very high, makes the absolute maximum production all over the world substantially \$100,000,000. The combined actual factory or works area of the world's coal-tar dye plants probably does not exceed one square mile.

GERMANY'S ALLEGED DEPENDENCE FOR COAL-TAR MATERIALS UPON FOREIGN COUNTRIES

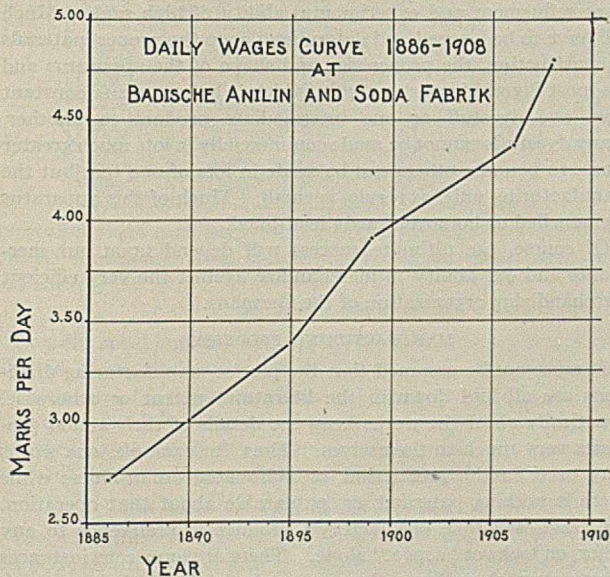
It has been urged that Germany is not wholly independent of outsiders for its coal-tar materials; possibly so. The foregoing 3.79 per cent of imports to exports may support that view.

By the same token the United States is dependent upon outsiders for hay, eggs, wheat, cotton and copper. For the years 1908-1914, both inclusive, the corresponding U. S. figures (low, average and high) are as follows:

	Low	Average	High
Hay.....	5.28	186.83	623.20
Eggs (1908-1912 only).....	1.68	6.06	12.63
Wheat.....	0.05	1.65	7.77
Cotton.....	3.19	3.60	4.24
Copper.....	24.24	31.89	36.95

THE WAGE QUESTION

In 1908 the average wage paid in Germany in this industry was about 4.80 marks per day inclusive of boys, common labor and skilled labor. With about 24 boys out of every 100 persons employed, and assuming each boy receives on the average 1/4 a man's pay, this makes the average man's wage M. 5.85 or \$1.40. Adding to this, \$750,000 annual welfare expense for a



total of 7000 employees and refiguring on the above ratio, makes the daily allowance for this item per man at 300 days per year 44 cents additional or a total of \$1.84, average daily adult wage. To this should be added the bonuses given to many of the workmen and also the works' contribution to the state old age pension and sick fund. Consequently, the average adult daily wage is actually in the vicinity of \$1.84.

This is reinforced by the detailed Table IV of the year 1906, wherein 40.32 per cent receive less than \$1.00 per day and 59.68

per cent receive more than \$1.00 per day of ten hours, with a grand average of \$1.04 per ten-hour day.

TABLE IV—THE BADISCHE ANILIN AND SODA FABRIK WAGE TABLE OF ABOUT 1906

Apart from bonuses, welfare expense and accident, insurance and pension fund

Daily pay in cents	Aliz-arin	Anilin dye factory	Azo dye factory	Acid and soda factory	Indigo factory	Con-struction de-part-ment	Machin-ery de-part-ment	Totals
78.5	2	23	...	...	6	8	...	39
80.9	1	8	...	2	30	...	...	41
83.3	2	31	21	50	55	2	42	203
85.8	23	52	54	81	75	49	11	345
88.2	15	39	31	72	71	3	13	244
90.5	15	49	37	72	87	36	25	341
92.9	11	32	35	72	52	5	30	257
95.3	19	30	50	72	54	73	29	327
97.7	46	35	68	64	74	15	54	356
100.1	62	70	68	73	66	161	71	571
102.4	55	48	53	71	31	26	121	405
104.8	94	78	47	41	9	36	14	319
107.2	74	58	42	37	5	19	38	273
109.6	25	16	21	21	2	15	59	159
112.0	11	13	23	19	...	38	67	171
114.3	1	12	12	13	...	39	71	148
116.7	9	7	3	...	...	18	22	59
119.1	...	10	5	...	...	93	47	155
121.5	1	6	1	...	...	30	19	57
123.9	...	3	...	...	...	88	35	126
126.3	...	2	...	2	...	56	29	89
128.6	...	...	...	...	...	95	23	118
131.0	...	...	4	...	...	107	19	130
133.4	...	...	...	...	...	33	31	64
135.8	...	...	...	...	...	19	18	37
138.2	...	4	...	...	...	28	31	63
140.5	...	...	6	...	...	2	22	30
142.9	...	...	...	...	...	16	13	29
145.3	...	4	...	15	...	7	21	47
147.7	...	...	6	...	...	8	19	33
150.1	...	...	...	...	...	6	6	12
152.4	...	...	...	...	...	12	19	31
154.8	...	...	...	...	...	...	6	6
157.2	...	...	5	...	...	4	...	9
159.6	...	...	...	...	...	6	3	9
162.0	...	...	...	...	...	7	...	7
164.3	...	...	...	...	...	2	...	2
166.7	...	...	15	...	...	8	...	23
176.1	...	...	5	...	...	...	...	5
Total employees	466	630	652	777	617	1170	1028	5340
Gross pay roll in dollars	473	620	659	740	567	1372	1166	5597
Average day pay in dollars	1.01	0.98	1.01	0.95	0.92	1.17	1.13	1.04

NOTE—These figures assume payment for ten hours only, although the men work in shifts from 6 A.M. to 6 P.M. for day work, and from 6 P.M. to 6 A.M. for night work. If the pay is for 12 hours, then each of these figures for average day, pay being based upon hourly wage-rate, must be increased 20 per cent over their present values, i. e., they would become \$1.21, \$1.18, \$1.21, \$1.14, \$1.10, \$1.40, \$1.36 and \$1.25, respectively.

THE INCREASED COST OF LABOR IN GERMANY

The following table presents the figures per head per working day (i. e., boys, skilled and common labor):

	Marks	Dollars	Per cent
1886.....	2.71	0.645	100.0
1890.....	3.01	0.716	111.1
1895.....	3.38	0.804	124.8
1899.....	3.91	0.926	144.3
1906.....	4.37	1.040	161.3
1908.....	4.80	1.142	177.0

or an average annual increase of 3.5 per cent of the 1886 pay.

However, it must be remembered that in Germany the day is a two-shift day with two hours and twenty minutes taken out for all men for meals and rest and for about one-third the men an additional thirty minutes for washing up; so that one-third work twelve hours less two hours and fifty minutes, and two-thirds work twelve hours less two hours and twenty minutes, or an average day of 9 1/2 hours net actual average working time for which they receive at least ten hours pay and it may be twelve hours pay; the above figures, as stated, were based on hourly rate of pay assume pay for ten hours, only, and not for twelve hours.

In the United States the day is a three-shift day.

PARTICIPATION OF LABOR CHARGE IN FINISHED DYES

Labor participates to a small extent only in the final cost of the finished dye; it probably never exceeds 15 and is, as a rule, more nearly 10 per cent.

As an illustration: in 1906, Germany's export of synthetic indigo was worth about \$4,750,000; the 617 men in the Badische

indigo factory made at least 50 per cent of that export value, or \$2,374,000 worth. These 617 men represent a daily pay roll of not more than \$678.70, and it may be as low as \$567.50 (dependent upon pay being for twelve hours or ten hours); at 365 days per year this means \$247,725 or \$207,137, or 10.43 or 8.72 per cent, respectively, on half of the above indigo export value; assuming bonuses, welfare expenses and the like to double that daily pay roll, it makes the labor participation 20.86 and 17.44 per cent, respectively; however, this frees the indigo manufactured and consumed in Germany from all labor charges.

However, these 617 men no doubt in 1906 had a greater participation than 50 per cent of the export and it is, therefore, reasonable to assume that 15 per cent participation by labor in the finished product is ample and very likely high.

#### A TYPICAL GERMAN COAL-TAR DYE FACTORY

A German coal-tar dye works in good order and of considerable magnitude will have a daily use for 1000 tons of coal, 40 tons ice, 40,000,000 gallons of water (about 1/7 of Manhattan and the Bronx), 2,500,000 cu. ft. of gas.

The works area is about 500 acres, of which 100 acres are occupied by buildings, and requires about 42 miles of railway within the factory walls to transport the various materials among the several hundred factory buildings.

Power generation and transmission require 158 boilers, 386 steam engines and 472 electric motors. Over 400 telephones are needed within the works.

In order to convert the nine products obtained from coal-tar into intermediate products, and then into dyes, these works need as auxiliary chemicals: sulfuric acid, hydrochloric (muriatic) acid, nitric acid, liquid chlorine, caustic soda, carbonate of soda, acetate of soda, acetic acid, acetic anhydrid, bromine and iodine—in large amounts, which, for obvious reasons, cannot be distributed as to the total amounts produced or used.

The following figures, taken from Dr. Brunck's 1900 Indigo Lecture, may give an idea of the magnitude of some of these items; these figures are now more than 14 years old and have no doubt immensely increased; at that time the Badische Anilin and Soda Fabrik made about 50 per cent of the world's consumption of indigo. Today all the German works make practically 95 per cent of the world's consumption; it is fair to double the following figures to get an approximate notion of today's figures; 50,000 tons of sulfuric anhydrid (equal to 40,000 tons pyrites), 4,400,000 lbs. of glacial acetic acid, which require not less than 5,200,000 lbs. liquid chlorine and produce 5,850,000 lbs. caustic soda as well, and the equivalent of about 7,800,000 lbs. or 3,900 tons of commercial muriatic, and an investment of \$4,500,000.

At that time (1900) the total world's consumption was estimated at 11,000,000 lbs. dry weight (100 per cent) indigo; in 1913 Germany exported 15,000,000 lbs. (100 per cent) indigo.

The world's annual consumption of indigo is today not far from 8200 tons (100 per cent) indigo or 27 tons per day.

#### PATENTS AND THE COAL-TAR DYE INDUSTRY

The development of the coal-tar dye industry called for 8062 German patents in the years 1876-1912, or 224 per year; corresponding patents have been taken out in other countries, e. g., 2432 in the United States.

But it is authoritatively said that only 1 in 100 of the German patents is a money maker and, as a matter of fact, in the case of the 921 dyes in the world's markets at the end of 1912, only 485 U. S. patents and 762 German patents were involved, or 19.94 per cent of the total U. S. and 9.46 per cent of the total German patents. Of these 921 dyes, 50 per cent, were never patented in the United States; the U. S. patents on 26 per cent have now expired leaving 24 per cent still covered by existing U. S. patents, but many of these expire in 1915.

#### THE PRIMARY COAL-TAR PRODUCTS AND THE INTERMEDIATE PRODUCTS

The nine different crudes from coal-tar which form the basis of the coal-tar dye industry are first converted into materials, themselves not dyes, but different from the nine original compounds. These nine compounds make about 270 intermediate products and these 270, by suitable combination, make the 900 and more different dyes of the present world's markets.

The above number of intermediate products by no means exhausts those that are possible, nor do the 900 dyes exhaust those theoretically possible; there are probably over 2000 intermediate products possible, but only about 270 that have found use and there are many thousands of millions of dyestuffs wholly distinct from each other embraced in the 8,000 German patents; but of these thousands of millions of dyes only 400 individuals have survived and are of use. It is extremely doubtful that in the remainder of these millions upon millions there are any dyes of any striking utility not covered by those already in use. It is safe to say that the German coal-tar dye industry has gone over all of the known fields in fine-tooth-comb fashion and the results thereof are laid down in their patents and are shown in the goods that they market. The Germans are, of course, searching for new fields; in the last 10 years only one new field has been opened and while that is limited it promises to be of great value.

#### THE FUNCTION OF RESEARCH IN ESTABLISHING THE PRESENT INDUSTRY IN THE U. S.

Therefore, a research laboratory, in the narrow sense of the word, is not necessary for the development of a real coal-tar dye industry in the United States. What we do need is a semi-manufacturing laboratory in which to ascertain the most favorable conditions for carrying out those operations which the work of the Germans both in their patents and in their commercial exploitation of them has shown to be needful or worthy of prosecution. That, however, is no child's play task; it calls for engineering skill of the highest order, for chemical knowledge of great refinement and experimental ability of high rank. Much will have to be learned and determined as to the proper materials of construction, the proper size and shape of the apparatus and the most favorable working unit, which is by no means constant from one dyestuff or one intermediate product to another. Many dyestuffs cannot be made commercially in lots much greater than 110 pounds; others can be made in lots of one ton, but the manufacturing unit, as a rule, is small. Much of this apparatus is enamelled or homogeneously lead-lined.

Of course, the ultimate success will depend upon our merchants and our ability to merchandize against the very efficient merchandizing organization of the Germans.

#### MANUFACTURING PROCESSES

It must not be assumed that the precise manufacturing directions are all laid down in the literature, patent or otherwise. Practically all of the works keep the details of their actual processes very much to themselves. Thus, for example, one works may excel in the production of sulfonated anilin-blues; while there is nothing patented or patentable about that operation, the trade will take one factory's product in preference to any other, on looks or "aspect" alone. There are numerous instances where even these large German works with all their research facilities and with all their engineering ability have been unable to outflank an original patentee or original producer, either as to price or as to quality of the goods whose patent has expired, even years after the expiration of that patent. This has also occurred in the case of non-patented products and in one instance, at least, Americans can and do produce a dye from German intermediates and sell that dye back to the Germans at a price and of a quality the Germans cannot meet. We must, therefore, be prepared to expect that our goods would not sell in open competi-



tion with foreign makes of the same goods; for perhaps one or more years after we had attempted to market them.

ACQUIRING PROCESSES

Furthermore, on account of the necessity of having good, careful, uniform manufacture at all points it is quite out of the question for any one chemist to acquire valuable manufacturing experience, except in only a very limited number of chemical transformations. Therefore, successful purchase of recipes or engagement of competent manufacturing chemists to make whole lines of dyes is practically out of the question although it may succeed for a limited number of dyes or operations. We shall have to rely on our own ingenuity, skill and ability to devise successful commercial methods of manufacture.

THE MARKETING OF COAL-TAR DYES

In 1897 the total number of different brands or commercial varieties of dyes sold by a single German concern all over the world amounted in round numbers to 8,000. Each one of these 8,000 brands has its own peculiar advantage over each of the others. These 8,000 brands, which have, no doubt, increased in number now, are used by those who use dyestuffs and produce with them thousands upon thousands of different shades and tints upon materials of the greatest diversity. This necessitates, of course, the constant production of sample cards by the

diagrams have been constructed to show in the simplest and most direct manner the genetic relationships between crudes, intermediates and finished dyes; these charts are, therefore, not to be taken as expressing all details or all possible modes or even the very best modes of making the various products and transformations. What they are intended to express is the order of production of the principal transformations and to indicate very briefly merely the outline of one way of accomplishing that change; they are indicative or directive only and are by no means to be regarded as presenting complete actual manufacturing operations or anything approaching that.

THE KETONE DYES (FIG. III)

This synthesis has been selected for the purpose of illustrating a group of twenty-four dyes closely related chemically, as well as from a manufacturing point of view; they are all good sellers and have been in the world's markets for upwards of 30 years with the exception of one or two which are only 8 or 10 years old. Eight were never patented in the United States. On 11 the U. S. patents have expired, on 3 the U. S. patents expire in 1915 and one each in 1916 and 1925. They represent only 1/40 of the entire number of dyes but exemplify and typify the interlocked and interlaced manufacturing dependency as simple as possible. Other groups are far more complex, chemically

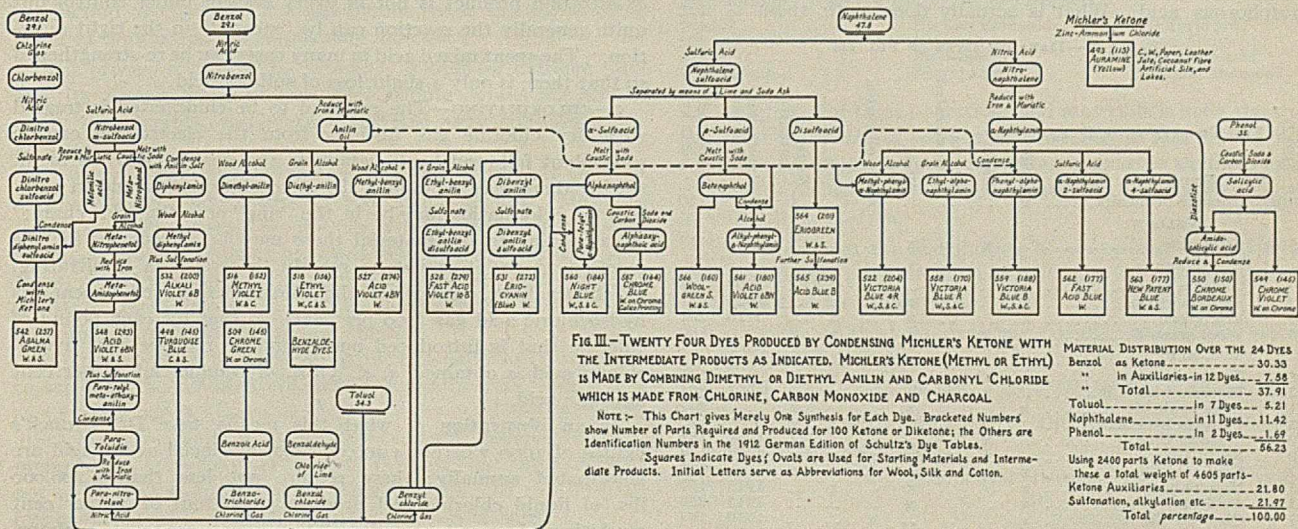


FIG. III.—TWENTY FOUR DYES PRODUCED BY CONDENSING MICHLER'S KETONE WITH THE INTERMEDIATE PRODUCTS AS INDICATED. MICHLER'S KETONE (METHYL OR ETHYL) IS MADE BY COMBINING DIMETHYL OR DIETHYL ANILIN AND CARBONYL CHLORIDE WHICH IS MADE FROM CHLORINE, CARBON MONOXIDE AND CHARCOAL.

NOTE:—This Chart gives Merely One Synthesis for Each Dye. Bracketed Numbers show Number of Parts Required and Produced for 100 Ketone or Diketone; the Others are Identification Numbers in the 1910 German Edition of Schultz's Dye Tables.

Squares Indicate Dyes; Ovals are Used for Starting Materials and Intermediate Products. Initial Letters serve as Abbreviations for Wool, Silk and Cotton.

MATERIAL DISTRIBUTION OVER THE 24 DYES

Benzol as Ketone	— 30.33
in Auxiliaries in 12 Dyes	— 7.58
Total	— 37.91
Toluol	— in 7 Dyes — 5.21
Naphthalene	— in 11 Dyes — 11.42
Phenol	— in 2 Dyes — 1.69
Total	— 56.23
Using 2400 parts Ketone to make these a total weight of 4605 parts—	
Ketone Auxiliaries	— 21.80
Sulfonation, alkylation etc.	— 21.97
Total percentage	— 100.00

dyestuff-makers each season of each year to show how the fashionable shades and even staple shades can be made profitably and cheaply.

BY-PRODUCTS

Broadly speaking, the entire coal-tar dye industry is a complicated maze and net-work of interlocking and interlacing products and by-products; these are great in number but, in most cases, small in volume individually. In numerous instances the very existence of the by-products was the sole directing cause for the invention of new dyes and classes of dyes.

THE DYES OF THE WORLD'S MARKETS

The 921 different dyes on the world's markets at about the end of 1912 are divided into 17 separate chemical classes as follows:

Nitroso dyes	4	Chinolin dyes	4
Nitro dyes	4	Thiobenzenyl dyes	5
Stilbene dyes	10	Indophenol dyes	1
Pyrazolone dyes	12	Oxazin and thiazin dyes	48
Azo dyes	462	Azin dyes	38
Auramines	2	Sulfide dyes	52
Tri- and di-phenylmethane dyes	73	Anthraquinone and allied dyes	116
Xanthone dyes	34	Indigo dyes	48
Arcidin dyes	8	Total	921

THE CHARTS OR DIAGRAMS

For present purposes of illustration a number of charts or

as well as from the point of view of manufacture and sale. Fig. III probably represents the simplest and least complex relationships in the coal-tar dye industry.

It should be remembered that each of the 17 different classes is interlaced and interlocked with one or more other classes and that the interlacing between individuals of Fig. III is true in great and very important measure of the 17 large divisions.

"KETONE"—The starting material for the 24 dyes of Fig. III is called "Michler's Ketone" and is prepared from dimethyl anilin and carbonyl chloride. It was discovered in 1876.

Dimethylanilin is made from anilin, anilin salt and acetone-free wood alcohol; anilin itself from nitrobenzol and that from benzol and nitric acid.

Carbonyl chloride is made from equal volumes of carbon monoxide and chlorine by means of a contact agent, preferably animal charcoal; platinum has also been used. It is now said to be made chiefly by the process of Michalske (U. S. Pat. 808,100 of December 26, 1905). In this process calcium chloride is heated with lime and coke breeze in an electric furnace; the carbonyl chloride is condensed as a liquid at 8° C. (about the freezing point of benzol). The carbonyl chloride gas is passed into the liquid dimethyl anilin at ordinary temperature until the weight increases 40 per cent; the mixture is then heated to

100° C. for several hours to complete the reaction; the product is a solid melting at 174° C.

By using grain alcohol in place of the wood alcohol, above, the corresponding ethyl product is obtained. It is not so important as the methyl product. "Ketone" is the nickname applied to the product made from dimethyl anilin, and "di-ketone" is that applied to the diethyl anilin product.

#### MAKING DYES FROM "KETONE"

In general, dyes are made from ketone by treating a mixture of it with phosphorus oxychloride or phosphorus trichloride with another coal-tar derivative; this operation is technically known as condensing. In Fig. III the dyes are represented by squares; the material combined with ketone to produce any one of these dyes is indicated on the oval next preceding the square.

Where phosphorus chlorides are used they are generally used in the proportion of 60 to 100 per cent of the ketone taken; toluol may also be used as a diluent when the amount of chloride can be reduced somewhat.

Many modifications have been introduced as to the condensing agent; zinc chloride, aluminum chloride, and sulfuric acid may, in special cases, be used in place of the phosphorus chlorides. In general, the phosphorus compounds are the best condensing agents in this method. They appear finally as phosphoric or phosphorous acid. What is actually done with them is not

TABLE V—DATA ON DYES OF FIG. III

Schultz No. (1912)	THE TWENTY-FOUR DYES								Expiration of patent	Parts from 100 parts ketone	
	RED	Acid	Basic	Cotton mordanted	Wool	Chrome wool	Silk	Never patented			
550(a)	Chrome bordeaux	x	..	..	..	x	..	x	..	150	
	YELLOW										
493(b)	Auramine	..	x	x	x	..	..	..	1901	113	
	GREEN										
509	Chrome green	..	x	..	..	..	x	..	1900	145	
542	Agalma green	..	x	..	..	..	x	..	1925	237	
564	Eric green	..	x	..	..	..	x	..	1916	201	
566	Wool green S	..	x	..	x	..	x	x	..	160	
	BLUE										
498	Turquoise blue	..	x	x	..	..	x	x	..	145	
522	Victoria blue 4 R	..	x	x	..	..	x	x	..	204	
531	Eriocyanin A	..	x	x	..	..	x	x	1901	272	
558	Victoria blue R	..	x	x	..	..	x	x	..	170	
559	Victoria blue B	..	x	x	..	..	x	x	1901	188	
560	Night blue	..	x	x	..	..	x	x	..	184	
562	Past acid blue	..	x	x	..	..	x	x	..	177	
563	New patent blue	..	x	..	..	..	x	x	1915	177	
565	Acid blue S	..	x	..	..	..	x	x	1915	239	
567	Chrome blue	..	x	..	..	x	..	..	1910	164	
	VIOLET										
516	Crystal violet	..	x	x	..	x	x	..	1900	152	
527	Acid violet 4 BN	..	x	..	x	..	..	..	1903	274	
528	Past acid violet 10 B	..	x	..	..	..	..	x	..	279	
548	Acid violet 6 BN	..	x	..	x	..	x	..	1910	293	
549	Chrome violet	..	x	..	..	x	..	..	1909	145	
561	Acid violet 5 BNS	..	x	..	x	..	..	..	1915	180	
518	Ethyl violet	..	x	x	..	x	..	..	1900	156	
532	Alkali violet 6 B	..	x	..	x	..	..	..	1903	200	
TOTALS		15	9	7	17	5	11	8	11	4605	

(a) Also calico printing.

(b) Also paper, leather, jute, coconut fiber, artificial silk and lakes.

definitely stated but their conversion into phosphorus chlorides seems feasible and obvious.

The course of materials in making ketone and condensing it may reasonably be represented as follows:

A—Carbonyl chloride (33.21) + dimethylanilin (90.31), yield ketone (100) + 100 per cent hydrochloric acid gas (21.24).

The figures in parentheses give the *theoretical proportions* for 100 parts of ketone; no account is here taken of losses.

B—Phosphorus oxychloride (100) + ketone (100) + intermediate material, yield phosphoric acid (11.87) + 100 per cent hydrochloric acid gas (13.25) + recoverable phosphorus oxychloride (81.47) + dye (x).

BY-PRODUCTS OF THESE 24 DYES—Therefore, in making 100 lbs. of ketone and making dye therefrom, 34.49 lbs. of 100 per

cent hydrochloric acid gas or roughly 100 lbs. of 33 per cent commercial muriatic acid are produced; of this only 30.51 per cent are usable in making the hydrochloric salts of such of the dyes made in this class as are basic; the remainder, or 70 lbs., of commercial muriatic is available for other purposes.

Table V gives relevant data as to the 24 dyes of the class here considered; of these only 9 are basic and in the case of all the other 15 the whole of the commercial muriatic producible is available for other purposes. Data as to the relative amounts produced of these 24 dyes are not available and any statement as to such relationship would have to be nothing but the baldest kind of guess.

#### THE CHEMICAL TRANSFORMATIONS

The manufacture of these 24 dyes calls for the following eleven chemical operations, each of which is briefly described below.

1 Nitrating	5 Oxidizing	9 Condensing
2 Chlorinating	6 Caustic-melting	10 Carboxylating
3 Sulfonating	7 Alkylating	11 Diazotizing and coupling
4 Reducing	8 Liming	

1—NITRATING—The material to be nitrated is treated with "mixed acid," *i. e.*, a mixture of nitric acid with sulfuric acid; generally only mono-nitration is effected; dinitrating and trinitrating are less frequently performed; the differences are wholly of proportions, times and temperatures. The kind or quality of nitration product is not in every respect under control but quite generally the reaction can be "steered" in the right direction. The spent mixed acid in many cases can be re-strengthened so that there is only a slight loss of sulfuric acid.

2—CHLORINATING—The material to be chlorinated is treated with dry chlorine gas (usually from the electrolytic caustic soda plant followed by liquefaction and gasification); as in nitrating there may be mono-, di- or tri-chlorinating and in addition the chlorination may be in the "ring" or in the "side chain," so, according to the material there may be six courses for the reaction to go; it is not so readily "steered" as is nitrating. In chlorinating, one-half of the chlorine employed appears as hydrochloric acid gas (100 per cent), so that for each pound of chlorine that is introduced one pound of 100 per cent hydrochloric acid is obtained, *i. e.*, 3 lbs. of commercial 33 per cent muriatic acid.

As an illustration of what this means, take Dr. Brunck's figures of 1900 wherein 4,400,000 lbs. of glacial acetic acid are chlorinated annually; these require not less than 5,200,000 lbs. of liquid chlorine and produce 3,900 tons of 33 per cent muriatic acid, or 11 tons daily. These figures are today, perhaps, doubled for the indigo industry alone. It is hardly to be expected that this amount of acid is thrown away.

Further, the above quantity of chlorine corresponds to about 5,850,000 lbs. or 2925 tons of caustic soda annually or 8.5 tons daily.

3—SULFONATING—The material to be sulfonated is treated with 98 per cent or with fuming acid, *i. e.*, oleum, according to the product desired. As a rule, the amount of sulfuric taken is several times that required to do the chemical work, the excess acting as a vehicle. Mono-, di- and tri-sulfonating may occur, and the course can be "steered" with difficulty except in a few cases. The excess sulfuric is as a general thing lost, either as calcium sulfate or as a weak and highly contaminated sulfuric acid of which a part only can be strengthened up; it is, as a rule, run into the sewer. In sulfonating, in general, much of the sulfuric doing chemical work is divided over a number of products and of these some are far less useful than others and the art of making both ends meet in this phase is dependent upon how fully these different sulfonation products can be used in dyestuff making.

4—REDUCING—As a rule, only nitro bodies (the products of nitration) are reduced; when reduced they yield amido bodies, *e. g.*, nitrobenzol yields amidobenzol, otherwise known as anilin. Reduction is, as a rule, effected by the use of iron in

the form of powder, filings, drillings, etc., with the aid of acetic or of hydrochloric acid. The iron residue is very largely reconverted into metallic iron. The world does not use enough iron salts to make even a dent in the amount of these residues available.

5—OXIDIZING—This is effected largely by means of lead peroxide; manganese dioxide and also permanganates are used; hydrochloric acid is generally used in connection with them although sulfuric acid is also used. The manganese residues are generally re-worked to peroxide while the lead residue is used for lead chromate and similar articles. Potassium bichromate (residue chrome alum) and chlorate of potash (residue chloride of potash) are also used for oxidation purposes.

6—CAUSTIC MELTING—The substance to be subjected to the caustic melt is, as a rule, a sulfonation product, and the purpose of this melt is to remove the sulfuric acid portion and put the hydroxyl group in its place. For example, benzol mono-sulfoacid yields hydroxy-benzol, *i. e.*, phenol or carboic acid; naphthalene monosulfoacid yields alpha-naphthol or beta-naphthol, depending upon which particular monosulfoacid of naphthalene was used. The sulfuric portion re-appears as sulfite of soda. As a rule, the amount of caustic soda taken is greater than that required for the chemical work; the excess is lost as carbonate in weak water solution, carrying the sulfite; this is used for bisulfite production or Glauber's salt production, or is thrown into the sewer as commercial conditions may indicate.

This process is not easily "steered;" it calls for extreme care, and its success depends upon very minute details not always easily discoverable, and when discovered very conscientiously kept secret.

7—ALKYLATING—This is the introduction of methyl or ethyl groups into hydroxyl groups or into amido groups. Methylation is generally effected by the use of wood alcohol and hydrochloric acid under pressure in closed vessels at elevated temperatures; sometimes methyl chloride must be used. Ethylation is similar to methylation, using grain alcohol for the wood alcohol and ethyl chloride for the methyl chloride.

8—LIMING—This is generally applied to sulfonation products to separate the different chemical substances from each other; as a general rule the lime salt of one or more is soluble and of the other insoluble; lime or chalk may be used; generally lime is preferred on account of absence of frothing, but where that is not objectionable limestone or chalk is used. In this case all free sulfuric acid is rendered useless as sulfate of lime.

In another phase of liming, however, caustic lime is necessary, as in separating benzal chloride from benzo-trichloride; the former gives benzaldehyde which is blown off by steam and the latter gives benzoate of lime, which is further decomposed to give benzoic acid.

9—CONDENSING—This covers all those processes where two different substances (or two molecules of the same substance) unite to form a new compound by the loss or elimination of water or its equivalent between them; among the most common equivalents for water-loss is loss of hydrochloric acid or of ammonia.

Sulfuric acid is a common condensing agent and for this purpose is used in considerable excess; in general, it reappears as a very weak acid and is lost to the works; the other condensing agents such as chlorides of phosphorus and of sulfur, zinc chloride, aluminum chloride, antimony chloride and the like can, as a rule, be recovered in usable form and returned to the cycle at a slight additional cost.

10—CARBOXYLATING—This is generally performed by the action of an excess of caustic soda and pure carbon dioxide gas upon a hydroxylated, *i. e.*, phenolic or naphtholic substance; for example, phenol or carboic acid yields salicylic acid and alpha-naphthol yields alpha-oxy-naphthoic acid. Salicylic acid has wide application in the coal-tar dyestuff art. The caustic is recoverable only as a salt (sulfate or chloride, etc.).

11—DIAZOTIZING AND COUPLING—An amido compound such as alpha-naphthylamine on treatment with nitrous acid yields a compound called diazonaphthalene; this operation is called diazotizing. When this result is brought into contact with salicylic acid in the presence of sodium carbonate or acetate it yields a new substance; this operation is called coupling. This product on reduction yields a new compound, amido-salicylic acid, and the original alpha-naphthylamine. The amido-salicylic acid is itself very useful in the coal-tar dyestuff art.

These two operations are the most ubiquitous and widely applied reactions in the entire industry; they serve to help in making intermediate products and to produce the multitudes of substances known as azo-dyes which make up more than 50 per cent of the individual dyes of the world's market. This group of azo-dyes is a terrific and bewildering maze of interlocked and interlaced substances and operations compared with which the 24 dyes here charted are the merest alphabet of simplicity, as is shown later under the benzidine dyes.

MAKING MICHLER'S KETONE

In making the ketone for the 24 dyes in Fig. III, four operations are employed:

Nitrating	Reducing	Alkylating	Condensing
The following twelve materials are needed:			
Benzol	Nitrobenzol	Anilin	Wood alcohol
Carbon monoxide	Chlorine	Phosphorus	Nitric acid
Sulfuric acid	Iron filings	Muriatic acid	Animal charcoal

The product of these operations and materials is *not* a dyestuff but must be *condensed* with other products; in fact we are now only ready to begin to make a dye but only *after* we have made several other substances—to be accurate 18 additional compounds to make these 24 dyes.

Table VI shows the distribution of operations and materials over the things other than "ketone" that are to be combined with "ketone" to make dyes.

For twelve of these 24 dyes *one* member of the four classes of organic materials, namely,

I = Fatty series II = Benzol III = Toluol IV = Naphthalene

is sufficient; for the other twelve the following combinations of materials are necessary:

Classes	No. of dyes	Classes	No. of dyes
I and II.....	4	III and IV.....	1
II and III.....	1	I, II and III.....	3
II and IV.....	1	I, II and IV.....	2

The operations required are a total of 118. In Table VI "xx" indicates that the operation has to be performed twice in making one dye.

TABLE VI—MATERIALS AND OPERATIONS OF THE 24 DYES

Dye No.	MATERIALS TRANSFORMATION No. (pp. 1020 and 1021)											Totals					
	Totals	I	II	III	IV	1	2	3	4	5	6		7	8	9	10	11
550.....	1		x						x	x					x	x	4
493(a).....	1																(a)
509.....	1		x					x	x	x					x		4
542.....	1		x					x	x	x					x		6
565.....	1								xx	x					x		5
566.....	1							x	x	x					x		5
498.....	1		x							x							3
522.....	3	x	x			xx			xx						x		6
531.....	3	x	x	x				x	x	xx					x		7
558.....	3	x	x			xx			xx						x		5
559.....	2		x			xx			xx						x		6
560.....	2			x		x			x	x					x		6
562.....	1					x			xx	x					x		6
563.....	1					x			xx	x					x		6
564.....	1					x			x	x					x		4
567.....	1					x			x	x					x		6
516.....	2	x	x														3
527.....	3	x	x	x				x	x						x		5
528.....	3	x	x	x				x	xx	x					x		7
548.....	2		x	x		xx			xx						x		8
549.....	1		x							x							3
561.....	3	x	x			x			x	x					x		6
518.....	2	x	x			x			x						x		3
532.....	2	x	x			x			x						x		4
TOTALS..	41	9	14	7	11	21	5	13	31	12	5	8	8	11	3	1	118

(a) No. 493 (auramine) uses double chloride of zinc and ammonia only, in addition to "ketone."

## COAL-TAR PRODUCTS PARTICIPATION IN THE 24 DYES

In making the quantities of each of the 24 dyes given in Table V the material participation is as follows:

	Per cent	
Ketone.....	52.11	
Benzol.....	7.58	...
Toluol.....	5.21	...
Naphthalene.....	11.42	...
Phenol.....	1.69	25.90
Sulfonation, alkylation, etc.....	...	21.97
TOTAL.....	99.98	

Of the ketone 58.21 per cent are benzol so that the benzol participation in the 4605 parts of the above 24 dyes is a grand total of 37.91 per cent. That is, of the 4605 parts of these 24 dyes:

	Per cent	Per cent
Benzol.....	37.91	...
Toluol, makes up.....	5.21	...
Naphthalene.....	11.42	...
Phenol, makes up.....	1.69	...
TOTAL.....	56.23	
Ketone production makes up.....	21.80	
Sulfonation, alkylation, etc., make up.....	21.97	

It must not be forgotten that these 24 dyes are by no means made and sold in the proportions given in Table V. Therefore, in order intelligently to plan a works for these 24 dyes it must be known how these 24 individuals are to be distributed over the whole production in order to avoid waste of space, apparatus, material and time in laying out the relative position of buildings and their respective sizes.

## MAKING THE TWENTY-FOUR DYES

To carry out the 118 operations it is not intended to say that 118 sets of apparatus are necessary; the different sets of apparatus are 11 or a multiple thereof and how great that multiple is depends upon the relative amounts of each of the 24 dyes to be made and the time at which they must be manufactured. Further, one and the same apparatus is not necessarily adapted for any one operation on different compounds, *e. g.*, nitrating each of the three different materials to be nitrated, namely, benzol, toluol and naphthalene; nor will the same chlorinating apparatus do for all kinds of chlorinating, nor the same condensing apparatus for all condensations and so on through the list.

## UNIFORMITY OF PRODUCT

It must be borne in mind that Fig. III does not in any way attempt to show the different manufacturing operations and steps that are necessary to accomplish the indicated results; neither is it attempted to show on Fig. III the filtering operations, the precipitation operations, the blowings off with steam and other means of mere mechanical separation; between each and any two successive chemical alterations there are one or more mechanical operations not indicated, as well as secondary chemical changes such as the conversion of sulfo-acids into salts; bases into salts; the separation of the salts from their liquids and their purification, their drying, their storing. In addition to all this, of course, there is the large amount of testing that must be done at all stages of each operation and the exhaustive and careful test of each lot of final product before it is passed from one step to the other and of the finished dye before it is placed in the warehouse. The number of these operations is merely a matter of calculation and consideration but such a presentation would add nothing of moment for present purposes; on the contrary it would make Fig. III so complicated as to rob it of most, if not all, of its utility. Suffice it to say, that the tests are in many cases rapid and short but in other cases and particularly in the case of the finished products they are very refined, allow but a small margin for error or variation and require a great deal of care and painstaking in their execution. For example, in making beta-naphthol some alpha-naphthol is always formed and the users of beta-naphthol have become so refined in their requirements and demands that if a sample of beta-

naphthol carries more than  $\frac{1}{600}$  per cent of alpha-naphthol, that is, one part of alpha-naphthol in 50,000 parts of beta-naphthol, it stands a very good chance of being rejected. In making alpha-naphthol some beta is always formed and its presence in alpha is just as objectionable as is the presence of alpha in beta.

Therefore, not only are there a large number of operations, but these operations while not always under accurate control must, nevertheless, be carried out with great refinement and great exactitude and with great uniformity of final product in the majority of the cases; there are a number of cases where such refinement is not necessary but, needless to say, works that make only the rough goods could not hope to survive in competition with works that make both classes of goods. The buyers of dye-stuffs, as a rule, subject the purchased goods to severe tests and even if they do not, the competition between the various makers of dyestuffs is so keen that they themselves have effectively and effectually raised the standard of the goods to be made.

That this industry is complex, interlaced and interlocked not only from the manufacturing point of view but the merchandizing viewpoint also must be clear from Fig. III which purports to present in the sketchiest of outline the interrelationship of only  $\frac{1}{40}$  of the individuals of the industry.

## INTERLOCKING AND INTERLACING

In Fig. III there are several instances of the production of two or more things side by side in one and the same operation and all of these must be utilized somewhere in the works in order not to be a dead loss.

Take, for example, treatment of toluol with chlorine; three substances are unavoidably formed: benzyl chloride, benzal chloride and benzo trichloride in greater or lesser proportions. In Fig. III benzyl chloride is used in three dyes, benzotrichloride in one dye and benzal chloride in a group of dyes, itself much larger than this particular group of dyes; but each of these three compounds has uses in other dyes and groups of dyes. Merchandizing effort must be directed to keeping the products of all these three materials in alignment so that excess production of none takes place over market requirements. It is a much more complicated merchandizing operation than, for example, the alignment of the salt-cake and muriatic acid markets, and still it is easier in some respects because of the greater number of outlets available. Nevertheless, it is a task requiring great skill and much careful and painstaking attention.

In treating toluol with nitric acid only one product is shown, namely, the para variety; however, another variety is also formed—the ortho variety which is commercially far more important than the para variety. In effect, therefore, the utilization of the para variety in this and other classes of dyes is merely making use of a substance unavoidably a by-product from another manufacture (*e. g.*, tolidine manufacture) so as to avoid useless waste and loss; if one maker does not the other will and thereby gain a commercial advantage. For example, the ortho variety is used in tolidine making and the para variety in magenta making (see Fig. VIII); both produce para and ortho respectively, in addition, which they respectively cannot use but *together* they can consume all of each *provided* their respective sales are properly adjusted; if not, additional uses are needed.

Other examples of such interlaced, interlocked simultaneous results are shown on Fig. VI; for example, the sulfonation products of beta-naphthol where one monosulfoacid and two disulfoacids must be kept in line; or the sulfonation of beta-monosulfoacid by means of oleum where at least two products, one disulfoacid and one trisulfoacid must be managed; direct loss of product with no use in this class is shown in the treatment of beta-monosulfoacid with nitric acid as described later on.

Study and examination of these charts or diagrams will dis-

close more and more how really intricate and complex as well as interdependent are these products. Nevertheless, simple inspection of these charts shows a real and important interlocking and interdependence of not only the intermediates but of the finished dyes themselves.

In Figs. IV, V and VI are presented the diagrams for 82 additional dyes and their needed intermediates; these 82 dyes are themselves important and large sellers. With the 24 ketone dyes just described they make up one-eighth of the individuals of the present world's market. The complex nature of the relationships of the relevant intermediates is obvious at a glance.



THE BENZIDINE DYES—FIG. IV

About one-tenth of the individual dyes on the world's markets have benzidine as a substantial and necessary ingredient. This can be made from nitrobenzol, caustic soda, zinc dust and hydrochloric acid and requires three chemical transformations, beginning with benzol as shown at Fig. IV. Benzidine itself,

FIG. IV.—BENZIDINE AND TOLIDINE DIAGRAMS

however, is no dyestuff and, unlike anilin, it cannot be used for the production of black or any other shade upon fiber without the cooperation of some other coal-tar product. The benzidine must first be treated with nitrous acid to form its tetrazo-compound which is itself then combined with other coal-tar derivatives to produce finished dyes. In the production of the 82 benzidine dyes in the world's markets the materials or finished intermediates with which the benzidine is to be combined,

The original treatment of naphthalene, Fig. VI, is divided into three classes, namely, by nitric acid, by oil of vitriol and by fuming sulfuric acid. The nitric acid treatment followed by other suitable treatments yields 5 of these finished intermediates. The oil of vitriol treatment coupled with caustic melt, nitric acid treatment, reduction, treatment with nitrous acid and heating with water or with oil of vitriol yields 21 of these finished intermediate products; the treatment with the fuming acid yields but one finished intermediate.

When these 44 compounds are combined with benzidine to produce the 82 dyes, they are used two at a time, three at a time and four at a time or each one twice and it is self-evident from the possible permutations and combinations that there is a wide field opened up by these 44 finished intermediates; however, only 82 individuals have been found to be of lasting commercial value.

The benzidine dyes, which are valuable because they are direct cotton dyes (that is, dye cotton fiber without the use of a mordant), are incomplete of themselves for the commercial range of shades and colors in this class of materials and as a complement the tolidine dyes are employed. Toluidine is made from nitro-toluol (the ortho variety) in the same manner that benzidine is made from nitro-benzol (see Fig. IV). Toluidine, in turn, is combined with finished intermediates over and above those shown on these charts and their genetic relationship is quite as complicated as that shown for the benzidine finished intermediates. Of the above compounds found in coal-tar only two are useful as such for union with benzidine and tolidine; they are phenol and cresol but the role they play in that capacity is rather subordinate.

The number of intermediate steps from naphthalene (Fig. VI) to finished intermediate is at a maximum in the case of 2.7

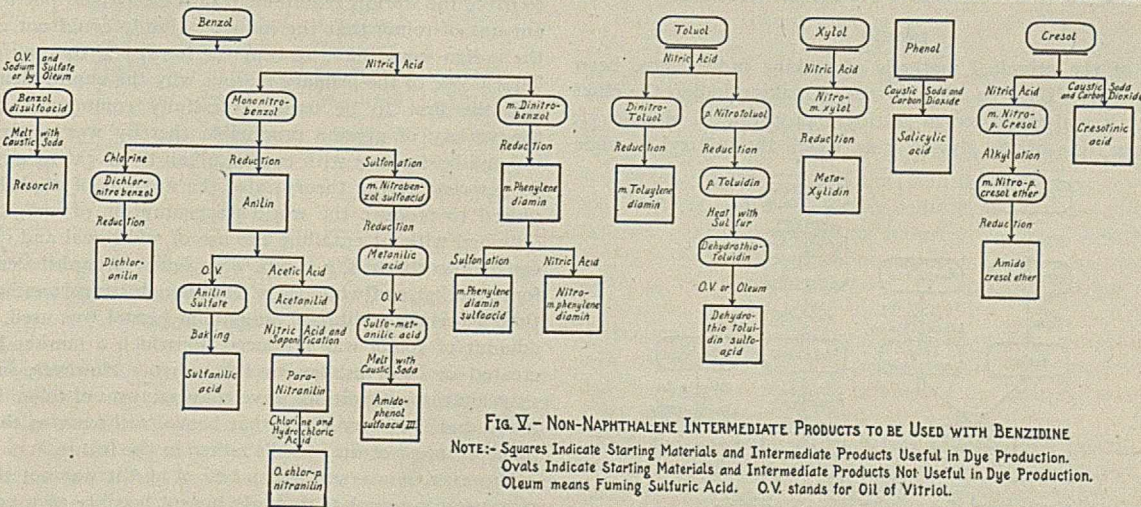


FIG. V.—NON-NAPHTHALENE INTERMEDIATE PRODUCTS TO BE USED WITH BENZIDINE

NOTE:—Squares Indicate Starting Materials and Intermediate Products Useful in Dye Production. Ovals Indicate Starting Materials and Intermediate Products Not Useful in Dye Production. Oleum means Fuming Sulfuric Acid. O.V. stands for Oil of Vitriol.

number 44. These 44 compounds are made from benzol, toluol, xylol, phenol, cresol and naphthalene and the making calls for the intermediate production of 55 substances that have, so far as these dyes are concerned, no other use than to serve as intermediate products.

Benzol, Fig. V, is treated with oil of vitriol or with nitric acid to form two different classes of benzol derivatives, the former having but one member and the latter having 9; toluol on treatment with nitric acid and three separate additional chemical treatments yields two finished intermediates. Xylol on treatment with nitric acid yields but one finished intermediate. Of course, other operations are necessary, such as the caustic soda melt, sulfonation, reduction, chlorination and baking. Phenol on carboxylation yields salicylic acid, and cresol on carboxylation yields cresotinic acid and on treatment with nitric acid and subsequently by alkylation and reduction yields amido cresol ether.

diamido naphthalene 3.6 disulfo acid; in that case six intermediate products must be prepared, no one of which has any use in this class of dyes, other than the production of this one finished intermediate. None of these starting materials yields a finished intermediate with one chemical operation except in the case of phenol and cresol; for all others at least two chemical steps must be taken before a finished intermediate is arrived at.

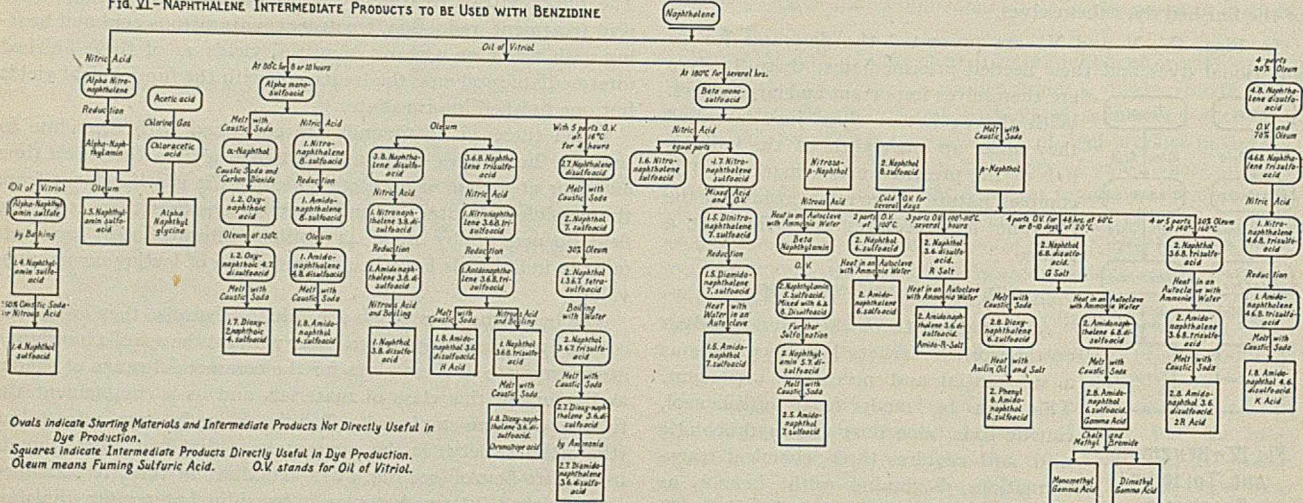
In addition to benzidine and to tolidine, 6 other substances of a similar nature are employed to complete this commercial series of direct cotton dyes and they in turn make use of some of these finished intermediates and in addition others not here charted.

Going back on Fig. VI, to the treatment of naphthalene beta-nitrosulfoacid with nitric acid it will be noted that the chart states that two nitration products are formed in equal parts; so far as this particular class of dyes is concerned one of those equal parts of nitration product is useless. It becomes a burden

to the other part so that the 1,5 di-amido naphthalene 7 sulfoacid must bear the entire cost of nitrating the beta-mono-sulfoacid although only one-half of that nitric acid and one-half of the beta-mono-sulfoacid is available for it; the other part

syntheses are divisible into 2 classes; three of them start from benzol and the remaining one starts from naphthalene and they all come together at the indoxyl point and from that point are all substantially identical. The salient point is at the pro-

FIG. VI.—NAPHTHALENE INTERMEDIATE PRODUCTS TO BE USED WITH BENZIDINE



goes to form a waste heap unless utilized in some other branch of the industry.

The 167 direct cotton dyes of the diphenyl type of the present world's markets are distributed as follows, among the various diphenyl derivatives:

Benzidine.....	82	Benzidine-mono-sulfoacid ...	2
Tolidine.....	43	Benzidine-disulfoacid .....	4
Dianisidine.....	28	Ethoxy-benzidine.....	4
o-Nitrobenzidine.....	1		
Di-chlorbenzidine.....	3	TOTAL.....	167

INDIGO

Four of the principal methods of making indigo have been charted (Fig. VII). In all processes of making indigo the chief difficulty has always been in getting a proper yield of indoxyl; the preparation of the glycine from which the indoxyl is made

duction of indoxyl. The method first to be used successfully commercially was to melt the glycine with caustic soda; whed starting from anilin the yield rarely exceeded 45 per cent anfor a long time no means was discovered for producing any substantial increase in that yield; admixture of burnt lime to the caustic soda was tried without materially increasing the yield. Moreover, all methods that started from benzol had to take account of the possibility of the drawback that to produce enough benzol to make the world's requirement of indigo would pile up such an amount of toluol that the industry simply could not use it and the indigo would have to bear the burden of the unused toluol. That is one of the primary reasons why the naphthalene method was the first to be used successfully commercially; further, the variety of glycine producible thereby was converted into indoxyl by melting with caustic alkali to an extent approaching 90 per cent of the theory; also the amount of naphthalene required to produce the world's consumption of indigo could be obtained without entailing the use of additional and other coaltar hydrocarbons; i. e., there was plenty of naphthalene looking for a market and while there was enough benzol available, every time a certain additional amount of benzol was used, a certain amount of toluol was produced for which a market had to be created or be a burden to the indigo. However, in the last 15 years those conditions have changed; uses of toluol have been found and it is very likely that benzol will serve as the starting point for most of the world's indigo in the future.

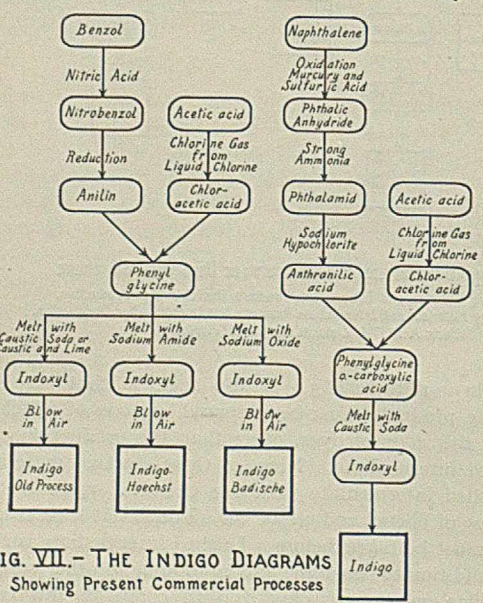


FIG. VII.—THE INDIGO DIAGRAMS Showing Present Commercial Processes

has in itself not offered any very great difficulty but the strategic point of the whole indigo synthesis is at that conversion, and it is at that point that most of the energy of chemists has been expended. It would not be at all surprising if on examination it were to turn out that at least 50 distinct and different modifications of operations at that point have been patented and of these probably not more than 3 survive to this day. These 4 indigo

However, it was not cheap benzol and it was not the finding of a use for toluol that made benzol feasible as a commercial starting point for indigo. The discovery that sodium amide would convert the glycine into indoxyl practically quantitatively was the particular event that made the use of benzol commercially feasible; sodium oxide has also been found to be a substitute of equally good quality for the sodium amide. Reverting to Fig. VII it will be of interest to note that the first step from naphthalene to phthalic anhydride today calls for the production of an amount of sulfuric anhydride equal to 80,000 tons of 50 per cent pyrites per annum. The step of passing from acetic acid to chlor-acetic acid today calls for over 9,000,000 pounds of glacial acetic acid and over 10,000,000 pounds of liquid chlorine.

AMERICAN ATTEMPTS TO DEVELOP A DYE INDUSTRY—FIG. VIII

The hydroquinone diagram in Fig. VIII illustrates what American manufacturers have been doing with domestic benzol; it requires a total of four chemical operations and produces two

compounds, each of them usable as such, *i. e.*, anilin, used for the production of black on cotton without the aid of any other coal-tar product and hydroquinone, used as a photographic developer. This diagram will give some measure of the difficulties that may be expected in an attempt to develop the finished intermediates necessary for the production of the 24 ketone dyes of Fig. III and the 82 benzidine dyes of Figs. V and VI.

Magenta requires benzol and toluol; the former must be converted into nitrobenzol and then into anilin and the latter into nitrotoluol (largely the para variety) and then reduced to toluidine by taking a suitable mixture of anilin and toluidine with nitrotoluol or nitrobenzol (as indicated in Fig. VIII), magenta base is produced, and this, on treatment with hydrochloric acid, yields the hydrochloride which is the commercial form of magenta.

A book of over 280 pages was published in 1889 and contained plates and drawings of apparatus and lay-out of works and minute directions for magenta manufacture; even this and the absence of all patents has not enabled American manufacturers to make this product in competition. It is true that magenta is still made in this country but it is made almost entirely from magenta base imported from abroad. Roughly and approximately speaking, in \$80,000 worth of magenta there are \$450 worth of commercial muriatic acid. The remainder of the value is made up by the magenta base.

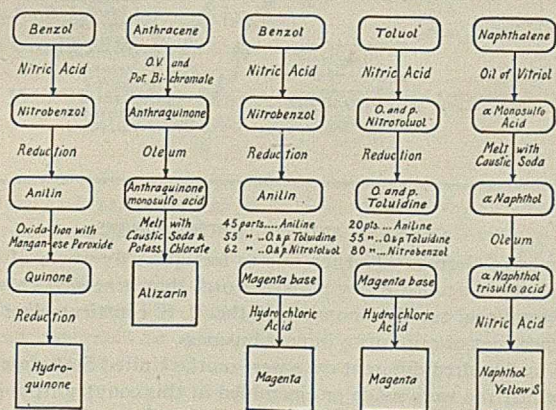


FIG. VIII.—SYNTHESIS OF SOME DYE-STUFFS ALL EXCEPT ALIZARIN ATTEMPTED IN THE UNITED STATES AND DRIVEN OUT BY FOREIGN COMPETITION

The Naphthol Yellow S patent has been dead for over 17 years and yet none of this dye has ever been successfully manufactured from naphthalene in this country. Whatever has been manufactured in this country has been made from alpha-naphthol-trisulfoacid, imported from abroad, which is merely treated here with nitric acid and carbonate of soda and even that manufacture has now disappeared almost entirely.

Alizarin manufacture involves three chemical transformations of anthracene which has always been as cheaply laid down from England in the United States as in Germany; the reputation of alizarin as a money-maker and money-getter has always been world-wide, and the United States has always been a good consumer of alizarin, yet no concern in this country has ever taken up the manufacture of alizarin. It is possible that the fact that alizarin never was protected by tariff may have prevented any such effort; certainly with the patent dead for 28 years it cannot well be urged that patent rights have stood in the way.

Many of the other dyes said to be made in the United States are made in just about the same way as the Magenta and Naphthol Yellow S; that is, the bulk of the chemical work is carried out in Germany and merely the finishing touches (the "as-

sembling") is done in this country. Obviously the bulk of the profit is not in the "assembling."

#### WORKING CLAUSES

These two examples show very clearly how a working clause in the patent law does not necessarily produce a coal-tar dye industry. The patent is taken out on the commercial form and any product prior to the commercial form is *not* the subject of the patent. It requires no lengthy dissertation to show that merely putting on the finishing touches is a long way from a true industry. France has had a working clause for a great many years, Great Britain for only seven, yet neither country today can make its dyestuffs simply because they have both been purchasing from Germany materials which bear the same relationship to the finished product that magenta base bears to commercial magenta and alpha-naphthol-trisulfoacid bears to Naphthol Yellow S. A true industry requires making all materials from the crudes.

#### GEOGRAPHY OF THE GERMAN DYE FACTORIES

In Germany the coal-tar dye plants and the principal coke oven districts are all contained within an area described by a square 300 miles on each side (see map). With but one exception the really important ones are all along the Rhine or a short distance up its tributaries. This whole district could be put inside the State of Wyoming, is much smaller than the state of New Mexico, or is smaller than New York and Pennsylvania combined. With cheap water routes and short rail hauls for the transportation of materials from one factory to another or to sea port, these dyestuff factories are most advantageously located and with the added short rail and water hauls to them from the coke regions the transportation of the raw materials to the dyestuff works is economically profitable.

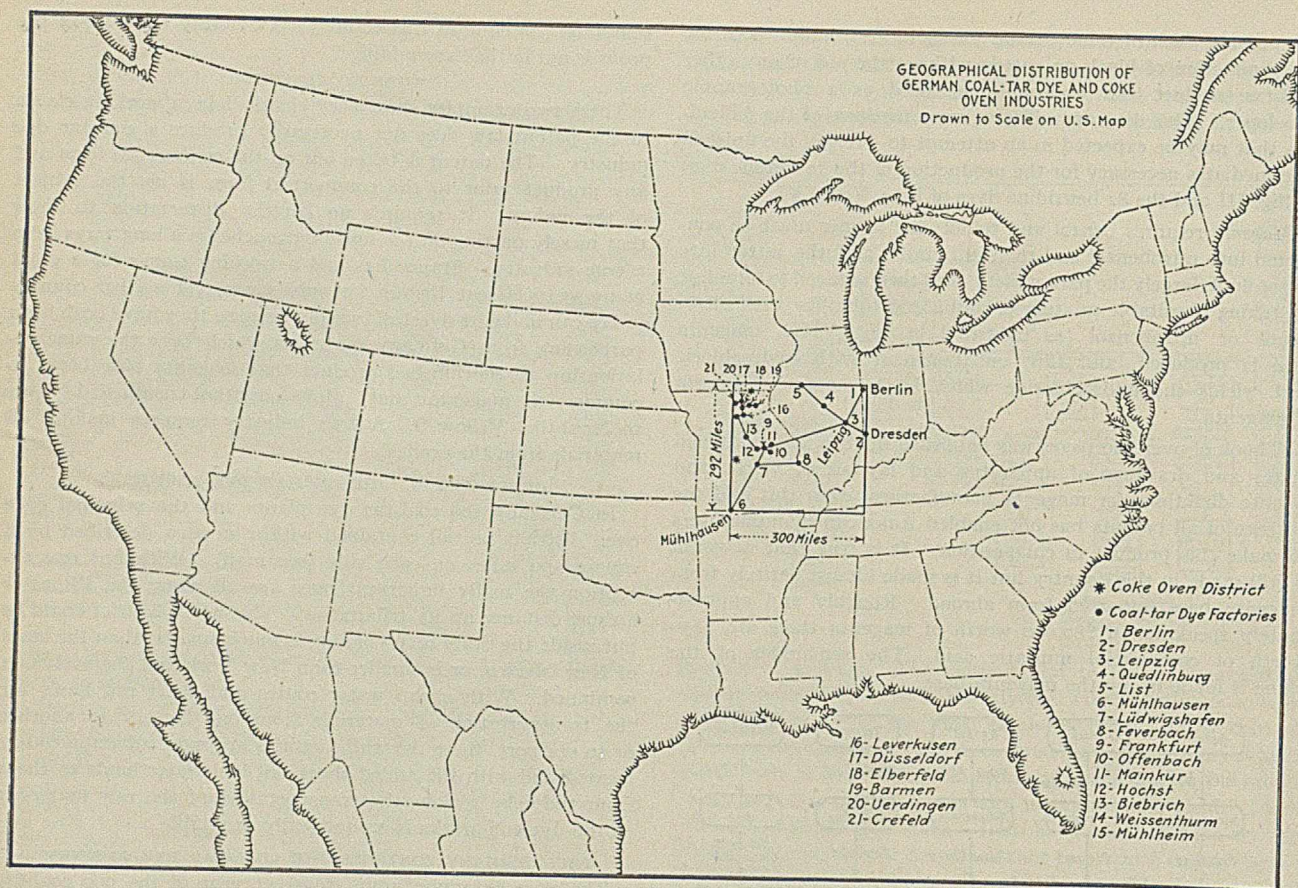
#### WHY GERMANY CONTROLS THE COAL-TAR DYE BUSINESS

The average annual unit gross per year of the 900 coal-tar dyes, exclusive of alizarin and indigo, all over the world outside of Germany, has previously been shown to be about \$41,000. Add to this the interlocked dependence of intermediates and finished dyes just shown and the facts that the German works have long ago fully paid for their plants, their experience and their sales organization and the result is what seems to be a complete answer to why Germany controls the world's coal-tar dye market. In fact, the whole industry, taking everything into account, is just about a one-nation business. It is a business made up of a large number of small units with all units essential to success.

Germany has this business established in 33 other countries; it is evident that any country starting in now would be greatly handicapped thereby if it attempted to enter the race for the full distance.

Although Germany has relied upon Great Britain for its crudes, *i. e.*, its benzol, its toluol, its naphthalene and its anthracene, up to the middle of the 90's and perhaps later, England has not been able to make any headway as competitors in dye manufacture, but on the contrary has lost ground. Many of these non-patented world's dyes are also non-patented in England yet most of Great Britain's requirements of those materials have always been supplied by Germany.

The answer to the question as to why Great Britain has not succeeded against Germany cannot be that Great Britain is not a nation with highly developed chemical industries. A German chemist as well equipped as any other living man to express an opinion and to compare German industries with British industries has said the following: "To be sure, we know that several of the European countries, *e. g.*, England, are still ahead of us in many branches of the chemical industry, especially in inorganic manufacture. But in no country on earth are those branches of the chemical industry which demand versatility of thought, and particularly a large body of scientifically trained employees, so well developed as with us. Our



synthetic dye, synthetic drug, and perfumery industries are foremost throughout the world, and there is probably no country in which the heads of factories are so imbued with the conviction that their employees must needs cast a glance beyond domestic boundaries."

Each one of the large chemical manufacturing countries of Europe, without exception, buys more intermediate products from Germany than it sells to Germany and all of the countries but one, namely, Switzerland, buy more dyestuffs from Germany than they sell to Germany. In other words, and broadly speaking, all the rest of the world, outside of Germany, merely assembles intermediates purchased from Germany, into finished dyes; Germany alone makes all its own intermediates; that is, Germany makes all the dye-parts and the rest of the world merely assembles these dye-parts into finished dyes. Needless to say, the one who controls the manufacture of dye-parts actually controls the manufacture of dyes.

Where Austria, Belgium, France, Great Britain, Italy, Russia and Switzerland singly and combined have failed, in spite of their other large chemical industries, to take away this business from Germany, the American chemist should not be blamed nor found fault with because he has not succeeded, nor should it be assumed that transplanting of the whole industry can be done at once and is a perfectly easy thing to do, as so many seem to think. The transplanting of that industry out of Germany is an undertaking properly and fitly to be described as titanic.

Why the other countries have failed is probably due to the fact that they contributed little or nothing to the real upbuilding of the business, and to its creation, for the coal-tar dye business is a *created* business; those who aided in its creation were first in the position to reap the benefits—an advantage they have no doubt earned and deserved through the effort they expended and the risks they assumed.

#### GERMANY AND THE UNITED STATES

In 1913 Germany had for sale to foreigners \$3 worth of these products as against every dollar's worth that it needed at home; the total coal tar dye imports of the U. S. constitute less than 0.4 per cent of our entire import business.

Nine hundred different dyes were on the United States markets of which 100 were made or assembled in this country from intermediates purchased from Germany. Yet these 100 do not seem to be enough for American dye-users.

How much less than the full 900 will satisfy American users is known to them and to the importers. The latter cannot be expected to divulge that information; if the former want substantial help from American chemical makers *they* must divulge that information; no other way of ascertaining it is available.

In 1909 the United States produced \$3,462,436 worth of artificial dyes which are probably anilin dyes in the strict sense. Compared with Switzerland's \$3,200,000 production, *i. e.*, "assembly," in 1896 this is an achievement of which Americans need not be ashamed. The wonder is not that we have not done more but that in the face of the well organized manufacturing plants of Germany and of Germany's very much superior facilities for foreign trade, both banking and carrying, that we have done as much as we have. Blame should not be parcelled out for what American chemists have not done, but credit, which has been withheld so far, should be given for what has been done in spite of obstacles abroad and obstacles at home. The users of dyestuffs have invariably opposed any tariff enactment that would substantially encourage a domestic production of coal-tar dyes. That so many are produced in this country as are being produced is due to no coöperation of dyestuff users but has been accomplished in spite of their obstruction and if today the users are in serious difficulty through a lack of dyestuffs they have their own shortsightedness to blame and cannot, by any argumentation whatever, shift the blame to American chemists.



With proper help and encouragement the American chemist will be able to increase the domestic production of coal tar dyes and to inaugurate the making of intermediates; in the course of time this country may then ultimately look forward to a substantial share of the world's coal-tar dye business.

Hardly any of the valuable or useful intermediates ever were patented. A considerable number of non-German chemists have invented and patented finished dyes made from non-patented intermediates. These inventors had perfect freedom to make the needful intermediates and an *exclusive* right to make, sell and use their new dyes therefrom, yet they bought their intermediates from Germany rather than make them themselves. The patent situation is, therefore, really, that Germany excelled the rest of the world in making patentable combinations from non-patented and non-patentable intermediates and further in making those intermediates in open competition with the rest of the world. So, from one point of view, it appears that the rest of the world, inclusive of the United States, lay back, let the Germans do all the hard work and when the rest of the world finally woke up to the value of what the Germans had accomplished they became very busy making excuses and explaining instead of making a determined, directed, united and effective attempt to recover the ground so lost. That such recovery will require the hardest kind of work on the part of all—users, capitalists, consumers and makers alike—is self-evident and obvious and the question is: Do we want to pay the price? It can be done, if the price be paid.

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## GAS MANUFACTURE FROM THE POINT OF VIEW OF PHYSICAL CHEMISTRY<sup>1</sup>

By W. F. RITTMAN

In past practice, gas manufacture has been primarily an engineering problem, with the chemist a more or less necessary adjunct for the analysis of coal, coke, oxide, etc. The research chemist, who deals with the processes of manufacture and the phenomena of reactions involved, has been looked upon as a burden unwarranted by returns. In view of the present available raw materials for gas manufacture on the one hand, and the demands of the public on the other, the advisability of continuing the policy of the past becomes a serious question.

There are few industrial operations which, from the standpoint of physical chemistry, are more complex in their nature than the treatment by heat of coal, oil and water in the production of coke, gas, tar, ammonia and cyanogen. In gas manufacture practically all the variables of chemical phenomena are involved. While this fact greatly complicates such industrial problems theoretically and practically, at the same time it greatly enlarges their possibilities; it strongly emphasizes the need of continued scientific research and investigation in connection with them. The heat treatment of coal, oil and water necessitates dealing with the chemical reactions of solids, liquids and gases, and with all the laws, both physical and chemical, which govern these reactions. The finest equipment in the world, designed with utmost mechanical precision, but without regard for the laws which govern the reactions carried out in it, is likely to be less useful than apparatus of the most wretched mechanical construction, but which does consider the chemical changes involved. Obviously, the aim of any industrial operation is perfection, both of process and apparatus.

Problems that are primarily chemical, and which can be attacked most efficiently from a chemical point of view, are common enough in gas manufacture. Who of the gas men present have not, at some time or another, faced the problems resulting from naphthalene, drip oil, fluctuating candle power, deposited carbon, ammonia, sulfur, cyanogen, or any one of a dozen other

<sup>1</sup> Presented with permission of the Director of the Bureau of Mines before the Chemical Section of the Ninth Annual Meeting of the American Gas Institute, New York City, October 22, 1914.

factors? Further, every new development in gas manufacture will create new problems. Every improvement will involve some question or questions peculiar to it. The greater the number of researches, the greater is the progress in a given field, and the greater becomes the number of new problems.

Hitherto, the greatest progress in American gas manufacture has been made along mechanical lines, and, as Americans, we may be proud of this progress. Chemical development, however, has been far behind the mechanical and operative improvements. It may be said that we have been spending too much of our energy investigating the machine rather than what is going on inside of the machine. Were the machine the end product of vital importance, improvements of this character would be unquestionable but the gas factory of the future will earn, or fail to earn, its dividends as it turns out, or fails to turn out, the best relative yields of coke, gas, tar and ammonia. It is true that the machine and the process are vitally related; there may be objections to this point because engineers are constantly working to perfect processes. It seems in gas manufacture, however, that too many of the purely theoretical chemical problems have been left to the mechanical or erecting engineer for solution. A mechanical, electrical or civil engineer, whose primary profession is the building and operation of machines and equipment, whose academic training consisted in the study of chemistry and physics during a part of two years, should not be expected to be as efficient in chemical research as the man who devoted himself exclusively to the study of chemical and physical phenomena; it is the latter, furthermore, whose primary profession to-day is the study of chemical and physical phenomena. To carry out high-grade research and investigation in any line, well-paid specialists must be employed. The able and efficient chemist and chemical engineer can do better things than analyze coal and iron oxide, however efficient he may be at the latter.

The day is past when gas-making is primarily a mechanical operation. Carbureted water gas constitutes approximately two-thirds of the gas made to-day, and it is no longer possible to buy a high-grade paraffin gas oil for 3 cents a gallon. Consequently, the petroleum supply becomes a most vital and important problem to the American gas manufacturer to-day. The importance of the oil problem as related to gas manufacture can be conveyed by the fact that in 1913 Greater New York alone used approximately 3,860,000 barrels of oil in the manufacture of carbureted water gas.<sup>1</sup> During 1913 the same plants used approximately 1,600,000 tons of coal. On the basis of heat units involved, oil has become as important in American gas manufacture as coal. Furthermore, Greater New York constitutes but one center for gas manufacture. I need not elaborate on the importance and seriousness of this oil problem, because you are fully acquainted with it. During the last decade, the increasing price of oil for gas manufacture has created what many gas men regard as a "dangerous" situation; and this is true despite the fact that never before in the history of the United States has so much oil been produced as to-day.

Why is it, then, that gas oil is expensive? Why should hundreds of millions of dollars' worth of oil-carbureting machinery be threatened? What is it that makes the economical use of petroleum one of the chief problems of the gas manufacturer? It is, first, the scientific progress in petroleum refining, and, second, the changing character in composition of the oil from newly discovered fields. Through careful scientific investigation, and through the application of physical-chemical principles, pure and simple, the refiner has perfected processes whereby the oil which you used to buy at 3 cents a gallon is now converted into gasoline and other end products which sell at several times that price. A representative example of this progress can be

<sup>1</sup> *Gas World*, 61 (1914), 76.

had from the testimony of Mr. Frank B. Lewis,<sup>1</sup> Jr., Manager of the Standard Oil Company Refinery at Whiting, Indiana, regarding the Burton process; this was offered at a recent court hearing in Chicago:

Q. Your Whiting plant is running exclusively on Mid-Continent oil, is it?

A. Yes, sir.

Q. Now tell us, Mr. Lewis, what percentage of the crude oil is refined into gasoline?

A. With the present method of distillation you can refine it all into gasoline if you wish to.

Q. The entire percentage?

A. You can take it all and convert it all into gasoline, except what coke is left in the still, and a little wax or petroleum tailings.

Q. How long has that method been in use?

A. About one year.

Q. Is that method in use at the Whiting plant to-day?

A. Yes, sir.

Q. To what extent?

A. To convert the fuel oil that we don't have any sale for into lighter product; fuel and gas oil we don't have any sale for and contracts for, into lighter products, making them up into motor fuel, which is practically gasoline."

Furthermore, oil refiners all over the country are working on methods to convert every pound of gas oil into more valuable products. Facing facts, this means that if gas men are to continue the use of petroleum in carbureting water gas, they must resort to one of two alternatives:

1—Greatly increase the yield of gaseous hydrocarbons from a given amount of oil, or

2—Perfect methods of using the millions of barrels of fuel oil which to-day are considered unfit for carbureting water gas.

One often hears the statement that these so-called fuel oils cannot be used in carbureting water gas. What right does any one have to make this statement? Is it the result of scientific study and investigation, or is it the result of experiments carried out under the same old conditions which prevail in the use of Pennsylvania, Ohio or Indiana petroleum?

The purpose in emphasizing the gravity of the petroleum situation in connection with gas manufacture is not to destroy hope nor to disseminate pessimism for the future. On the contrary, I believe that as soon as the gas manufacturer faces facts as they are, and seriously attacks the problem, increased efficiency and economy will result with petroleum still of primary importance as a raw material. Never in the history of the world has so much oil been produced as is being produced to-day. It is estimated that Oklahoma<sup>2</sup> alone will mine 80,000,000, and California<sup>3</sup> will contribute 100,000,000 barrels. Never in the history of the United States has so much oil been in storage as to-day. We are not facing an oil famine. We are facing a famine of knowledge concerning the chemical behavior of inferior petroleums which will facilitate their substitution for higher grade petroleums.

If we accept the statement that the various so-called fuel oils cannot be used to carburete water gas, the necessity for scientific chemical research becomes more acute than ever. It means that carbureted water gas is entering a rapid decline, and is to be replaced by coal gas, by-product coke-oven gas, or some other process gas not developed to-day. The problems involving physical chemistry will not be eliminated. The phenomena of chemical change are involved in any process wherein a solid or liquid is converted into a gas of different constitution.

The machine becomes of vital importance when it favors or hinders optimum conditions for the end products desired. Aside

from operating costs, the relative merits of horizontal *vs.* inclined *vs.* vertical retorts depend entirely upon the influences of the retort's position on physical and chemical changes involved. The relative merits of any mechanical structure used in gas manufacture depend upon its influence on the chemical reactions which produce the ultimate end products. The vertical retort completely filled yields more tar and less gas than the practice of partially filling the vertical retort, simply because the vapors are subjected to different physical conditions which influence the degree of cracking and tend to bring about equilibria concordant therewith. This difference in end products, using the same type of machine, indicates the complexity of the chemical reactions of gas manufacture and the close relations which exist between prevailing conditions and end products obtained. Both coke-oven gas and retort gas are made by the application of heat to coal, yet the two gases vary considerably in their composition. Therefore, should we not look forward to a complete understanding of the composition of the raw materials, coal and petroleum, and the changes and mechanisms of the changes that take place in them under different physical conditions?

When pointing out the seriousness and the dimensions of the gas man's chemical problems, and when referring to the efforts and accomplishments of petroleum refiners, it would be unjust to overlook the excellent research work which has been started within the last three to five years. However, practically all of these investigations deal with coal. They are concerned with determining:

1—The composition of the coal.

2—The initial decomposition products.

3—The final decomposition products under varying temperatures and pressures.

4—The nature of the tars produced under varying temperatures and pressures.

I refer to the valuable work of Parr and Olin,<sup>1</sup> Burgess and Wheeler,<sup>2</sup> Ame and Pictet,<sup>3</sup> Pictet and Bouvier,<sup>4</sup> Rau and Lambris,<sup>5</sup> the Bureau of Mines, the United Gas Improvement Company, The Barrett Manufacturing Company, and numerous other investigators.

Much of this work may appear too academic, and questionable from a practical point of view. On the other hand, our industry progresses as the result of just such investigations. Regardless of whether a low-temperature process, for example, is valuable for direct application, the information obtained as to the constitution and chemical behavior of the coal is of utmost importance. The same information with respect to petroleum is equally essential. As a matter of fact, prior to the works above referred to, the extent of change that takes place in the destructive distillation of coal was a question. In other words, do the end products occur in coal as such, or are they formed in the operation? Does benzene occur in coal as benzene, or is it formed in the distillation? To-day these questions appear unnecessary and out of place. We now believe that benzene does not occur perceptibly in the original coal, nor does it occur in appreciable quantities in Eastern gas oils. The fact that it does occur considerably in both water-gas and coal-gas tars of to-day, indicates conclusively that benzene is made in the course of the gas-making process. There has been a transformation, a chemical change. That this change is not a simple one can be observed from the investigations referred to. Further, it is found that when coal is distilled under a vacuum, very little benzene is formed. When the mechanism of benzene formation is fully understood, it will be a relatively simple

<sup>1</sup> Bull., Univ. of Illinois Engr. Expt. Sta., 1912; *Compt. rend.*, 137 (1913), 779.

<sup>2</sup> *Trans. Chem. Soc.*, 1910, p. 1917; 1911, p. 649; 1914, p. 131.

<sup>3</sup> *Compt. rend.*, 157 (1913), 779.

<sup>4</sup> *Jour. f. gasb.*, 56 (1913), 533, 557, 589.

<sup>5</sup> *Compt. rend.*, 1912, p. 1514.

<sup>1</sup> *The Petroleum Gazette*, July, 1914, p. 5.

<sup>2</sup> *Oildom*, Aug., 1914.

<sup>3</sup> *Petroleum Review*, 30, 599, 687, 717; 31, 3.

matter to increase or decrease the yield. Benzene is referred to purely as an illustration. The same reasoning applies to all tar, ammonia and cyanogen formation in connection with gas manufacture. If naphthalene is an undesirable product in gas manufacture, its appearance is not conclusive proof that its production cannot be avoided.

The variation in the tar obtained from different processes of coal, oil and coke-oven gases, is entirely due to variations in the prevailing physical conditions. It is a fact that these tars do differ, yet the initial materials used in the process of manufacture may be the same. With the reason for these differences fully understood, the optimum conditions for manufacture of both tar and gas will be understood and better realized. The tars which result from the destructive distillation of coal or oil, under different physical conditions, vary as widely as do the physical conditions under which they are made. In the course of a research carried out by Prof. M. C. Whitaker and the writer,<sup>1</sup> on the destructive distillation of petroleum, it was found that the tar made under greatly diminished pressure was radically different from that obtained by cracking the same oil under atmospheric or increased pressure. The vacuum tar was of much lighter specific gravity; it contained practically no free carbon; no naphthalene or anthracene settled out of the heavier distillates of the tar; the tar combined readily with 1.82 sp. gr. sulfuric acid. Tars resulting from cracking the same oil under increased pressure contained much free carbon; they were of considerably higher specific gravity; naphthalene and anthracene settled out of the distillates; they contained benzene; they would not combine readily with 1.82 sp. gr. sulfuric acid. The gas made under the two conditions was of equally different composition. The vacuum gas was a "dry" gas, in that it contained practically no benzene; on the other hand, it was high in ethylene homologues. The volume of uncombined hydrogen obtained under vacuum conditions was very much less than when the machine was under increased pressure. Further, there was practically no deposit of free carbon when working under a vacuum, whereas when the pressure on the machine was increased to three atmospheres, over fifty per cent, by weight, of the original oil was deposited as carbon.

principally with the machine under atmospheric pressure. Experiment shows that the moment we change the pressure, new results are obtained and a new series of experiments suggested. Certain it is that much remains to be done in the field of concentration, pressure and contact-surface changes. The application of various conditions for different periods of time still offers field for investigation.

I repeat that even if such investigations do not result in radically new processes, they will yield valuable information for a better understanding of, and improvement in, present-day processes. From a practical viewpoint, we may not as yet be able to see the advantages to be gained from the application of such scientific investigations, and, on the contrary, we may see disadvantages. However, this should not prevent our exploring the field. Industrial experience has again and again proven that the theory of to-day is the practice of tomorrow. In the absence of theoretical considerations, applied chemistry to-day would be in the medieval stages. As a typical example, the investigations of Haber<sup>1</sup> concerning the manufacture of ammonia from hydrogen and nitrogen were on a purely theoretical basis. From an initial yield less than 0.25 per cent, the process has been perfected to give a yield of well over 10 per cent of ammonia. From the idea of a man whose principal tools were theoretical chemistry, mathematics and physics, laboratory experiments developed into a process of commercial importance. The same laws maintain in the ammonia production of the gas plant that maintain in Haber's experimental and industrial apparatus.

The combination of nitrogen and carbon in the formation of cyanogen compounds is influenced by varying physical and chemical conditions just as surely as is the production of ammonia, whether from coal distillation or directly from the elements.

The application of physical chemistry, in mathematical terms, to industrial problems furnishes a means for quantitatively expressing yields and reactions taking place. I refer to the equilibrium relationship. Under some conditions it is highly important that the system reach a state of chemical equilibrium; under another condition, it would be fatal for the system to reach such equilibrium. Let us consider a few typical examples:

No.	Reactions	Heats of reaction	Volume changes	Partial pressures	Approximate $K_{600}$	Approximate $K_{900}$
1.....	$C + 2H_2 = CH_4$	+18900	2 to 1	$K = \frac{CH_4}{(H_2)^2}$	0.077	0.003
2.....	$2C + H_2 = C_2H_2$	-58100	1 to 1	$K = \frac{C_2H_2}{H_2}$	$1.1 \times 10^{-12}$	$5.7 \times 10^{-10}$
3.....	$3C_2H_2 = C_6H_6$	+163000	3 to 1	$K = \frac{C_6H_6}{(C_2H_2)^3}$	$9 \times 10^{23}$	$1.2 \times 10^{12}$
4.....	$C + H_2O = CO + H_2$	-29300	1 to 2	$K = \frac{CO \times H_2}{H_2O}$	0.2	25
5.....	$CH_4 + H_2O = CO + 3H_2$	-48200	2 to 4	$K = \frac{CO \times (H_2)^3}{CH_4 \times H_2O}$	0.06	3.46
6.....	$CO_2 + C = 2CO$	-39650	1 to 2	$K = \frac{(CO)^2}{CO_2}$	0.1	59

Let us see how far the variables common to any gaseous chemical reactions have been investigated with respect to illuminating and heating gas. They are five in number:

I—Temperature

II—Pressure

III—Concentration (mass action)

IV—Duration (time)

V—Contact surface

On the basis of combinations and permutations, it becomes evident that a great variety of manufacturing conditions can be obtained. Opinions naturally differ as to when a field has been properly and sufficiently investigated, and I, therefore, do not pretend to determine what proportion of the work remains to be done. It remains for each individual to form his own opinion. The field of temperature has been widely investigated, but

It becomes evident that for some reactions an elevation in temperature favors the preservation and formation of hydrocarbons, whereas for other reactions the same temperature is destructive. Considering equations 4 and 5, two of the most vital in present carbureted water-gas manufacture, one finds that a temperature of 900° C. is favorable to the CO and H<sub>2</sub> formation of both 4 and 5, but it is unfavorable to the methane preservation of 5. On the other hand, a temperature of 600° C. is unfavorable to the formation and preservation of CO and H<sub>2</sub>, but is decidedly more favorable than 900 to the hydrocarbon preservation of 5. At this lower temperature, however, the CO<sub>2</sub> of 6 predominates. From reaction 1 it becomes evident that methane is destroyed by high temperatures.

Numerical equilibrium expressions permit of quantitatively indicating the influence of three of the most important varia-

<sup>1</sup> THIS JOURNAL, 1914, pp. 383, 472.

<sup>1</sup> Z. Elektrochem., 1913, p. 53.

bles of a gaseous reaction, *i. e.*, temperature, pressure and concentration. The value of the equilibrium constant increases or decreases with the temperature. Although pressure and concentration variations do not change the value of the equilibrium constant for a given temperature, the use of such equilibrium enables one to calculate the influence of changes in pressure or concentration for any given temperature. In reactions 1 and 3, referred to above, there is a decrease in the number of volumes due to the reaction; in reactions 4, 5 and 6 there is an increase in the number of volumes due to the reaction; in reaction 2 there is no change in the reacting volumes. According to the principle of Le Chatelier, pressure stimulates those reactions involving contraction, and vacuum stimulates those involving expansion. Pressure and vacuum are without influence on those reactions involving neither contraction nor expansion. For detailed consideration of the application of numerical equilibrium relationships, see articles by Whitaker and Rittman<sup>1</sup> and Rittman.<sup>2</sup> By a correlation of equilibrium conditions for the various reactions involved in gas manufacture, much help can be had in determining the course of experiments. Unfortunately, equilibrium relationships, as shown, do not indicate the speed of the reaction involved; they indicate the state of affairs after complete reaction has taken place and the system is balanced. Therefore, the information indicated by an equilibrium relationship is not complete in itself. No single reaction can be considered exclusively by itself. All the reactions in a process are vitally inter-related, though any single reaction, or set of reactions, may be extremely important as indicating a tendency.

The shape of the machine cannot change the equilibrium constant for any given reaction. It is easily possible to reach the same equilibrium in entirely different types of machines. The machine is vitally important in so far as its design provides conditions for a favorable or unfavorable equilibrium; or in so far as its design hastens or retards the system in reaching equilibrium. It would be an easy matter to expand indefinitely on the importance and practical application of equilibrium relationships with respect to gas manufacture, but it seems advisable to await further experimental evidence.

In conclusion, I would say that the application of physical chemistry to gas manufacture is stimulating, because gas manufacture is a chemical and chemical-engineering problem. It involves solids, liquids and gases with all the chemical and physical laws governing these three states of matter. The questions of energy and heat transformations determine profit or loss. Nowhere is the question of chemical equilibrium more important. Vapor pressure, surface tension, solubility, dissociation, diffusion, polymerization, catalysis, decomposition, specific heat, latent heats of reaction, speed of reaction constitute fundamentals in physical chemistry, and are all vital to the gas man. The five variables—temperature, pressure, concentration, duration, and contact surface—offer a flexibility which should permit equal flexibility in the character of the end products obtained. Complicated problems become elementary in the light of physical chemistry. The pendulum swings to the extreme where gas manufacture becomes primarily a problem involving theoretical and applied chemistry. Without its application the industry cannot develop. However, in view of the work which has recently been done and which is being done, we can feel that gas manufacture as a chemical problem is gradually coming into its own.

CHEMICAL SECTION OF PETROLEUM DIVISION  
BUREAU OF MINES  
PITTSBURGH, PA.

<sup>1</sup> THIS JOURNAL, 6 (1914), 383, 472.

<sup>2</sup> *Jour. Soc. Chem. Ind.*, 1914, p. 626; THIS JOURNAL, 6 (1914), 684; and *Metall. Chem. Eng.*, 1914, p. 475.

## THE BROADER APPLICATIONS OF CHEMISTRY BY THE MUNICIPALITY

By HERMANN W. MAHR

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Chemistry has for the last decades been a valuable aid in securing the health and well-being of the dweller in American cities. Its fields of activity have been the inspection of foods, the all-important duty of controlling the quality of the water supply and the disposal of sewage. Beyond this, the science has only in rare instances been called upon for regular aid by the municipality.

In the meantime chemistry has been becoming an important factor in the industrial field. Chemists have improved processes and brought forth new products, many of which are finding wide use in civic housekeeping. The position now occupied by applied chemistry has led the far-seeing to herald the near future as the age of chemistry. With the advance in the industrial field have come additions to the knowledge and improvements in the methods of the science which now enable it to successfully attack special problems confronting our cities.

The chemists at present engaged in the all-important work of aiding in the conserving of the public health are often too well occupied with their duties to give time or attention to the technical problems which arise. Municipal engineers attempt to solve these questions, but are handicapped by a lack of knowledge of industrial chemistry and the ability to think chemically. These conditions give rise to opportunities for the chemist to aid the engineer and become his active co-worker. Members of the profession entering this work must necessarily be well acquainted with the processes of applied chemistry, and the methods of analysis and testing of industrial products, particularly the materials of engineering.

Our federal government has been a pioneer in this respect and its researches have redounded to its material advantage. It now has in its service well informed experts in many branches of industrial chemistry. The results of their investigations have been published and many of them are invaluable to the municipality. The latter should have in its service chemists able to apply the results of these governmental and of other technical investigations to the problems of the city.

A large portion of the expenditure of the municipal corporation is for the purchase of supplies. The value of the chemical laboratory in connection with this work has long been recognized. Some of our railroads were the first organizations to avail themselves of scientific supervision and inspection in this connection. The federal government has followed their lead and carried on the work through the Contracts Laboratory and similar testing stations in the large departments.

The first duty of the chemist concerned with the purchase of supplies is the inspection of materials delivered. Study of the various commodities and the framing of requirements is second only to the work of testing. Many proprietary compounds, of supposedly secret composition, with alleged wonderful properties, are urged on purchasing officials. On being subjected to chemical analysis these materials often prove to be composed of cheap ingredients for which a price greatly in excess of their value is asked.

The fuel bill of the municipality is probably the largest item of its budget for supplies. Competitive bidding, in accordance with well drawn specifications, has been universally adopted among large coal buyers as the best solution of the problem. In spite of its manifest advantages, city officials have hitherto been backward in putting a purchasing method of this nature into operation. The chemist can aid here greatly by studying the composition and heat value of the available coal supplies, drawing up requirements and testing shipments.

His labor in relation to fuel should, however, extend to over-seeing its proper and economical use. The importance of the

fuel question has, within recent years, assumed such proportions that chemists designated as fuel engineering chemists now make a specialty of the subject of fuel burning. A chemist, in municipal service, devoting himself to the wider application of chemistry, can make profitable studies of the methods of coal burning in schools and other public buildings. Wasteful grates may be found which require changes in the size of coal, and possibly expensive coals are burned where cheaper grades would adequately and economically furnish the required heat. Poor methods of stoking often allow opportunities for improvement with consequent saving.

Closely connected with the fuel question is that of obtaining proper boiler water. This part of municipal housekeeping is often entirely neglected, with a resulting increased consumption of fuel and decreased life of the heating or power apparatus. In some cases the man in charge is persuaded to buy a solution of sal soda and soda lye for a price many times in excess of its value. This mixture may or may not be adapted for use with the water in question. An examination of the water supply from the feed water standpoint will reveal the causes of trouble and enable the chemist to prescribe an inexpensive compound or the proper method of treatment.

There are many commodities purchased in large amounts whose composition is well enough known for them to be bought on specifications and subjected to test. One of the chief of these materials is soap, the cost of which is a considerable part of the amount expended for supplies. The federal government and railroads have long bought soap on well drawn requirements.

Within recent years the fact that "there is paper and papers" has been recognized. Large concerns are now paying attention to the quality of this material. The paper experts of the German government have made investigations and devised tests and methods of analysis for ascertaining the value of various papers. The uses of these methods have become known and are taken advantage of in the paper trade and by large users. Our municipalities are among the latter and can gain materially by scientifically scrutinizing paper supplies.

Rubber hose is an expensive necessity purchased in considerable amounts. On its quality and strength much depends. This has led insurance underwriters to require that hose for use in insured buildings be of the highest grade. Inspection of rubber requires it to be subjected to thorough chemical analysis and severe chemical tests. Cities should demand and make certain that hose for use by their fire departments and in public buildings is of the best quality.

Construction work of various kinds consumes a large portion of the civic bank credit. To obtain lasting structures and roads and prevent the use of inferior materials, the latter must be continually examined. Iron and steel should be subjected to chemical and microscopical analysis. Cements require chemical as well as physical tests. Results obtained by the chemist on a concrete containing one part cement to twelve of aggregate instead of one to six will often furnish grounds for civil or criminal action against an unscrupulous contractor. The water-proofing of concrete has occupied the attention of the engineer and technologist within the last few years. The importance of the subject has resulted in the appearance of many worthless water-proofing compounds whose nature and value can be best revealed by chemical analysis.

Paints and protective coatings have been investigated to good effect by our American chemists and their results have put this subject on a scientific basis. An understanding of these principles and knowledge of the properties of paints is necessary for the adequate protection of municipal buildings and structures.

Modern traffic conditions have been instrumental in bringing more of the products of applied chemistry into use by the city

than any other influence. The ingenuity and experience of the oil and coal tar chemists have been drawn upon to solve the problems arising from the use of the automobile. Various forms of pavement with permanent bituminous binders have come into wider use. The manufacture of new asphalts from oils in order to supplement the natural deposits owes its impetus to the demand thus created. Treatment of coal tar for use in tar macadam and as a semi-permanent surface binder has occupied the attention of the chemical technologist for the same reason. The lighter tar and oil products have also been studied and experimented with in the effort to produce dust preventatives. Treated wood block pavements are meeting with increased favor. Upon a knowledge of the properties of various treating media and thorough inspection and testing rests the success of these pavements and the comfort of those compelled to use them.

The city is called upon to apply the principles of preventative medicine on a large scale. Municipalities thus consume large amounts of antiseptics in their health departments. Disinfecting compounds flood the market. They, however, vary widely in ability to kill the various pathogenic organisms. The use of scientific tests for disinfecting value is not wide-spread in this country, but their introduction and use would result in a saving to the municipality with increased surety of the effect of treatments. Scientific inspection of disinfectants is a subject which also touches the household. It should be placed on the same plane as food inspection. Use of an inefficient antiseptic will often lead to more serious consequences than the consumption of a sophisticated food product.

Fire authorities have recently directed their energies toward the prevention of fires rather than their extinguishment. To make sufficient and effective rules governing the use and transportation of combustibles and enforce them requires the advice and service of members of the chemical profession. Within recent years the wide-spread establishment of garages has greatly increased sewer explosions. Chemical investigation is required to control this problem and place the blame at the proper source. The ultimate solution of the difficulty rests on chemists working in collaboration with the plumbing and sanitation experts of departments having authority over the erection of buildings.

Fire-proofing and requirements in regard to it also occupy the attention of the latter departments. We owe our modern fire-resisting materials largely to the work of technologists in the chemistry of ceramics. The national government has appreciated this fact and now maintains a department of the Bureau of Standards for testing and research in ceramics.

A problem which has been given much thought and attention by municipal officers is the disposal of refuse, especially garbage. No satisfactory or altogether profitable method of disposal has been evolved. The treatment of this waste has not as yet been well studied by the chemist. The field of work, being comparatively unexplored, offers commensurate reward to members of the profession who shall bend their energies to the work. The most apparent method of increasing the value of garbage is that of rendering available the nitrogen of tankage, which is now mostly in forms of little value for fertilization.

Legal investigations have in many important instances been aided by the services of chemists. The opportunities for their work in this connection are more varied and numerous than have been realized. This leads to the belief that the future will see a chemist with his microscope and laboratory attached to many police departments. His work will be not only the present well-known toxicological investigation, but he will devise and apply delicate methods to the interpretation of clues which have in the past been closed books. The service rendered by that new branch of chemistry, metallography, is one instance of this. Boiler explosions have been difficult to trace to their origin, but microscopical examinations will often reveal faults in the

heat treatment or structure of the metal which have caused disaster.

The foregoing outline suggests only a few of the possibilities for assistance that chemists may render our municipalities. An appreciation of the value of the science is necessary in the progressive civic official. More frequent attempts to throw the

light of chemical research on problems will lead to satisfactory and even gratifying results. Surely the science of Liebig, Perkin and Bunsen can render increased aid to our American cities.

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## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

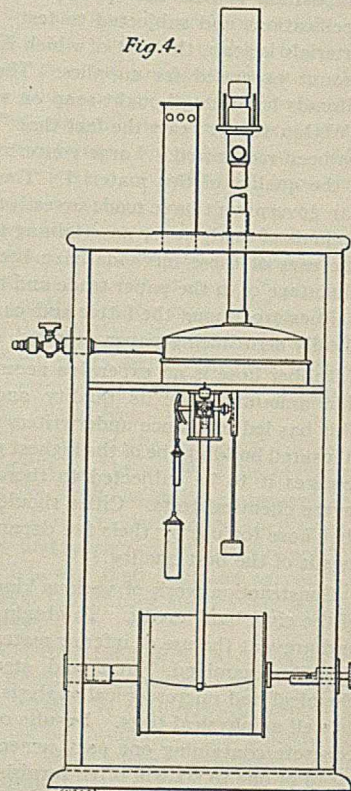
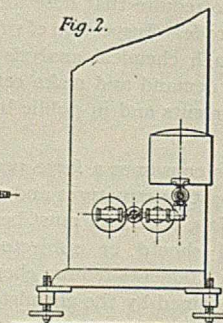
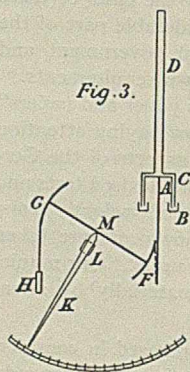
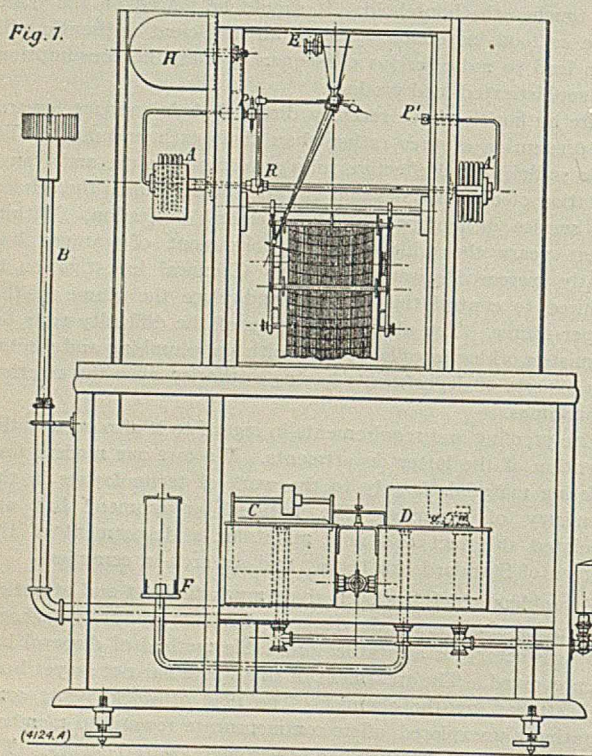
### INSTRUMENTS FOR TESTING GAS

At the Munich Gas Exhibition, Messrs. Alex. Wright and Co., London, showed instruments for testing gas, two of which—the caligraph and the gravimeter—are described in *Engineering* (London), 98 (1914), 362. The caligraph, which attracted much attention, is an instrument by means of which the calorific value of a gas is automatically recorded.

The principle on which it operates may be described as follows: A constant volume of gas is burnt. The heat from this combustion is caused to warm a certain quantity of air which then passes over one diaphragm of a differential thermometer, the other diaphragm being affected only by the room temperature. The indication of the differential thermometer, which is thus a measure

of a tube, B, at the top of which it is consumed by a small flame. This is prevented, by means of a special burner, from heating the gas in the tube. Any variation in specific gravity of the gas will obviously cause a difference in weight of the column of gas in the tube B, and will thus alter the pressure in the left-hand bell C. This alteration in pressure will cause the bells to move and actuate the gas-admission valve. In this way a constant supply of gas to the burner F is assured, no matter what the density of the gas may be.

The differential thermometer consists of two metal diaphragm boxes, A and A', filled with air, one at each end of a glass rod, R. Any movement of this rod is recorded, by means of a pen actuated by link-work, on a chart wrapped round a revolving



of the heat given off from the gas on combustion, is marked by means of a pen, actuated by suitable link-work, on a chart passing over a clock-drum.

Referring to Figs. 1 and 2, the constant consumption of gas is obtained by means of a governor consisting of two bells, C and D, which are connected and swing on needle-points. The gas passes through a dry governor (to take up any sudden variation in pressure) into the right-hand bell D by means of a valve. The extent of opening of this valve is determined by the position of the bells. The gas passes out of the bell D through a gold nipple of standard size to the burner F, where it is consumed. At the same time the gas can also pass from the dry governor into the left-hand bell C by means of a by-pass cock. This gas passes out of the bell C through

drum, which is driven by clock-work. As the temperatures of the diaphragms vary, the air in them will expand or contract, thus causing a movement of the glass rod, and as the right-hand diaphragm is affected by the room temperature only, while the left-hand one is affected by the heat from the flame as well as by that from the room temperature, the movement of the rod, being the difference of the two effects, is proportional to the heat obtained from the combustion of the gas at F. It will be observed that any alteration in temperature and in atmospheric pressure will affect the air being heated in the same way as the gas burnt, thus automatically compensating for any change in the number of the tables of constants which are used in connection with the instrument.

The essential principle of the gravimeter is illustrated in

Figs. 3 and 4. The instrument is essentially a gas-balance, in which the specific gravity of the gas under test is compared with that of the surrounding air. This is accomplished differentially, the weight of a column of gas and the weight of an equal column of air being arranged to act on opposite sides of what is virtually a scale-pan, and the difference in weight registered.

The bell of the gravitometer may be considered as a scale-pan on which the pressure below is due to the pressure of the atmosphere on the lower surface, and the pressure above to the pressure of a column of gas added to the pressure of the atmosphere at the top of that column, the aggregate being less, in the case of coal-gas, than that of the atmospheric pressure below the bell. Gas is always passing up the tube to supply the burner at the top, and under these conditions is under absolutely the same conditions of temperature and pressure as that of the surrounding air. It will thus be seen that the pointer of the gravitometer indicates the weight of that column of gas of a height equal to that of the tube. For example, with a bell of 6 in. diameter and a height of tube of 30 in., the gas of, say, 0.9 specific gravity is 15.9 grams.

The pressure or weight on the top of the bell is in direct proportion to the specific gravity of the gas in the tube, and is, in addition, proportional to the height of the tube. Thus, if the tube were 60 in. in height instead of 30 in., the pressure on the bell, due to the weight of the gas, would be 30.38 grams, and the movement of the pointer across the scale would be twice that in the case of the 30-in. tube. Mechanical considerations constitute the only reason for not using a longer scale; indeed, by employing tubes of sufficient height, it is possible to measure specific gravity to any required degree of accuracy.

Referring to Fig. 3, which shows diagrammatically the action of the gravitometer, A represents a light aluminium bell, sealed in oil contained in the annular tank B. The Bell is covered by a shell, C, which is not in contact with it. The top of the shell carries a tube, D. The bell is free to move up and down, and is carried by a vertical support connected to the end of the balance-beam G by a hanging chain. The other end of the beam carries a hanging weight, H. The chains connected to both H and A pass over circular arcs. A pointer, K, and a gravity-control weight, L, complete the essentials of the instrument. On a stream of gas passing slowly over the bell A and up the tube D, the pressure on the top of the bell is diminished and the pointer K swings into a new position of equilibrium. The scale over which the pointer moves is graduated to read or to record specific gravity directly.

### THE IMPERMEABILITY OF CONCRETE

In a paper recently read before the Western Society of Engineers and quoted in *Engineering* (London), 98 (1914), 483, Professor M. O. Withey described the results of a series of tests on the permeability of concrete, which have been made at the University of Wisconsin. The materials used were Portland cement, sand ranging in weight from 104.5 lbs. to 112.2 lbs. per cu. ft., and gravel weighing from 107.3 lbs. to 190.3 lbs. per cu. ft. Eighty-eight of the test-pieces were made with a 1 : 1½ : 3 mixture by volume, and sixty-seven with a 1 : 2 : 4 mixture, and there were ninety-eight specimens proportioned with 1 part by weight of concrete to 9 parts by weight of aggregate. None of the concretes proved absolutely water-tight in the sense that they would not absorb water, but most were so impervious that there was no visible evidence of flow. The signs of dampness on the bottom of the specimens increased with increasing humidity of the atmosphere. With mixture of 1 part of cement to 7 parts of aggregate the average rate of flow during a period of fifty hours was under 0.001 gal. per sq. ft. per hr., when the pressure was 40 lbs. per sq. in. With the 1 to 9 mixtures, prac-

tically water-tight concrete could, it was found, be obtained by suitably grading the sand and gravel. Richer mixtures, such as the 1 : 1½ : 3, proved very impervious, but Professor Withey remarks that such rich mixtures show considerable volume changes when alternately wetted and dried. To secure impermeability great care is needed in mixing the concrete, especially when the proportion of cement is small. If mixed too dry, the concrete cannot be properly compacted. The best results were obtained by mixing the materials dry for ¼ to ½ min., and then continuing the process after adding the water for 1½ to 2 min. with 1 to 9 concrete, or for 1 min. with the rich 1 : 1½ : 3 mixture. Proper curing of the concrete greatly adds to its impermeability. Premature drying destroys the imperviousness of the lean mixture, seriously impairs that of the 1 : 2 : 4 mixture, and appreciably diminishes the watertightness of the rich mixture. Thus, thin sections of 6 in. to 8 in. in thickness should be, he concludes, kept damp for one month for lean mixtures, or two weeks for a rich one.

*Engineering* also quotes (*vol. cit.*, 446) from *Science Conspectus*, a publication of the Society of Arts of the Massachusetts Institute of Technology, some particulars of an interesting series of experiments now being carried out by the Aberthaw Construction Company in order to disprove the theory that the combined effects of sea-water and frost rapidly destroy concrete structures.

With this object in view, twenty-four concrete columns, 16 ft. long, 16 in. square, and reinforced with bars near the corners, were constructed in January, 1909, and immersed in the water at Boston Navy Yard. They were suspended in such a manner that at high tide the water reaches nearly to the top of the column, and falls at low tide nearly to the bottom. In cold weather the columns are thus alternately thawed and frozen as the tide rises and falls. The columns were made with various qualities of concrete mixed dry, plastic, and very wet. Different qualities of cement were used, and the effects of waterproofing materials, clay, and other additions to the concrete are being studied. One of the columns was mixed with salt water, but this was unfortunately lost in handling.

No final conclusions are, of course, possible yet; many years must, in fact, elapse before it will be possible to say which kind of concrete is most permanent. When examined in December last many of the specimens were practically unaffected, but others were badly eroded. As might be expected, the best results were given by the specimens richest in cement and mixed wet. For instance, of two columns made with 1 part of cement to 1 of sand and 2 of stone, the one mixed dry was badly eroded over the whole of its length; whereas the other, which was mixed very wet, was only slightly pitted. Again, of two specimens made with slag cement in the ratios of 1 : 1 : 2 and 1 : 3 : 6, respectively, and both mixed wet, the former was in excellent condition, with only very slight pitting, while in the latter all the corners had gone and the reinforcement was exposed in places. The part of this specimen which was continuously immersed was, however, in very fair condition. The experiments are being continued, and doubtless some very interesting results will be obtained in time.

### PUTTING ELECTROTYPING INDUSTRY ON MORE SCIENTIFIC BASIS

At a meeting in New York on October 7, 1914, the International Association of Electrotypers appointed a committee to cooperate with the Bureau of Standards in a study of the conditions in the electrotyping industry, with a view to assisting in placing it upon a more scientific basis. A preliminary circular giving simple directions for testing and adjusting the density and the acidity of the copper electrotyping solutions has been prepared, and may be obtained upon request from the Bureau of Standards, Washington, D. C.

THE BALANCE OF TRADE IN CHEMICALS BETWEEN THE UNITED STATES AND GERMANY IN 1913

In an article in THIS JOURNAL, 6 (1914), 274, by B. C. Hesse, it was shown that the tonnage of chemicals exported from this country to Germany was considerably in excess of that imported from Germany, the difference in our favor being 404,295,500 kg., or in round numbers, 890,000,000 lbs.

Recently the values of the separate items, listed according to the German official classification, were published [Chem. Ztg., 38 (1914), 962], and it became possible to estimate the value of the trade balance as follows: the total value of the German

import or export taken from the above mentioned German table was multiplied by the percentage of weight of total German import or export originating in or sent to the United States, and this value changed to dollars. These results together with Hesse's figures are given in Table I following. Table II summarizes Table I and shows also the balance in each class in favor of one country or the other. The total balance is in favor of the United States and amounts to over \$95,000,000.

This balance is not strictly comparable with the smaller one of \$21,000,000 calculated for 1904 by Hesse in THIS JOURNAL, 6 (1914), 2, because the later list is much more extensive, con-

TABLE I—CHEMICAL TRADE OF THE UNITED STATES WITH GERMANY—1913

Official sub-class	UNITS OF 100 KG. VALUE (a) IN = 0.1 LONG TON \$1000 UNITS				Official sub-class	UNITS OF 100 KG. VALUE (a) IN = 0.1 LONG TON \$1000 UNITS			
	U. S. to Germany	U. S. from Germany	U. S. to Germany	U. S. from Germany		U. S. to Germany	U. S. from Germany	U. S. to Germany	U. S. from Germany
<b>I—MALT, OIL FRUITS, INDUSTRIAL PLANTS, FRUITS AND PLANT JUICES</b>									
30 Hops		11,119	29	952					
32 Madder, quercitron and other dye plants	3,403		165						
60a Opium			29						
<b>II—INDUSTRIAL OR MEDICINAL VEGETABLE PRODUCTS</b>									
72c Lichens, herbs, berries, leaves and buds	4,567	5,499	114	200					
73 Vegetable wax			1	030					
89 Sawdust and excelsior		27,671		48					
<b>III—TANNING EXTRACTS</b>									
384e Miscellaneous tanning extracts		3,213		16					
<b>IV—RESINS, LACQUER AND VARNISH GUMS, ADHESIVES</b>									
97a Turpentine rosin	770,100	2,619	4,585	17					
97c Damar; hard and soft gums and resins	11,168	560	300	20					
97e Shellac		1,179		45					
97f Gum acacia, Bassora gum, etc.		1,027		22					
97g Gum tragacanth		625		40					
342 Alcohol and shellac varnishes	84		2						
343 Miscellaneous and coach varnishes	4,447	1,975	71	55					
345 Putty and miscellaneous putties	829		14						
346 Asbestos paint and putties	668		7						
<b>V—CAOUTCHOUC AND CAMPHOR</b>									
98a Caoutchouc, crude or refined	364	20,019	53	2,582					
98b Gutta percha, crude or refined	272	911	33	76					
98d Rubber scrap and waste	3,145	13,741	24	229					
<b>VI—ANIMAL AND VEGETABLE FATS AND OILS</b>									
126a Hog lard	1,011,812		26,700						
126b Oleomargarine	196,328		4,880						
126c Goosefat, beef-marrow, etc.	1,091		21						
128b Prime beef tallow	85,998		2,171						
129 Beef and mutton tallow	35,498		579						
130 Bone-fat, fat-waste, stearin-tar	16,809	37,005	208	335					
131a Fish oils	6,417		72						
166d Peanut oil		16,058		323					
166h Cotton-seed oil	99,950		1,550						
166l Beechnut, bone, corn, poppy, sunflower, etc., oils	19,127		286						
170 Cocoa-butter		4,798		316					
171b Cotton-stearin	3,335		55						
171c Palm oil		136,684		280					
171e Cocoonut oil		2,150		39					
172 Oleic acid, olein, etc.	5,875		84						
205b Edible vegetable fats		345		8					
<b>VII—ANIMAL PRODUCTS</b>									
142 Spermaceti		135		6					
156f Bones and hoofs		10,821		30					
<b>VIII—STARCH AND SUGAR</b>									
173a Potato starch, wet, dry or ground		15,222		109					
173c Corn, wheat and other starches	5,833		58						
174 Starch-gums (dextrin), roasted starch and gluten		19,460		174					
176c Beet sugar, all forms, refined		22,112		716					
176f Beet sugar, raw		101,504		492					
177a Glucose, etc.	5,217		31						
<b>IX—ALCOHOL, ACETIC ACID, YEAST, MINERAL WATERS</b>									
190 Mineral waters, inclusive of bottles		20,419		103					
<b>X—MINERAL AND FOSSIL RAW MATERIALS</b>									
223a Clay (potter's pipe, fire, etc.)		223,922		70					
224d Graphite, crude, ground and washed	10,763		63						
225a Pumice and tripoli, crude, ground and washed	1,761		9						
225c Mineral abrasives polishes and rouges		6,675		27					
227b Magnesite		10,856		57					
227d Phosphate rock and other mineral phosphates	4,212,124		4,970						
230a Portland, etc., cement		104,423		89					
231b Asbestos, crude and in fibers	48,151		422						
231e Mica	575		442						
232a Heavy spar and celestite		350,196		232					
236a Boronatrocalcite, etc.	2,088		111						
236c Miscellaneous earths, e. g., Fuller's earth, etc.	41,987		30						
<b>XI—ORES, IRON AND SLAGS</b>									
237a Antimony ores and matte		210		2					
237f Gold ores		4		506					
237g Copper ores and cuprous cinder	2,501	25,854	9	58					
237h Manganese ores		4,610		8					
237o Zinc ores	132,088		366						
237q Uranium, molybdenum and other miscellaneous ores	6,731		239						
<b>XII—FOSSIL FUELS</b>									
238d Coke		185,492		114					
238h Vegetable charcoal		6,664		11					
<b>XIII—MINERAL OILS AND OTHER FOSSIL RAW MATERIALS</b>									
239a Mineral lubricants		1,024,673		8,415					
239b Crude petroleum, etc.		1,619		3					
239c Heavy benzene, patent-turpentine		18,194		97					
239d Gas oil		55,468		656					
239e Refined petroleum		5,747,587		12,690					
239f Crude benzene		418,159		2,220					
239g Benzene, ligroin, misc. light distillates		15,712		120					
239h Miscellaneous crude mineral oils		18,746		49					
250b Crude hard paraffin		87,028		1,231					
251 Soft paraffin		100		1					
240a Asphalt and asphaltic minerals		68,116		72					
241 Crude ozokerite, etc.		11,443		135					
249 Refined ozokerite, etc.	52	5,214	2	129					
243a Pitch		8,078		154					
<b>XIV—COAL-TAR OILS AND PRODUCTS</b>									
245b Anthracene and heavy oils		159,944		206					
246a Naphthalene		7,242		18					
246c Phenol, crude or refined		12,098		230					
246d Cresol		2,152		25					
246e Anilin oil and salt		24,282		476					
246f Naphthol and naphthylamin		6,379		149					
246g Anthraquinone, nitrobenzol, toluidin, resorcin, phthalic acid, etc.		9,651		242					
<b>XV—WAXES</b>									
247a Beeswax		1,116		82					
<b>XVI—SOAP AND FAT PRODUCTS</b>									
254 Soft and textile soaps; Turkey-red oil, etc.		6,208		59					
256 Soap in cakes, powder, liquid, etc.		481		16					
257a Crude glycerin		5,037		128					
257b Refined glycerin		1,307		45					
258 Vaselin and lanolin		10,285		147					
260 Lubricants made of fats or oils		68,384		617					
262 Shoe polish		243		6					
264 Stearin, paraffin materials		395		14					
<b>XVII—CHEMICAL AND PHARMACEUTICAL PRODUCTS</b>									
266 Alkali and other metals		411		18					
270 Sulfur and Spence metal		71,535		187					
276 Oxalic acid and potassium oxalate		26,066		319					
277 Acetic anhydride		832		13					
278 Lactic acid and lactates		2,040		31					
279a Tartaric acid		1,235		72					
280c Crude salts of 12-15 per cent K <sub>2</sub> O		5,412,614		3,215					
280e Salts of more than 15-19.9 per cent K <sub>2</sub> O		412,926		338					
280e Fertilizer salts and fertilizers with 38 per cent K <sub>2</sub> O		2,168,204		3,695					
280f "Abraum" and miscellaneous salts		131,626		64					
283 Barium chloride		13,434		32					
289b Caustic potash, solution or solid		38,173		192					
290 Potassium carbonate		78,339		632					
292 Bleaching powder, barium and hydrogen peroxide, etc.		82,634		290					
295a Potassium sulfate		536,741		2,287					
295b Potassium phosphate		13		300					
298a Alums, aluminum acetate, alumina, etc.		7,605		38					
304b Barium nitrate		4,794		33					
306 Potassium manganate and permanganate		6,078		48					
308a Potassium and sodium ferro- and ferricyanide		3,978		65					
308b Potassium and sodium cyanide		10,179		248					
309a Acetate of lime		25,619		845					
311 Crude and refined argols	203,643		1,162						
312 Tartar emetic and other antimony products		1,284		51					
314 Strontium carbonate, oxide and chloride		2,077		62					
315 Zinc chloride and other zinc salts		903		5					
316b Carbides of aluminum, silicon, etc.		489		5					
317a Sulfate of ammonia	18,261		695						
317b Arsenious acid		56,296		329					
317c Epsom salts		10,947		139					
317d Chlorides of magnesium and calcium		46,816		51					
317e Potassium chloride		68,771		82					
317f Potassium magnesium sulfate		2,611,137		9,220					
317h Lime-nitrogen, nitro-lime and other fertilizers		222,978		509					
317m Nitrites		231,976		635					
317n Salicylic acid and salicylates; santonin; benzoic acid and benzoates		4		050					
317o Ammonium chloride		2,672		229					
317s Sodium sulphhydrate, lead compounds and misc. metalloids, acids, salts		19,127		222					
		32,939		88,971					482,1602

(a) M 1.00 = \$0.238.



TABLE I—CHEMICAL TRADE OF THE UNITED STATES WITH GERMANY—1913—(Concluded)

Official sub-class	UNITS OF 100 KG. VALUE (a) IN = 0.1 LONG TON \$1000 UNITS				Official sub-class	UNITS OF 100 KG. VALUE (a) IN = 0.1 LONG TON \$1000 UNITS			
	U.S. to Germany	U.S. from Germany	U.S. to Germany	U.S. from Germany		U.S. to Germany	U.S. from Germany	U.S. to Germany	U.S. from Germany
<b>XVIII—MISCELLANEOUS CHEMICAL AND PHARMACEUTICAL PRODUCTS</b>					<b>XXI—VOLATILE OILS, SYNTHETIC PERFUMES, TOILET ARTICLES</b>				
371 Scrap Welsbach mantles.....		32		21	352 Wood tar oil; caoutchouc oil; animal oil		65		500
372 Dried or powdered egg albumen.....		1,308		74	353a Turpentine, pine needle oil and spirits				
373 Casein and products for technical uses.....		1,658		16	353b Turpentine.....	269,945		3,840	
375a Glue exclusive of albumen.....		23,180		471	353c Oil camphor, anise, elder, rosemary and other volatile oils; menthol and menthol pencils.....				
375b Gelatine.....		4,839		403	354 Terpeneol, vanillin, anethol and similar synthetics.....	1,374	2,711	673	941
376 Gelatine capsules.....		540		64	358 Toilet and tooth powders.....		1,842		409
378 Wood and peat tar creosote.....	1	180		125		298			658
380a Quinine, salts and compounds.....		625		436	<b>XXII—ARTIFICIAL FERTILIZERS</b>				
380b Other alkaloids and their compounds.....		444		16	359a Animal fertilizers.....		23,996		56
386 Artificial balsams and non-odoriferous watery extracts.....		389		240	360 Bone-meal.....		82,838		182
388 Proprietary remedies.....		416		59	361 Thomas-meal.....		105,481		103
390a Miscellaneous medicinals.....		968		379	362 Superphosphates, etc.....		42,160		766
390b Miscellaneous chemicals for photographic cleansing and other uses.....		5,521		377	<b>XXIII—EXPLOSIVES, AMMUNITION AND COMBUSTIBLES</b>				
— Misc. pharmaceuticals and chemicals.....		280		26	366 Loaded cartridges.....		119	953	10
<b>XIX—DYES AND DYE MATERIALS</b>					370 Fuses, etc.....		2,847		96
318b Animal kirries, carmine, sepia.....		25		4	<b>XXIV—WOOD FIBER, CHEMICAL PAPER</b>				
319 Anilin and other coal-tar dyes.....		138,547		7,290	650b Straw, esparto and other fibers; paper stock.....	7,545	352,468	32	1,649
320a Alizarin-red.....		4,926		178	664 Tracing, blue-print, gelatine, fly, ozone and test papers.....		348	1,752	17
320b Alizarin dyes from anthracene.....		21,636		1,285	<b>XXV—METALS</b>				
321a Indigo synthetic and vegetable.....		34,609		1,319	769d Gold scrap.....		36		15
322 Prussian blues, chrome and zinc greens.....		1,056		24	769e Platinum, iridium, osmium, palladium, rhodium, ruthenium: cast, raw and not alloyed.....		2	9	254
324b White lead.....		4,848		52	772a Silver alloys.....		190		340
325 Blanc fixe.....		24,208		399	772c Silver scrap.....		312		33
326a Zinc oxide.....		18,850		224	777a Pig iron.....			24,400	
326b Zinc dust.....		8,337		97	777b Ferro-aluminum, chrome, manganese-nickel, etc.....			117,331	
326c Lithopone.....		7,328		40	844 Aluminum plates and metal.....		8,367	10,186	318
327 Red cinnabar.....		306		36	850 Pig lead and lead scrap.....		162,727		1,421
328a Logwood extract.....		2,775		45	855a Zinc.....			17,697	
328b Fustic, Brazil wood and similar extracts.....		1,225		24	860 Tin and tin scrap.....		9,285	10,412	903
329c Umber, sienna and earth colors.....		18,716		71	864 Nickel and nickel coins.....		21,566		1,744
330 Lamp and similar blacks.....		9,537		222	869a Copper (see note below).....	2,116,702		75,000	
331 Bronze and metal colors.....		6,616		473	869b Copper coins, copper scraps, etc.....		5,111	1,977	164
332b Copper pigments.....		8,530		54	869c Copper alloys.....		23,162	5,931	506
334 Printing ink.....		573		15	869e Spiers glance.....			1,545	
336a Ready-made paints ground in oil.....		879		52	869f Chrome, cadmium, tungsten and similar metals.....			5,094	
336b Artists' colors.....		295		20					784
338 Graphite in manufactured forms.....		217		1	<b>XX—ETHERS AND ALCOHOLS</b>				
340 Lead and colored pencils, crayons.....		2,210		262	348 Fusel oils; amyl, butyl and propyl alcs.....		669		38
<b>XX—ETHERS AND ALCOHOLS</b>					349a Crude wood alcohol.....		50,707		724
348 Fusel oils; amyl, butyl and propyl alcs.....		669		38	351 Acetaldehyde, paraldehyde.....		45		2
349a Crude wood alcohol.....		50,707		724					
351 Acetaldehyde, paraldehyde.....		45		2					

taining 201 in comparison with the other list's 55 items; the list for 1913 for example includes metals (Class XXV) which do not appear in that for 1904, and in this class alone the United States' exports exceeded Germany's by \$76,000,000 (see note below).

Tables I and II completely confirm the contention of the author of the articles cited above, that the common belief in the preponderance of the value of Germany's chemical exports over our own is erroneous.

NOTE—The figures for copper in *Chem. Ztg.*, 38 (1914), 176 are evidently wrong, for while the whole German importation is given as 2,253,920 dz., the U. S. is credited with 3,946,378 dz. The figure in Table I, 2,116,702, was obtained by adding the German imports listed from all other countries and subtracting this figure from the total imports; the value in dollars was calculated from this.

TABLE II—TRADE IN CHEMICALS BETWEEN U. S. AND GERMANY IN 1913—SUMMARY OF TABLE I

Official German class	UNITS OF 100 KG. = SUBSTANTIALLY 0.1 LONG TON				VALUE IN DOLLARS			
	U.S. to Germany	U.S. from Germany	BALANCE IN FAVOR OF U.S.	U.S. to Germany	U.S. from Germany	BALANCE IN FAVOR OF U.S.	U.S. to Germany	U.S. from Germany
I Malt, oil fruits, plants, etc....	3,403	11,284		29,000	1,120,000		1,091,000	
II Industrial or medicinal vegetable products.....	4,567	33,171		114,000	248,030		134,030	
III Tanning extracts.....	3,213		3,213			16,000		16,000
IV Resins, gums and adhesives.....	787,296	7,985	779,311	4,979,000	199	4,780,000		
V Caoutchouc and camphor.....	3,781	34,671		110,000	2,887,000		2,777,000	
VI Animal and vegetable fats and oils.....	1,482,240	197,040	1,285,200	36,606,000	1,301,000	31,305,000		
VII Animal products.....	135	10,821		6,000	30,000		24,000	
VIII Starch and sugar.....	11,050	158,298		89,000	1,521,000		1,432,000	
IX Alcohol, acetic acid, mineral waters.....		20,419			103,000		103,000	
X Mineral and fossil raw materials.....	4,317,449	696,514	3,620,935	5,680,000	505,000	5,175,000		
XI Ores, iron and slags.....	141,320	30,678	110,642	614,000	574,000	40,000		
XII Fossil fuels.....		192,156			125,000		125,000	
XIII Mineral oils and like fossil raw materials.....	7,466,897	21,707	7,445,190	21,736,000	344,000	21,392,000		
XIV Coal-tar oils and products.....		221,748			1,346,000		1,346,000	
XV Waxes.....		1,116			82,000		82,000	
XVI Soap and fat products.....	79,307	13,033	66,274	784,000	248,000	536,000		
XVII Chemical and pharmaceutical products.....	326,378	12,327,989		12,001,611	2,526,000	25,616,350		23,080,350
XVIII Miscellaneous chemical and pharmaceutical products.....	809	40,825			112,090	3,305,000		3,192,910
XIX Dyes and dye materials.....	39,276	299,178			641,000	11,972,000		11,331,000
XX Ethers and alcohols.....	50,707	714	49,993		724,000	40,000		684,000
XXI Volatile oils, synthetic perfumes, toilet articles.....	271,319	4,916	266,403		4,513,000	2,008,500		2,504,500
XXII Artificial fertilizers.....		254,475				1,107,000		1,107,000
XXIII Explosives and combustibles.....	119	3,800			10,000			166,000
XXIV Wood fiber and chemical paper.....	7,893	354,220			49,000	1,729,000		1,680,000
XXV Metals.....	4,177,136	194,582	3,982,554		80,698,000	4,284,000		76,414,000
TOTALS.....	19,174,295	15,131,340	17,609,715	13,566,760	156,036,090	60,860,880	142,846,500	47,671,290
Balance of exports in favor of the U. S.	4,042,955		4,042,955		\$95,175,210		\$ 95,175,210	

## NOTES AND CORRESPONDENCE

### STRONTIUM IN THE BEET SUGAR INDUSTRY

*Editor of the Journal of Industrial and Engineering Chemistry:*

No more interesting commentary on the trade that is bound to accrue to American chemical manufacturers through the failure of continental suppliers to meet the demands of the American market, can be made than the foundation of a new industry directly traceable to the present chaos existing in the industrial world abroad. This is the manufacture of various strontium salts, which heretofore have been produced solely on the Continent. Within the past month over 300 tons of strontia ore (celestite, strontium sulfate) have entered the United States at the port of Philadelphia through the agents of the only commercially productive deposit in the world. It has been estimated that this quantity will no more than meet the pressing demands of certain consumers who, prior to the war, imported the refined salts chiefly in the form of strontium nitrate at figures entirely out of keeping with the known cost of production. Prior to August 1st of this year, the refined nitrate was offered in commercial lots at 8 cents per lb., but since the above date, the price of the salt has advanced 200 per cent. So far as statistics show, this is the largest quantity of strontium ore ever brought into the United States. Scarcity of raw material and the higher labor costs in this country have evidently deterred manufacturers from entering the world's market as producers of strontium compounds. For the American manufacturer to meet his foreign competitor on the same footing, it was necessary to secure a cheap and reliable source of supply, but now, with raw material at a price approximating that paid by foreign manufacturers, we shall be able to not only meet the demands of the domestic market but, in all probability, export a considerable portion of our total production.

The commercial demands for strontium nitrate are not so diversified as for certain other chemical products, but the total annual consumption in the United States seems to fully warrant the American manufacturer entering upon this new field with the confidence that once his market is established, he need no longer fear ruinous competition from the foreign producer.

The principal salts of strontium that appear on the commercial market are, in the order of their importance: strontium hydroxide, strontium nitrate and strontium chloride. Of the above salts, however, the nitrate is the only one that has been imported in large quantities, but the world consumption of this salt is very small in comparison to that of the hydroxide, which is used in the refining of beet sugar molasses. So far as is known, the major portion of the nitrate imported annually is consumed in the manufacture of railway signals or Coston lights, and the manufacture of so-called red fire used extensively by the pyrotechnists.

For reasons best known to the continental sugar refiners, the price of the hydrate has never been within the reach of our domestic consumers, but inquiries made among large beet sugar refiners in this country indicate that there would be a very large consumption of the compound, provided a stable source of supply could be secured.

The conversion of celestite, or strontium sulfate, into soluble strontium compounds, is effected through the reduction of this salt by heating with carbon in rotary furnaces, thus producing the soluble strontium sulfide, from which the hydroxide or nitrate can be readily prepared with suitable reagents.

In the desaccharization of beet sugar molasses, containing generally some 40 to 50 per cent of sugar, which, owing to the presence of small quantities of certain inorganic salts will not crystallize out, there are at present three methods employed to

effect desugarization: 1—Strontia process, 2—Osmosis process, 3—Lime process.

Of these three, the most effective, efficient and economical is the strontia or Scheibler process. This depends on the reaction that occurs when an excess of strontium hydroxide is added to a dilute sugar solution at a temperature exceeding 100° C. The work is carried out in suitable boilers provided with steam coils and agitators, a 20 per cent to 25 per cent solution of the hydroxide being first heated and the molasses added in amount equal to about one-third that of the strontium solution. The liquid is then rapidly agitated, the temperature being kept above 100° C., when there occurs a granular, sandy precipitate of strontium disucrate. This is rapidly filtered and washed with a boiling 10 per cent solution of strontium hydroxide, the disucrate being insoluble in hot solutions. After the precipitate has been thoroughly washed, it is dissolved in a cold solution of the hydroxide and allowed to stand for several days in crystallizing tanks. At the end of this time, about 50 per cent of the hydrate separates in crystalline form and the saccharine solution is decanted and the crystalline residue centrifuged to free it from the solution. Carbon dioxide is then passed through the sugar solution, thus causing a precipitation of the balance of the strontium as the carbonate. This compound is reconverted into the hydroxide by calcining and dissolving the resultant oxide in water. The ratio of the total strontium hydroxide required for the precipitation of sugar in the beet molasses is approximately 2½ : 1. A remarkably pure sugar solution is obtained by the strontia process, so that the sugar, after crystallization, can be placed directly on the market without further refining.

At the present time the methods in vogue in this country are the osmosis and lime or Steffen process. The former is rather slow and necessitates the handling of the same solution a number of times. The lime process requires special cooling apparatus, as the temperature of the sugar solution must be kept below 15° C. during the precipitation of the tricalcium sucate, which is readily soluble at a higher temperature. There are numerous other minor objections to both of these processes, so that although the initial cost of the strontia process may be more than either of these, it can be readily seen that it is much more effective and rapid.

In connection with the regeneration of strontium hydrate, an American patent has just been issued describing a process for the rapid conversion of strontium carbonate into the oxide through the use of certain fluxes such as fluorspar, soda ash, etc. In the past, some difficulty has been experienced in treating the impure strontium carbonate precipitated from sugar solutions, owing to its being contaminated with lime, silica and certain organic substances.

Statistics show that Germany desaccharizes annually about 100,000 tons of beet sugar molasses. As nearly all the continental beet molasses is desugarized by the strontia process, this would indicate that over 100,000 tons of strontium hydroxide are employed in Germany alone. It must be remembered, however, that this does not indicate the annual consumption, which is probably very much less than this figure, owing to the fact that the strontium compounds are nearly all recovered by various regenerative processes, so that the percentage of loss is rather small.

The American beet sugar industry is still in its infancy compared to that of Europe. During the last few years the production fluctuated between 600,000 and 700,000 tons annually, all of which was for domestic consumption. It would not be safe to predict at the present time just what increase in this annual production the introduction of the strontia process would

effect, but with the coöperation of the American chemist, the process is likely to play an important part in the American technology of beet sugar.

FOOTE MINERAL CO., PHILADELPHIA  
November 14, 1914

H. C. MEYER

### THE EFFECT OF STEAM UPON MAGNESITE BRICK OR CALCINED MAGNESITE

*Editor of the Journal of Industrial and Engineering Chemistry:*

Carbonate of magnesia or magnesite is found chiefly in Greece, Austria-Hungary, Africa, India, and in California in the United States. The deposits of Greece and California are of the white massive character and as a rule of very pure quality. They are not as suitable for refractory purposes in metallurgical processes as the Austro-Hungarian magnesite, on account of composition and high cost of preparation. The white magnesites are used principally in paper manufacture, in caustic form as flooring cement, and for the manufacture of carbonic acid gas, the carbonate as mined containing approximately 50 per cent of CO<sub>2</sub>, which may be driven off at a comparatively low temperature. A few refractory brick are made from white magnesite, but difficulties of manufacture and high cost render the demand very slight.

It is with the Austro-Hungarian magnesite that the users of magnesite in this country are most interested. The material occurs in a crystalline formation and is gray in color with tinges of brown. In comparison with the white magnesite it differs in composition and formation. The chemical composition is the most important difference. Comparative analyses of the two kinds of magnesite, calcined, are as follows:

	Austro-Hungarian	White
Silica (SiO <sub>2</sub> )	2.75	2.50
Alumina (Al <sub>2</sub> O <sub>3</sub> )	0.50	0.25
Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )	7.00	1.00
Lime (CaO)	2.50	2.25
Magnesia (MgO)	87.00	93.00
Loss on ignition	0.75	1.00

The impurities in the Austro-Hungarian render it less refractory, and it will frit more readily at operating temperatures, which is a very important property, especially in open hearth steel practice in building the bottom and repairing the slag line. In the calcined form, for commercial uses, Austro-Hungarian magnesite has a rich brown color and white magnesite is either white or a very light brown, depending on the thoroughness of calcination.

The chief uses of magnesite brick are in open hearth steel furnaces, copper converters, reverberatories and settlers, and electric furnaces. Their use is spreading considerably where strong basic slags, mill cinder and strongly metallic slags are encountered, such as the bottoms of forging, heating and welding furnaces.

It is an interesting fact, and one of importance to all users of magnesite, that when subjected to the action of steam, magnesite in calcined form, or even the most thoroughly burned brick, will hydrate, similarly to the action of calcined lime when water is added. This hydration takes place to equal degree in all brands of magnesite brick made in the United States or Europe. The effect of the hydration is disintegration to an almost impalpable powder. It does not seem to bear any relation to the content of lime or other impurities, as the tests showed the same results for the Austro-Hungarian as for the white or very pure Grecian magnesite.

Tests were conducted by placing brick in a steam-tight cylinder and subjecting to steam at 100 lbs. pressure for a period of two hours, all brick tested showing hydration to the same degree, though it is reasonable to conclude that the action would be somewhat retarded under lower pressure or less severe conditions.

Difficulties of this nature have been experienced in open hearth furnace bottoms by laying the brick and magnesite bottom over a bed of refractory materials mixed with water. Upon heating up, steam is formed and the bottom may be very badly damaged by hydration of the magnesite.

This fact, which has not been well established until recently, no doubt accounts for a number of similar troubles which have occurred in years past. It also explains cases of disintegration of burned magnesite brick which have been in contact with steam leaking from coils or steam-heated floors used in manufacturing magnesite brick. It should be made a matter of common knowledge, therefore, so that users of magnesite will be able to guard against trouble of this kind, especially during the initial heating period.

HARBISON-WALKER REFRACTORIES CO.  
PITTSBURGH, September 15, 1914

R. H. YOUNGMAN

### CONVERSION TABLE FOR GLUES

In connection with the use of the Weinhagen Glue Hydrometer, which reads percentage by weight of air-dry glue, it is necessary to calculate the number of pounds of glue in a gallon of the dry product, as well as to determine the capacity of tanks and other glue containers in terms of air-dry or bone-dry glue. In determining the following values by experiment, a hide glue was used and the methods employed were of a degree of accuracy commensurate with technical use. The percentages selected are those generally dealt with in commercial glues.

Per cent air-dry glue (Hydrometer)	Corresponding percentage bone-dry glue	LBS. PER GALLON WHEN	
		Air-dry	Bone-dry
0.0	0.000	8.3360	8.3360
0.5	0.424	8.3550	8.3570
1.0	0.848	8.3650	8.3690
1.5	1.272	8.3750	8.3810
2.0	1.696	8.3860	8.3930
2.5	2.120	8.3970	8.4060
3.0	2.544	8.4080	8.4190
3.5	2.968	8.4190	8.4320
4.0	3.392	8.4300	8.4440
4.5	3.816	8.4410	8.4570
5.0	4.240	8.4515	8.4700
5.5	4.664	8.4625	8.4820
6.0	5.088	8.4730	8.4945
6.5	5.512	8.4840	8.5080
7.0	5.936	8.4950	8.5210
7.5	6.360	8.5050	8.5330
8.0	6.784	8.5160	8.5460
8.5	7.208	8.5270	8.5590
9.0	7.632	8.5380	8.5715
9.5	8.056	8.5480	8.5840
10.0	8.480	8.5590	8.5970
10.5	8.904	8.5700	8.6100
11.0	9.328	8.5800	8.6225
11.5	9.752	8.5910	8.6340
12.0	10.176	8.6015	8.6460
12.5	10.600	8.6130	8.6600
13.0	11.024	8.6230	8.6715
13.5	11.448	8.6340	8.6840
14.0	11.872	8.6450	8.6970
14.5	12.296	8.6550	8.7100
15.0	12.720	8.6660	8.7225
15.5	13.144	8.6770	8.7360
16.0	13.568	8.6880	8.7490
16.5	13.992	8.6990	8.7610
17.0	14.416	8.7090	8.7740
17.5	14.840	8.7200	8.7870
18.0	15.264	8.7310	8.8000
18.5	15.688	8.7420	8.8130
19.0	16.112	8.7530	8.8260
19.5	16.536	8.7640	8.8390
20.0	16.960	8.7740	8.8520

BAEDER, ADAMSON & Co.  
PHILADELPHIA, August 1, 1914

ISMAR GINSBERG

### CAP FOR BUNSEN BURNER USED WITH NATURAL GAS

*Editor of the Journal of Industrial and Engineering Chemistry:*

Special burners adapted for natural gas are already in much use. But Bunsen burner and other modifications of this can be rendered serviceable for natural gas by providing caps made of ordinary wire gauze, say about 22 mesh. A cap made of wire gauze and put on a Bunsen burner or this type of burner gives a steady flame, not extinguishable even by a strong air draught. Such a cap can easily be made by pressing a piece of

wire gauze down over the aperture of an iron tube. One square inch wire gauze, 22 mesh, will answer the purpose. The flame of the wire gauze capped burner can be regulated very easily by the air regulator.

NATIONAL CARBON CO.  
CLEVELAND, OHIO, June 1, 1914

GREGORY TOROSSIAN

### A SHAKER FOR THE MECHANICAL ANALYSIS OF SOILS— NOTE

*Editor of the Journal of Industrial and Engineering Chemistry:*

In THIS JOURNAL, 6, 517, Mr. C. C. Fletcher takes exception to my claim that my Soil Shaker is better than that used by the Bureau of Soils at Washington. I should like to consider his objections and further substantiate my claim.

I. NUMBER OF BOTTLES—It is true that the Bureau machine carries 48 bottles, while mine carries only 16. But the comparison becomes fairer by considering the power required to run the two machines. In the description of the Bureau machine<sup>1</sup> it is stated that "the machine is driven by an ordinary stock 1/4 H. P. motor." Determinations recently made on my machine by the Department of Mechanical Engineering of Yale University, show that 0.000766 H. P. is required to run it at the prescribed rate and loaded to full capacity. We then have a comparison of powers as follows: 0.25 vs. 0.000766—a ratio of 1 to 326+. Even if only one-tenth of the power of the motor were really used to operate the Bureau machine, that same amount of power would be sufficient to operate more than 30 of my machines at once, with a total carrying capacity of 480 bottles. One should bear in mind, also, the fact that my machine is strictly "home-made." If it were nicely constructed, mounted on bearings, etc., the efficiency would be even more striking.

II. SPEED—It is true that if the wheel were turned very rapidly there would be centrifugal effects. But it is expressly stated in my article that the wheel should *not* be run rapidly. Surely, the mechanical difficulties of running a wheel slowly instead of rapidly are not insurmountable! And indeed, the slower the wheel is turned the less energy is required. The "merely pouring" of the contents of the bottle from one end to the other, consequent upon slow turning of the wheel, is a distinct advantage over hitting the soil particles swiftly together by a sudden jerking motion.

III. ELEMENT OF TIME—Mr. Fletcher explains the 7 hours required by the Bureau machine by saying "in some rare instances as long a time as this has been found necessary. The majority of soils, especially sandy soils, do not need 7 hours." In other words, 7 hours is the maximum required. Well, similarly for my machine, the 3 hours mentioned is a maximum time requirement. The average soil can be successfully treated in a much shorter time. Mr. Fletcher also states that even if 7 hours are used it is no loss of time to the operator, because he is busy anyway. Certainly, in this age of conservation and efficiency engineering, one should not countenance waste of power and energy in running a machine longer than necessary!

Another argument not as yet presented may be stated here. In the Bureau machine the bottles are in a horizontal position. With a moderate jerking back and forwards of the bottle only the upper portion of the soil is shaken; with more vigorous jerking the whole mass of soil is in movement, but, on account of the friction on the bottle, the lower part moves more slowly than the upper, and may move but slightly or not at all. Also, in order to have all the sample in action at the same time the upper portion is driven backwards and forwards with more violence than it really requires. As a result, there is a tendency for the particles to abrade one another. Obviously this breaking down of the soil particles should not be very appreciable or the method is a failure. In treatment by my machine the

bottle is slowly ended over and over. The whole sample thus falls from one end of the bottle to the other through a column of water twice in every revolution of the wheel. The lack of violence in the process of "merely pouring," coupled with shorter time of treatment, reduces abrasion to a negligible factor. It should be clear why my method is shorter than the Bureau method for all the particles are receiving equal treatment all the time.

FREEMAN WARD

SHEFFIELD SCIENTIFIC SCHOOL, YALE UNIVERSITY  
NEW HAVEN, CONN., October 16, 1914

### AMERICAN INSTITUTE OF CHEMICAL ENGINEERS 7TH ANNUAL MEETING, PHILADELPHIA DECEMBER 2-5, 1914

#### PROGRAM OF PAPERS

- Address of Welcome. MAYOR BLANKENBURG.  
Distribution of Industrial Opportunities. GEORGE OTIS SMITH, Director of the U. S. Geological Survey.  
The Manufacture and Application of the Artificial Zeolites (Permutite) in Water Softening. D. D. JACKSON.  
Feldspar as a Possible Source of American Potash. ALLERTON S. CUSHMAN AND GEO. W. COGGESHALL.  
Hydrometallurgical Apparatus and Its Use in Chemical Engineering. JOHN V. N. DORR.  
The Hardwood Distillation Industry. E. H. FRENCH AND JAMES R. WITHROW.  
The Chemical Industries of Japan. JOKICHI TAKAMINE.  
Need of Up-to-date Manufacturing Statistics. BERNHARD C. HESSE.  
Ore Flotation, a New Hydrometallurgical Development. S. P. SADTLER AND S. S. SADTLER.  
Aspects of Some Chemical Industries in the United States Today. EDWARD GUDEMAN.

#### EXCURSIONS

Atlantic Refining Co. of the Standard Oil Co. at Point Breeze on the Schuylkill River. This plant has the new Burton process for the distillation of petroleum and the manufacture of motor fuel.

United Gas Improvement Co. This plant has new water gas generators with waste heat boilers. The physical research laboratory was visited and recent developments in artificial illumination and photometric apparatus were inspected.

Welsbach Works, Gloucester, N. J. Nitrating and collodion manufacture, thorium nitrate and mantle manufacture, solvent recovery, metal working, nickel plating and finishing were seen.

New York Shipbuilding Co., Camden, N. J.

Farr & Baily Linoleum Works, Camden, N. J.

Commercial Museums, West Philadelphia. Address by Dr. Wm. P. Wilson on the work of the Museum.

Laboratories of the University of Pennsylvania.

Barrett Manufacturing Co., Chemical Department, Frankford, Philadelphia. The working up of the light and middle oils, the refining of naphthalene, the small scale preparation of carbolic acid, etc., were shown.

### COMMUNICATION FROM THE ANALYTICAL COMMITTEE RUBBER SECTION, AMERICAN CHEMICAL SOCIETY

From the reply of The Joint Rubber Insulation Committee, THIS JOURNAL, 6, 515, it is evident that some discussion of the results as published in THIS JOURNAL, 6, 514, is necessary to prevent any misunderstanding as to their bearing. Since this reply appeared it was impossible to hold a meeting of The Analytical Committee until this date.

In presenting the results of their work, The Analytical Committee voted to confine their published report to the facts brought out by their analysis and omit all discussions, as a publication of these discussions in full would have occupied more space than this committee could reasonably have asked for and it was by no means certain how much of it would be of general interest.

<sup>1</sup> U. S. Dept. Agr., Bur. Soils, Bull. 84, p. 15.

The three compounds selected for analysis were designed to test the accuracy of the methods for analysis of the Acetone Extract as affected by the presence or absence of the two hydrocarbons used in commercial practice. The amount of rubber and the fillers were varied only slightly to avoid the influence of extraneous factors on the results. The selection of fillers and the respective proportions were designed to fall within the limits prescribed by the 1913 Railway Signal Association's specification for 30% Fine Para insulation, as this was considered to be the most important type of material to which the methods of The Joint Rubber Insulation Committee were likely to be immediately applied. The methods of The Joint Rubber Insulation Committee were intended to be applicable to the analysis of just such compounds. Therefore, if the errors have been magnified due to the constituents, the methods should be revised to meet such conditions.

The Analytical Committee, before issuing its report, took into consideration the discrepancies of Analyst No. 3 under waxy hydrocarbon, which in all probability were due to the Solution of Alcoholic Potash used. They also took into consideration the results of No. 4, under Free Sulfur, which were obtained by the use of a different type of extractor, for comparative purposes. Inasmuch as no conclusions drawn from either of these results were adverse to the methods of The Joint Rubber Insulation Committee, no exception was made to the decision of the committee to publish only the results and conclusions.

These discrepancies and the reasons for the same were brought to the attention of the Rubber Section at the Cincinnati meeting and were fully discussed at that time. Two members of The Joint Rubber Insulation Committee, who were instrumental in drawing up the comments printed in THIS JOURNAL, 6, 515, were present at this meeting and were fully acquainted with the facts.

A clerical error which appeared in the published report should be corrected as follows: Under Sample A, Analyst I:

11/20—Total waxy hydrocarbons should read 2.14 per cent

11/21—Total waxy hydrocarbons should read 2.55 per cent

Referring to the comments on the work of Analyst No. 2,

The Joint Rubber Insulation Committee state, "The results indicate that the Acetone Extraction was not properly made." Comparison of the results of Analyst No. 2 with those of Nos. 1, 4 and 5, which are taken as a standard for comparison, does not substantiate this statement, as these results are consistent with Nos. 1, 4 and 5 and the duplicate results are particularly consistent; furthermore, the analyst states that the Acetone Extraction was made absolutely in accordance with the procedure.

The fact that the averages of a large number of determinations are "about what we would expect from this compound" proves only that positive and negative errors are equally probable and does not substantiate the claim that the determination of saponifiable extracts by this method will give accurate results, since the individual results show that the probable error of a single determination is large.

This procedure is given as a method for 30 per cent Hevea rubbers, therefore the Analytical Committee was justified in making its first investigation on Fine Para.

E. W. BOUGHTON G. H. SAVAGE P. H. WALKER  
W. A. DUCCA J. B. TUTTLE D. W. WHIPPLE, *Chairman*  
114 LIBERTY ST., NEW YORK CITY  
November 16, 1914

#### THE SPECIFIC HEAT OF CALIFORNIA PETROLEUMS A CORRECTION

In my article under the above title in THIS JOURNAL, 6, 727, the formula used for the calculation of the specific heats given

in the results was  $c = \frac{CM(T-t)}{m(t-t_0)} - \frac{W}{m}$  and not that given in the article as originally printed.

3333 19TH STREET HAROLD E. WALES  
SAN FRANCISCO, CAL., November 7, 1914

#### THE EXPLOSIBILITY OF GRAIN DUSTS—A CORRECTION

In the article printed under the above title, in THIS JOURNAL, 6, 934, the name of Mr. David J. Price as joint author was omitted by error.

BUREAU OF CHEMISTRY, WASHINGTON HAROLD H. BROWN  
November 16, 1914

## PERSONAL NOTES

The University of Pittsburgh announces the following course of Special Evening Lectures on Chemical Engineering during 1914-15: *Nov. 9th*—"Our New Knowledge of Coal," H. C. Porter, Chemist, U. S. Bureau of Mines, Pittsburgh. *Nov. 16th*—"Recent Researches on the Combustion of Coal," Henry Kreisinger, Engineer in Charge of Fuel Tests, Bureau of Mines, Pittsburgh. *Nov. 23rd*—"Some Applications of Pulverized Coal," Richard K. Meade, Consulting Chemist, Baltimore. *Nov. 30th*—"Producer Gas," J. K. Clement, Physicist, Bureau of Mines, Pittsburgh. *Dec. 7th*—"The Softening of Water for Industrial Purposes," James O. Handy, Director of Research, Pittsburgh Testing Laboratories. *Dec. 14th*—"The Classification of Clays," Edward Orton, Head of Department of Ceramics and Dean of the College of Engineering, Ohio State University. *Jan. 4th*—"The Effect of Heat on Clays," A. V. Bleining, Director Technological Laboratory, U. S. Bureau of Standards, Pittsburgh. *Jan. 11th*—"The Manufacture of Structural Clay Products," A. V. Bleining. *Jan. 18th*—"The Manufacture of Refractories," Kenneth Seaver, Chief Chemist, Harbison-Walker Refractories Co., Pittsburgh. *Jan. 25th*—"The Manufacture of Porcelain," Ross C. Purdy, Chief Chemist, Norton Co., Worcester, Mass. *Jan. 25th*—"Glazes and Enamels," A. V. Bleining. *Feb. 1st*—Symposium: "Special Phases of the Glass Industry," C. H. Kerr, Pittsburgh Plate Glass Co.; S. R. Scholes,

Assistant Director Mellon Institute of Industrial Research; Alexander Silverman, University of Pittsburgh. *Feb. 8th*—"Special Methods of Pyrometry," H. S. Stupakoff, Director Stupakoff Laboratories, Pittsburgh. *Feb. 15th*—"The Present Status of the Chemical Technology of Vanadium," B. D. Saklat-Walla, Chief Chemist, American Vanadium Co., Pittsburgh. *Feb. 22nd*—"The Manufacture of Steel Tubing," F. N. Speller, National Tube Co. *Mar. 1st*—"The Manufacture of Steel in the Electric Furnace," F. Crabtree, Professor of Metallurgy, Carnegie Institute of Technology. *Mar. 8th*—"The Corrosion of Iron and Steel," D. M. Buck, American Sheet and Tin Plate Co., Pittsburgh. *Mar. 15th*—"Catalysis," M. A. Rosanoff, Professor of Research Chemistry, Mellon Institute. *Mar. 22nd*—"Recent Developments in the Electrochemistry of Organic Compounds," Harold Hibbert, Research Fellow, Mellon Institute; and "Industrial Applications of the Phase Rule," M. A. Rosanoff.

The North Carolina College of Agriculture and Mechanic Arts has made the following additions to the staff of its Chemistry Department: C. F. Miller, E. L. Frederick, J. T. Dobbins and H. I. Cox.

Mr. James J. Bajda, formerly connected with the Chemical Department of Sulzberger & Sons, is now Chemist and Chemical Engineer for the San-I-Genic Company of Winnipeg, Canada.

J. D. Mackenzie is now employed in the laboratory of Armour and Company at Chicago.

Mr. W. D. Richardson, of Swift & Co., Chicago, spent his vacation bear hunting in Oregon.

Prof. M. A. Rosanoff, for the past seven years director of the Department of Chemistry in Clark University, has accepted a professorship of Chemical Research in the Mellon Institute of Industrial Research and the Graduate School of the University of Pittsburgh.

Dr. Harvey W. Wiley celebrated his seventieth birthday recently by a dinner party. Among the guests were Prof. Chas. E. Munroe, one of Dr. Wiley's instructors at Harvard; Dr. W. D. Bigelow, for many years with Dr. Wiley in the Bureau of Chemistry; Dr. G. L. Spencer, a student under Dr. Wiley at Purdue University 40 years ago, and Prof. Frank W. Clarke, of Washington.

The Royal Canadian Institute in Toronto, Canada, plans to inaugurate work on the lines of the Mellon Institute of the University of Pittsburgh. Dr. Raymond F. Bacon, director of Mellon Institute, was invited to address the Canadian Institute and spoke before them on "Industrial Research" on November 7th. The lecture was given in the University of Toronto, the alma mater of the late Dr. Robert Kennedy Duncan, founder of the system of industrial research at the Mellon Institute.

Prof. J. H. Mathews, of the University of Wisconsin, will give an illustrated lecture on "Color Photography" before the Kansas City Section of the A. C. S. on December 12th.

The program for the December 11th meeting of the New York Section of the A. C. S. is as follows: "A Surficial Burn, Produced by an Unknown Radiation," C. A. Doremus; "Past, Present and Future of Electrochemistry in America," E. F. Roeber; "Research in Applied Chemistry," W. H. Walker; "Industrial Research," Raymond F. Bacon.

The Executive Committee of the International Congress of Mining, Metallurgy, etc., London, 1915, decided on September 4th to adjourn the holding of the Congress *sine die* on account of the war.

Prof. J. G. Shearer gave an illustrated lecture on "Some Phases of the Development of Roentgen Rays and Their Applications," before the Cornell Section of the A. C. S., on November 16th.

Mr. Carl Hambuechen, of the American Carbon and Battery Co., addressed the November 9th meeting of the St. Louis Section of the A. C. S. on "Some Problems in the Manufacture of Dry Batteries."

The Hedley F. Jobbins glycerine plant at Aurora, Ill., and one of the largest of its kind in the world, was completely destroyed by fire on August 23rd. The loss of a very well equipped laboratory and the destruction of hundreds of tons of finished glycerine made the fire an exceedingly costly one.

The New York Section of the American Electrochemical Society met in joint session with the American Gas Institute and the Illuminating Engineering Society on November 18th. The topic for the evening was "The Effect of Chemical Research on Lighting," and the speakers were: H. S. Miner, W. C. Moore, R. E. Myers, R. D. Bailey, D. MacFarlan Moore and H. E. Ives.

Dr. P. F. Trowbridge, of the University of Missouri, spoke on "Some Problems in Nutrition," on November 9th, at the University of Rochester, before the Rochester Academy of Science and the Rochester Section of the A. C. S.

At the October 31st meeting of the Puget Sound Section of the A. C. S. at Seattle, the following articles were read: "Fish Oils," J. W. Brandel; "Fertilizer and Other By-Products of the Fishing Industry," E. A. Stoppel.

The Maryland Section of the A. C. S. held its 2nd regular meeting on November 14th. Papers were read by J. Bosley Thomas, "Present and Future Methods for the Purification of the Baltimore City Water Supply," and Wm. Royal Stokes, "Bacteriological and Sanitary Results Obtained by the Treatment of the Baltimore City Water Supply."

The following papers were read at the Connecticut Valley Section of the A. C. S. in Hartford on November 7th: "Recent Studies on the Theory of Dyeing and the Chemistry of Wool Fiber," Frederic Danneth; "The Control of Plating Solutions," Arthur DeF. Cowperthwait.

Prof. Harry McCormack, of Armour Institute of Technology, lectured on November 13th before the Chicago Section of the A. C. S. on "Why We Do Not Manufacture Aniline Dyes."

The Eastern N. Y. Section of the A. C. S. met at Union College, Schenectady on October 30th. The following papers were presented: "The Commercial Production of Oxygen and Nitrogen," G. L. Fonda; "The Influence of Composition on the Magnetic Properties of Steel," W. E. Ruder.

The Highway Engineering Department of Columbia University offers the following illustrated lectures during December, 1914: Dec. 3rd—"Specifications for Sizes and Physical Properties of Broken Stone," Arthur W. Dean, Chief Engineer, Mass. Highway Commission. Dec. 7th—"The Essential Physical and Chemical Properties of Creosote Oils for Wood Blocks," S. R. Church, Manager Research Department, Barrett Manufacturing Co., New York. Dec. 9th—"Details of Construction of American Wood Block Pavements," A. W. Dow, Chemical and Consulting Paving Engineer, New York. Dec. 11th—"European Wood Block Pavements," George W. Tillson, Consulting Engineer to the President of the Borough of Brooklyn, New York. Dec. 14th—"The Construction and Maintenance of Cement-Concrete Pavements," Edward D. Boyer, Cement and Concrete Expert, The Atlas Portland Cement Co., New York. Dec. 16th—"Specifications for Physical Properties of Paving Bricks and Stone Blocks," William A. Howell, Engineer of Streets and Highways, Newark, N. J. Dec. 23rd—"Planning of Streets and Street Systems," Nelson P. Lewis, Chief Engineer, Board of Estimate and Apportionment, New York. Dec. 28th—"Production of Bermudez and Trinidad Asphalts," C. N. Forrest, Chief Chemist, Barber Asphalt Paving Co., Maurer, N. J.

The program of the November 16th meeting of the Rochester Section of the A. C. S. was as follows: "Notes on the Determination of Antimony," H. E. Howe; "Some of the Impurities of Photographic Chemicals," M. B. Punnett; "Military Explosives," C. E. K. Mees.

Dr. Edgar Fahs Smith, Provost of the University of Pennsylvania, addressed the Philadelphia Section of the A. C. S. at its November 19th meeting.

Mr. F. B. Sherwood, B.S. 1912, North Carolina A. & M. College, has been appointed Assistant Chemist to the North Carolina Agricultural Experiment Station.

The program of the Wisconsin Section of the A. C. S. for November 18th included the following papers: "Apparatus for Precise Cryoscopic Measurement at Elevated Temperatures," Prof. J. H. Mathews; "The Effect of Temperature Control in the Destructive Distillation of Wood," R. C. Palmer.

Dr. Alfred Springer gave an illustrated lecture on "An Egyptian Trip," before the Cincinnati Section of the A. C. S. on October 28th.

A series of seven lectures on "Sanitation as Applied to Cities" was given during November at the Worcester Polytechnic Institute, by Prof. George C. Whipple, of Harvard University.

Mr. Chas. Boulton, of the Carborundum Co., gave an illustrated lecture on carborundum before the Columbus Section of the A. C. S. on November 5th.

Prof. Harry McCormack is giving a course of lectures on "Industrial Chemistry" at Armour Institute of Technology; these lectures are given on Tuesday evenings, from 7.30 to 9.30 o'clock, and the course will continue for three terms.

Dr. George Oliver Curme, of Evanston, Ill., was one of few Americans abroad this summer who successfully escaped the war embargo. He arrived in this country at about the time the storm broke in Belgium. Dr. Curme was in Berlin doing some special work in chemistry. He took his doctor's degree at Chicago in 1913 and went abroad shortly afterwards.

Mr. H. E. Jordan gave an illustrated lecture on "Some Features of Water Purification before the Indiana Section of the A. C. S. on November 14th.

The Milwaukee Section of the A. C. S. met on November 20th. Prof. E. B. Hart, of the College of Agriculture, University of Wisconsin, spoke on "Recent Developments in Agricultural Chemistry."

At the November 11th meeting of the Lexington Section of the A. C. S. the following papers were given: "Some Curiosities of Chemical Literature," Dr. Garnett Ryland; "Note on a Specimen of Vivianite from Marshall Co., Ky.," Dr. A. M. Peter.

Dr. Charles H. Viol, Director of the Radium Research Laboratory, Pittsburgh, gave an illustrated lecture on Radium and Radioactivity before the Pittsburgh Section of the A. C. S. on November 12th.

The N. Y. Section of the Society of Chemical Industry were addressed by John H. Hall on "Manganese Steel" and by George F. Comstock on "Titanium and Its Effects on Steel" at their meeting on November 20th.

Mr. W. R. Gilard has resigned as Chemist with the Pittsburgh Testing Laboratory to accept a position as research chemist with the Pittsburgh Plate Glass Co.

On invitation of the Brown Chapter of the Society of the Sigma Xi, the Rhode Island Section of the A. C. S. attended an illustrated lecture on "X-Rays and Crystals" on November 20th by William Henry Bragg, A.M., F.R.S., Professor of Physics in the University of Leeds, England.

The U. S. Bureau of Mines has begun the collection of a general library of petroleum literature, under the direction of W. A. Williams, chief petroleum technologist. The details of this work have been assigned to Dr. David T. Day, recently transferred from the U. S. Geological Survey as petroleum technologist, who will also assist in a thoroughly organized research into the chemistry of oils, which is being developed by the Bureau of Mines. In view of the importance of such a library, the Bureau hopes that all technologists will aid in the work by exchanging with it all available books and maps on the subject.

Dr. Frederick B. Power will retire from the directorship of the Wellcome Chemical Research Laboratories, London, on December 1st, in order to return to the United States, where, for family reasons, he will make his future home.

Dr. Frank L. Pyman, whose researches and contributions to chemical science are well known, will succeed Dr. Frederick B. Power as director of the Wellcome Research Laboratories, London, England.

President A. C. Humphreys, of the Stevens Institute of Technology, will act as president of the International Gas Congress, which meets in San Francisco next September.

## GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**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. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

### GEOLOGICAL SURVEY

**Production of Anthracite in 1913.** EDWARD W. PARKER. Advance chapter from Part 2, Mineral Resources, 1913. 16 pp. Including the coal recovered from old culm banks by washeries, and a small quantity dredged from Susquehanna River, the production of anthracite in 1913 amounted to over 81 million long tons valued at \$195,000,000. This is an increase of nearly 10 per cent over the production of the previous year. No unusual influence affected the 1913 trade but the increase is rather greater than average. "The increase in the use of artificial gas and of coke for domestic purposes will probably keep pace with the increase of population in the markets supplied by anthracite, and there is little probability that the production of anthracite will show any marked increase in the future. Changes in temperature and labor conditions will continue to be the most important factors affecting the production of anthracite." The standard screens used in the preparation of anthracite have the following dimensions, the percentage of the total production of each size being indicated in the last column:

### STANDARD SIZES OF ANTHRACITE

Size	Through	Over	Percentage of total production
Lump and steamboat.....			0.51
Broken or grate.....			4.92
Eggs.....	4 inches square	2 <sup>3</sup> / <sub>4</sub> inches square	12.59
Stove.....	2 inches square	1 <sup>3</sup> / <sub>8</sub> inches square	19.53
Chestnut.....	1 <sup>3</sup> / <sub>8</sub> inches square	3 <sup>3</sup> / <sub>4</sub> inch square	24.08
Pea.....	3 <sup>3</sup> / <sub>4</sub> inch square	1 <sup>1</sup> / <sub>2</sub> inch square	11.51
Buckwheat No. 1.....	1 <sup>1</sup> / <sub>2</sub> inch square	1 <sup>1</sup> / <sub>4</sub> inch square	13.33
Buckwheat No. 2 or rice.....	1 <sup>1</sup> / <sub>4</sub> inch square	1 <sup>1</sup> / <sub>8</sub> inch square	7.90
Buckwheat No. 3 or barley.....	1 <sup>1</sup> / <sub>8</sub> inch square	1 <sup>1</sup> / <sub>16</sub> inch round	5.17
Screenings.....	1 <sup>1</sup> / <sub>16</sub> inch round		0.46

**Production of Peat in 1913.** CHARLES A. DAVIS. Separate from Part 2, Mineral Resources, 1913. 19 pp. "Up to the present time, however, practically none of these attempts (in the U. S.) at the production of a serviceable fuel from peat have been commercially successful." However, in almost every case, where material properly prepared has been offered for sale, it has found a ready market at prices which were ample to have paid a profit upon the operation. European methods for the production of peat in form suitable for fuel either as "cut peat" or "machine peat" are described. The various processes for pressing water from peat and briquetting it are also described. Despite the general belief to the contrary it should be noted that "only a single peat-briquette factory is known to be in operation in Europe at the present time." Among the various uses for peat discussed are the following: Peat powder, peat coke or charcoal, as fuel for steaming, as fuel for producer-gas generation, as fuel in special industries, as fertilizer filler or as fertilizer (the latter in case of peats rich in combined nitrogen), stock food, paper stock, and stable litter. The production in 1913 in short tons for the various purposes shows as follows: Fertilizer 28,400,000, valued at

\$169,600; for stock food 4,800,000, value \$27,600; and for stable litter, all of that being imported material, 10,983, valued at \$55,719.

**Barytes.** JAMES M. HILL. Separate from Part 2, Mineral Resources, 1913. 10 pp. The production of crude barytes in the United States in 1913 was 45,298 short tons valued at \$156,275, an increase of 20 per cent in quantity over 1912. The average price per ton in 1911 was \$3.19, in 1912 \$4.09, and in 1913 \$3.45. However, it is noted that considerable difference in average price per ton is found for the production in different localities, that in Missouri reaching \$3.78 per ton in 1913, whereas that of Tennessee and Kentucky was only \$1.70 per ton for the same period.

The 1913 imports of unmanufactured barytes amounted to \$61,000; the manufactured product amounted to \$38,000. The imports of barium compounds during the same period were as follows:

Barium carbonate, natural.....	\$ 13,116
Barium carbonate, manufactured.....	38,949
Barium binoxide.....	239,000
Barium chloride.....	37,620
Blanc-fixe, or artificial barium sulfate.....	62,785
Total.....	\$391,470

This report describes the mineral characteristics, the uses and the occurrence of barytes in the United States.

**Strontium.** JAMES M. HILL. Note from Mineral Resources, 1913. During 1913 no strontium was reported as mined in the United States, probably because of the limited market. "No strontium carbonate, oxide, or protoxide was imported in either 1911 or 1912, but in 1913 the total value of imports of these salts was \$2,284. Probably some strontium nitrate was imported for use in 'red fire,' but it is not possible to obtain figures of the imports of any salts of strontium except those named above."

**The Production of Salt, Bromine, and Calcium Chloride in 1913.** W. C. PHALEN. 16 pp. The marketed production of salt in 1913 was over 34,000,000 barrels of 280 pounds each, having a total value in excess of \$10,000,000. It is noted that the price of salt has been slowly rising throughout the last several years. A classification is given of the several methods of production, and the production by grades and by localities is given in detail. It is noted that a total value of imported salt was \$421,745 and the exports \$515,194 during 1913.

The production of bromine in 1913 amounted to 572,400 pounds having a value of about \$110,000. The calcium chloride production in the same period was 19,611 short tons valued at \$130,000.

**Asbestos.** J. S. DILLER. Separate from Part 2, Mineral Resources, 1913. 16 pp. "The production of asbestos in the United States is small, but in manufactured asbestos products the United States surpasses any other country. The total output of asbestos in this country for 1913 was about 1,100 short tons, and all of it came from 2 producers in Georgia and 1 in Arizona." Not only was the production very much less during this period but the value per ton (\$10) was also lower than in any previous year, except 1907. As a matter of fact, the price of asbestos in the United States is controlled by the Canadian market, since the world's supply of asbestos is largely drawn from the province of Quebec; however, a rapid development of the Russian asbestos is making that country an important factor. It is noted that an advance of 10 per cent to 15 per cent in price is to be expected during 1914, owing to the demands for increase in wages. The asbestos imported in 1913 amounted to \$2,307,666, nearly 90 per cent of this being unmanufactured material. The occurrence and character of asbestos found in this country, as well as the Canadian and Russian deposits, are given in some detail and the summary of some recent investigations concerning these asbestos is included.

**The Gypsum Industry in 1913.** RALPH W. STONE. Separate from Part 2, Mineral Resources. 17 pp. In 1913 over 2,500,000 short tons of raw gypsum were mined, this being an increase of about 4 per cent over the previous year. The applications of this product are shown by the following table, which indicates the application of the marketed product of gypsum in the United States during 1913:

SOLD CRUDE	Quantity	Value	Average price per ton
For Portland cement.....	408,221	\$ 600,913	\$1.47
As land plaster.....	54,815	95,953	1.75
For other purposes.....	100	200	2.00
Total.....	463,136	\$697,066	\$1.51
SOLD CALCINED			
As plaster of Paris, wall plaster, Keene's cement, etc.....	1,680,157	5,858,785	3.49
For dental plaster.....	861	4,168	4.84
To glass factories.....	10,942	21,797	1.99
For Portland cement and other purposes.....	81,889	193,006	2.36
Total.....	1,773,849	\$6,077,756	\$3.43

The report also includes a discussion of the production of other countries, trade and manufacturing conditions, the character of gypsum products made, and the occurrence of gypsum and gypsite in the United States.

**The Production of Fluorspar and Cryolite.** ERNEST F. BUCHARD. Separate from Part 2, Mineral Resources, 1913. 8 pp. The total quantity of domestic fluorspar reported as marketed in 1913 was 115,580 short tons, valued at \$736,000. This was a slight decrease as compared with the previous year. The conditions of the industry, the character and composition of the supply which has been marketed, the uses of fluorspar, and the occurrence are described in some detail.

As a note, the imports and prices of cryolite are given as follows:

"No cryolite is produced in the United States, the entire supply used in this country being imported from Ivigtut, an Eskimo hamlet on the southern coast of Greenland.

"The quantity of cryolite reported to have been imported for consumption into the United States in 1913 was 2,559 long tons, valued at \$52,557, as compared with 2,126 long tons, valued at \$48,293, in 1912. The average price per ton declared in 1913 was apparently \$20.54, as compared with \$22.72 in 1912. Cryolite was imported free of duty in 1913."

**The Production of Mineral Waters in 1913 with a Discussion of their Radioactivity.** R. B. DOLE. 48 pp. The statistics given in this report are intended to include natural waters that are bottled and sold in practically their natural state, but it is not intended to include natural still waters that have been changed materially in chemical character or waters that are sold by flat or meter rates. No distinction has been drawn between the "table water" and "medicinal water," since the practice in differentiating by these two varies greatly. There are 746 commercial springs reporting, which indicate over 62,000,000 gal. sold at an average price of 11 cents per gal. About one-third the total value is classed commercially as "medicinal water." The range in price indicated shows a few springs selling at less than 2 cents or over 50 cents per gal.; the large majority, however, are between 2 cents and 10 cents. The imports in 1913 amounted to 3,364,000 gal., valued at \$950,000. The report gives in great detail the production by states indicating the name and location for all springs reporting.

In the portion discussing the radioactivity of mineral waters, the methods of measurement of radioactivity and the units used are briefly discussed, and a tabulation is given indicating the radioactivity of the considerable number of spring waters in this country and in Europe. A brief bibliography is appended.

**The Production of Magnesite in 1913.** CHARLES G. YALE AND HOYT S. GALE. Separate from Part 2, Mineral Resources, 1913. 14 pp. The 1913 production of magnesite was over 8



per cent less than in 1912, being 9,600 short tons valued at \$77,000. The report indicates the sources, prices, imports, and traffic regulations regarding this mineral. The more important uses of magnesite are indicated as follows: Refractories; in paper-making as bisulfite; for the manufacture of carbon dioxide; as oxychloride or "Sorel" cement. These and miscellaneous applications are discussed, particular attention being given to magnesia cement which is discussed in detail.

**Statistics of the Pottery Industry, 1913.** JEFFERSON MIDDLETON. Separate from Part 2, Mineral Resources, 1913. 15 pp. In this report are given full data as to the production of various classes of pottery in different parts of the United States. The value of all domestic pottery marketed in 1913 was approximately \$38,000,000, an increase of more than 4 per cent over 1912. The imports, which combine almost exclusively high-grade work, show a slight increase over the previous year, amounting to about \$10,000,000.

**Clay Products of the United States.** JEFFERSON MIDDLETON. Special tabulation without number. 1 p. This circular gives the value, quantity, and average price per unit for various kinds of brick, tile, terra cotta, and other clay products produced during 1913. The total value is in excess of \$181,000,000. Data are given separately for each of the several states.

**Production of Spelter in 1913.** C. E. SIEBENTHAL. Special leaflet, unnumbered. This circular indicates the variation in price of spelter at London and at St. Louis. Of 60 per cent of zinc concentrates at Joplin there is shown the weekly sales for the period 1906-1913, inclusive. The zinc smelting capacity of each of the various plants reporting is indicated, and tables are given showing the production by states and by foreign countries for the same period. In 1913 the primary spelter produced amounted to 346 tons; the consumption of primary spelter in the United States was less than 300,000 tons; the world's production of spelter was 1,100,000 tons.

**Quicksilver Production in 1913.** H. D. McCASKEY. 15 pp. The production indicated for 1913 amounts to 20,213 flasks of 75 pounds each, valued at \$813,000, the large majority of the product coming from California. Owing to the low prices during the year, the quicksilver industry was even less prosperous in 1913 than in the previous year. It is of particular interest to note that "the market has been very quiet during the last two years and some large producers are understood to have stored some of their output from time to time and others to have reduced their production until the demand and prices for the metal improve." Labor legislation for protection of labor in the mines is said to have added somewhat to the difficulty of profitable production in California. Data are given as to the production and resources for the different parts of this country as well as the world's production and the imports and exports. The New York price for 1913 averaged \$39.54 per flask of 75 pounds, about \$3 less than during the previous year.

**Gold, Silver, Copper, Lead, Etc., in 1913.** VARIOUS AUTHORS. Separate from Part 1, Mineral Resources, 1913. Sixteen sections of this volume are devoted to various phases of this subject, some of these being already in print. There are general reports for gold, silver, copper, lead, and zinc and special reports (called Mines Reports) for the several districts of the country arranged as follows: Eastern States, Central States, Alaska, Arizona, California and Oregon, Colorado, Idaho and Washington, Montana, New Mexico and Texas, South Dakota and Wyoming, and Utah. These reports are too detailed to permit of a review. Any of them can be secured as separates as soon as issued.

#### BUREAU OF STANDARDS

**Measurement of Standard of Radiation in Absolute Value.** W. W. COBLENTZ. Scientific Paper 227. 14 pp. Measurements are given of the radiation from the Hefner lamp and from a standard sperm candle relative to that from a black body and

data are given for more refined measurement of radiation from standard incandescent lamps.

**An Experimental Study of the Koepsel Permeameter.** CHARLES W. BURROWS. Scientific Paper 228. 30 pp. Of interest in the study of that type of instrument for use in accurate measurements of permeability and hysteresis curves.

**Various Modifications of Bismuth-Silver Thermopiles Having a Continuous Absorbing Surface.** W. W. COBLENTZ. Scientific Paper 229. 57 pp. This paper is largely of physical interest, but the construction of thermopiles is fully discussed, and appendices are included which take up the following subjects: Galvanometer mirrors, vacuum galvanometers, the most efficient combination of thermopile and galvanometer resistance, test of stellar thermoelements on stars, the maintenance of high vacua by means of metallic calcium.

**Lead Acetate Test for Hydrogen Sulfide in Gas.** R. S. MCBRIDE AND J. D. EDWARDS. Technologic Paper 41. 46 pp. The effect of practically all the factors which can influence the sensitiveness of the test when utilized in a commercial way for the testing of a city gas supply has been examined. The method of testing recommended is intended for commercial use and not for the most precise scientific work. However, the experiments described in detail indicate the methods of varying the test to make it of greatest sensitivity.

**Testing of Electrotype Solutions.** Preliminary circular, unnumbered. 4 pp. This circular indicates in a preliminary way the general problems met in the control of copper electrotyping solutions and gives in simple form preliminary suggestions for maintenance of the proper acidity and density of the solutions. No new experimental work is reported since the circular is intended to aid only non-technical operators in commercial plants.

#### BUREAU OF MINES

**Production of Explosives in the United States during 1913.** ALBERT H. FAY. Technical Paper 85. 15 pp. For purposes of comparison, explosives are grouped as black blasting powder, high explosives and permissible explosives. The production is given by states for these 3 groups. The totals reported are as follows: Black blasting powder, 194,146,000 lbs.; high explosives, other than permissible, 241,682,000 lbs.; and permissible explosives, 27,685,000 lbs.; a grand total of 463,514,000 lbs. The coal production per pound of explosives in 1913 was 2.72 tons, an increase of 0.36 ton over 1913.

**A Study of the Oxidation of Coal.** HORACE C. PORTER AND O. C. RALSTON. Technical Paper 65. 30 pp. This paper discusses the oxidation of coal at ordinary temperature, spontaneous heating of coal, the initial action of oxygen on coal, factors affecting the ignition of coal and affecting the rate of oxidation of coal, and closely related topics; analyses are given of the coals tested to indicate the nature of the change.

#### CONSULAR REPORTS—OCTOBER, 1914

The war has offered a market for American oleomargarine in England. Oleomargarine used in Europe usually consists of a mixture of cottonseed and copra (cocoanut) oil. (P. 13.)

As practically all the copra (dried cocoanut) from the Philippines was formerly shipped to France, the price has fallen to practically nothing, so that efforts are being made to develop a market in the United States. (P. 14.) See also P. 411 for a description of the copra industry of the Philippines.

Uranium ores are being prospected in India. (Pp. 20, 335.)

The output of the Government iron foundry at Walamatsu, Japan, amounts to 216,000 tons, and will soon be increased to include galvanized iron. (P. 24.)

The manufacture of buttons from ivory nuts, formerly carried out in Germany, should be a profitable industry in the United States. (P. 104.)

The methods of graphite mining in Ceylon are described. (P. 164.)

A committee appointed by the British Government has recommended among others the following regulations for patent medicines, *viz.*, (1) control by one department under the ministry of Public Health, (2) registration of the composition of all patent medicines, to be confirmed by confidential government analyses, (3) prohibition of the sale of any objectionable patent medicines; (4) that pure drugs sold under patent names be no longer exempt from duty. (P. 278.)

The camphor industry of India is described. (P. 288.)

Efforts are being made to develop the petroleum resources of India. (P. 443.)

The principal imports of graphite into the United States come from Ceylon, Mexico, Canada and Japan. (P. 455.)

Tungsten ore is being mined in Siam, the output in 1912-13 being over 300 tons. (P. 460.)

The manganese ore industry of Brazil is described. (P. 476.)

Carnauba wax, obtained from the leaves of the carnauba palm, is one of the principal exports of Brazil to the United States. It is used for the manufacture of phonograph records, shoe polish, candles, etc. (P. 477.)

Newly organized industries in Trinidad, include a cassava starch factory, a cocoanut fiber factory, and a tannery. (P. 489.)

The jute industry of India is prosperous, the United States being the principal consumer. (P. 508.)

The new oil-bearing nut discovered in the Philippines has been identified as belonging to the family Meliaceae. The seeds contain 45 per cent of a dark fatty oil. (P. 536.)

The New Zealand Government is attempting to grade kauri gum, one of their principal exports to the United States, where it is used in the manufacture of varnishes. (P. 540.)

Seeds of the plant "Jatropha curcas," cultivated in Argentina, contain 49 per cent of oil, suitable for the manufacture of soap. (P. 541.)

The cultivation of the soya bean in Argentina is being urged, experiments having shown that it grows well there. (P. 541.)

The whale oil industry of Vancouver has had a very successful season. (P. 507.)

The British Government has just purchased 900,000 tons of raw sugar in the East Indies at \$97.00 per ton, the largest purchase of sugar ever made. (P. 512.)

Correction (see THIS JOURNAL, 6, 965).—The statistics of the U. S. production of dyestuffs which appeared in Daily Consular and Trade Reports for Sept. 16, 1914, included the entire output of dyestuffs and-extracts. The production of artificial dyestuffs alone totaled \$1,764,451 in 1904 and \$3,462,436 in 1909.

#### RECENT DEMANDS FOR AMERICAN GOODS (PP.)

NOVA SCOTIA—70	NEW BRUNSWICK—	AZORES—311
Glass	219	Caustic soda
Drugs	Window glass	Cement
Chemicals	Sheet zinc	Cornstarch
Earthenware	Pig lead	Electrical supplies
Ink	Block tin	Fertilizers
Vegetable parchment	White lead	Glassware
PANAMA—80 and 155	Zinc white	Hardware
Sugar	Galvanized iron	Ink
Glassware	Sulfur	Linoleum
China	Tin plate	Linseed oil
Aluminum ware	Cream of tartar	Lubricating oil
ONTARIO—108, 138	SPAIN—224	Paints
Carbolic acid	Carbolic acid	Soap
Oxalic acid	Formic acid	Sugar
Citric acid	Naphthalene	Tallow
Salicylic acid	Aluminum	Varnishes
Tartaric acid	Alum	NORWAY—315
Camphor	Aniline dyes	Chemicals
Cocaine	Dextrin	Copra
Codeine	Glass	Dyestuffs
Cream of tartar	Copper and iron ware	Rubber
Glycerine	Ocher	Iron and steel products
Hydroquinone	Soda	Sugar
Menthol	Thermometers	Linoleum
Morphine	Waxes	Linseed oil
Castor oil	China clay	Olive oil
Olive oil	Emery	Salt
Potassium chlorate	SWEDEN—246	Soda
Potassium permanganate	Coal	Sulfur
Shellac	NEW ZEALAND—259	Tin plate
Sodium benzoate	Drugs	PARAGUAY—372
Sodium salicylate	Chemicals	Drugs
Santorine	Glassware	Electrical supplies
Cottonseed oil	Porcelain	Glassware
PORTUGUESE AFRICA	SANTO DOMINGO—273-7	Paper
—125	Beer	Tinware
Cement	China	SWITZERLAND—410
Sugar	Porcelain	Coal
Steel	Glassware	Coke
CHINA—125	Iron ware	Petroleum
Photographic supplies	Tin	Leather
Paper	Paper	Iron
Drugs	CARTAGENA—347	Steel
Tin	Drugs	Copper
Galvanized iron	Hardware	Edible oils
SWITZERLAND—125	Beer	Turpentine
Petroleum	Wines	WEST AFRICA—412
Gasoline	SWITZERLAND—362	Cement
Copper	Dyestuffs	Hardware
Tin	Petroleum	Glassware
Steel	Gasoline	Earthenware
Leather	JAMAICA—365	Candles
Coal briquets	Condensed milk	Kerosene
Lead	Butter substitutes	COSTA RICA—522
Lard	Beer	Beer
AZORES—140	Matches	Cement
Lubricating oils	Soap	Condensed milk
Sugar	Hardware	Paints
Candles	Paints	Varnishes
Gelatine	Crockery	Structural iron
Rubber goods	Paper	JAPAN—504
		Hides
		Paper pulp

#### STATISTICS, ETC., ON EXPORTS DURING 1912 AND 1913 TO THE U. S. (PP.)

CETTE, FRANCE—38	VANCOUVER—176	BRITISH SO. AFRICA—
Argols	Brewer's rice	232-241 and 357
Bauxite	Fertilizer	Hides
Fertilizer	Glycerine	Horn
Gentian	Gold bullion	Chrome ore
Glycerine	Hides	Aloes
Rags	Whale oil	Argols
Verdigris	Coal	Berry wax
VENEZUELA—59	Copper ore	Buchu
Balata	FRENCH OCEANICA—	Diamonds
Rubber	193	ZANZIBAR—261
Hides	Copra	Ebony
Gold	Phosphate	Ivory
Tonka beans	Vanilla	Skins
Copaiba balsam	VENEZUELA—193-201	BRITISH HONDURAS—
Chicle	Balata	313
HULL, ENGLAND—69	Balsam	Chicle gum
Alum	Mangrove bark	Hides
Ammonium sulfate	Bones	Logwood
Carbolic acid	Chicle	Rubber
Cement	Copaiba	JAMAICA—368
Chalk	Copper ore	Annato
Creosote	Fustic	Fustic
Cresol	Gold	Hides
Fertilizers	Hides	Kola nuts
Glue	Rubber	Logwood
Iron oxide	Tonka beans	Orange oil
Castor oil	ST. PIERRE—214	JAVA—369
Creosote oil	Fertilizers	Benzine
Linseed oil	Fish glue	Copra
Rape oil	Skins	Cubebs
Soya bean oil	SAMOA—218	Damar
Sunflower oil	Cocoa	Gambier
Paints	Copra	Peanuts
Ultramarine	BERMUDA—252	Gum benzoin
Whiting	Arrow root	Gum copal
PERNAMBUCO—84	Hides	Gutta percha
Castor beans	TRIPOLI—298	Hides
Hides	Hides	Kapok
Rubber	NUREMBERG, GER-	Citronella oil
Carnauba wax	MANY—310	Quinine
ARGENTINE—88	Cigar lighters	Rubber
Linseed	Bronze	Sugar
Hides	Electric carbons	Tapioca
Inebacho logs	Lupulin	Vanilla
Inebacho extract	Drugs	Paraffin wax
SAN SALVADOR—132	Percussion caps	TRINIDAD—404
Balsam	Optical glass	Asphalt
Bullion	Mirror glass	Bitters
Hides	Plate glass	Copra
Indigo	Gold leaf	Petroleum
Rubber	Hops	Rum
Sugar	Enamel ware	Sugar
MANCHURIA—148	Metal leaf	BRITISH WEST INDIES
Hides	Paints	—420-422
Fusel oil	Paper	Aloes
Hemp seed	Porcelain	Balata
CEYLON—169	Soapstone	Gold
Rubber	Lithographic stone	Molasses
Cocoanut oil	Tin foil	Sugar
Plumbago	Copper foil	Hides
Citronella oil	Steel wire	Citrate of lime
	Brass wire	Lime oil

## BOOK REVIEWS

**Industrial Chemistry for Engineering Students.** By HENRY K. BENSON, PH.D., Professor of Industrial Chemistry in the University of Washington. New York: The Macmillan Company. 1913. About 12mo., xiv + 431 pages. Price, \$1.90.

In the words of the author, "The purpose of this text is to describe from the standpoint of chemistry, the most common materials used in the various branches of engineering. Emphasis is accordingly laid upon the occurrence, the mode of manufacture, the properties, and, to a limited extent, the uses of the various materials." It is stated to be "an elaboration of the author's lecture notes used during the last eight years in the courses of industrial chemistry for second year engineering students." The book includes the following chapters: General Processes and Apparatus; The Atmosphere; Industrial Water; Combustion and Destructive Distillation; Solid Fuels; Liquid and Gaseous Fuels; Petroleum and Lubricating Oils; Manufacture of Pig Iron; Commercial Forms of Iron and Steel; Industrial Alloys; Clay Products; Hydraulic Cements and Lime Products; Paving Materials and Wood Preservation; Paint and Varnish Materials; Plastics for Electrical Insulation; Cellulose Products; Explosive Materials.

Books of this kind will be in demand before long in engineering and technical schools as the increasing importance of the chemistry of engineering materials and operations, and the fact that many of their problems are essentially chemical ones, become impressed upon our engineers. Few engineering schools as yet have devoted time specifically to this purpose, very justly feeling that the inexperience of chemistry professors in engineering matters would seriously discount the value of the instruction. Such attention to the matter as is unavoidable is usually given in connection with specific engineering subjects by the engineer in charge. This treatment is succinct—a great advantage to the student, for while some engineers are reasonably good chemists, yet the average chemical intelligence of even engineering teachers is often pathetic to the same degree as is the engineering intelligence of chemistry teachers.

While not strictly the first, Dr. Benson is one chemist who has had the courage and the industry to attempt to be of service in this field. One might take exception perhaps to the calling of such a course as covered by this book, *Industrial Chemistry*, when it professes to be a course in the chemistry of engineering materials. The words *Industrial Chemistry* can doubtless be applied to such work, though many of us, I believe, would prefer that it be confined as is generally done, to the study of the chemical and engineering problems involved in the manufacture of chemical substances or the solution of industrial manufacturing problems by chemical means or operations, a matter not exactly germane to the training of civil or electrical engineers, for example. From the point of view of the author's expressed purpose the work in question should be called *Engineering Chemistry* or the *Chemistry of Engineering (Materials)*. The author was doubtless hampered by the fact that his college catalogue labeled his course *Industrial Chemistry* instead of *Engineering Chemistry* and, therefore, it is to be expected that this confusion would be difficult to repress in the book itself and an attempt made to cover both fields. The book lives up more closely to its title than to its purpose. It really is a series of chapters from *Industrial Chemistry* and, therefore, contains much material which has little general engineering interest though important to the industrial chemist or chemical engineer.

In commenting specifically upon the treatment of the different topics in the book the reviewer is attracted to those portions with which he is more familiar or with whose leaders he has had the most contact,

By "Charcoal Retorts," on p. 95, probably is meant the modern oven plants which with two exceptions in the U. S. are rectangular in shape. The common retort plants, of which there are still above twenty-five in the U. S., use cylindrical retorts exclusively but this type uses a retort of less than a cord capacity and never uses cars in the retort in this country. The statement that "acetic acid (2%)" and "methyl alcohol (7%)" is obtained from hardwood is not commercial experience. It may be the figures were intended to have been reversed. Vacuum evaporators are not yet a success on acetate of lime in this country, nor is *brown* acetate of lime made from redistilled pyroligneous acid. The product is gray acetate. Neither is the dried acetate of lime "usually . . . . moderately heated to volatilize the tarry matter which separates," etc. It is scarcely proper to say acetate of lime "is almost completely utilized in the manufacture of acetic acid" without intimating that our acetone supply comes from the destructive distillation of this same acetate of lime.

The obvious necessity for brevity has at times led the author into a position open to serious misinterpretation. For instance, the statement that the Semet Solvay and Otto Hoffman ovens "are identical in principle, the main difference being in the arrangement of the flues for the combustion of the gases used in heating them," hardly represents the facts. Then a few lines further both types are covered in a joint description, most of which deals with their *regenerative checker work systems*. This faces a full page illustration of sections through the Semet-Solvay type very properly showing no regenerative checker work whatever.

One wonders why students must be introduced solely to the German method of distilling Coal Tar, when American practice is so admirably and thoroughly handled by one who knows, in Rogers and Aubert's "Industrial Chemistry" in the Chapter by F. E. Dodge. This account—the best ever written—is not even cited.

In such a brief treatment of the clay-products, nine pages devoted to a classification of clays which is largely geological seems excessive even if it has the merit of being the hitherto unpublished work of an eminent authority (Dean Edward Orton, Jr.). The rational analysis of clay is given large space in proportion to its standing. Crushing strength, as well as the tensile strength mentioned, is used as a measure of cohesive strength of clays. Air shrinkage in drying clay products should have been given as running from two to fifteen per cent, averaging about five per cent. Quartz should have been included in the list specific gravities of clay constituents. The Citation: "The Uses of Hydraulic Cements," p. 310, is by Eno and not Bleining as given.

Cold curing of rubber is stated to be accomplished by treating a *solution* of rubber in carbon disulfide with sulfur monochloride, instead of treating the uncured or the compounded rubber with sulfur monochloride dissolved in carbon disulfide, etc. The description of "ethyl alcohol from sawdust" hardly leaves one sufficiently impressed with the fact that this industry is still in the "prospect" stage.

As may be seen from the list of chapters already mentioned the topics treated in the book are well selected from an engineering point of view. The illustrations are usually very good and for the most part quite modern and refreshing. The excellent bibliography at the end of each chapter is a very commendable feature of the book.

JAMES R. WITHROW

**Metallurgy of Copper.** By H. O. HOFMAN. 8vo. 556 pp. McGraw-Hill Book Company, New York. Price, \$5.00.

In his "General Metallurgy" Dr. Hofman promised to supplement it with special volumes dealing with the principal metals,

and has issued this, the first of them, with commendable promptness. The "Metallurgy of Copper" is a worthy successor to the other book and will prove of much value and interest, not only to copper smelters but to those engaged in other branches of metallurgy.

The introduction is followed by short, but sufficient, chapters on "Commercial Copper, Its Impurities and Their Effects," "Alloys," "Compounds" and "Ores." After this, the various smelting processes for sulfide ores are taken up in order—Roasting, Blast Furnace Smelting, Reverberatory Smelting, The Converter. In each case the necessary apparatus is fully described and well illustrated from current practice—from American practice wherever possible. The variations under different conditions are pointed out and the reasons for them explained, with their advantages and disadvantages. The conduct and theory of the operations are fully given and in such a manner that theory and practice go hand in hand.

The smelting of native copper and of oxidized ores are then described in the same thorough manner. This is followed by an excellent chapter on refining.

The next section of the work deals with hydrometallurgy, giving the methods that have been proposed and tried for ores, matte and metal. While many of the processes described have not succeeded, they are of interest and value. In many cases they are the basis of experiments now being undertaken with a better chance of success, owing to changed commercial conditions and the better means now available for handling large quantities of ores and solutions. In this, as in the earlier chapters, the descriptions are clear and full, and the amount of information given is very large.

The last chapter deals with Electrolysis, and describes the principles and process clearly and well, giving good descriptions of plants using each of the modifications of the process.

One of the most valuable features of this, as of his previous book, is the copious bibliography and its convenient arrangement as foot-notes to each page. The proof-reading has been better, and there are fewer errors due to carelessness in this respect. The paper and binding, unfortunately, are no improvement on the "General Metallurgy." Altogether, Dr. Hofman has produced an excellent book which can be heartily recommended to all interested in the subject.

GEORGE C. STONE

**Fixation of Atmospheric Nitrogen.** By JOSEPH KNOX, D.Sc., Lecturer on Inorganic Chemistry, University of Aberdeen. Published by D. Van Nostrand Company. Price, 75 cents.

The book is divided into three sections: Section I deals with the conversion of atmospheric nitrogen into nitric and nitrous acids and their salts. The first part briefly describes the physico-chemical researches made in order to determine: whether the reaction is thermal or electrical; the best yield of nitric acid in the arc; the processes for the absorption of the acids; etc. The second part describes the most important processes in existence for the technical manufacture of nitrates and nitrites.

Section II takes up the synthesis of ammonia and ammonium compounds from atmospheric nitrogen. A short description of the Haber process is given with the data obtained from the experimental furnace. The technical manufacture of ammonia is not described.

Section III discusses the conversion of atmospheric nitrogen into compounds which readily yield ammonia. The various nitrides are mentioned. Serpek's aluminum nitride and the calcium cyanamide processes are discussed, both from the scientific and technical aspects.

The bibliography given at the end of the book is fairly complete, and deserves attention.

Owing to the fact that the subject matter of this chemical

monograph is very extensive, one cannot expect the author to cover his subject in 102 pp. with any degree of thoroughness. The book may be recommended to those who wish to get a bird's-eye view of the subject of Fixation of Atmospheric Nitrogen, from the scientific as well as from the commercial point of view.

ALEXANDER LOWY

**Neues Handbuch der Chemischen Technologie.** Published by Friedr. Vieweg & Sohn in Braunschweig. Editor-in-Chief, Prof. Dr. C. Engler, Karlsruhe, Germany.

There are seven volumes in this "handbook" series, which, like the following three volumes, can be considered as separate books and bought as such. While this series is intended as a third edition of Bolley's "Handbuch der Chemischen Technologie," so many changes have been made in revising and modernizing the older editions that an entirely new title has been selected.

Vols. I and II. **The Coal-tar and Ammonia Industry.** By DR. GEORGE LUNGE AND DR. HIPPOLYT KÖHLER. Vol. I, **Steinkohlenteer**, 928 pp., and 354 illus. Price, 30 Marks.

This volume is divided into ten chapters as follows: 1—Coal as Raw Material of Coal-tar. 2—Sources of Tars for Raw Material in the Coal-tar Industry. 3—Properties of Coal-tar and of Its Constituent Parts. 4—Uses of Coal-tar without Distillation. 5—The First Distillation of Tar. 6—Pitch. 7—Anthracene Oil. 8—Heavy Oil. 9—Second Light Oils (phenol, cresole and naphthalene). 10—Light Oils. The book is clearly printed on a very good quality of paper and is profusely illustrated throughout. A great deal of attention is given to the mechanical side of the coal-tar industry, and while most of the illustrations are line drawings, in some cases actual photographs have been used, thus showing clearly the construction and operation of most of the apparatus used. The chemical side of the industry is equally well presented, and many tables of physical constants are given. There are also numerous references to the literature and patents. This book is very complete and should prove of great value to those chemists interested in coal-tar and should be in every reference library.

Vol. II, **Ammonia**. 462 pp. 163 illus. Price, 16 Marks.

There are eight chapters: 1—History of Ammonia; Development and Future of the Ammonia Industry. 2—Properties of Ammonia and Its Technically Prepared Salts. 3—Natural Occurrences of Ammonia and Suggestions for Its Industrial Manipulation. 4—Composition and Analysis of Ammonia Water. 5—Manufacture of Ammonia Water. 6—Production of Spirits of Ammonia and Liquid Ammonia. 7—Production of Ammonium Sulfate from Ammonia Water. 8—Manufacture of Other Technically Important Ammonium Salts (Chloride, Fluoride, Ferrocyanide, Sulfo-cyanide, Carbonate, Nitrate, Nitrite, Persulfate, Perchlorate, Thio-sulfate, Phosphate, Chromate, Formate, Acetate, Oxalate). The many advances and improvements in the manufacture of illuminating gas and the production of coke, especially the by-products, fully justify this new edition, which, like Vol. I, should prove a valuable reference book.

Vol. V. **Manufacture of Lamp Black and Charcoal.** By HIPPOLYT KÖHLER. 221 pp. 114 illus. Price, 8 Marks.

This, the third edition, is about the only book published which thoroughly covers the manufacture and uses of lamp black and charcoal. Dr. Köhler has brought this edition up to date and has paid considerable attention to the uses of charcoal as a decolorizing agent. The book is even more fully illustrated than Vols. I and II, and contains, as well, many analyses and valuable tables. It is divided into four chapters: 1—General Information of the Properties and Uses of Carbon. 2—Lamp Black. 3—Charcoal. 4—Examination and Investigation of Lamp Black and Charcoal.

This series of valuable books would be of even greater interest and value to American chemists and students if they were translated into English. German fashion, they are published in both

cloth and paper bindings, the paper binding being about 25 cents cheaper. The "Neues Handbuch" series should be well bound and on the shelves of all chemical libraries.

ROBERT K. MURPHY

**Examination of Lubricating Oils.** By THOS. B. STILLMAN, M.Sc., Ph.D. Easton, Pa.: The Chemical Publishing Co., 1914. 125 pp. Price, \$1.25.

The descriptions of the determination of specific gravity and cold test are very full and complete. For the determination of viscosity, among other instruments, the Saybolt "A" viscosimeter is described. His universal which has replaced the A, B, and C forms is not mentioned. The statement that "Tagliabue's Viscosimeter is used to a very large extent by the manufacturers of lubricating oils in the United States" would seem to be open to question as are also the readings obtained with it.

In the description of the flash test, the Abel tester for *burning oils* is given, and the apparatus perhaps most extensively used in this country for lubricating oils—the Cleveland Tester—barely noticed.

The book contains a number of tables, pp. 10, 12, 35, and 51. It would have economized space and detracted nothing from the use of the work to have condensed these into one, and it would have saved time for the user had the oils there given been arranged alphabetically. These tables are from results obtained in the author's laboratory; while they are valuable as showing American conditions, yet it would seem to have been advisable to have included as well the limits of the usual characteristics found. For example, the iodine number of neat'sfoot oil is given as 80-82; inasmuch as the highest figures usually reported are 72-76, it would seem as if these samples were suspicious.

The directions for the valuable Maumené and Iodine tests are very incomplete, the precautions necessary for their successful use not being fully given.

Nearly two pages are devoted to color tests for the different oils, notwithstanding the fact that they are notoriously unreliable; strangely enough the best one of them all—The Halphen test for cottonseed—is omitted. The method for the separation of mineral from the organic oils leaves something to be desired as the ethyl ether used dissolves some of the soap formed.

The references to the Proceedings of the American Society of Testing Materials, pp. 48, 60-65, are not clearly given, and in some cases material has been taken from this source without it being so indicated. Nor is the selection of testing machines a particularly happy one, those considered the best not being clearly mentioned.

The chapter on specifications for the various oils used by the various railroads, cities, and the federal government will be found valuable, as will also the procedure for the analysis and synthesis of cylinder oils, and the analysis of cylinder deposits.

A. H. GILL

**Laboratory Course in Electrochemistry.** By OLIVER P. WATTS, Ph.D. New York: McGraw-Hill Book Company. 150 pp. Price, \$1.00.

There are several books at present both in English and German dealing with this subject, but this manual by Dr. Watts is of special interest, as it evidently follows the work in applied electrochemistry as it is conducted at the University of Wisconsin.

The book deals with electrochemistry in aqueous solution and does not touch on the subject of the electric furnace either for thermic or electrolytic purposes. Beginning with a short description of suitable equipment and very excellent advice to the student, there is given a list of experiments covering Faraday's law, resistivity of electrolytes, electromotive force, discharge potentials, passive state corrosion, separation and plating of metals and electrolytic preparations. Particular attention is

given to the subject of electroplating and the treatment is excellent.

It would have been better to have had more sketches or diagrams in some of the experiments described as it would enable the student to grasp the meaning more quickly.

Comparatively little attention is given to the electrolytic separation of metals as it is recognized that this subject is treated very fully in other books on the subject.

An excellent feature of the book is in giving references as each subject is taken up.

Organic preparations are not touched on and the inorganic preparations are mostly taken from the several books dealing with this subject.

The appendix includes some useful tables and one of particular interest—giving the approximate potentials of the metals in various electrolytes as the data were obtained by the students in their regular work in the University.

The book will be found very helpful in the laboratory teaching of applied electrochemistry.

SAMUEL A. TUCKER

**Chemistry of Rubber.** By B. D. PORRITT, B.Sc., F.I.C., Chief Chemist to the North British Rubber Company and published by D. Van Nostrand Company, New York City, 1913; one of a series of Chemical Monographs edited by A. C. Cumming. Price, \$0.50.

The book contains 93 pages of subject matter. It is an admirable, briefly written review of the status of rubber chemistry up to the time it was printed. The author is to be commended for excellent English, brevity of expression and freedom from unduly emphasizing or advocating theories upon which there are several dissimilar points of view. It contains the following divisions:

I—The Properties of Crude Rubber. II—Constitution and Derivatives. III—Methods of Vulcanization. IV—Theories of Vulcanization. V—Waste Rubber and Its Utilization. VI—Synthetic Caoutchouc.

These are followed by a bibliography of the published work referred to in the body of the text and a brief index.

The book is an excellent one for students and for those who wish a brief statement of the essentials of rubber chemistry.

W. C. GEER

**A Chart of the Carbon Compounds.** Prepared by CHARLES W. CUNO, A.M. Published by the Department of Efficiency, University of Denver, University Park, Colo. Size, 31½ × 43½ in. Price, postage paid, \$0.30.

"The chart is designed for student use in Organic Chemistry, but may also be of value to chemists in organic work." It gives the divisions of organic compounds, such as hydrocarbons, halogen derivatives, alcohols, etc., in the horizontal rows and the different classes under each divisional heading in the vertical rows. This arrangement brings both aliphatic and aromatic compounds in the same general division and is very good. In each case are usually given the general formula, structure, methods of synthesis, and chemical properties as shown by reactions. The chart is printed plainly and is generally well arranged. Some of the structural formulas, however, are awkward, and it is unfortunate that there should be so many typographical errors in structural and empirical formulas and in the names of compounds. There are a number of statements which are misleading, and there are some to which many chemists would take exception. The chemistry is that of the text-books of a number of years ago. There is no mention of the important Grignard methods and of the many applications of metals and of catalytic reductions in syntheses.

A chart visualizes and correlates facts and relationships and therefore it will always be of service.

HARRY L. FISHER

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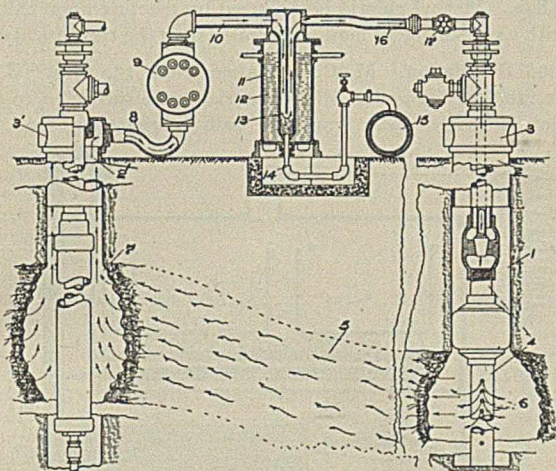
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## RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Ferment.** P. Altenfeld, August 4, 1914. U. S. Pat. 1,105,601. A dough is formed of malt, rye, corn-flakes and water and allowed to ferment at a relatively low temperature.

**Gasoline.** J. W. Waitz, August 4, 1914. U. S. Pat. 1,105,727. This process is designed for the production of the lighter hydrocarbon liquids, and vapors, notably gasoline, from the older developed territories where the natural gas pressure is reduced to such an extent that such hydrocarbons will not flow spontaneously from the wells which have been drilled into the



producing strata or where the supply of such hydrocarbons has been almost exhausted. Air or gas under pressure is passed at a comparatively low temperature through a stratum in which hydrocarbon fluids are contained; the resulting saturated air or gas is then put through a condenser to separate the desired hydrocarbons.

**Refining Vegetable and Animal Oils.** C. Baskerville, August 4, 1914. U. S. Pat. 1,105,744. The oil is agitated with fibrous vegetable material impregnated with an alkali, the fibrous material and contained impurities being later filtered out.

**Gas from Oil.** W. A. Hall, August 4, 1914. U. S. Pat. 1,105,772. A combustible gas is produced by subjecting a mixture of mineral oil and water to the action of metallic nickel at a temperature of about 650° to 750° C.

**Stannic Chlorid from Materials Containing Tin Oxid.** H. Goldschmidt, August 4, 1914. U. S. Pat. 1,105,902. Oxid of tin is reduced under conditions to produce a porous mass containing the tin in a metallic state and this mass is subjected to the action of chlorin gas.

**Gasoline from Fuel Oil.** W. M. Burton, August 4, 1914. U. S. Pat. 1,105,961. Fuel oil or other products of petroleum distillation having a boiling point of upward of 500° F. is distilled at a temperature of from about 650° F. to about 850° F., the volatile constituents of the liquid being conducted off and condensed under a pressure of from about 4 to 5 atmospheres. The volatile constituents of the residue are then distilled off under approximately atmospheric pressure. The product of the last condensation is then re-subjected to the first treatment.

**Isoprene.** Earle and Kyriakides, August 5, 1914. U. S. Pat. 1,106,290. The vapors of methylisopropylketone are passed over heated aluminum silicate and the isoprene is separated from the other products of the reaction.

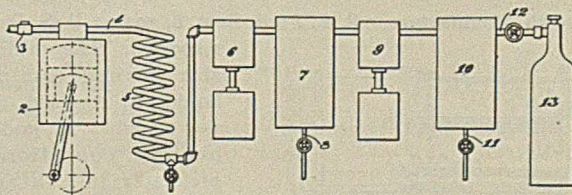
**White Lead.** E. Euston, August 11, 1914. U. S. Pat. 1,106,793. The composition is produced by the admixture of a precipitate formed by carbon dioxide gas from a basic lead acetate solution eventually approximately neutral with a precipitate formed by carbon dioxide gas from basic lead acetate solution eventually acid. The admixture is made in proportions to form a pigment containing 11.0 per cent to 14.5 per cent carbon dioxide.

**Argon and Rare Atmospheric Gases.** J. E. Bucher, August 11, 1914. U. S. Pat. 1,106,921. Argon and incidentally the other rare inert atmospheric gases helium, xenon, krypton, and neon are separated from atmospheric nitrogen by passing such nitrogen, free from oxygen, over a heated reactive mass containing finely divided catalytic material (preferably iron filings), associated with carbon and free alkali metal (preferably sodium) and collecting the gaseous residues of the reaction.

**Potassium Compounds from Silicious Materials.** T. B. Stillman, August 11, 1914. U. S. Pat. 1,106,984. The potash-bearing silicious material is ground, mixed with a sufficient quantity of carbonate of potash to convert all of the silica present into potassium silicate and the mixture fused at a high temperature. The fusion is ground and the potassium aluminate and potassium oxid are extracted with cold water. The solution is made more alkaline and then sufficient ammonium salt to precipitate all of the alumina in the aluminate of potash as hydrated aluminum oxid; the liquor is then separated from the precipitate and charged with a sufficient carbonic acid to convert the potassium hydroxide to carbonate of potash. The solution is then evaporated and the potash recovered from the cold-water-insoluble residue.

**Tanning Compound.** L. Pollak, August 11, 1914. U. S. Pat. 1,107,107. The composition is produced by condensing phenol, sulfuric acid and grape sugar.

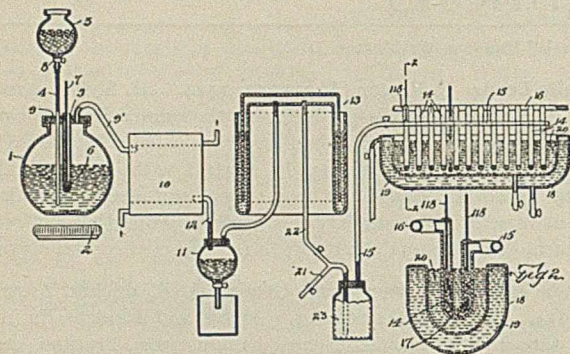
**Carbon Monoxid, Hydrogen, and Nitrogen.** Brownlee and Uhlinger, August 18, 1914. U. S. Pat. 1,107,581. Carbonaceous material, preferably gas or gasoline vapor, is mixed with an amount of air sufficient to support incomplete combustion of the mixture to produce a maximum amount of carbon monoxid and hydrogen and the mixture is exploded preferably in an



internal combustion engine. The carbon monoxid, hydrogen and nitrogen are then separated from the exhaust gases. The products of combustion, water vapor, carbon dioxide, carbon monoxid, hydrogen and nitrogen pass through the exhaust pipe 4 to a refrigerating coil, 5, where the gases are cooled and the moisture separated as water, thence to compressor 6 where the gases are compressed and the carbon dioxide is liquefied and collected in the holder 7. The hydrogen, carbon monoxid and nitrogen pass to a compressor, 9, where the gases are further compressed and the carbon monoxid and nitrogen are liquefied and collected in a holder, 10. The remaining hydrogen passes through outlet 12 to a receiver or holder, 13.

**Ethane.** Mulliken and Moore, August 18, 1914. U. S. Pat. 1,107,696. In this process exothermic compounds, such as ethane,

are produced from endothermic compounds, such as ethylene or acetylene, by subjecting the latter in the presence of a re-



ducing agent to catalytic action and simultaneously refrigerating the product to extract the heat liberated by the reaction.

**Boric Acid.** A. Burger, August 25, 1914. U. S. Pat. 1,108,120. Boric acid is produced by calcining a borate and heating the resulting products with carbon dioxide in the presence of water.

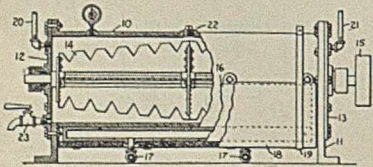
**Water-Repellent Cement.** C. Ellis, Sept. 1, 1914. U. S. Pat. 1,109,120. Waterproof concrete is produced by mixing with the cementitious material a composition containing mineral oil, a water-soluble soap in solution and a water-insoluble soap.

**Refining Petroleum and Its By-Products.** E. A. Starke, Sept. 1, 1914. U. S. Pat. 1,109,187. Aromatic hydrocarbons are separated from petroleum by adding sulfuric acid and subjecting the mixture to agitation in a closed vessel in the presence of heat until the specific gravity of the oil becomes constant and no longer decreases upon the addition of sulfuric acid. The sulfur dioxide produced by the reaction is not allowed to escape but is retained by the oil from which it is later separated by blowing in air or steam. The treated oil is allowed to settle until the sulfonic acids have separated from the petroleum and are drawn off.

**Stable Hydrogen Peroxid.** A. Schaidhauf, Sept. 8, 1914. U. S. Pat. 1,109,791. A neutral solution of hydrogen peroxid is rendered stable by the addition of soap.

**Softening Water.** H. Ley, Sept. 8, 1914. U. S. Pat. 1,109,849. The water is treated with a precipitate obtained by mixing a solution of phosphate of soda with a solution of an alkali-metal silicate.

**Varnish Manufacture.** S. E. Ford, Sept. 8, 1914. U. S. Pat. 1,109,979. The oxidizable varnish-forming liquid is confined in the chamber 10 under oxidizing conditions, preferably in contact with ozone, and heated and agitated to reduce it to a fine spray.



**Formaldehyde.** H. von Hochstetter, Sept. 8, 1914. U. S. Pat. 1,110,289. A mixture of methyl alcohol vapor and air is conducted over metallic silver with which metallic rhodium is associated, the vapor mixture being caused to contact with the metals at an elevated temperature.

**Aluminum Fluorid.** C. A. Doremus, Sept. 15, 1914. U. S. Pat. 1,110,675. Aluminum fluorid having variable amounts of water of crystallization (or none) is obtained by heating in a closed vessel a solution of aluminum fluorid, the proportion of water of crystallization diminishing as the temperature applied is raised.

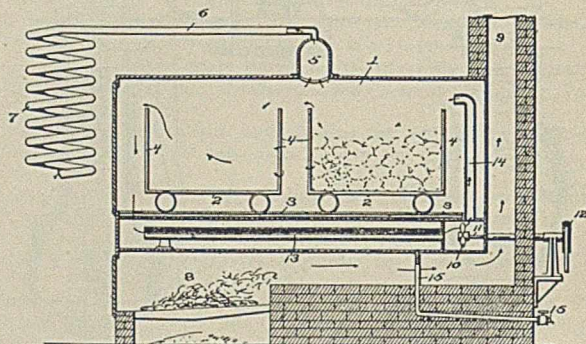
**Pure Turpentine.** T. W. Pritchard, Sept. 15, 1914. U. S.

Pat. 1,110,819. Pure turpentine is obtained from impure turpentine by drawing through it air warmed to a temperature of not substantially above 212° F. and condensing the vapors drawn off with the air.

**Treating Heavy Hydrocarbon Oils.** C. J. Greenstreet, Sept. 15, 1914. U. S. Pat. 1,110,923. Crude oil is converted into light hydrocarbons, liquid at ordinary atmospheric temperatures, by atomizing the crude oil with steam and passing the mixture continuously through a pipe system maintained at a substantially cherry-red heat. A portion of the hot product is ignited and the proportion of crude oil and steam varied so that the flame burns without smoking. The remaining product is condensed.

**Methyl Chlorid.** B. S. Lacy, Sept. 29, 1914. U. S. Pat. 1,111,842. Methyl chlorid is produced by reacting upon chlorine gas with a proportion of methane greater than the theoretical one.

**Wood Distillation.** M. C. Whitaker, Sept. 15, 1914. U. S. Pat. 1,110,850. Wood or other material to be subjected to distillation is spaced away from the walls of the retort and the



temperature of the contents of the retort equalized by the agitation of the gases and vapors within.

By regulating the heat applied to the retort and at the same time circulating the gases and vapors about the charge, it may be brought to any temperature desired and held there so as to effectively drive off all of any substance vaporizable at that temperature.

**Copper Ores.** C. S. Vadner, Sept. 29, 1914. U. S. Pat. 1,111,874. Sulfid ores of copper naturally oxidized and sufficiently roasted are dissolved in a solution of sodium chlorid saturated with sulfur dioxide gas in the presence of heat. The excess of sulfur dioxide gas is blown out and the copper precipitated as a basic copper carbonate by adding finely pulverized calcium carbonate to the cold solution and passing air through it.

**Alkali-Silico Aluminate Richer in Alkali than Feldspar.** A. H. Cowles, Sept. 29, 1914. U. S. Pat. 1,111,881. A mixture of clay, carbon and salt is formed into small masses and subjected in a rotary furnace to the action of water vapor and furnace combustion gas.

**Wax from Other Hydrocarbons.** W. M. Burton, Sept. 29, 1914. U. S. Pat. 1,112,113. A wax-free hydrocarbon of a high boiling point is distilled under a pressure of about four atmospheres and at a temperature of about 650° F. The residuum of this distillation is then distilled at a low pressure. The distillate of the second distillation is then chilled and the paraffin wax pressed out from it.

**Phosphoric Acid.** I. Hechenbleikner, Sept. 29, 1914. U. S. Pat. 1,112,211. Natural phosphate rock mixed with silicious material and carbon is heated to produce vapors of phosphorus. The furnace gases and vapors are withdrawn in a stream which is broken up and mixed with oxygen. The resulting acid is absorbed by water in towers operated on a countercurrent system.



# MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF NOVEMBER, 1914

## ORGANIC CHEMICALS

Acetanilid.....	Lb.	34	@	—
Acetic Acid (28 per cent).....	C.	1.75	@	1.90
Acetone (drums).....	Lb.	16	@	—
Alcohol, denatured (180 proof).....	Gal.	33	@	35
Alcohol, grain (188 proof).....	Gal.	2.60	@	2.65
Alcohol, wood (95 per cent).....	Gal.	45	@	47
Amyl Acetate.....	Gal.	2.75	@	—
Aniline Oil.....	Lb.	50	@	60
Benzoic Acid.....	Lb.	60	@	70
Benzol (90 per cent).....	Gal.	34	@	35
Camphor (refined in bulk).....	Lb.	55	@	—
Carbolic Acid (drums).....	Lb.	50	@	—
Carbon Bisulfide.....	Lb.	5 1/2	@	10
Carbon Tetrachloride (drums).....	Lb.	12	@	—
Chloroform.....	Lb.	30	@	35
Citric Acid (domestic), crystals.....	Lb.	65	@	67
Dextrine (corn).....	C.	2.87	@	3.12
Dextrine (imported potato).....	Lb.	—	@	—
Ether (U. S. P., 1900).....	Lb.	15	@	20
Formaldehyde.....	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....	Lb.	21 1/2	@	25
Oxalic Acid.....	Lb.	12	@	15
Pyrogallie Acid (bulk).....	Lb.	1.90	@	2.10
Salicylic Acid.....	Lb.	70	@	75
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	2.09	@	2.30
Starch (potato).....	Lb.	—	@	—
Starch (rice).....	Lb.	—	@	—
Starch (sago).....	Lb.	—	@	—
Starch (wheat).....	Lb.	5	@	10
Tannic Acid (commercial).....	Lb.	60	@	66
Tartaric Acid, crystals.....	Lb.	43 1/2	@	46

## INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 1/4	@	7 1/2
Acetate of Lime (gray).....	C.	1.75	@	1.90
Alum (lump).....	C.	2.75	@	3.00
Aluminum Sulfate (high-grade).....	C.	1.50	@	2.00
Ammonium Carbonate, (domestic).....	Lb.	9	@	10
Ammonium Chloride, (gray).....	Lb.	6 1/4	@	6 3/4
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/2
Arsenic (white).....	Lb.	4 1/2	@	6
Barium Chloride.....	Ton	75.00	@	90.00
Barium Nitrate.....	Lb.	15	@	16
Barytes (prime white, foreign).....	Ton	20.00	@	27.00
Bleaching Powder (35 per cent).....	C.	1.75	@	2.50
Blue Vitriol.....	C.	4.35	@	4.55
Borax, crystals (bags).....	Lb.	4 1/4	@	4 3/4
Boric Acid, crystals (powd.).....	Lb.	7 3/4	@	8 1/2
Brimstone (crude, domestic).....	Long Ton	22.00	@	22.50
Bromine (bulk).....	Lb.	40	@	50
Calcium Chloride (lump).....	Ton	11.70	@	12.00
Chalk (light precipitated).....	Lb.	5	@	6
China Clay (imported).....	Ton	14.00	@	16.00
Feldspar.....	Ton	8.00	@	14.00
Fuller's Earth (powdered, foreign).....	Ton	—	@	—
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.65
Iodine (resublimed).....	Lb.	3.75	@	4.00
Lead Nitrate.....	Lb.	8 1/4	@	8 1/2
Litharge (American).....	Lb.	5	@	5 1/4
Lithium Carbonate.....	Lb.	1.00	@	1.10
Magnesium Carbonate.....	Lb.	4 3/4	@	6
Magnesite "Calcined".....	Ton	40.00	@	50.00
Nitric Acid (36°).....	Lb.	37 1/8	@	41 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	28	@	28 1/2
Phosphorus.....	Lb.	35	@	95
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate.....	Lb.	12	@	14
Potassium Bromide.....	Lb.	70	@	80
Potassium Carbonate (calcined), 80 @ 85%.....	C.	12	@	15
Potassium Chlorate, crystals.....	Lb.	20	@	22
Potassium Cyanide (bulk), 98-99%.....	Lb.	25	@	30
Potassium Hydroxide.....	C.	32.00	@	40.00
Potassium Iodide (bulk).....	Lb.	3.15	@	3.25
Potassium Nitrate (crude).....	Lb.	—	@	—
Potassium Permanganate (bulk).....	Lb.	20	@	25
Quicksilver, Flask (75 lbs.).....	Oz.	50.00	@	55.00
Red Lead (American).....	Lb.	5 1/2	@	6
Salt Cake (glass makers').....	C.	55	@	65
Silver Nitrate.....	Oz.	31	@	33

Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	5	@	7
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	3 1/2	@	4
Sodium Bichromate.....	Lb.	4 3/4	@	5
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	16	@	18
Sodium Hydroxide (60 per cent).....	C.	1.55	@	1.57 1/2
Sodium Hyposulfite.....	C.	1.60	@	1.90
Sodium Nitrate (95 per cent, spot).....	C.	1.85	@	1.90
Sodium Silicate (liquid).....	C.	60	@	70
Strontium Nitrate.....	Lb.	15	@	17
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid (60° B).....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	9 1/4	@	10
Tin Oxide.....	Lb.	38	@	40
White Lead (American, dry).....	Lb.	5	@	5 1/4
Zinc Carbonate.....	Lb.	8 1/2	@	9
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 1/8	@	6 3/8
Zinc Sulfate.....	C.	2.35	@	2.70

## OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	45	@	57
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	8 1/4	@	9
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	5.35	@	5.45
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	33	@	34
Cottonseed Oil (p. s. y.).....	Lb.	5 1/2	@	6
Cylinder Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	12	@	13
Lard Oil (prime winter).....	Gal.	90	@	92
Linseed Oil (raw).....	Gal.	46	@	47
Menhaden Oil (crude).....	Gal.	33	@	—
Naphtha, 68 @ 72°.....	drums	—	@	17
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/8	@	3 1/4
Paraffine Oil (high viscosity).....	Gal.	27	@	28
Rosin ("F" grade) (280 lbs.).....	Bbl.	3.95	@	4.05
Rosin Oil (first run).....	Gal.	25	@	—
Shellac, T. N.....	Lb.	14	@	14 1/2
Spermaceti (cake).....	Lb.	28	@	30
Sperm Oil (bleached winter), 38°.....	Gal.	70	@	71
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9	@	11
Tallow (acidless).....	Gal.	64	@	66
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	48	@	48 1/2

## METALS

Aluminum (No. 1 ingots).....	Lb.	18 1/2	@	19
Antimony (Hallet's).....	Lb.	15 1/2	@	16 1/2
Bismuth (New York).....	Lb.	2.80	@	2.90
Bronze powder.....	Lb.	—	@	—
Copper (electrolytic).....	C.	12.07 1/2	@	12.12 1/2
Copper (lake).....	C.	12.12 1/2	@	12.25
Lead, N. Y.....	C.	3.90	@	—
Nickel.....	Lb.	—	@	—
Platinum (refined).....	Oz.	50.00	@	52.00
Silver.....	Oz.	49 1/8	@	—
Tin.....	C.	32.10	@	—
Zinc.....	C.	5.20	@	5.25

## FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2.55	@	2.62 1/2
Blood (dried).....	Unit	3.15	@	3.20
Bone, 4 1/2 and 50 (ground, raw).....	Ton	27.50	@	—
Calcium Cyanamid.....	Unit of Ammonia	2.30	@	2.35
Calcium Nitrate (Norwegian).....	C.	—	@	—
Castor meal.....	Unit	—	@	—
Fish Scrap (domestic, dried).....	Unit	3.00	@	10
Phosphate, acid (16 per cent bulk).....	Ton	7.50	@	—
Phosphate rock; f. o. b. mine:				
Florida land pebble (68 per cent).....	Ton	2.25	@	2.50
Tennessee (70-80 per cent).....	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent.....	Ton	—	@	nominal
Pyrites (furnace size, imported).....	Unit	13	@	—
Tankage (high-grade).....	Unit	3.15	@	10