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THE ANNUAL MEETING AT ROCHESTER

The Forty-eighth Annual Meeting of the American Chemical Society was held in Rochester, New York, September 8th to 14th. This is the first meeting held in the fall of the year under the newly adopted constitution, and is by far the most successful in the history of the Society. The large and representative attendance amply justifies the change in date for the annual meeting from the Christmas holidays to the fall of the year.

We publish elsewhere in this issue the program of papers presented to the general meetings and the various sectional meetings, and a study of the list will show an unusual number of valuable contributions to theoretical and applied chemistry. The greater portion of the papers in this program will be published in full in the Journals of the Society.

President Little's address was given on Wednesday morning at a general meeting in the East High School. The Sectional meetings were held in the Eastman Building, University of Rochester. The presidential address, which follows in full, is a most authentic and comprehensive treatment of the subject of Industrial Research in America, and its statements of the extent and thoroughness of this development in our more progressive industries will be a surprise to many of our readers. A careful reading of this address will undoubtedly suggest to delinquent American manufacturers that serious and genuine Industrial Research will offer the only means by which they may avoid the otherwise inevitable steam roller of crumbling tariff walls, foreign competition and antiquated methods and products.

The general meeting of the Society on September 9th was preceded by a meeting of the Board of Directors at the Hotel Seneca on Monday afternoon. The Rochester Section of the Society entertained the Council at dinner on Monday evening, after which the formal meeting of the Council was called to order by President Little. Dr. Chas. L. Parsons was elected Secretary of the Society and Dr. A. P. Hallock, Treasurer for a period of three years under the new constitution. The editors and editorial boards of the Society's journals were reëlected for the current year, and the editorial staff of the *Industrial Journal* was strengthened by the addition of two assistant editorships.

The first general session was held in the Assembly Hall of the Eastman Kodak Company plant at Kodak Park, on Tuesday morning, and was opened by a cordial address of welcome by Mayor Edgerton. Papers were presented by Messrs. J. O. Handy, C. E. K. Mees, B. C. Hesse, G. A. Soper and Henry Leffmann.

At the conclusion of the morning session, the members and their guests were entertained at luncheon by the Eastman Kodak Company. After luncheon the manufacturing departments and laboratories of the plant were thrown open to inspection, and under the guidance of the technical members of the Eastman staff the visitors were given an excellent opportunity to see one of the most highly developed industries in America.

The Rochester Section entertained the visiting members on Tuesday evening, at a smoker in Masonic Hall. The Entertainment Committee, under the direction of M. H. Eisenhart, ably assisted by large committees from the Rochester Section, provided a most elaborate program and feast for this occasion. Each guest was decked out in a commodious white apron, on which was inscribed, in bold letters, his name and address, and, as a protection against draughts a Chinese mandarin cap with pigtail. The liquid refreshments were provided in the form of a special brew supplied by the Moerlback Brewery. The Smoker program was arranged with great care and consisted of selections by professional talent interspersed with much music from an orchestra, songs from a membership quartet, unusually interesting and instructive moving pictures, and several impromptu parades by guests. The entire function was most thoroughly organized and executed and will stand as a monument to the skill and energy of the Rochester Section.

The annual banquet was set for Thursday night at Powers Hotel. Dr. L. H. Baekeland acted as toastmaster and the principal speakers were President Rees of the University of Rochester; Edward W. Morley, past honorary president of the Eighth International Congress; President A. D. Little; H. E. Howe of Bausch & Lomb Optical Co.; C. H. Herty of the University of North Carolina; S. L. Bigelow of Washington; and Secretary C. L. Parsons. A delightful feature of the banquet was the orchestral music and a number of soprano solos.

The excursions to the plants of the Bausch & Lomb Optical Company, Taylor Instrument Company, Curtice Bros. Company, J. Hungerford Smith Company, Moerlback Brewery, German-American Button Company, Genessee Reduction Company, Municipal Incinerator, Stecker Lithographic Company, and others, under the general direction of Mr. J. E. Woodland, Chairman of the Factory Excursions Committee, proved to be one of the most important features of the Annual Meeting. Rochester, being an industrial center, is admirably situated to provide this interesting and instructive feature of the program.

The Entertainment Committee had also made ample provision for the entertainment of the lady members and visitors in the form of a reception at the University Club, a card party at the Century Club, an excursion to Irondequoit Bay with luncheon at the Newport House and numerous automobile excursions through the city and neighborhood of Rochester.

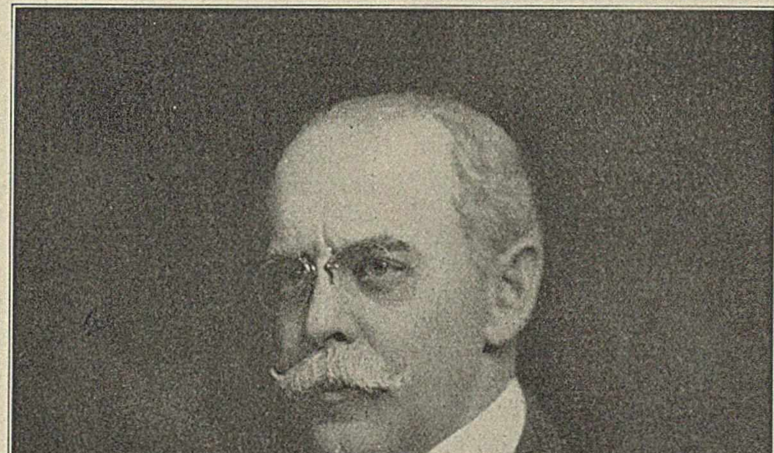
The success of the meeting is due to the work of the local committees and it was the unanimous opinion of the visiting members that to the Rochester Section belongs the credit of organizing and administering to the minutest detail the innumerable features which contributed to the complete success of the Forty-eighth Annual Meeting.

INDUSTRIAL RESEARCH IN AMERICA

PRESIDENTIAL ADDRESS

By Arthur D. Little

Germany has long been recognized as preeminently the country of organized research. The spirit of research is there imminent throughout the entire social structure. This is not the time nor place, however, nor is it necessary before this audience, to refer in any detail to the long record of splendid achievement made by German research during the last fifty years. It is inscribed in luminous letters around the rock upon which Germany now stands secure among the nations of the world.



PRESIDENT LITTLE

The virility and range of German research were never greater than they are to-day. Never before have the superb energy and calculated audacity of German technical directors and German financiers transformed so quickly and so surely the triumphs of the laboratory into industrial conquests. Never has the future held richer promise of orderly and sustained progress, and yet the preeminence of Germany in industrial research is by no means indefinitely assured. A new competitor is even now girding up his loins and training for the race, and that competitor is strangely enough the United States—that prodigal among nations, still justly stigmatized as the most wasteful, careless and improvident of them all.

To one at all familiar with the disdain of scientific teaching which has characterized our industry, and which still persists in many quarters, this statement is so contrary to the current estimate that its general acceptance cannot be expected. It will have served its purpose if it leads to a consideration of the facts which prove the thesis.

The country of Franklin, Morse and Rumford; of McCormick, Howe and Whitney; of Edison, Thomson, Westinghouse and Bell; and of Wilbur and Orville Wright, is obviously a country not wholly hostile to industrial research or unable to apply it to good purpose. It is, however, not surprising that with vast areas of virgin soil of which a share might be had for the asking; with interminable stretches of stately forest; with coal and oil and gas, the ores of metals and countless other gifts of nature scattered broadcast by her lavish hand, our people entered upon this rich inheritance with the spirit of the spendthrift, and gave little heed to refinements in methods of production and less to minimizing waste. That day and generation is gone. To-day, their children, partly through better recognition of potential values, but mainly by the pressure of a greatly increased population and the stress of competition among themselves and in the markets of the world, are rapidly acquiring the knowledge that efficiency of production is a sounder basis for prosperity than mere volume of product, however great. Many of them have already learned that the most profitable output of their plant is that resulting from the catalysis of raw materials by brains. A far larger number are still ignorant of these fundamental truths, and so it happens that most of our industrial effort still proceeds under the guidance of empiricism with a happy disregard of basic principles. A native ingenuity often brings it to a surprising success and seems to support the aphorism "Where ignorance is profitable, 'tis folly to be wise." Whatever may be said, therefore, of industrial research in America at this time is said of a babe still in the cradle but which has nevertheless, like the infant Hercules, already destroyed its serpents and given promise of its performance at man's estate.

The long-continued and highly organized research which resulted in the development of American agricultural machinery has led to the general introduction of machines which reduce the labor cost of seven crops $681,000,000 as measured by the methods of only fifty years ago.

The superhuman dexterity and precision of American shoe machinery, which has revolutionized a basic industry and reduced competition to the status of an academic question, present American industrial research at its best. They are not the result of the individual inspiration of a few inventors as is commonly supposed. They represent years of coördinated effort by many minds directed and sustained by constant and refined experimental research.

You need not be reminded that the ubiquitous telephone is wholly a product of American research. Munchausen's story of the frozen conversation which afterward thawed out is a clumsy fable. Think of the Niagaras of speech pouring silently through the New York telephone exchanges where they are sorted out, given a new direction and delivered audibly perhaps a thousand miles away. New York has 450,000 instruments—twice the number of those in London. Los Angeles has a telephone to every four inhabitants. Why should one care to project one's astral body when he can call up from the Club in fifteen seconds? Our whole social structure has been reorganized, we have been brought together in a single parlor for conversation and to conduct affairs because the American Telephone and Telegraph Company spends annually for research, the results of which are all about us, a sum greater than the total income of many universities.

The name of Edison is a household word in every language. The Edison method is a synonym for specialized, intense research which knows no rest until everything has been tried. Because of that method and the unique genius which directs its application, Italian operas are heard amid Alaskan snows and in the depths of African forests; every phase of life and movement of interest throughout the world is caught, registered, transported and reproduced that we may have lion hunts in our drawing-rooms and the coronation in a five-cent theatre. From his laboratory have come the incandescent lamp, multiple telegraphy, new methods of treating ores and a thousand other diverse inventions, the development of a single one of which has sometimes involved millions.

The development of the automobile, and especially of the low-priced American car, is a thing of yesterday. To-day a single manufacturer turns out two cars a minute, while another is expanding his output to 500 cars a day. Every 23 days the total engine horsepower of new cars of one small type equals the energy of the entire Mississippi river development at Keokuk. Every 46 days this engine output rises to the total energy development at Niagara Falls. The amount of gasoline consumed upon our roads is equal to the water supply of a town of 40,000 inhabitants, and its cost on Sundays and holidays is $1,000,000.

It goes without saying that any such development as that of the automobile industry in America has been based upon and vitalized by an immeasurable amount of research, the range and influence of which extends through many other industries. It has accelerated the application of heat treatment more than any other agency. One tire manufacturer spends $100,000 a year upon his laboratory. The research department organized by my associates for one automobile company comprised within its staff experts in automobile design, mathematics, metallography and heat treatments, lubrication, gaseous fuels, steel and alloys, paints and painting practice, in addition to the chemists, physicists and assistants for routine or special work.

The beautiful city whose hospitality has so greatly added to the pleasure and success of the present meeting of our Society is the home of two highly scientific industries of which any community may well be proud. The Bausch & Lomb Optical Company, through its close affiliation with the world-famed Zeiss works at Jena, renders immediately available in this country the latest results of German optical research. The Eastman Kodak Company is perhaps more generally and widely known than even the Zeiss works, and in capital, organization, value of product and profit of operation will bear comparison with the great German companies whose business is applied science. Like them, it spends money with a lavish hand for the promotion of technical research and for the fundamental investigation of the scientific bases on which its industry rests. As you have happily been made aware, this work is carried on in the superb new research laboratories of the company with an equipment which is probably unrivalled anywhere for its special purposes. The laboratory exemplifies a notable feature of American industrial research laboratories in that it makes provision for developing new processes first on the laboratory scale and then on the miniature factory scale.

To no chapter in the history of industrial research can Americans turn with greater pride than to the one which contains the epic of the electrochemical development at Niagara Falls. It starts with the wonderful story of aluminum. Discovered in Germany in 1828 by Wöhler, it cost in 1855, $90 a pound. In 1886, it had fallen to $12. The American Castner process brought the price in 1889 to $4. Even at this figure it was obviously still a metal of luxury with few industrial applications. Hall in America and Héroult simultaneously in Europe discovered that cryolite, a double fluoride of sodium and aluminum, fused readily at a moderate temperature, and when so fused dissolved alumina as boiling water dissolves sugar or salt, and to the extent of more than 25 per cent. By electrolyzing the fused solution aluminum is obtained. On August 26, 1895, the Niagara works of the Pittsburgh Reduction Co., started at Niagara Falls the manufacture of aluminum under the Hall patents. In 1911, the market price of the metal was 22 cents and the total annual production 40,000,000 pounds.

A chance remark of Dr. George F. Kunz, in 1880, on the industrial value of abrasives, turned the thoughts of Acheson to the problem of their artificial production and led to the discovery, in 1891, of carborundum and its subsequent manufacture on a small scale at Monongahela City, Pennsylvania. In 1894, Acheson laid before his directors a scheme for moving to Niagara Falls, when to quote his own words:

"To build a plant for one thousand horse-power, in view of the fact that we were selling only one-half of the output from a one hundred and thirty-four horse-power plant, was a trifle too much for my conservative directors, and they, one and all, resigned. Fortunately, I was in control of the destiny of the Carborundum Company. I organized a new board, proceeded with my plans, and in the year 1904, the thirteenth from the date of the discovery, had a plant equipped with a five-thousand electrical horse-power and produced over 7,000,000 pounds of those specks I had picked off the end of the electric light carbon in the spring of 1891."

The commercial development of carborundum had not proceeded far before Acheson brought out his process for the electric furnace production of artificial graphite and another great Niagara industry was founded. In quick succession came the Willson process for calcium carbide and the industrial applications of acetylene; phosphorus; ferro-alloys made in the electric furnace; metallic sodium, chlorine and caustic soda first by the Castner process, later by the extraordinarily efficient Townsend cell; electrolytic chlorates and alundum.

Perhaps even more significant than any of these great industrial successes was the Lovejoy & Bradley plant for the fixation of atmospheric nitrogen which was perforce abandoned. It is well to recall, in view of that reputed failure, that the present-day processes for fixing nitrogen have made little if any improvement in yields of fixed nitrogen per kilowatt hour over those obtained in this pioneer Niagara plant.

In the year 1800, a young assistant of Lavoisier, E. I. du Pont by name, emigrated to this country with others of his family and settled on the banks of the Brandywine, near Wilmington, Delaware. He engaged in the manufacture of gunpowder. To-day the du Pont Company employs about 250 trained chemists. Its chemical department comprises three divisions: the field division for the study of problems which must be investigated outside the laboratory and which maintains upon its staff experts for each manufacturing activity, together with a force of chemists at each plant for routine laboratory work; *second*, the experimental station which comprises a group of laboratories for research work on the problems arising in connection with the manufacture of black and smokeless powder, and the investigation of problems or new processes originating outside the company; *third*, the Eastern Laboratory which confines itself to research concerned with high explosives; its equipment is housed in 76 buildings, the majority being of considerable size spread over 50 acres. Since no industrial research laboratory can be called successful which does not in due time pay its way, it is pleasant to record that the Eastern Laboratory is estimated to yield a profit to its company of $1,000,000 a year. In addition to the generous salaries paid for the high-class service demanded by the company, conspicuous success in research is rewarded by bonus payments of stock.

In Acheson and Hall have been already named two recipients of the Perkin medal, the badge of knighthood in American industrial research. The distinguished and thoroughly representative juries which award the medal annually had previously bestowed it upon Herreshoff for his work in electrolytic copper refining, the contact process for sulfuric acid and the invention of his well-known roasting furnace, and upon Behr for creative industrial research in the great glucose industry. In 1912, it was received by Frasch, and this year it was awarded Gayley.

The Gayley invention of the dry air blast in the manufacture of iron involves a saving to the American people of from $15,000,000 to $29,000,000 annually. A modern furnace consumes about 40,000 cubic feet of air per minute. Each grain of moisture per cubic foot represents one gallon of water per hour for each 1000 cubic feet entering per minute. In the Pittsburgh district the moisture varies from 1.83 grains in February to 5.94 grains in June, and the water per hour entering a furnace varies accordingly from 73 to 237 gallons. In a month a furnace using natural air received 164,500 gallons of water, whereas with the dry blast it received only 25,524 gallons. A conservative statement according to Prof. Chandler is that the invention results in a 10 per cent increase in output and a 10 per cent saving in fuel.

Especially notable and picturesque among the triumphs of American industrial research is that by means of which Frasch gave to this country potential control of the sulfur industry of the world. There is in Calcasieu Parish, Louisiana, a great deposit of sulfur 1000 feet below the surface under a layer of quicksand 500 feet in thickness. An Austrian company, a French company and numerous American companies had tried in many ingenious ways to work this deposit, but had invariably failed. Misfortune and disaster to all connected with it had been the record of the deposit to the time when Frasch approached its problem in 1890. He conceived the idea of melting the sulfur in place by superheated water forced down a boring, and pumping the sulfur up through an inner tube. In his first trial he made use of twenty 150 H. P. boilers grouped around the well, and the titanic experiment was successful. The pumps are now discarded and the sulfur brought to the surface by compressed air. A single well produces about 450 tons a day, and their combined capacity exceeds the sulfur consumption of the world.

An equally notable solution of a technical problem which had long baffled other investigators is the Frasch process for refining the crude, sulfur-bearing, Canadian and Ohio oils. The essence of the invention consists in distilling the different products of the fractional distillation of the crude oil with metallic oxides, especially oxide of copper, by which the sulfur is completely removed while the oils distill over as odorless and sweet as if from the best Pennsylvania oil. The copper sulfide is roasted to regenerate the copper. The invention had immense pecuniary value. It sent the production of the Ohio fields to 90,000 barrels a day and the price of crude Ohio oil from 14 cents a barrel to $1.00.

Turning from these examples of individual achievement so strongly characteristic of the genius of our people in one aspect, let us again consider for a moment that other and even more significant phase of our industrial research, namely, that which involves the coördinated and long-continued effort of many chemists along related lines.

Chemistry in America is essentially republican and pragmatic. Most of us believe that the doctrine science for science's sake is as meaningless and mischievous as that of art for art's sake, or literature for literature's sake. These things were made for man, not for themselves, nor was man made for them. Most of us are beginning to realize that the major problems of applied chemistry are incomparably harder of solution than the problems of pure chemistry, and the attack, moreover, must often be carried to conclusion at close quarters under the stress and strain induced by time and money factors. Under these circumstances it should not excite surprise that a constantly rising proportion of our best research is carried on in the laboratories of our great industrial corporations, and nowhere more effectively than in the research laboratory of the General Electric Company under the guidance of your past president, Dr. Whitney. As to the laboratory method Dr. Whitney says in a personal letter: "We see a field where it seems as though experimental work ought to put us ahead. We believe that we need to get into the water to learn to swim, so we go in. We start back at the academic end as far as possible, and count on knowing what to do with what we find when we find it. Suppose that we surmise that, in general, combustible insulation material could be improved upon. We try to get some work started on an artificial mica. Maybe we try to synthesize it and soon come to a purely theoretical question; *e. g.*, is it possible to crystallize such stuff under pressure in equilibrium with water vapor corresponding to the composition of real mica? This may lead a long way and call in a lot of pure chemistry and physical chemistry. Usually we just keep at it, so that if you haven't seen it on the market we're probably at it yet."

In striking contrast to the secrecy maintained between individual workers in large German research laboratories, is the almost universal custom in America to encourage staff discussion. In the General Electric Laboratory, as in many others, the weekly seminars and constant helpful interchange of information has developed a staff unity and spirit which greatly increases the efficiency of the organization and raises that of the individual to a higher power.

Many evenings could profitably be spent in discussing the achievements of this laboratory. Their quality is well indicated by the new nitrogen tungsten lamp, with its $^1/_2$ watt per candle, which combines the great work of Dr. Coolidge on ductile tungsten with the studies of Langmuir and others of the staff on the particular glass and gas and metal which are brought together in this lamp.

Any attempt to adequately present the enormous volume of research work, much of which is of the highest grade, constantly in progress in the many scientific bureaus and special laboratories of the general government or even to indicate its actual extent and range, is of course utterly beyond the limits of my attainments or of your patience. The generous policy of the government toward research is unique in this, that the results are immediately made available to the whole people. Heavy as some of the government reports are, they cannot be expected to weigh more than the men who write them. Some, like the Geochemistry of F. W. Clarke, are of monumental character. A vast number are monographs embodying real and important contributions to scientific knowledge or industrial practice. Some, as would be expected, are little more than compilations or present the results of trivial or ill-considered research.

The United States is still essentially an agricultural country and agriculture is, in its ultimate terms, applied photo-chemistry. The value of our farm property is already over $42,000,000,000, and each sunrise sees an added increment of millions. Even small advances in agricultural practice bring enormous monetary returns. The greatest problem before the country is that of developing rural life. While our people still crowd into already congested cities, some are beginning to realize that Long Acre Square is not a wholly satisfying substitute for Long Acre Farm, and to question whether the winding, fern-fringed country roads of Vermont may not be a better national asset than the Great White Way.

Chief, therefore, among the Government Departments, in the volume of industrial research is of course the Department of Agriculture, which includes within its organization ten great scientific bureaus, each inspired by an intense pragmatism and aggressively prosecuting research in its allotted field. The magnitude of these operations of the Department may be inferred from the fact that it spent for printing alone during the fiscal year just ended $490,000. The activities of its army of agents literally cover the earth, and its annual expenditure runs to many millions. The Bureau of Soils, the Bureau of Plant Industry, the Bureau of Animal Industry and the Forest Service have to do with the very foundations of our national existence and prosperity, and their researches have added billions to the national wealth. The Bureau of Chemistry, through its relation to the enforcement of the Pure Food Law and the inspection of meats before interstate shipment, is as ubiquitous in its influence as the morning newspaper and touches the daily life of the people almost as closely. The consumer is by no means the only one benefitted by its activities. Manufacturers are protected from the unfair competition of less scrupulous producers. The progress of research is stimulated not only by investigations within the Bureau, but by their reaction upon the manufacturers of food products who are rapidly being brought to establish laboratories of their own. The food work of the Bureau is supplemented and extended by the laboratories of the state and city boards of health, of which that of Massachusetts has been notable for productive research. Special laboratories within the Bureau carry its influence and investigations into other fields as in case of the Paper and Leather Laboratory.

The Office of Public Roads of the Department, mindful of the fact that less than ten per cent of the total road mileage of the country has ever been improved, maintains a large organization of engineers, chemists and other scientists to conduct investigations and compile data, the ultimate purpose of which is to secure efficiency and economy in the location, construction and maintenance of country roads, highways and bridges.

The research work of the Department of Agriculture is greatly augmented and given local application through the agency of 64 state agricultural experiment stations established for the scientific investigation of problems relating to agriculture. These stations are supported in part by Federal grants, as from the Hatch and Adams funds, and for the rest by state appropriations. Their present income exceeds $3,000,000. All are well equipped; one of them, California, includes within its plant a superb estate of 5400 acres with buildings worth $1,000,000.

The station work is organized upon a national basis but deals primarily with the problems of the individual states. The efficiency of their work is stimulated by the requirement of the Adams Fund that appropriation shall be confined to definite projects. The number of such projects during 1910 was 335 and during 1911, 290. The reduction in number in no way implies diminished activity, and is due to more careful selection and preparation, with elimination of trivial and merely demonstrational projects. While the work of the stations necessarily covers a wide range of subjects, many of which would not be regarded as chemical in nature, a notable proportion has to do directly with chemical projects. Only the briefest reference can be made to a few of these:

At Connecticut, Osborne's studies of proteins and their feeding values have developed differences as great in their assimilability as those existing between the different carbohydrates.

Kansas has a department for the study of problems in handling and milling grain with an experimental baking plant for testing the bread-making capacity of flours. The millers are actively coöperating.

Minnesota has a similar thoroughly modern baking and testing laboratory for studies in wheat and flour chemistry and technology.

Arizona finds that date ripening may be so hastened by spraying the immature fruit with acetic acid that choice varieties are caused to ripen in that region.

The Cornell Station has demonstrated that the growth of a legume with a non-legume gives the latter a greater protein content than when grown alone.

Wisconsin has established the significance of sulfur as a plant food; grain crops, for example, remove nearly as much sulfur as they do phosphoric acid, whereas the soil supply of sulfur is far less.

Vermont is studying the forcing of plants by means of carbonic acid gas.

Idaho has raised the protein content of wheat by 50 per cent. Kentucky has developed a method for the detection of *Bacillus typhosus* in water, and North Dakota is conducting very extensive field tests on the durability of paints and oils.

These are of course mere surface references which hardly touch the real work of the stations. An enormous amount of research and routine work on fertilizers is constantly carried on by methods standardized by the Association of Official Agricultural Chemists. The theory of the action of fertilizers engages the effort of many research workers who find the problem far more complex than the old plant food theory assumed.

It may be said without fear of contradiction that through the combined efforts of the Department of Agriculture, the Experiment Stations, the Agricultural Colleges and our manufacturers of agricultural machinery there is devoted to American agriculture a far greater amount of scientific research and effort than is at the service of any other business in the world.

No other organic substance occurs in such abundance as wood, and few if any are more generally useful. About 150,000,000 tons of wood are still wasted annually in the United States. The Forest Products Laboratory which is maintained by the Forest Service in coöperation with the University of Wisconsin has for its purpose the development and promulgation of methods for securing a better utilization of the forest and its products, and its research work is directed to that end. The laboratory is splendidly equipped with apparatus of semi-commercial size for work in timber physics, timber tests, wood preservation, wood pulp and paper and wood distillation and chemistry.

In the United States Patent Office, Dr. Hall has developed a remarkably comprehensive index to chemical literature which now contains 1,250,000 cards and which is open to every worker. The Bureau of Fisheries devotes $40,000 to a single study and the Geological Survey, $100,000 to the investigation of the mineral resources of Alaska. It spent, in 1913, $175,000 for engraving and printing alone. The superb Geophysical Laboratory of the Carnegie Institution of Washington is also constantly engaged in the most refined researches into the composition, properties and mode of genesis of the earth's crust. The Smithsonian Institution is honored throughout the world for the efficiency of its effort to increase and diffuse useful knowledge among men.

The Bureau of Mines of the Department of the Interior was established to conduct in behalf of the public welfare fundamental inquiries and investigations into the mining, metallurgical and mineral industries. Its appropriation for the current fiscal year is $662,000, of which $347,000 is to be devoted to technical research pertinent to the mining industry. The Bureau has revolutionized the use of explosives in mines. Over $8,000,000 worth of coal is now bought on the specification and advice of the Bureau while more than 50 of the larger cities, a number of states, and many corporations have adopted the Bureau plan of purchase. Our own

Dr. Parsons, as chief mineral chemist of the Bureau, is carrying its researches into new and interesting fields.

Perhaps no better evidence could be adduced of the present range and volume of industrial research in America than the necessity, imposed upon the author of such a general survey as I am attempting, of condensing within a paragraph his reference to the Bureau of Standards of the Department of Commerce. Its purpose is the investigation and testing of standards and measuring instruments and the determination of physical constants and the properties of materials. To these objects it devotes about $700,000 a year to such good effect that in equipment and in the high quality and output of its work it has in ten years taken rank with the foremost scientific institutions in the world for the promotion of industrial research and the development and standardization of the instruments, materials and methods therein employed. Its influence upon American research and industry is already profound and rapidly extending. The Bureau coöperates with foreign governments and institutions, and is constantly consulted by state and municipal officials, technical bodies, commissions and industrial laboratories as a court of highest appeal.

I cannot better conclude this cursory and fragmentary reference to governmental work in applied science than with the words of the distinguished Director of the Bureau of Standards:

> "If there is one thing above all others for which the activities of our government during the past two or three decades will be marked it is its original work along scientific lines, and I venture to state that this work is just in its infancy."

In view of the evidence offered by Germany of the far-reaching benefits resulting from the close coöperation which there obtains between the university laboratory and the industrial plant, it must be admitted with regret that our own institutions of learning have, speaking generally, failed to seize or realize the great opportunity confronting them. They have, almost universally, neglected to provide adequate equipment for industrial research, and, what is more to be deplored since the first would otherwise quickly follow, have rarely acquired that close touch with industry essential for familiarity and appreciation of its immediate and pressing needs. There are happily some notable exceptions. Perhaps foremost among them stands the Massachusetts Institute of Technology with its superb engineering and testing equipment, its Research Laboratory of Applied Chemistry and the meritorious thesis work of its students in all departments. The Biological Department has been especially active and successful in extending its influence into industrial and sanitary fields, while unusual significance attaches to the motor vehicle studies just concluded and the more recently inaugurated special investigations in electricity, since both were initiated and supported by external interests. About two years ago the Institute brought vividly before the community the variety and extent of its wide-spread service to industry by holding a Congress of Technology, at which all of the many papers presented recorded the achievements of Institute alumni.

The Colorado School of Mines, recognizing that $100,000,000 a year is lost through inefficient methods of ore treatment, has recently equipped an experimental ore dressing and metallurgical plant in which problems of treatment applicable to ores of wide occurrence will be investigated. The Ohio State University has established an enviable reputation for its researches in fuel engineering. Cornell has been especially alive to the scientific needs of industrial practice, and a long experience with technical assistants enables me to say that I have found none better equipped to cope with the miscellaneous problems of industrial research than the graduates of Cornell. It may in fact be stated generally that the quality of advanced chemical training now afforded in this country is on a par with the best obtainable in Germany, and that home-trained American youth adapt themselves far more efficiently to the requirements and conditions of our industries than do all but the most exceptional German Doctors of Philosophy who find employment here.

Several of the great universities of the middle west, notably those of Wisconsin and Illinois, have placed themselves closely in touch with the industrial and other needs of their communities and are exerting a fundamental and growing influence upon affairs. In the east, Columbia has recently established a particularly well equipped laboratory for industrial chemistry and is broadening its work in this department.

The Universities of Kansas and of Pittsburgh are carrying forward an especially interesting experiment in the operation of Industrial Research Fellowships supported by the special interests directly concerned. These Fellowships endow workers for the attack of such diverse subjects as the chemistry of laundering, the chemistry of bread and baking, that of lime, cement and vegetable ivory, the extractive principles from the ductless glands of whales, the abatement of the smoke nuisance, the technology of glass, and many others. The results obtained are intended primarily for the benefit of the supporters of the individual Fellowships but may be published after three years. The holder of the fellowship receives a proportion of the financial benefits resulting from the research, and the scale of sums allotted has progressively risen from $500 a year to $2500 and even to $5000. While some doubt may reasonably be expressed as to the possibility of close individual supervision of so many widely varying projects, the results obtained thus far seem entirely satisfactory to those behind the movement, which has further served to strongly emphasize the willingness of our manufacturers to subsidize research.

The present vitality and rate of progress in American industrial research is strikingly illustrated by its very recent development in special industries. It has been said that our best research is carried on in those laboratories which have one client, and that one themselves.

Twenty-five years ago the number of industrial concerns employing even a single chemist was very small, and even he was usually engaged almost wholly upon routine work. Many concerns engaged in business of a distinctly chemical nature had no chemist at all, and such a thing as industrial research in any proper sense hardly came within the field of vision of our manufacturers. Many of them have not yet emerged from the penumbra of that eclipse and our industrial foremen as a class are still within the deeper shadow. Meantime, however, research has firmly established itself among the foundation stones of our industrial system, and the question is no longer "What will become of the chemists?" It is now, "What will become of the manufacturers without them?"

In the United States to-day, the microscope is in daily use in the examination of metals and alloys in more than 200 laboratories of large industrial concerns.

An indeterminate but very great amount of segregated research is constantly carried forward in small laboratories which are either an element in some industrial organization or under individual control. An excellent example of the quality of work to be credited to the former is found in the development of cellulose acetate by Mork in the laboratory of the Chemical Products Company, while a classic instance of what may be accomplished by an aggressive individualism plus genius in research is familiar to most of you through the myriad and protean applications of Bakelite. The rapidity of the reduction to practice of Baekeland's research results is the more amazing when one considers that the distances to be traveled between the laboratory and the plant are often, in case of new processes and products, of almost astronomical dimensions.

Reference has already been made to the highly organized, munificently equipped and splendidly manned laboratories of the du Pont Company, the General Electric Company, and the Eastman Kodak Company. There are in the country at least fifty other notable laboratories engaged in industrial research in special industries. The expenditure of several of them is over $300,000 each a year; the United States Steel Corporation has not hesitated to spend that amount upon a single research; the expenses of a dozen or more probably exceed $100,000 annually. The limits of any address delivered outside a jail unfortunately preclude more than the merest reference to a very few. One of the finest iron research laboratories in the world is that of the American Rolling Mills Co. Equally deserving mention from one aspect or another are the laboratories of the Fire Underwriters, the National Carbon Co., the Solvay Process Co., the General Bakelite Co., Parke, Davis & Co., the Berlin Mills Co., the United Gas Improvement Co., the National Electric Lamp Association, Swift & Co., the Pennsylvania Railroad, and many others.

Research in the textile industries has been greatly stimulated by the various textile schools throughout the country, of which the Lowell Textile School with its superb equipment is perhaps best known. The fermentation industries have been brought upon a scientific basis largely through the efforts of the Wahl-Henius Institute at Chicago and other special schools. In the paper industry, general research is mainly confined to the Forest Products Laboratory at Madison, its branch laboratory for wood pulp at Wausau, the Bureau of Standards, the Paper and Leather Laboratory of the Agricultural Department, and the laboratory of Arthur D. Little, Inc., at Boston. Our own special equipment for this purpose includes, as does that of some of the other laboratories named, a complete model paper mill of semi-commercial size.

There is no school of paper-making in the country, and one of our most urgent industrial needs is the establishment of special schools in this and other industries for the adequate training of foremen who shall possess a sufficient knowledge of fundamental scientific principles and method to appreciate the helpfulness of technical research. The Pratt Institute at Brooklyn is fully alive to this demand and has shaped its courses admirably to meet it.

The steel industry in its many ramifications promotes an immense amount of research ranging from the most refined studies in metallography to experimentation upon the gigantic scale required for the development of the Gayley dry blast; the Whiting process for slag cement; or the South Chicago electric furnace. This furnace has probably operated upon a greater variety of products than any other electric furnace in the world. Regarding the steel for rails produced therein, it is gratifying to note that after two and one-half years or more no reports of breakage have been received from the 5600 tons of standard rails made from its output. The significance of this statement will be better appreciated when we consider that in 1885 the average total weight on drivers was 69,000 lbs. It had risen to over 180,000 lbs. in 1907, and reached a maximum of 316,000 lbs. in that year. The weight of rails during the same period had increased from 65–75 lbs. to 85–100 lbs. In 1905, conditions were so bad that out of a lot of 10,000 tons, 22 per cent were removed the first year because of depressions in the head. In 1900, the American Railway Engineering Association took the matter in hand and studied the influence and extent of segregation of specific impurities. The work was at first confined to phosphorus but has been extended to other constituents. Fay called attention to the highly deleterious influence of sulfide of manganese.

The great railway systems have been quick to coöperate in these researches which with others of fundamental importance have been extended by the American Society for Testing Materials, the Master Car Builders' Association, and other organizations. Materials of construction have constituted a fertile subject of inquiry in the Structural Materials Testing Laboratory of the United States Geological Survey.

There could well be a further great enlargement of the field of industrial research in special industries through the initiative and support of National trade associations, to the great benefit of their membership. The American Paper and Pulp Association, for example, should subsidize studies in the utilization of waste sulfite liquors, the paper-making qualities of unused woods and fibers, the hydration of cellulose, new methods of beating the yields from rags, the proper use of alum and so on. The American Brass Founders'

Association could not do better than initiate investigations into zinc losses, the physical properties of alloys, and the production of alloys to specifications defining the properties desired, the application of the electric furnace to the industry and the preparation of new alloys by electric or other methods. A similar opportunity knocks at the door of the American Foundrymen's Association. Some few associations like those of the Bakers and the Laundrymen are already active to good purpose; others like the Yellow Pine Lumber Manufacturers' Association are aroused, but to the great majority of those powerful organizations, research is still an academic question to be discussed by their members individually if they so choose. Every industry has, however, its broad research problems, and its points especially vulnerable to research attack, among which it should be easy to select those of general interest to the industry as a whole.

There are in the country many analytical, testing and commercial laboratories, and, in most of these, special researches are conducted for clients, often with gratifying results. It is to be regretted, however, that there is not a more general appreciation among commercial chemists of the scale and quality of equipment and organization essential for really effective industrial research. As this broader viewpoint is attained, and the engineer's habit of mind acquired, we may expect a great extension of independent research, and the cessation of complaint regarding the trend of prices for analysis.

Among the relatively few private or incorporated laboratories with highly organized staff, and adequate special equipment, should be mentioned those of the Institute of Industrial Research at Washington, which has done notable work on the corrosion of metals, paint technology, canning, road material, cement, and special mill problems; the electrochemical laboratories of FitzGerald and Bennie at Niagara Falls, which have so successfully specialized on the construction and operation of electric furnaces to meet the requirements of special processes and products; the ore sampling and treating plant of Ricketts and Banks; and the Pittsburgh Testing Laboratory.

Industrial research is applied idealism: it expects rebuffs, it learns from every stumble and turns the stumbling block into a stepping stone. It knows that it must pay its way. It contends that theory springs from practice. It trusts the scientific imagination knowing it to be simply logic in flight. It believes with F. P. Fish, that, "during the next generation—the next two generations there is going to be a development in chemistry which will far surpass in its importance and value to the human race, that of electricity in the last few years. A development which is going to revolutionize methods of manufacture, and more than that is going to revolutionize methods of agriculture," and it believes with Sir William Ramsay that "The country which is in advance in chemistry will also be foremost in wealth and general prosperity."

With these articles of faith established in our thought, let us consider where they lead us. Within the last few days Frank A. Vanderlip, than whom no one speaks with more authority upon financial matters, has told the assembled representatives of the electrical industries that they are facing a capital requirement of $8,000,000 a week for the next five years—a total within that period of $2,000,000,000. As chemists, we are ourselves entering upon an era in which the capital demands of industries now embryonic or not yet conceived, will in the not distant future be equally insistent and even more insatiable. Have we as chemists given a thought to this aspect of the development of our science, or planted the seeds of the organization which may some day cope with it? In the electrical and other established engineering professions, it is significant that the great industrial applications of the sciences involved have been in large part due to the activities of firms and organizations like Stone and Webster, J. G. White & Co., Blackwell, Viehle & Buck, and the United Gas Improvement Co., which, by an orderly but inexorable evolution, passed from the status of engineers to that of engineers and bankers. Our own profession has not yet evolved the chemist and banker, but such an evolution, or at least the close alliance of chemistry and banking is a fundamental prerequisite if the results of industrial research are to find their full fruition in America. Let me add that no field within the purview of the banker is more ripe for tillage or capable of yielding a richer harvest.

We need, however, to lead the banker to the chemical point of view, and even more do we ourselves require to be taught the financial principles involved in the broad application of chemistry to industry. To the ideals of service which inspire our profession, and which are so finely exemplified in Cottrell and made effective in the Research Corporation, we should add a stronger impulse to direct personal initiative in affairs. We shall need for years to prosecute a vigorous campaign for a better understanding by the general public of what chemistry is and what research is. The popular imagination is ready to accept any marvel which claims the laboratory as its birthplace, but the man in the works still disbelieves that two and two in chemical nomenclature make four. We need a multiplication of research laboratories in special industries, each with an adequate staff of the best men obtainable and an equipment which gives full range to their abilities. In nearly every case this equipment should include apparatus of semi-commercial size in which to reduce to practice the laboratory findings. Nothing is more demoralizing to an industrial organization, and few things are more expensive, than full-scale experimentation in the plant.

These laboratories should each be developed around a special library, the business of which should be to collect, compile and classify in a way to make all instantly available, every scrap of information bearing upon the materials, methods, products and requirements of the industry concerned. Modern progress can no longer depend upon accidental discoveries. Each advance in industrial science must be studied, organized and fought like a military campaign. Or, to change the figure, in the early days of our science, chemists patrolled the shores of the great ocean of the unknown, and seizing upon such fragments of truth as drifted in within their reach, turned them to the enrichment of the intellectual and material life of the community. Later they ventured timidly to launch the frail and often leaky canoe of hypothesis and returned with richer treasures. Today, confident and resourceful, as the result of many argosies, and having learned to read the stars, organized, equipped, they set sail boldly on a chartered sea in staunch ships with tiering canvas bound for new El Dorados.

ORIGINAL PAPERS

DESIGN OF SURFACE COMBUSTION APPLIANCES

By Charles Edward Lucke[1]

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Manufactured gaseous fuel is and always will be more costly per unit of heat carried than natural fuel, and yet may yield cheaper and better service; cheaper if the process and apparatus used for the combustion of the gas is efficient enough, and better if it is so designed as to liberate the heat in a sufficiently more available form. It is this fact that justifies the general interest now shown in the process that has been termed Surface Combustion, which promises both cheaper and better gas service, the realization of which depends on the accumulation of much new data for the design of apparatus of commercial form. Some of this information has been worked out, and commercial apparatus of one or two classes designed therefrom. The process of development that has resulted in the establishment of surface combustion on an engineering basis whereby apparatus can now be designed to meet specific conditions is reported briefly in this paper.

ASSUMPTIONS OF NEW PROCESS

The new process assumes that gas to be burned should be supplied with no more air than will furnish the required amount of oxygen for the combustion reaction, and that the air and gas should be thoroughly mixed previous to combustion, so that the reaction may take place instantly, once the ignition temperature is reached. Excess air is regarded as not only useless but harmful because its heat absorption prevents the attainment of the highest temperatures so desirable when the heat of combustion is to be communicated to other bodies, and carries away as flue heat, quantities that would otherwise be of use. Premixture is regarded as desirable because thereby each particle of fuel may be brought positively into intimate contact with its required oxygen before it is needed, instead of depending on the accidental dissipation of the products formed on the edge of a flame jet, before the central core of gas can secure air from a surrounding and supporting atmosphere. This premixture, in conjunction with suitable proportioning, prevents the escape of unburned fuel in any form. Thus, premixture of air and gas in combining proportions at once insures protection against two important sources of loss in combustion: (1) that due to excess air and (2) that due to incomplete combustion. As an incidental accompaniment, another advantage of no less importance follows, and that is development of the heat of combustion in a form more available for absorption by the bodies to be heated, and for the heating of which the gas is burned. Heat will be absorbed most readily from a fire when the temperature of the gases leaving the first is highest and when the fire zone is most radiant. All heat absorbed from the fire by direct contact of the absorber with the hot gaseous products is absorbed at a rate directly proportional to the excess of the temperature of the gases over that of the absorber; hence, the hotter these gases the more heat will a given absorbing surface take up, other things being equal. Heat is, however, much more rapidly absorbed by bodies when the source is radiant, because radiant heat readily pierces the insulating dead gas films adhering to the surface of the absorber and resisting by its low thermal conductivity all transmission from passing hot gas streams. The superior transmitting value of radiant heat has been well known as long as physicists have studied the sun's rays, but it has been lacking in most, though not all, gas burners because of the very low radiant value of hot gases as compared with solid bodies at the same temperature. The premixture of the gas and its supporting air makes it very easy to secure a large amount of the heat of combustion in a radiant form, because the combustion, being entirely independent of any atmosphere into which the products may be discharged, can be carried on behind layers of solid granules, in the crevices between them, in holes in solid plates, or behind solid plates of any convenient form, all of which, attaining the temperature of the gaseous products of combustion, radiate heat at a rate immensely superior to that of the gases themselves.

With all these prospective advantages in the direction of superior efficiency of this gas burning apparatus over all other modes of supply, the question naturally arises as to why the principles involved have not been more commonly practiced, and why there should be any delay in at once proceeding to the design of suitable appliances. The answer is to be found in the peculiar physical properties possessed by the gas and air over those now commonly in use, which make them difficult to control in the absence of detailed knowledge of their characteristics. In fact, without such knowledge, design of apparatus is quite impossible and it becomes feasible just in proportion as information of the needed sort is established by experimental research.

REQUIREMENTS OF PROCESS

The fundamental peculiarity of such mixtures is the property of self-propagation of flame through them, bringing them into the class of things commonly termed explosive. As all the mixture is in a condition suitable for combustion once the ignition temperature

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is reached, it naturally follows that as the combustion temperature is much in excess of that of ignition, the burning of however minute a quantity of mixture at a point of ignition will promptly heat neighboring layers of mixture far above their ignition temperature so that the flame will, of itself, proceed through the whole mixture mass if it be isolated in a chamber. The only way such a self-propagation can be stopped is by preventing the heating of a fresh layer by the combustion of its neighbor, such prevention taking the form of a heat absorption by some solid screen at a rate great enough to permit the screen to take up the heat of combustion of all mixture in contact with one side without itself becoming hot enough to warm the mixture on its other side to the ignition point. It is easy to make such flame interrupting screens that will stop the propagation of flame through an explosive mixture once or twice, but difficult or impracticable to make them so as to be able to continue to do so indefinitely. With the exception of the internal combustion gas engine, gas burning apparatus requires a continuous burning of gas as supplied in a definite place termed the burner or furnace. When explosive gaseous mixtures are supplied to such continuous fires, the property of self-propagation operates to defeat localization of the combustion unless specific means are provided in the design of the structure to make the treatment of the mixture conform to its physical properties, in which case the combustion can be more definitely localized than otherwise.

For any given mixture there is a definite normal rate of propagation which may be equal to, less or greater than the velocity of flow of the mixture into the fire, and it is clear that localization of combustion will depend primarily on the relation of these two rates, that of flame propagation and that of flow. If they are equal, that is, if the flame can burn back toward the source of mixture supply, just as fast as, but no faster than the mixture reaches the flame, then will the flame remain fixed or be definitely localized. In fact, the above is the primary condition for localization of the combustion of explosive mixtures, because otherwise the flame would travel back to the source of supply or be blown out by the physical pushing away of the faster flowing fresh stream of mixture. Of course, localization may also be secured if the mixture be fed through a flame-interrupting partition at a flow rate inferior to that of propagation, in which case the localization takes place on the face of the partition, which must, of course, have a large capacity for heat absorption indefinitely, *i. e.*, it must be able to dissipate or transmit to some other body the amount of heat it is receiving—otherwise it would rise in temperature to the point where it, by igniting the mixture on the supply side, would cease to be an interrupter.

Mixtures of the sort that seem best from the standpoint of efficiency of apparatus, having this explosive property, require a special treatment to permit of their use in commercial apparatus, which special treatment has for its first object the definite localization of the flame. The means employed must, moreover, be so positive as to be unaffected by long-continued operation; that is, the localization must be permanent. There are, however, still other conditions to be met, such as control of rate of combustion per sq. ft. of fire or per cu. ft. of furnace, a cook stove requiring a low and a crucible furnace a high rate, and as such mixtures have what might be called a natural rate corresponding to the normal rate of propagation, it is clear that specific means must be available for burning slower or faster per sq. ft. of gas stream cross section. Furthermore, any one burner or furnace designed for some definite or normal rate of combustion or gas consumption, would be valueless commercially unless it would operate quite as positively at a wide range of variation, both above and below that normal rate. In other words, localization of the flame must not only be positive, and any desired rate of combustion be attainable by design, but in addition—hand or automatic interference with the designed rate of consumption must not in any way interfere with the localization.

In some cases it is desirable that the burner be capable of reaching its normal or steady working state in a short time, *e. g.*, in a domestic cook stove burner, while on the other hand a slow heating corresponding to a large heat storage in the furnace is necessary when articles are constantly being thrust in to be heated and then drawn out, without too much change of temperature in the furnace: hence, control of heat capacity of the burner must be available. Finally, there must be provided mechanical means for making the desired mixtures and for maintaining the desired proportions sufficiently, means so simple and automatic to require no more skill or attention on the part of the operator than appliances now in use.

Accordingly, this review of the work of development of the first commercial surface combustion appliances is divided into the following divisions:

I. Localization of Combustion Zone: *initially* on starting cold apparatus and *permanently* on attainment of the steady state of the fire.

II. Rate of Combustion per sq. ft. of Bed or Hearth for High Rates and Low.

III. Control and Adjustment of Radiating Surface.

IV. Auxiliary Apparatus.

V. Efficiency of Surface Combustion Appliances.

The experimental work here reported has all been done by or under the direction of the writer, partly in his laboratory at Columbia University, but largely in the laboratory of the Gas and Oil Combustion Co. in the Chemists' Building. Acknowledgment is freely made of the contributions of the laboratory staff, headed by Mr. Frank Creelman and including Messrs. E. J. Allen, H. L. Ocumpaugh, F. A. Wegener, W. B. Eddison and Prof. E. J. Hall of Columbia University.

Only the results of N. Y. City illuminating gas are here reported, though work has been done with other fuels and satisfactory results obtained that permit the statement that all fuels in the gaseous or liquid form are equally available for the process.

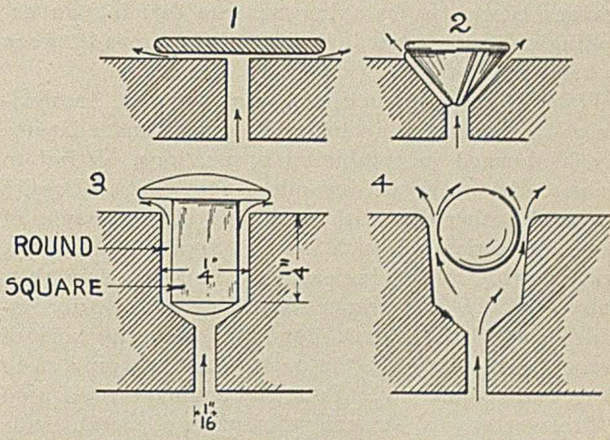
I. LOCALIZATION OF COMBUSTION ZONE

Reasoning from the fact that the flame cap or surface over which combustion is proceeding will be steady in location only when the velocity of the mixture approaching it is equal to the rate of flame propagation for such a mixture, the first step in the design of practicable apparatus is the formation of gas passages of suitably changing area, since the velocity of gas flow for small changes of pressure will vary inversely as the cross section of the flow path. The mixture should approach the fire zone through a small tube or orifice at a rate greater than the normal velocity of flame, but immediately beyond there should be an enlargement of the cross section of the passage to permit of velocity reduction which, if carried far enough, would finally cause flow velocity to drop to equality with flame velocity, which was at the point of entrance in excess. Mechanical construction that will permit of this can be designed in almost endless variety, many of them equally good, but for the best results certain precautions must be observed: notably (1) the tendency for a gas jet escaping from an orifice under pressure to resist sidewise expansion so that even if the passage offers an increasing area for flow, the gas stream may not fill it unless forced to do so by baffles or their equivalent; and (2) the tendency for free jets flowing through a gaseous atmosphere of, for example, products of combustion, to entrain or diffuse with the atmosphere at the edges, becoming so dilute as to not burn properly, if at all.

GAS PASSAGES

Perhaps the simplest apparatus would be a very narrow angle conical passage to which mixture is fed at the smaller end; the stream expanding sidewise to always fill the cone would reduce in velocity and permit the location of a combustion surface quite definitely. In time such a conical tube would get hot; in fact, at the section where the flame surface located, it would become incandescent almost immediately if of refractory material, or melt off if of metal, and, of course, the narrower section along which the fresh mixture approaches would heat by conduction and warm the feeding gas. This mixture heating would tend to increase flow velocity and push away the flame surface if another counter influence did not prevent it; *i. e.*, the increase of flame propagation rate, which is due partly to rise of mixture temperature and partly to the accelerating effect of the hot solid walls. This counter influence accelerating combustion and drawing the flame surface back against the supply current is really stronger than the pushing away effect of velocity increase due to expansion of the stream by heating. Such cones are not in most cases good forms for the purpose because of the limit imposed on adjustment of rate of supply which if varied very much would cause a blow off or back flash of the flame, unless they were extremely long. When, however, a steady-rate apparatus is needed and flow is fixed, there may be just enough sidewise expansion of the jet issuing from a mere hole in a plate to locate the flame, but the practical uses of such apparatus are very small.

To meet the needs of every-day service there must be a more positive localization of the combustion surface, insensible to variation of mixture pressure or flow rate over a wide, though definite service range; this requires specific provision for stream baffling so that the gas stream will increase in cross section rapidly beyond the supply point of minimum area and safe maximum flow velocity. Perhaps the simplest of these flame spreaders is a plate over the hole through which the mixture escapes as in Fig. 1. By placing the baffle away from the plate carrying the orifice, a distance equal to one-quarter of the diameter of the orifice, the stream direction will be turned through a right angle without changing the flow velocity until the stream moves out under the plate beyond the hole, when, of course, the velocity will be reduced inversely as the diameter of the circle the gas occupies at any one time. With a hole $^1/_{16}$ of an inch in diameter a plate spaced $^1/_{64}$ of an inch away could reduce flow velocity when cold to $^1/_8$ of its entrance value if the plate were $^1/_2$ inch in diameter. This would permit an eightfold change in the rate of flow when cold, keep the flame surface always under the plate and give to the flame surface the form of a short cylinder. Such a construction offers some difficulties as in operation both plate and hearth would get very hot and unequally so; starting at the center the plate would remain dark, becoming incandescent from the flame zone out to the edge, which would crack most plates refractory enough to resist fusion even if a practical way of making such plates and holding them in position were available.



Figs. 1 to 4—Means for Velocity Reduction to Control Localization of Combustion Surface

An easier construction is shown in Fig. 2, in which a solid (alundum cement) cone with three small ribs is placed in a counterbore of the feed hole. This is self-locating when in the position shown but not otherwise. Still another form that holds the baffle definitely against side movement is shown in Fig. 3, in which the baffle is shaped somewhat like a mushroom with a square-section stem fitting loosely in an enlargement of the feed hole so that the flow area does not change materially until the escaping mixture strikes the underside of the head and is deflected outward. The dimensions given are those used on some that gave good service with mixture pressures up to three inches of water though a little troublesome to make and apt to break if not gently handled. The most permanent form of this class of molded baffles is the refractory ball in a conical hole as shown in Fig. 4 and it is interesting to note that the ball, remaining suspended in the jet and keeping, by reason of its weight, a constant velocity of the jet around it, insures the location of the flame above it, keeping it cooler than otherwise, so that fire clay balls have remained uninjured when the same clay a short distance above readily fuses. The physical action is here slightly different than in the previous cases, the escaping mixture forming an expanding and velocity reducing jet of ring form between the ball and its seat.

While, in the construction shown as typical, localization of the combustion surface is definite and mixtures may be burned in combining proportions, all fail to produce the uniform incandescence that is easily obtainable otherwise with such mixtures, though, of course, a series of such baffles spaced uniformly, approach this result; instead of a uniform glow they have a spotty appearance from black to truly incandescent. It is found, however, that any sort of porous screen placed in the path of the escaping gases will get uniformly hot. Such screens have been used of three sorts: (1) A perforated plate of metal, made of one of the non-oxidizable alloys such as are used in electric heaters. (2) A layer of granulated refractory material. (3) A diaphragm of bonded granular material, the most satisfactory of which were made of Norton alundum. Of course, the less mass given to the screen the more rapidly it reaches incandescence initially and in this respect the metal screen is best; one of these placed $^{3}/_{8}$ inch over a hearth $4^{1}/_{2}$ inches diameter supplied with 55 holes each $^{1}/_{16}$ inch diameter and $^{1}/_{4}$ inch ball baffles heated in six seconds, while diaphragms thick enough to be mechanically strong may take five minutes, though, of course, the latter are more permanent. With the same arrangements except that the mushroom baffles were used instead, the following consumptions of gas were measured at the corresponding pressures and gave a steady dull red at the lowest rate and correspondingly brighter heats at the higher rates: 7.25, 9.1, 10.9, 12.2, and 14.2 cu. ft. of gas per hour at 1.00, 1.5, 2.0, 2.5 and 3.0 inches of water pressure. A similar set of mushroom baffles placed in a vertical hearth and having a screen of crushed fused silica $^{5}/_{8}$ inch deep of size between $^{20}/_{64}$ inch and $^{13}/_{64}$ inch, held in place by a second screen of wire mesh, heated to incandescence in $3^{1}/_{2}$ minutes at a supply pressure of 2 inches of water.

All the previously described baffling means intended to assist the spreading of the mixture stream beyond the point of high velocity supply, and many others of the same class, are used to counteract the natural tendency of gas jets to remain intact and resist sidewise expansion. It is possible, however, to make use of this natural tendency of jets and incidentally secure a very high degree of incandescence, higher in fact than is possible by any other known means, using air and the same gas. Moving the nozzle away from the baffle and making the baffle porous (using for convenience in experimental work a pile of refractory granules), the top or impact surface may be shaped to conform to the natural mushroom of the jet as it strikes. For any degree of porosity and jet velocity or supply pressure there is a best distance and a corresponding impact face shape, that permits all mixture striking whether at the center or edges to have just the right velocity, that of propagation, in contact with the material, so that combustion takes place in contact with the outer or radiating surface which then has the maximum possible temperature. It is essential that the impact face be porous so that the products may readily escape through instead of forming dead gas films which separate the combustion surface from the solid faces and insulate the latter from the heat of the former. In this manner a surprising degree of radiance is obtained due to the high rate of combustion of a mixture containing no excess air except possibly at the outer edges by entrainment. At 3.2 inches mixture pressure, 40 cu. ft. of gas per hour were burned over about four square inches of surface, which corresponds to over 1400 cu. ft. per sq. ft. per hour and more than 800,000 B. T. U.'s per hour per sq. ft. Higher rates of combustion than this are obtainable but not all developed on the radiating surface itself.

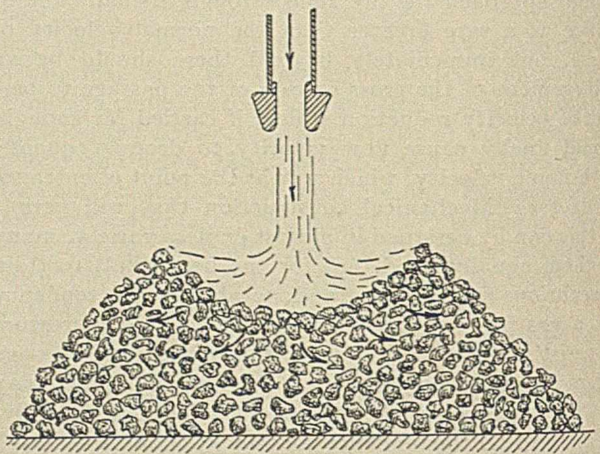


FIG. 5—MEANS FOR LOCALIZING THE COMBUSTION ZONE AT THE EXTERNAL RADIATING SURFACE

PROPERTIES OF GRANULAR BEDS

In view of the importance of developing as large an amount of heat as possible in the radiant form, in addition to the localization of the combustion zone, and considering that loose granules or a porous diaphragm of refractory may serve the double purpose of the radiating screen and of the actual baffling or mixture stream spreader, everything else may be abandoned in favor of these refractories except perhaps for certain special purposes for which special forms may be best. Nearly all the work done has been concentrated on an effort to learn how these granular beds and bonded diaphragms should be handled to yield commercial apparatus, and by reason of the simplicity of the loose bed it has been consistently favored for most uses over the bonded.

A uniform grained bed of loose granular material will act as a substantially perfect spreader of the mixture issuing from an orifice covered by the bed but the quantitative effect of variations in size of grain, imperfections in shape or non-uniformity of size, together with shape of bed and its relation to shape, size and position of the feed orifice, are all to be determined by experiment only. Most of the detailed data of this sort will be omitted as not of general interest but the following series of experimental determinations illustrate the most important of the general principles that must be observed for successful operation: One of the simplest imaginable arrangements is shown in Fig. 6, where a single nozzle $^{5}/_{16}$ inch in diameter projects $1^{1}/_{4}$ inches into a bed of broken fire brick which material is very convenient for studying the ultimate position and shape of the combustion zone as it will fuse and bond at that place. The bed was held in a square brick box $6^{3}/_{4}$ inches on a side and 5 inches deep and the nozzle was fed with mixture at 3.2 inches pressure. Starting with coarse grains $^{1}/_{2}$ inch to $^{3}/_{8}$ inch, the mixture on ignition flashed instantly down through the bed, locating below, quite near the nozzle as was shown later by the more or less spherical lump that fused there. The same action took place with smaller grain as it was reduced in size successively from $^{3}/_{8}$ inch to $^{5}/_{16}$ inch, $^{5}/_{16}$ inch to $^{1}/_{4}$ inch, $^{1}/_{4}$ inch to $^{3}/_{64}$ inch, $^{3}/_{64}$ inch to $^{5}/_{32}$ inch and $^{5}/_{32}$ inch to $^{3}/_{32}$ inch, but a further reduction in size resulted in a different action. On using grains from $^{3}/_{32}$ inch to $^{1}/_{16}$ inch in size, the mixture on ignition burned on top instead of flashing down through the voids to its normal surface about the nozzle. In a few minutes the top layer became hot and then seemed to cool; but on scraping away the top it could be seen that the combustion surface had receded; after running a sufficient time this progressive heating from the outside down toward the nozzle resulted in a final location of the combustion zone about where it was in the coarser material, in which it flashed back *instantly* to its normal position. Of course, in either case, the whole bed gets hot in time, but with coarse grains it heats from the normal combustion zone near the nozzle out and upward, while with small enough grain the outside top heats first, the flame drawing down slowly, a difference in action which requires an explanation.

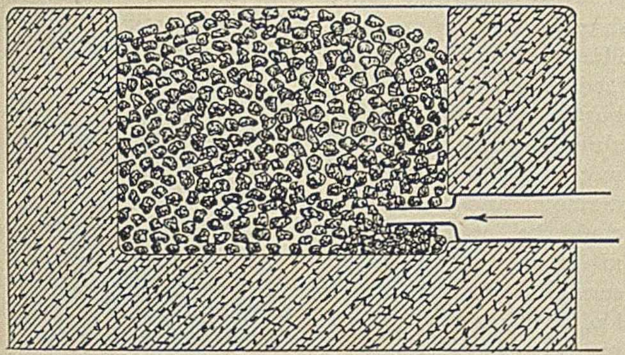


Fig. 6—Apparatus for Demonstrating the Spherical Form of the Combustion Surface when Mixture is Supplied from a Nozzle Surrounded by Granular Refractory

When the grain is fine enough it acts like a flame interrupting screen, each little crevice between neighboring grains discharging so little mixture that its heat of combustion can for an appreciable time be absorbed by the solid grain in contact without raising the lower side to the ignition point, radiation from the outside surface helping to keep down the temperature. In time, however, the lower side of the top layer gets hot and the combustion surface recedes, doing so more rapidly once it has passed under the top layer because then radiation cooling is lessened, leaving more heat for the grain to take up. It follows also that as with the finer grain less total mixture will escape from such a round nozzle as it tends to fill the orifice, so the total amount of heat developed will be less than with coarse grain. To show that the stoppage of the nozzle by the grain reducing the total gas flow and heat generation with fine grain is not responsible for the difference in flame action at the start as compared with coarse grain but that the difference is due to the difference in the mode of gas flow through the bed itself with corresponding more intimate contact between mixture and grain the smaller the latter, the same series of results were obtained in a pyramidal chamber, shown in Fig. 7, in which the nozzle is a pair of hacksaw cuts in a 1-inch pipe cap, the whole being shown in the photo, Fig. 8. With such slot outlets for the mixture the flow is substantially the same for all the different sizes of grain given, yet not only did the top heat first with the $^{3}/_{32}$ inch to $^{1}/_{16}$ inch grain and then burn back but also with the larger $^{5}/_{32}$ inch to $^{3}/_{32}$ inch with which it required ten minutes to draw the combustion zone down through the bed to its normal place and fuse a lump of granules over the cross slot.

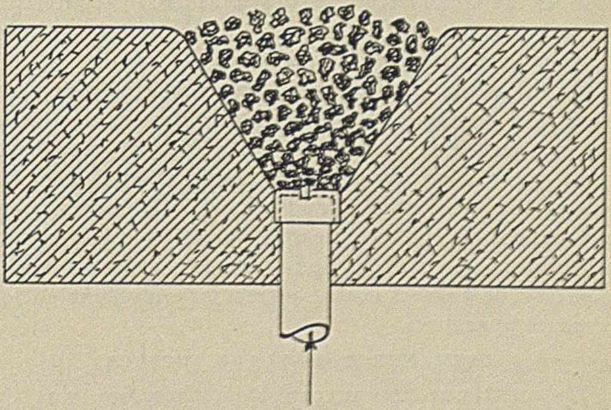


Fig. 7—Apparatus for Demonstrating Uniformity of Position of Combustion Surface with Different Sizes of Grain

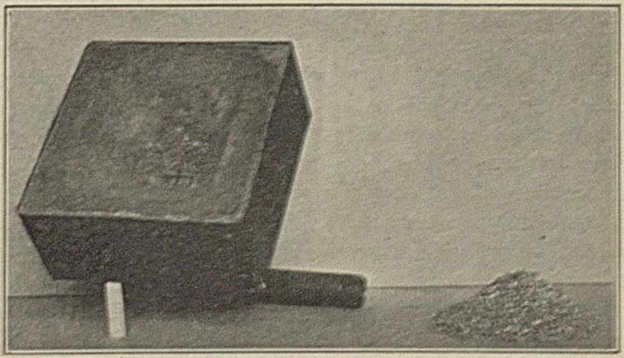


Fig. 8—Apparatus for Demonstrating Uniformity of Position of Combustion Surface with Different Sizes of Grain

In establishing the action just described the use of fire brick for the grain was most satisfactory as each test gave a fixed record (in the form of a fused lump) of what had happened, but once it was clear that the size of grain made only a starting or temporary difference in action, then longer runs became desirable to bring out the possible heating effect on the nozzles; for these refractory grain was used, including magnesite, chrome ore, both natural lumps and broken brick, fused silica, lime and alundum. With these materials the long runs showed that some forms of feed orifices became heated so as to ignite the mixture in the feed pipe while with others this action did not take place, permitting operation for an indefinite time. It was not clear at the time just what caused the trouble since it frequently happened that the nozzle that worked best was really much hotter than another that flashed back almost as soon as the steady state was established. At any time an increase in the pressure at which the mixture was supplied would have so increased the volume of flow as to drive the combustion surface to a safe distance from the nozzle but it was deemed unwise to leave the matter here because, *first*, all domestic apparatus must operate on low pressure, lower than that of the gas in the local mains, and *second*, all industrial apparatus for which gas pressure boosting would not be objectionable would, at some time, be operated at part capacity or turned down, which is equivalent to low pressure operation.

PERMANENCE OF FLAME SURFACE

The next question investigated, therefore, was this permanence of the localization of the flame surface or combustion zone, and the discovery of means for securing an indefinite time of operation without disturbance from long-continued heating even over several days and with mixture pressures so low as to heat the hearth end of the nozzle above the ignition point. It is clear at the start that iron, or in fact any *metal*, must be kept away from the feed orifice proper, which in effect means that in order that appliances may operate on low pressures it is necessary that the mixture enter the fire chamber through a refractory orifice, or when the burner is lined with refractory, as it should be, the mixture must enter through a hole in the lining or what might be properly called the hearth. Using different mixture entrances a long series of experiments were made that were for a time extremely puzzling but which finally could be summed up in a very few words. All feed holes will become incandescent at the fire end with low gas pressures; heat will flow back through the bounding material of the hole and these hot walls will heat the mixture passing through. No harm will result, however, even from a bright red heat on the walls of the hole, provided the latter is of uniform bore over the heated part and has no enlargement of cross section with its corresponding low mixture flow velocity except at points that never get hotter than the point of ignition. To put it otherwise, the mixture passageway may be at any temperature without harm if of uniform bore and if when cold the flow velocity is great enough to prevent back flash. Under these conditions localization of the combustion will be permanent. Naturally anything that will reduce the temperature of the supply tube, like radiation to the air, will also shorten the length of the necessary uniform bore portion as will also the use of more non-conducting material. Finally it was found that the length of uniform bore feed pipe that would be cool enough at its supply end to be joined to a larger mixture header or box, was greater for large than for small holes or that the allowable length was a definite number of diameters. For example, in an apparatus such as is illustrated in Fig. 9, with a single refractory lined tube feeding a cylindrical combustion chamber, all of alundum cement encased in metal, a hole of $^1/_4$ inch diameter and 6 inches long could be operated indefinitely at 1 inch water pressure even after the chamber had been made very hot by previous operation at much higher pressures, whereas a $^7/_{16}$ inch diameter hole of the same length flashed back at 1.5 inches water pressure, and continued to do so after periods ranging about three hours even after its length had been increased to 15 inches. Small diameter orifices of say $^1/_{16}$ inch diameter have, on the other hand, been operated indefinitely on pressures as low as 0.2 inch of water when about $1^1/_2$ inches long. Back flash after long periods of operation by heating up of the supply system may, therefore, be prevented by proper design; *i. e.*, by selection of suitable proportions in accordance with the announced principles and the established data, localization of the combustion zone will be correspondingly insured against disturbance.

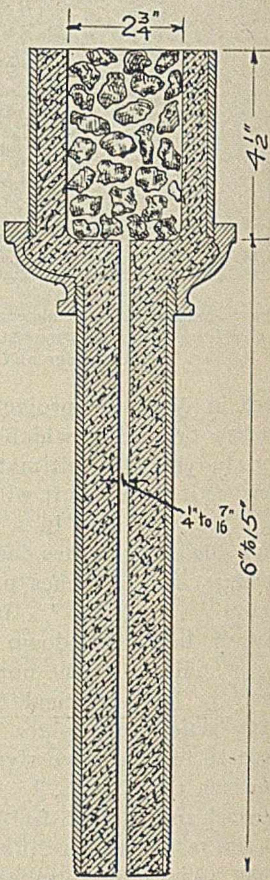


FIG. 9—APPARATUS FOR DETERMINING THE RATIO OF LENGTH TO DIAMETER OF FEED HOLE TO CONTROL "BACK HEATING"

II. RATE OF COMBUSTION PER SQ. FT. OF BED OR HEARTH

Passing now from the discussion of localization of the combustion zone or flame surface and the means for keeping it permanently localized, the next question of importance is that of control of rate of heat generation per sq. ft. of fire bed, which is a problem of distribution of the burning mixture over surfaces as large or small as may be demanded and of maintaining high or low degrees of incandescence over these surfaces. This now seems a very simple matter but for a considerable time it seemed even more elusive than the prevention of back flash through nozzles, which was annoying enough. There are really two problems here and though related, the relation is not as clear as it may seem. *First*, the problem of the high rate—At how high a rate may gas be burned and how may the structure be formed so as to permit of steady supply and combustion at this rate over any given surface? *Second*, the problem of the low rate—Can such mixtures be burned so slowly as to keep a surface just hot enough for fusing for example; may such a burner be turned down to a so-called simmering point without giving trouble and if so, what ideas must be incorporated in the construction?

HIGH RATE OF COMBUSTION

The problem of the high rate is the simpler of the two, as this may properly be termed the natural rate, assuming, of course, that suitable refractories are obtainable for the corresponding high temperatures and that the principles of permanent localization of the combustion zone are understood and incorporated in simple constructions of apparatus. When the whole cross section of bed is taken up by the burning gas stream or when the combustion zone occupies the whole of the bed cross section, then mixture is being supplied as fast as it can be burned within the space available and any increase in rate of supply will tend to push the combustion zone away or result in the phenomenon of blow off. This is the condition at the limiting high rate of combustion and is the natural rate, because the advancing stream of mixture fills the whole available cross section of fire zone and combustion surface coincides with bed cross section in area. To establish this high rate it is necessary that at first when everything is cold, the mixture be supplied at a lower rate and then after the bed is heated, its accelerating effect may be relied upon to hold localized a very much increased rate of mixture supply up to a certain maximum, which is the natural or high rate of combustion. This natural high rate is intimately associated with the pressure of the mixture at the point of supply, or more properly, the drop in pressure through the feed holes or orifices, for holes of any given size. For example, in such a simple apparatus as that of Fig. 9, where a single feed hole supplies a combustion chamber of larger cross section, carrying a loose granular bed, it is evident that at some low pressure the combustion surface will just cap the feed hole and the rate of combustion will be natural for a bed area equal, not, to the actual bed of $2^3/_4$ inches diameter, but on the contrary, equal to that of the feed hole, a fraction of an inch in diameter. Increase of mixture supply pressure will push the combustion surface away from the hole until finally it will extend across the whole bed and have a form approximating a section of a spherical surface lying within a cylinder, the axis of which passes through the center of the sphere, which latter will be located at the center of the feed hole. It is this latter condition that gives the high rate and to secure it the supply pressure must be big enough to send through a small feed hole, say $^1/_4$ inch in diameter, enough mixture to spread out and fill the voids in the bed $2^3/_4$ inches in diameter, which will exceed half the free cross section, while at the same time the flow velocity through the enlarged cross section must be as great as the rate of flame travel backward. If the ratio of bed area (with a given percentage of voids) to feed hole area is large, then high mixture pressures must be used to secure the natural high rate; so if only small mixture pressures are available then the free flow area of the bed may not exceed the area of the feed hole by very much. In any case large beds may be heated by the high rate of combustion, only by multiplication of orifices spaced at distances equal to the diameter of the combustion surface natural to the supply pressure in use. Before such spacing of feed holes for high natural rates of combustion can be found, it is first necessary to investigate the action for a single hole in a given bed, to find the relation between feed pressures and the ratio of active bed area to feed hole area that will cause the combustion surface to fill the whole bed between the enclosing walls. As an illustration of the method of procedure, it being impossible here to record much of this sort of data, the results of a single series on the apparatus shown in Fig. 9 will serve. In this series the pressures were never extended above 12 inches of water at the point of mixture supply and began with a single hole $^5/_{16}$ inch in diameter, discharging into a cylinder $2^3/_4$ inches in diameter, area 6 sq. inches, but as increase of pressure to the maximum noted failed to supply as much mixture as could be consumed in the available area, there was added a second, a third and finally a fourth hole, even then not reaching the limit.

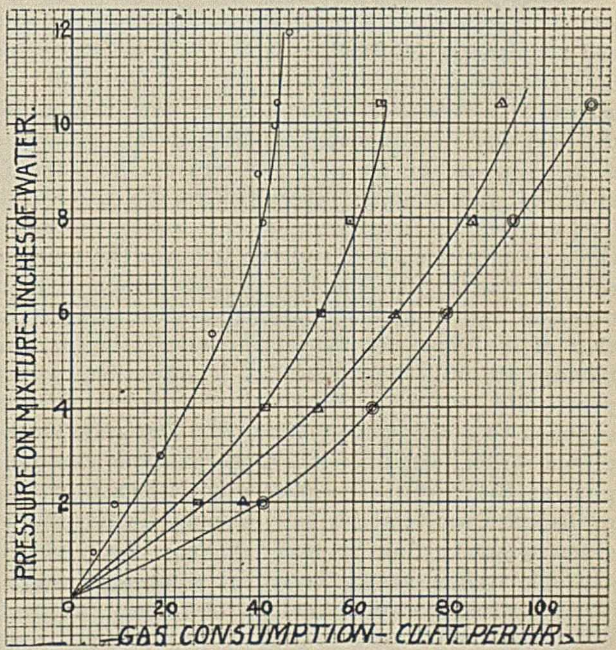


Fig. 10—Rate of Flow of Mixture through Different Numbers of 5/16" Feed Holes at Various Pressures

With the four holes and at a pressure of $16^1/_2$ inches of water, there was attained a rate of combustion consumption of 2460 cu. ft. of gas per sq. ft. of bed per hour, which on a calorific value of 600 B. T. U. per cu. ft. is equivalent to 1,584,000 B. T. U. per hour per sq. ft. There was no indication that the limit had been reached, but as the rate was high enough for practical purposes and so high as to give trouble with available refractory materials, this series was not carried beyond these limits, though it could easily have been done with high pressures or with a larger feed area than from $^5/_{16}$ inch hole (= 0.3 sq. in.). The conclusion here is, that rates higher than have been known are easily obtainable and rates higher than any refractory in common use can resist; hence, if any service arises that demands such rates, the need can be met. It might be noted here that of several refractories tried, the most satisfactory found was white alundum, with linings of alundum cement, preferably mixed with alundum grain of several sizes, properly proportioned dry to fill the voids, then mixed wet, rapidly dried and finally baked at a bright red heat. The size of grain in the loose bed and the depth of bed each exert an important influence within limits but in general for these high rates the larger the grain the better, though there is little, if any, advantage beyond one inch diameter, the depth in any case being little more than sufficient to prevent the gases lifting the grain off the hearth. The resistance in the bed is always appreciably less for round grain than for flat and in this respect the form of fracture of white alundum is most satisfactory. In the above mentioned series white alundum from $^1/_2$ inch to $^3/_4$ inch diameter was used and the depth averaged 2 inches. The results of this series are given in curve form, Fig. 10.

LOW RATE OF COMBUSTION

Probably the most difficult of these experimental problems was that of finding a suitable structure for the permanent localization of the combustion surface for very low supply pressures, while at the same time securing any desirably low rate of combustion over the bed with a uniform incandescence at the surface such as would be suitable for cooking, for example. It is clear that the lower the pressures the closer to the feed hole will the combustion surface locate, the smaller the area of bed heated, and the stronger the tendency to back flash. This fact led to early attempts to secure low rate heat distribution by other means than that of feed hole supply with a series of spots, each having natural high rates of combustion, located practically at the mouth of the holes. Mixture supplied to a passageway filled with fine granules or a porous brick, will flow much the same as through a pipe as the porosity supplies a multiplicity of small paths more or less mutually communicating, and a given quantity flowing would have a mean velocity through such a porous layer the same as through a pipe of cross section equal to the voids except for differences in friction. Mixture fed into such a fine bed in any convenient way, ranging from a single hole under a thick bed to a great number of holes under the whole bed obtainable by a metallic screen support for loose granules or the under surface itself of a bonded diaphragm, would discharge the mixture uniformly from the top of the bed, however the supply was arranged, if the bed were thick enough. This seemed to be at first the most promising idea to follow for low rate heat distribution especially as changes of area of flow path so necessary for localization can be obtained by two means quite conveniently: *first*, by using two layers with the upper coarser and, therefore, with more free voids than the lower fine bed; *second*, by changing the diameter of the containing walls that hold the porous bed.

At first only loose granules were used in apparatus such as shown in Fig. 11, where a perforated metal plate of 306 holes per sq. in., diameter 0.033 inch, and 27.8 per cent free opening is supplied by a $^3/_4$ inch pipe, discharging into a conical space under the screen. On the top of the screen rests a one-inch bed of granules $^8/_{64}$ inch to $^6/_{64}$ inch and over it another one-inch layer of larger grain, $^{24}/_{64}$ inch to $^{20}/_{64}$ inch diameter. On lighting the mixture supplied at 2 inches water pressure the combustion zone instantly locates between the layers at the point of change of free flow space, due to the difference in voids, but as the heat penetrates the lower or fine bed, the combustion zone works back to the screen, which happens with these conditions in about ten minutes. All sorts of changes in the relative sizes of the material and thickness of the two beds or number of layers yield no difference in the result except as to the time it takes the combustion zone ultimately to work back to the screen, burning it out, causing a flash back, or both. This is clearly due to insufficient velocity of flow at the supply end of the bed and suggests a contraction of the walls toward the lower end, as in Fig. 12, where a slot supply is substituted for the screen as it does not burn out so readily if by accident the flame should work down that far. As before, however, the combustion zone worked down close to the nozzle but not so quickly as before, suggesting a further narrowing at the bottom to form a neck as in the forms successively tried, and shown in Figs. 13, 14 and 15. As the neck is thus narrowed the combustion surface no longer approaches the nozzle so closely, stopping, in Fig. 13, about 1 inch above after $^3/_4$ hour at $3^1/_2$ inches pressure, in Fig. 14 about $1^1/_2$ inches above, while in Fig. 15 it did not enter the lower cylindrical portion at all.

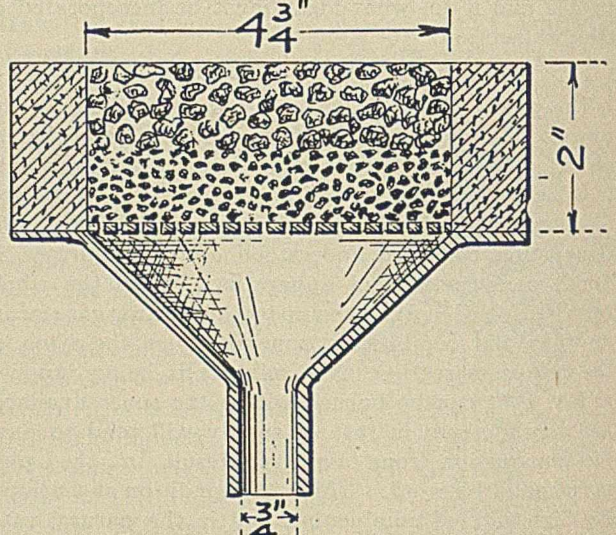
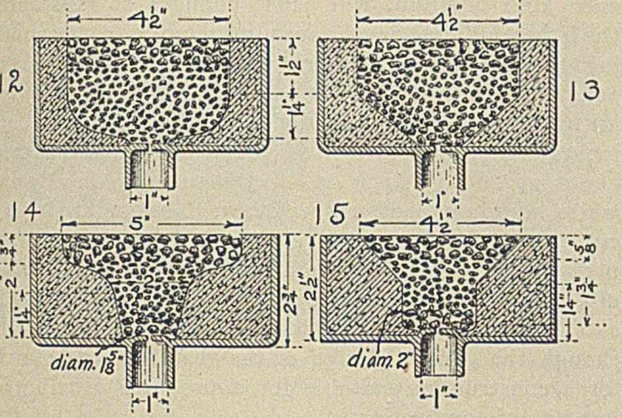


FIG. 11—MEANS OF CONTROLLING SURFACE DISTRIBUTION OF HEAT BY MIXTURE SUPPLY TO FINE GRANULAR BED ON THE SCREEN

By adjusting the space between the walls, the flow velocity through the lower or fine bed can, therefore, be kept high enough to control the location of the combustion zone, regardless of the manner of feeding the mixture to its narrow bottom part, but the problem is by no means solved. All these latter forms are bad in another respect because with the thickness of bed above the combustion zone the top is hot in the center and cool at the edges. To get an even top heat, a greater thickness of bed above the combustion zone would be required but this is already too thick to give a quick initial heating, so another change in construction is suggested, incorporating a different relative position of the narrow lower neck of fine material in the top surface maintaining about the same relative areas as in the last case, which were found sufficient to hold the combustion zone above the cylindrical portion. Such an alteration was made by enlarging the cylindrical portion and inserting a solid core $3^1/_2$ inches in diameter so the mixture rose in a thin ring $^1/_4$ inch thick around the core filled with fine material and then spread out at the top, heating a bed of 5 inches diameter. This gave a better top heat distribution but took too long to reach a steady state—almost an hour. After many trials of various proportions it became clear that if uniform top temperatures are to be quickly obtained with low rates of gas consumption over an extended surface that single feeds through single or double porous beds will not suffice and some other plan must be employed.



Figs. 12 to 15—Apparatus for Controlling Position of Combustion Surface for a Given Heat Distribution over the Radiating Surface

USE OF MULTIPLE FEED ORIFICES

The failure of the single point supply to distribute mixture so as not to flash back and yet quickly and uniformly heat the top of a radiating bed, with a low rate of combustion, leads to the conclusion that multiple feed orifices must be used, so spaced as to give the heat distribution desired at the available pressure, a surface bed or radiating screen of sufficient thickness serving to localize the combustion and to equalize the otherwise spotty appearance. It might appear that this could be done by drilling holes in a plate and dividing the combustion chamber from the mixture supply chamber, but from what has been said about the conditions for permanent localization of the combustion zone, it is clear that such an orifice plate will sooner or later heat through, becoming hot enough on the supply side to ignite the mixture there before its entrance into the feed holes. Any sort of feed hole plate is out of the question unless provided with means for removing heat received on the combustion chamber face, fast enough to balance heat conduction through it toward the source of supply, and effective enough to prevent that side from becoming a point of ignition.

Since it has been shown that a single long feed hole supplying a combustion zone can be proportioned so as to permanently resist backward heat flow well enough to insure indefinite periods of operation, it naturally follows that several feed holes might be grouped so as to be fed from a common point, discharging mixture at the other end over as large an area as needed for any desired surface rate of combustion, and so proportioned as to resist heat flow as effectively as with one, if the necessity for the latter is kept clearly in mind. This conception is the basis of the construction shown in Fig. 16 which has 30 holes molded in alundum cement by wires held in hole plates at the end and radiating from a $1^1/_2$-inch bottom chamber in the iron container casting, to a $4^1/_4$-inch diameter circular top bed. To insure the supply chamber end of these feed holes against a rise of temperature to the ignition point, it is necessary only that the distance between this point and the hearth be long enough. When it is, the dissipation of heat from the side walls will be large enough to balance the heat carried down through the solid material surrounding the holes, and the dimensions shown in the sketch have proved to be adequate for this purpose.

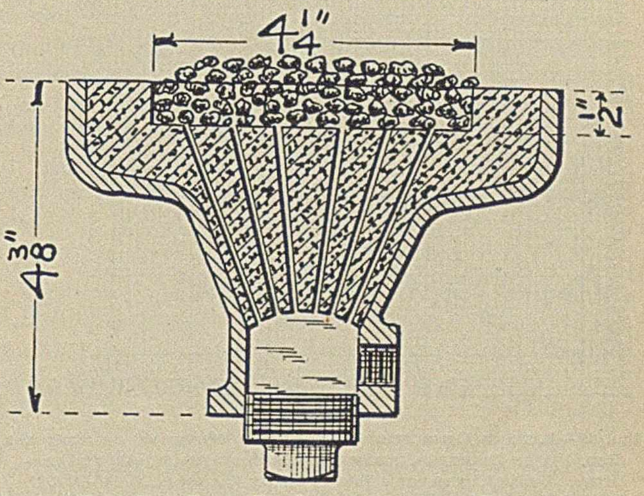
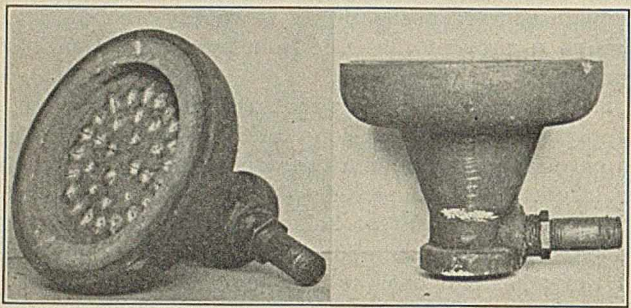


Fig. 16—First Cook Stove Top Burner in which Localization of Combustion Surface, Back Heating, Distribution of Heat over Radiating Surface Are All Controlled

FIRST PRACTICAL STOVE BURNER

In Figs. 17 and 18 are shown two photographic views of the first reasonably practical burner for stove service operating on surface combustion principles—but still imperfect in some respects. To uniformly heat the top bed of loose grain of white alundum or broken fused silica, half an inch thick, thirty-four holes were molded, as shown, by wires $^1/_{16}$ inch in diameter and spaced in three rings. This arrangement gave a quite uniform top heat and was operative at low gas and mixture pressures for an indefinite time, for although the holes of the central group were often red hot for



FIGS. 17 AND 18—FIRST SUCCESSFUL COOK STOVE TOP BURNER, SOLID TYPE

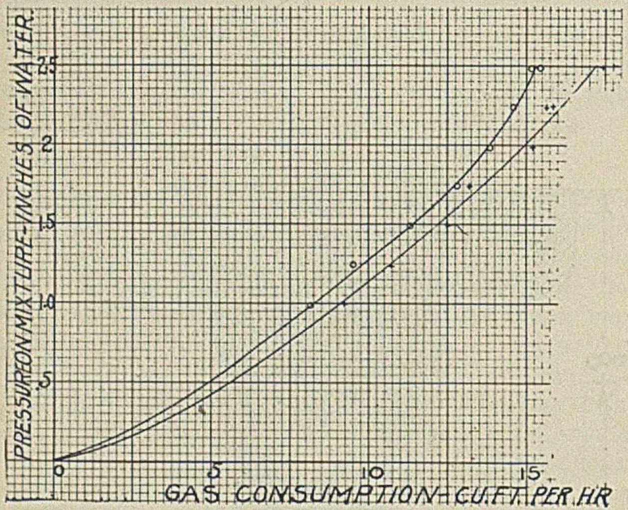


FIG. 19—RATE OF COMBUSTION AT VARIOUS PRESSURES ON CIRCULAR BED, 4¼" IN DIAMETER, SUPPLIED BY 34 HOLES, EACH 1/16" IN DIAMETER. UPPER CURVE FOR A BED OF WHITE ALUNDUM, 20/64"–24/64" GRAIN, 1/2" THICK. LOWER CURVE FOR A BED OF FUSED SILICA 20/64"–24/64" GRAIN, 1/2" THICK

over an inch below the hearth the heat dissipation from the sides was always sufficient to prevent the lower end of the holes ever reaching the ignition temperature. The proportions used were selected to give consumption somewhere near those of the standard top burners of ordinary gas cook stoves, that is, at mixture pressures of $2^1/_2$ inches water the consumption was intended to be about 15 cu. ft. of gas per hour, which is equivalent to about 100 cu. ft. of mixture. Naturally, variations in bed thickness, size of grain or even kind of grain, will cause changes of resistance, the latter due to the variations in the voids, corresponding to different characteristic fractures. The characteristic consumption tests at various low pressures are given in curve form, Fig. 19, showing that at 2.5 inches water pressure this stove burner consumed about 17 and $15^1/_2$ cu. ft. of gas with the silica and white alundum beds, respectively, the standard of 15 cu. ft. per hour being equivalent to 150 cu. ft. per hour per sq. ft. By varying the diameter length and spacing of holes, keeping the general arrangement here indicated, practically any desired rate is obtainable though the general design is the result of the search for a construction suitable for a properly distributed low rate of combustion.

ADAPTATIONS OF TYPE BURNER

To illustrate the ease of adaptability of this general type construction of surface combustion burner to any desired rate over any surface, three other burners are shown, one each designed for a muffle furnace, a crucible furnace and a steam boiler fire, respectively.

The first of these, intended for placing below an assay muffle, is shown in sketch form in Fig. 20 and photographically in Figs. 21 and 22, on which latter the chalk line indicates the beginning of the feed holes. This burner had a rectangular hearth, 6 inches by 10 inches, supplied by 96 holes, molded in alundum cement in a cast iron casing and at 3 inches of water mixture pressure consumed 120 cu. ft. of gas per 60 sq. inches, equivalent to 288 cu. ft. per hour per sq. ft.

A still higher rate over an annular hearth was obtained in the small crucible furnace burner of the same general type as shown in Fig. 23, the combustion zone lying between the side insulation and a central cylindrical muffle used to keep the crucible chamber clear but not at all essential to the operation, though it helps to keep the crucible bottom cooler than it would be otherwise. In this burner 20 holes, each 0.14 inch in diameter, were distributed so as to be on the surface of a cone supplying a hearth lying between two circles, $4^1/_2$ inches and $2^3/_4$ inches in di-

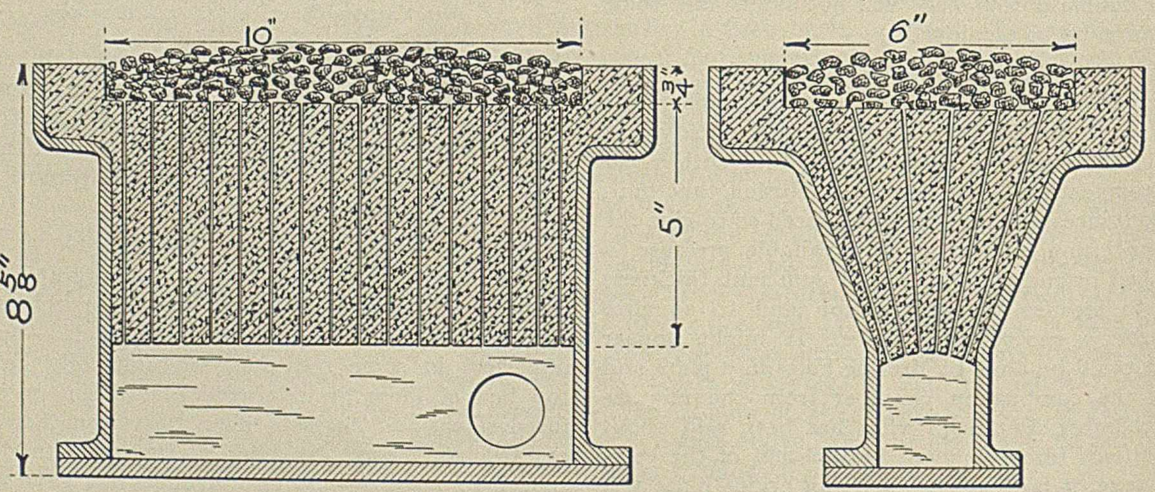


FIG. 20—FIRST FORM OF MUFFLE FURNACE BURNER, SOLID TYPE

ameter, the area of which is, therefore, 15.9 — 5.9 = 10 sq. in. The combustion was 40 and 47 cu. ft. per hour at 2.5 inches and 3.0 inches, respectively, which are equivalent to 576 and 677 cu. ft. per hour per sq. ft. of hearth.

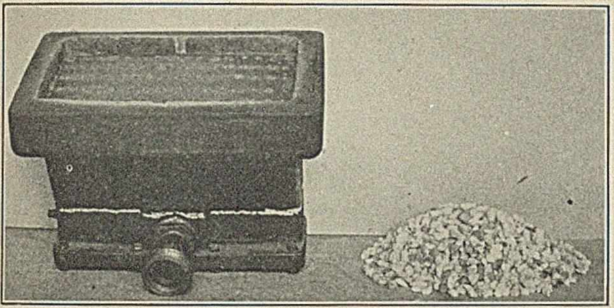


Fig. 21—Top View of Solid Type of Muffle Furnace Burner and White Alundum Loose Granular Bed

An example of how this type construction may be adapted to extension of hot surface or hearth over large areas without excessive length of holes in the solid group is shown in the photograph, Fig. 24, where three sections of wedge form, each 1 x 3 ft., make together a hearth of nine sq. ft. This burner was tried out in the fire box of the Baldwin locomotive in the Mechanical Engineering Laboratory at Columbia University as to its capacity and the proper design of fan blast and pipe connection. Mixtures were supplied through a twelve-inch header to three five-inch branches, one to each burner, and gas supplied through a six-inch main from the street was measured in a Wylie proportional meter, loaned for the purpose by the Equitable Meter Co. At 10 inches water pressure the rate would be 20,000 cu. ft. of gas per hour.

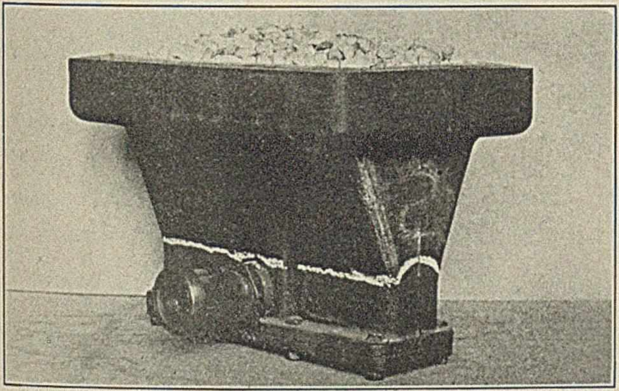


Fig. 22—Side View of Solid Type Muffle Furnace Burner; Bed in Place

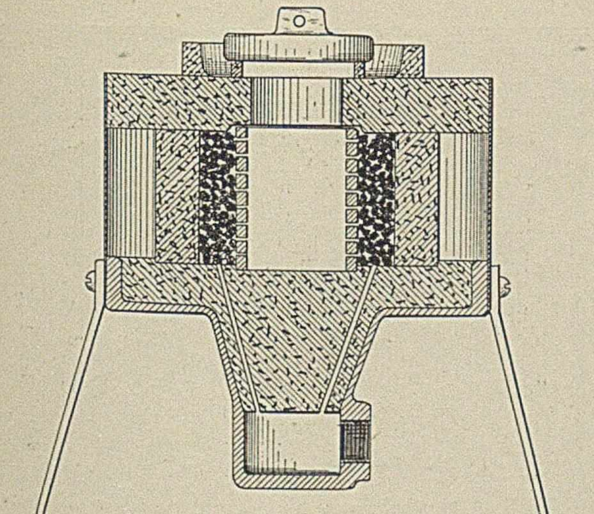


Fig. 23—Construction of Small, Solid Type Muffle Furnace

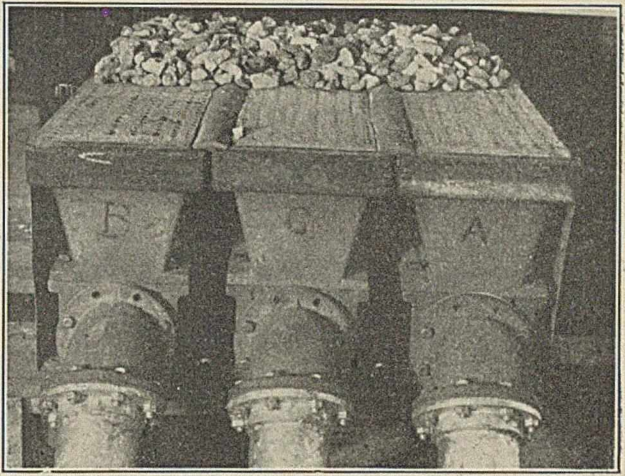


Fig. 24—View of Three Large Solid Type Burners, Forming an Active Bed, 3 Ft. Sq., Capable of Burning 20,000 Cu. Ft., of Gas Per Hour

PROBLEM OF FEED HOLES

While the molding of groups of feed holes in tapered banks, long enough to keep the mixture chamber from reaching the ignition temperature, is a perfectly feasible mechanical construction and capable of insuring indefinitely long operation at any desired rate of combustion per sq. ft. of hearth, it has certain disadvantages that warrant a search for an improvement that will remove them. In the first place it is somewhat troublesome to mold the plastic material between casing and wires so as to secure a solid mass that will not crack on subsequent unequal heating, and when large these sections are very heavy and easily broken by shocks that may come when setting them in place. They are, moreover, necessarily high, too high for many locations, such as a cook stove or boiler furnace if present proportions of frames and settings are to be maintained. These with some others of minor value are sufficient objections to warrant a search for a better form though not serious enough to cause abandonment of this form if no better were available.

Fortunately a better form, and one that is completely satisfactory in all respects, has been found and it naturally follows from a little analytical reasoning. The holes through which the mixture is to be supplied must be cooled, and the cooling must be effective enough to keep the supply end above the temperature of ignition, but no more cooling than will do this is necessary or of value. In addition, the holes must be spaced at the hearth for proper distribution of heat and the desired rate of combustion per sq. ft. of hearth. Banking them in groups, as has been shown, will accomplish this, but it is clear that complete or partial structural independence of the holes by forming them in tubes so each may be cooled independent of the other or even forming them in ribs with independent cooling in at least two directions, is better and more effective than a form in which the heat to be dissipated from an inner hole must be conducted past an outer one also developing heat of its own.

PRACTICAL BURNERS

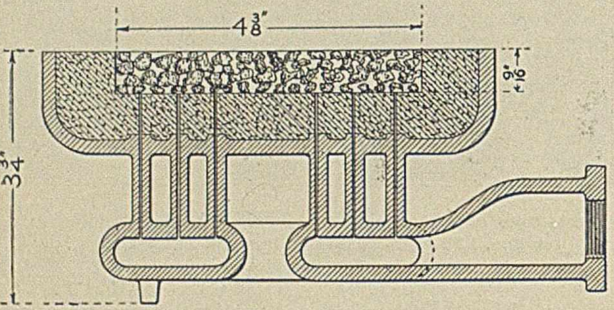


Fig. 25—Second Typical Form of Construction of Active Cook Stove Burner (Top). Heat Distribution Controlled by Spacing Feed Holes. Rate of Combustion by Number and Size of Holes. Localization by Velocity Reduction at Outlet from Holes and Back Heating by Separate Cooling of the Walls of each Hole

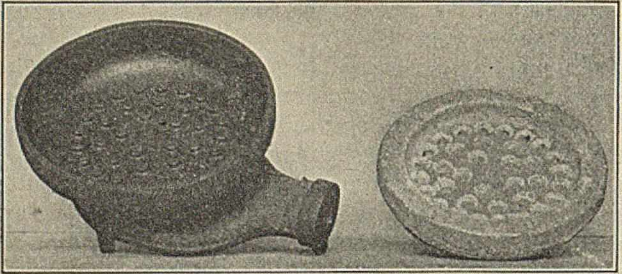


Fig. 26—Top View of Second Form of Cook Stove Burner; Casting before Drilling and Fire Brick Lining

Accordingly, this principle has been incorporated, and burners constructed that seem, in every way, to be satisfactory commercial forms for the essential element of all sorts of surface combustion apparatus. The construction of the first of these designed as a top burner for a domestic cook stove is shown in the sketch, Fig. 25, and photographically in Figs. 26 and 27, the casting and fire brick lining separate, and Fig. 28, the lining secured in place after drilling the feed holes in each of the separately formed cast posts.

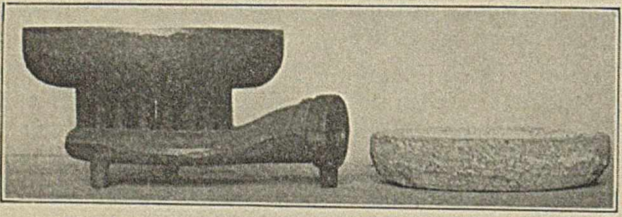


Fig. 27—Second Form of Cook Stove Burner; Casting before Drilling and Fire Brick Lining

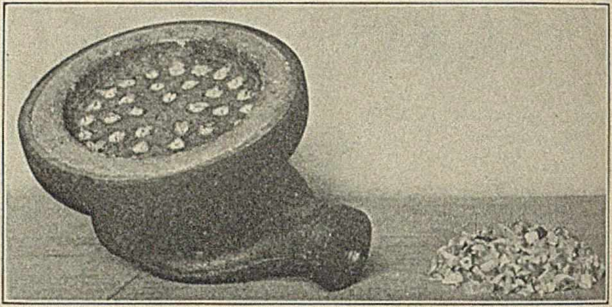


Fig. 28—Second Form of Cook Stove Burner; Fire Brick Lining in Place and Loose Refractory Filling

To insert the lining, wires are inserted in the drilled holes while pressing the lining in place, the cement forming a perfect hole in the hearth, exactly registering with the drilled hole in the casting.

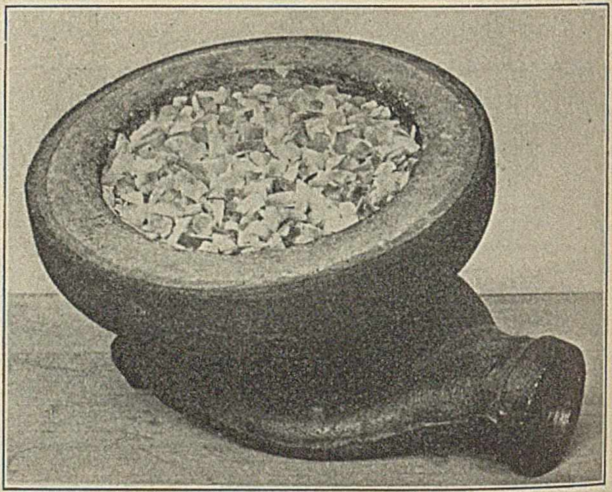


Fig. 29—Second Form of Cook Stove Burner Complete and Ready for Operation

Fig. 29 shows the completed burner with the granular bed in place, in this case crushed and sized fused silica.

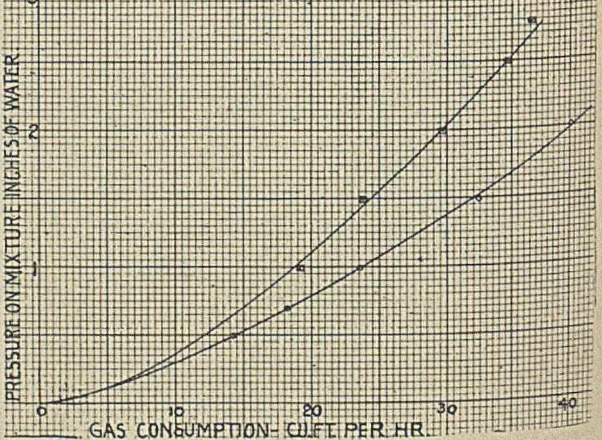


Fig. 30—Rate of Combustion at Various Pressures on Circular Hearth of Cook Stove Top Burner, $4^3/_8$" in Diameter with 35 Holes, each 7/64" in Diameter for Lower Curve, 3/32" for Upper Curve

This burner has 35 holes each $^1/_{16}$ inch in diameter but other diameters have been used, as well as other material for the bed of all sorts of thicknesses and while the consumption and top temperature vary with each, practically everything works well and any result desired by the designer is obtainable merely by selection of suitable dimensions. In Fig. 30 are shown a pair of characteristic consumption curves. Burners of this class have been thoroughly tested under both laboratory and kitchen service conditions, separately and as incorporated in complete cook stoves, having in addition inverted broiler burners with 60 holes, $^1/_{16}$ inch diameter in two rows and a long narrow rectangular hearth with loose granulated material held in place by wire mesh screens. Three of these placed in the top of the Vulcan hotel broiler shell gave consumptions of 38, 43 and 50 cu. ft. of gas per hour at pressures of 1 inch, $1^1/_2$ inches and 2 inches, respectively, all making a bright broiling heat that gives excellent service.

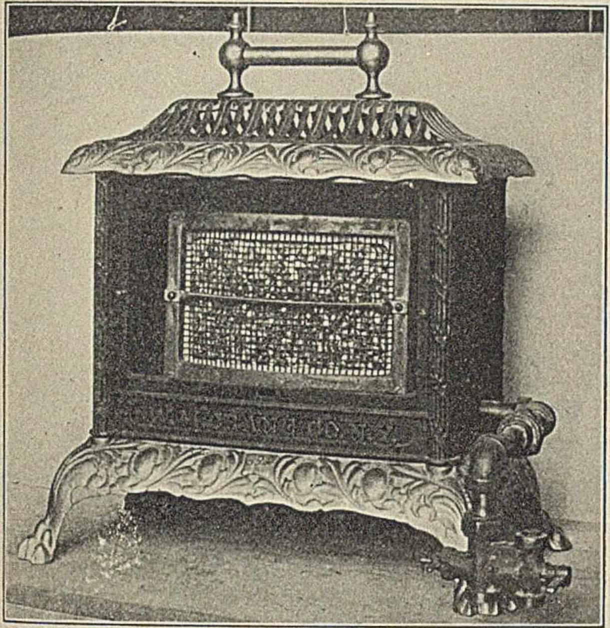


FIG. 31—RADIANT ROOM HEATER EQUIPPED WITH SECOND FORM OF TUBULAR TYPE BURNER, SET IN ORIGINAL SHELL OF STANDARD VULCAN HEATER. LOOSE BED HELD IN PLACE BY WIRE MESH NICHROME SCREEN

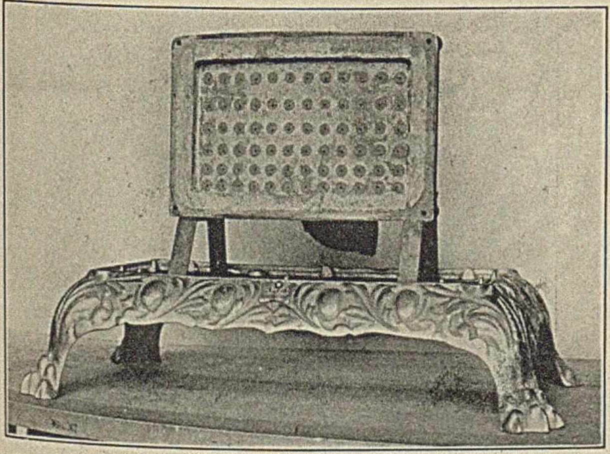


FIG. 32—RADIANT ROOM HEATER BURNER ON BASE WITHOUT BED OR SHELL

This screen construction is well shown by the illustrations of a curved face room-heater burner, designed to fit in a Vulcan heater shell in the photographs, Figs. 31, 32 and 33. The first shows the new heater complete with an automatic proportioning mixing valve, to be described later, while the latter two show the burner without its bed, as set on the base and a separate side view. This burner has a rate of 14, $16^1/_2$ and $17^1/_2$ cu. ft. per hour at 1 inch, $1^1/_4$ inches and $1^1/_2$ inches pressure, respectively, on a hearth $8^1/_2 \times 5$ inches = $42^1/_2$ sq. in. supplied with 72 holes, $^1/_{16}$ inch diameter, and in operation gives as strong a radiation of heat as is consistent with non-blistering of varnish on chair legs or ignition of carpet. While the refractory material is brightly hot, the No. 18 B. & S, four per inch wire of the screen does not seem to be above a faint dull red, and at this temperature all the alloys used in electric heater elements intended for operation at bright red heats up to 2000° F., without serious oxidation, will give good service in this location as will also common cast iron grids. Burners of any shape or size suitable for all sorts of household and hotel cooking and heating service can be produced along these lines to work in any position by the ordinary processes of design, involving no more complex mental processes than are required to select suitable materials and dimensions with the aid of established data or obtainable by simple experiment in any laboratory.

This same principle of supplying mixture through more or less independently cooled feed holes formed in metal walls and discharging into registering holes in refractory hearths, has been applied to higher rate appliances than those for domestic service such as the muffle and crucible service, and one each of these is shown by the photographs Figs. 34 to 36 both with feed holes drilled in ribs, which allows the same casting to be used for a wide range of capacities by changing drill sizes and center distances. The assay muffle is illustrated in Fig. 34, showing the two ribs carrying the feed holes with a few separate tubes placed at the side and front to develop enough extra heat to counteract the open front end muffle cooling, and equalize the temperature throughout the muffle. At the left-hand side is shown a single orifice sampling burner with open bed, consuming two feet of gas per hour and used to adjust the mixture proportions, slight changes in which are readily recognizable by the appearance of this small open fire. The main burner is operated normally at 116 cu. ft. per hour and with the above arrangement always gives a very

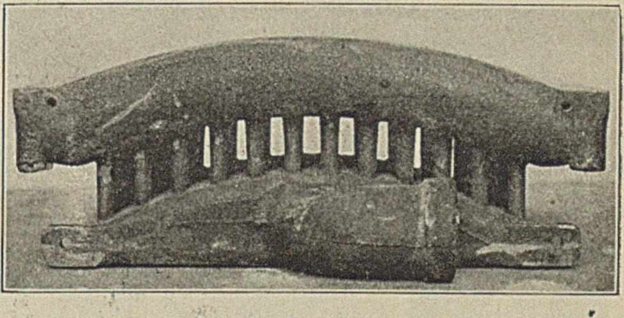


FIG. 33—SIDE VIEW OF TUBULAR BURNER OF RADIANT ROOM HEATER

good thermal gradient, as shown by the following figures:

Thermal Gradient in Muffle with Flue at Front

Top distance from front of muffle	Door closed No draft Temp. ° F.	Door open Good draft Temp. ° F.
2″	1760	1600
4″	1870	1742
6″	1900	1820
8″	1910	1852
10″	1900	1840
Back 12″	1900	1820

The really significant thing here, however, is the ease with which any gradient desired can be obtained by changing the quantity of mixture supplied at different points, entirely independent of flue location. The crucible furnace shown in Figs. 35 and 36 is fed with two rows of holes drilled in a series of radial ribs and discharging in the annular space between insulation and muffle as can be seen in the first illustration with the top removed, which view also shows a sampling burner. The first view shows the side appearance and bottom mixture chamber from which the feed ribs run upward to the base, all cast in one piece. The mixture holes discharge into a hearth of alundum cement on which rests the cylindrical alundum muffle and after one run at about 10 inches water pressure, both muffle and hearth softened as shown by Fig. 37 on which the permanent shrinkage cracks clearly show as do also some pieces of white alundum that adhered to both muffle and hearth. By a change of alundum bonding mixture both of these parts may be made more refractory, sufficiently so for a considerable quantity of very high temperature work. It is not difficult, however, to consume, in such a furnace, enough gas to produce temperatures that will soften any available refractory, but by simply changing mixture pressures it is easy to maintain practically any temperature desired. If for any special purpose it should be necessary to maintain a secondary hot zone at any particular point, then separate mixture supplies can be led to that point and burn without interference with the products of combustion passing from another combustion zone, a condition peculiar to surface combustion, to which the well known "smothering" of common burner flames is unknown.

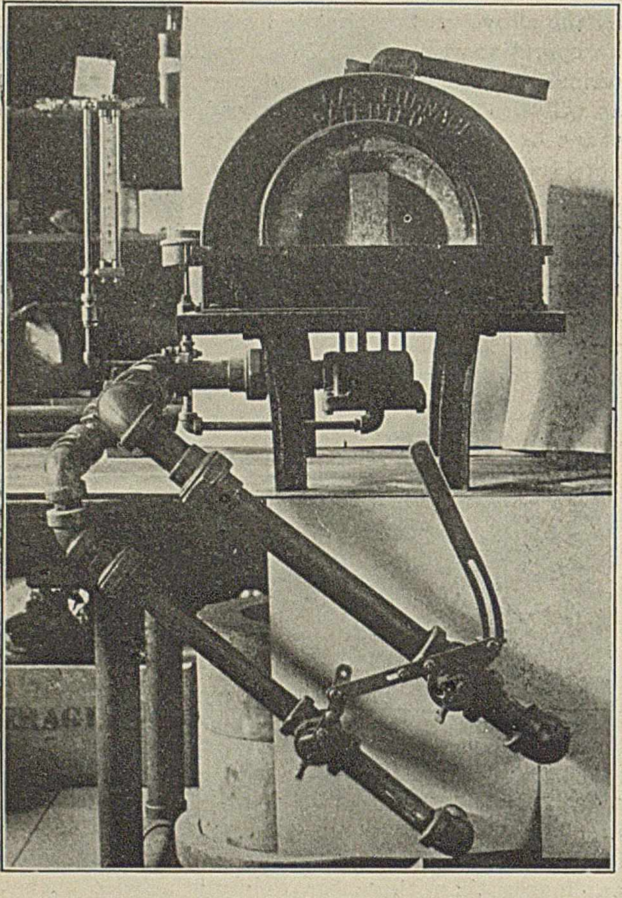


Fig. 34—Front View of Muffle Furnace, Showing Ribs, Carrying the Mixture Feed Holes

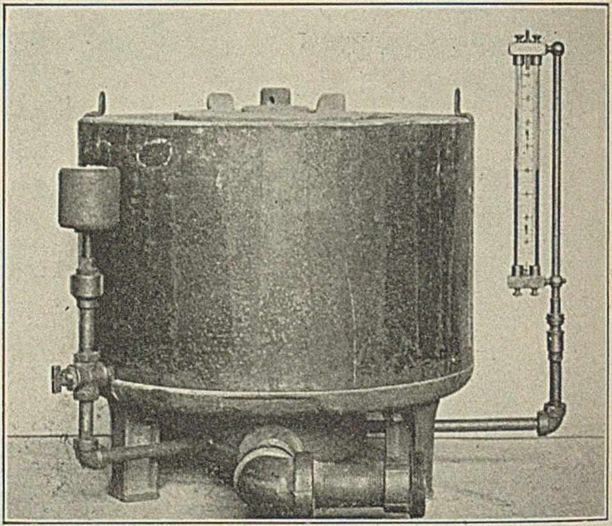


Fig. 35—Side View of Crucible Furnace Supplied by Holes Drilled in Radial Ribs between Mixture Chamber and Furnace Box. Mixture Sampling Burner is Shown at the Left

III. CONTROL AND ADJUSTMENT OF RADIATING SURFACE

By the application of the principles of construction so far developed, it is possible to make a surface combustion burner for any desired rate of combustion per sq. ft. of hearth that will operate for indefinite periods of time without disturbance or adjustment, but for

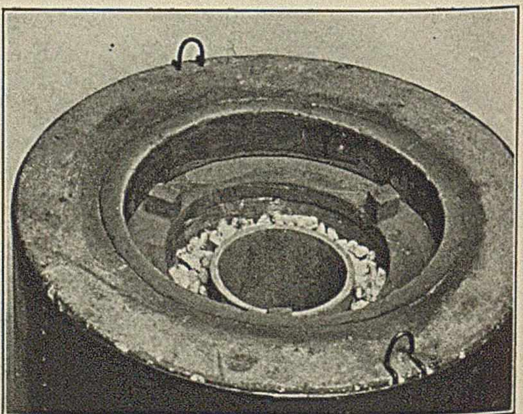


Fig. 36—Top View of Crucible Furnace with Cover Removed

commercial apparatus even more than this is needed. One additional property that must be present is a suitable range of control of the rate, as few, if any, burners are operated in practice at a constant rate of combustion whether used for domestic or industrial purposes. It must be possible, therefore, to adjust the consumption of any burner from a minimum low, to a maximum high rate and to operate safely and surely at any one, no matter what the previous adjustment or the time of operation. Furthermore, some classes of service require a very prompt change in the radiating bed temperature after adjustment, which includes a very quick initial heating after lighting cold, while other classes of service require a slow change after adjustment or a sluggish response to changes. With any given range of adjustment of rates for safe working, there may be associated the requirement of a prompt or a sluggish response after a change, but fortunately in no one burner is it ever necessary or even desirable to provide for more than a limited range of adjustment associated with either prompt heating or sluggish, never both. These conditions can be met in the sort of burners described sufficiently well to meet practically all service requirements consistent with maintaining the advantages of surface combustion as a process.

Fig. 37—Side View of Crucible Furnace Muffle and Hearth, Showing the Effect of Softening of Muffle by Heat. Material of Both, Alundum Mixture

RANGE OF CONTROL OF RATE OF COMBUSTION

The range of control of rate of combustion depends primarily on the size of the feed holes and on the effectiveness of their cooling, and it is easily possible to make holes small enough in separate tubes or ribs to absolutely prevent back flash even when the mixture is turned off and the velocity of flow reduced to zero. By imposing sufficient mixture pressure on enough of these holes per square inch of hearth, any maximum rate of combustion may easily be associated with this minimum rate of zero. Certain practical considerations such as the extra cost of forming small over large feed holes and the increased possibilities of stoppages in them make it desirable to use larger holes than correspond to a minimum rate of zero when that is not necessary, and it has been found that holes $^1/_{16}$ inch in diameter are small enough for safe operation at rates as low as most service requires. Holes of this size in cook stove top burners, broilers and room heaters, can be safely operated at two- or three-tenths of an inch pressure, giving thereby at least as great a range of adjustment as is possible with Bunsen burners of the ordinary form without back flash. Such holes seem to keep free of stoppages and are cheap to form if not much over one inch in length. Apparatus intended normally for much higher rates than the domestic class would naturally be given larger holes, and, therefore, have a higher minimum operating pressure, but the range desired even with this higher minimum is easily obtained by using a correspondingly higher maximum. Thus while the maximum pressure available for operating domestic apparatus without gas boosting, which is out of the question here, is a little less than that of the street main, say 3 inches of water, that for an industrial furnace for which gas boosting is not objectionable may be made even with small fans as high as 12 inches and with positive blowers several pounds. Assuming the holes in the latter case to be such that the minimum safe pressure is 1 inch, there is a pressure range of 12 : 1 for adjustment of rate. Correspondingly, if the domestic apparatus has a minimum safe pressure of 0.2 inch, then it has an adjusting pressure range of 15 : 1. It must not be understood that these are limiting figures, for they are not, being offered merely as examples, since the real range may be made whatever is desired, a thing thought to be impossible in the early days of surface combustion development.

TIME OF HEATING

The time of heating is likewise within control though not through so wide a range; *i. e.*, by adopting suitable constructions the burner may be made to heat up from the initial cold to the normal working state in a short or long time, and will be correspondingly quick or sluggish in response to pressure rate adjustments while in operation. Sluggishness is obtained by using a thick bed of great mass and, therefore, large heat storage capacity, while sensitiveness follows the use of beds or radiating surfaces as light as possible. It is clear that, taking for example the cook stove top burner, a bed only $^1/_4$ inch thick will heat quicker and respond more positively to valve adjustments than a bed 1 inch thick, other things being equal, and the time of heating the latter would approximate four times that of the former if there were no interfering influences. These influences are, however, present and are somewhat difficult to understand at first, but clear enough after study.

In the first place, a reduction in the thickness of bed may leave it so thin that it is no longer effective in reducing mixture velocity at the hearth orifices, so that mixture will blow off at various points where the grain does not properly baffle a jet. The escape of this mixture actually reduces the heat developed in the bed, delays its heating and so counteracts the expected gain from bed mass reduction; at the same time it causes a smell from the escape of the unburned gas which, of course, ceases once the bed is heated even when the baffling is very poor. This is one of the difficulties encountered in the effort to reduce the initial heating time by reduction of bed thickness. It would seem that if, starting with grain $^{1}/_{4}$ inch in diameter a reduction of bed thickness was carried so far as to cause partial blow off by insufficient baffling, this could be corrected by a reduction of size of grain and this is so, but here again limits are met. In no case may the grain be so small as to fall into the end of the tube, but with small holes used, even before this occurs two other things are noted: (1) A thin layer of fine grain on the flat hearth will not heat uniformly with the hole spacing satisfactory for larger grain; a series of bright spots above each hole with dark areas separating them will replace the uniform color of a thicker and, therefore, more sluggish bed. (2) The fine grain bed will not heat initially in the same way that the coarse one will, for below a certain grain size the combustion locates initially on the outside surface, which heats first, the combustion zone gradually working back toward the orifices, while with a larger grain, offering fewer and wider mixture passages in the voids, the combustion zone locates instantly about the holes, flashing directly through the bed. In other words, the fine grain bed heats from the surface *inward* while the coarse heats from the inside *outward*, and though for two such beds of equal weights of material it would seem that equal times must elapse before each had reached a steady state, as a matter of fact the one that heats first from the outside will be quicker because of the non-escape of unburned mixture while heating.

QUICK HEATING TOP BURNERS

This reasoning leads naturally to one of the successful forms of quick heating top burners which becomes incandescent and uniform at the normal rate of combustion in about half a minute, the ordinary half-inch thickness of large grain bed requiring three to four minutes, depending on the material. This one is formed by counter-sinking the outlet side of the $^{1}/_{16}$ inch feed holes to $^{1}/_{2}$ inch, filling the tape holes with silica of size $^{10}/_{64}$–$^{2}/_{64}$ inch, and also covering the hearth to a depth of $^{1}/_{4}$ inch, as indicated in the sketch, Fig. 38.

Reduction of mass to be heated without interference with the effectiveness of the baffles and by using materials that are permanent is a definite problem for which there are many solutions and no doubt others will appear as long as specific attention is given to it, but it is a serious question whether reduction of time below one minute, or even to this time, is really advisable. There is available one type group of construction already explained under localization, and that is the formed baffle, of which the flat plate mushroom plug and ball in tape hole are examples, and over which may be placed the radiant screen, of metal, perforated or woven, a thin layer of loose grain, or a diaphragm of refractory perforated or otherwise formed, to be porous enough to allow the free passage of gases; all these have been used as well as some others that proved unsatisfactory. In the latter class fall a layer of picked asbestos fiber which heats as quickly as an illuminating mantle but which has no life; a $^{1}/_{4}$ inch layer of hollow cylinders or short thin silica tubes like straight beads, $^{1}/_{8}$–$^{1}/_{4}$ inch diameter and $^{3}/_{8}$ inch long, which heats in less than one minute and is permanent but too expensive; and a thin plate of alundum cement perforated freely with $^{1}/_{8}$ inch holes, which becomes incandescent in one minute but is too fragile. In the former class fall the perforated metal non-oxidizing alloy plate over some form of direct baffle, and the molded porous diaphragm directly over the holes serving as both baffle and radiator, the former giving a very quick heating but not so permanent as the latter which, however, heats more slowly. For the metal plate, two materials have been used, Nichrome II and Excello, the analyses of which are given below, as determined by Whitaker and Metzger:

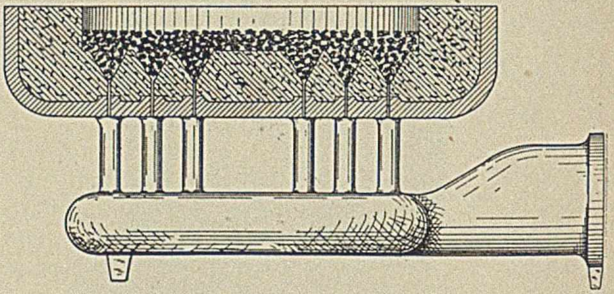


FIG. 38—MODIFICATION OF TUBULAR TYPE COOK STOVE TOP BURNER FOR QUICK INITIAL HEATING

ANALYSIS OF NON-OXIDIZING ALLOYS (PERCENTAGES)

	Nichrome II			Excello
	Sample No. 1	Sample No. 2		
Nickel	56.4	59.9	Nickel	83.43
Chromium	10.6	10.8	Chromium	14.72
Iron	30.6	26.2	Iron	1.30
Manganese	2.1	2.3	Silica	Trace
	99.7	99.2		99.45

The former has been most used and as applied to the problem of quick heating was in sheet form, 0.032 inch thick, perforated with holes 0.073 inch diameter and about one diameter apart. This was cut circular to fit the top burner hearth $4^{3}/_{8}$ inches diameter and heats to normal in about half a minute when set over baffles of the mushroom or plate type, and in about ten seconds with ball baffles. Such plates have a fair life if not operated at too high a temperature; about one cu. ft. of gas per hour for each two sq. in. of radiation is a satisfactory rate and gives a good red heat. This construction may, therefore, be adapted as a direct competitor of the electric heater, using the same radiant material at the same temperature, but with gas as the source of heat instead of electric current. A series of consumption curves of one of these quick heating nichrome radiating plates, $4^{3}/_{8}$ inches diameter, set over 35 holes, 1/16 inch in diameter, in the cook stove top burner hearth with mushroom baffles plugs is given in Fig. 39.

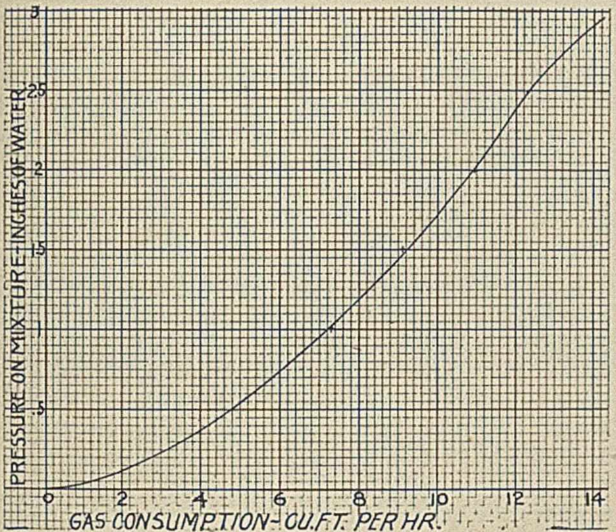


FIG. 39—RATE OF COMBUSTION OF TUBULAR TYPE COOK STOVE TOP BURNER HAVING 35 HOLES, EACH 1/16" IN DIAMETER, DISCHARGING UNDER SQUARE STEMMED MUSHROOM PLUGS, SHOWN IN FIG. 3 AND PROVIDED WITH PERFORATED NICHROME RADIATING PLATE

REDUCTION OF HEATING TIME

It is a serious question whether the reduction of heating time should be carried so far, even in domestic apparatus in spite of a demand on the part of users for it, because of the corresponding small heat storage. The top burner carrying a half-inch loose bed has so much heat storage that it will resist interference from the spilling on it of large quantities of water or grease, amounts of which sufficient to be serious with Bunsen burners have no effect here whatever, but the more this heat storage is reduced by constructing for quick heating the less this resistance. Another advantage of heat storage in the incandescent bed is inherent in all intermittent heating such as the heating of laundry irons, which may thereby absorb heat for a time faster than it is being generated by drawing on the bed storage; these always heat faster on the surface combustion burner than on a common burner of equal gas consumption. One trial showed that with two irons on a surface combustion burner a laundress could do as much work as with three irons on the Bunsen, the former consuming about half the gas that the latter used and heating the iron in less time.

INFLUENCE OF SERVICE CONDITIONS

In applying these surface combustion burners a new study of service conditions is necessary as they have some characteristics, not possessed by the old burners, that permit and even demand adaptation of burner design to service. There will always be some cases where quick heating is important, *e. g.*, in toasters; others where heat storage is important; top burners for intermittent service and those that are much used and likely to receive spillings; also others that will demand the smooth self-supporting surface of the bonded diaphragm, which is operative in all positions and which has properties all its own.

USE OF DIAPHRAGMS

The application of the bonded diaphragm to general service conditions is a problem in itself, as the localization of combustion is not so readily controlled under wide ranges of mixture pressures within the limits imposed by the ordinary domestic gas service. All such diaphragms except those of very great porosity and, therefore, necessarily thick, will heat from the outside inward and in all, the heat will work back, the combustion zone following until back flash takes place under some supply pressures and times of heating. Assuming that general service apparatus will be operated at a variable rate and at such variable pressures, the localization combustion by diaphragms is not to be depended upon; but they will still be useful as baffles and radiators when placed over a hearth, such as described, and which latter insure localization.

Placing a bonded diaphragm over such a hearth as that of the cook stove top burner, it will, on ignition, heat from the outside first; the combustion zone will then work down and through it until a back flash occurs and the combustion zone locates between the hearth and bottom face, extending from each hole into the diaphragm a little way if it lies directly on the hearth. As the heat works back unevenly, due to non-homogeneity of voids and size of grain, there will be at the moment of ignition below it only one hot spot, all the rest of the bottom and the hearth being cold. Up to this moment the outer surface has been hot and radiating, but now the heat will be practically all absorbed by the hearth and lower space until they become incandescent, and in this period the top radiating surface will cool and then slowly recover its temperature, after which it will operate indefinitely without change. The time it takes for the outer surface to begin to radiate, and for the back flash to occur are both dependent on the relation of porosity to pressure or rate of supply, but the time of recovery after back flash is largely controlled by diaphragm uniformity. If the combustion zone works back equally fast all over the diaphragm the bottom face will be hot all over when bottom ignition takes place, instead of only one spot, and thus the top temperature will be recovered most rapidly.

A great many small diaphragms of all sorts of grain materials and bonds have been tried and all abandoned in favor of alundum; these have been prepared by the Norton Co., to whom considerable credit is due for the spirit of coöperation displayed in opening up a new field, absolutely without data. Without reciting the details, it may be noted that satisfactory results are obtained with Norton alundum diaphragms fed through the self-cooling mixture holes and set over the discharge hearths. These are structurally quite strong if the bond used is not intended for very high temperatures, in which case they are delicate but still useful for some purposes. Two consumption tests of such diaphragms set in the hearth over 35 holes, 1/16 inch diameter, the porous part being 4 inches diameter and 1/2 inch thick, are given in Fig. 40, comparing a Norton alundum diaphragm of No. 4 grain with an English fire clay diaphragm, which latter fused in time on the hearth side, the former remaining unchanged. In Fig. 41 are given similar results for a series of alundum diaphragms $5^{1}/_{8}$ inches diameter, $^{7}/_{16}$ inch thick, set over the same hearth after enlarging. These were of four sizes of grain No. 8, No. 6, No. 4 and No. 2, and three different processes of working. Change of curvature indicates that the main flow resistance has been transferred from feed holes to diaphragm.

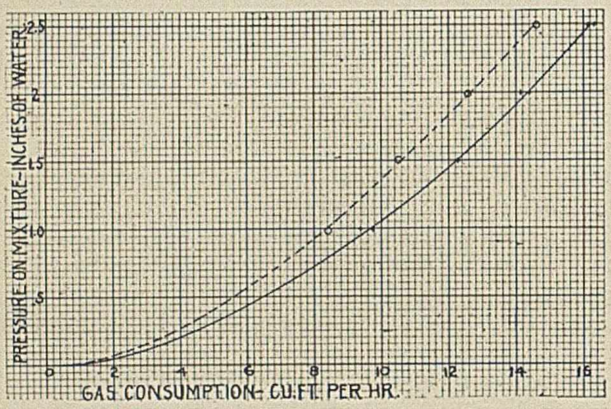


FIG. 40—RATE OF COMBUSTION OF COOK STOVE TOP BURNER HAVING 35 HOLES, EACH 1/16" DIAMETER, DISCHARGING TO BONDED DIAPHRAGMS. TOP CURVE DIAPHRAGM OF NORTON ALUNDUM MIXTURE. BOTTOM CURVE ENGLISH FIRE BRICK MIXTURE

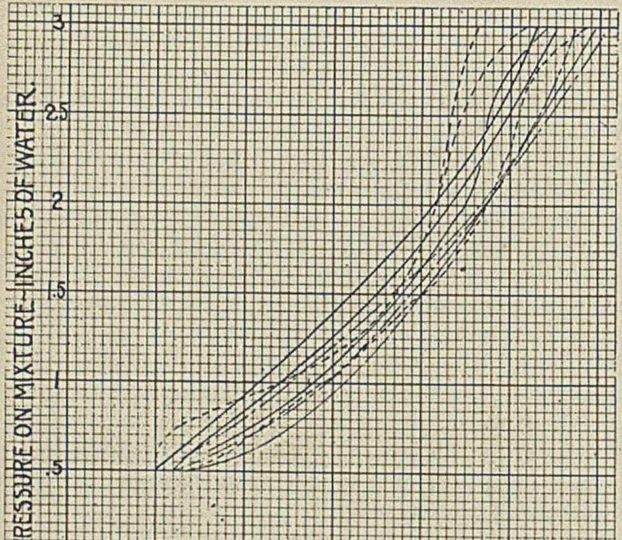


FIG. 41—RATE OF COMBUSTION OF COOK STOVE TOP BURNER HAVING 35 HOLES, EACH 1/16" IN DIAMETER, DISCHARGING THROUGH NORTON ALUNDUM DIAPHRAGMS OF DIFFERENT CONSTRUCTION. EACH DIAPHRAGM $5^{1}/_{8}$" DIAMETER AND 7/16" THICK. VARIATION IN CURVATURE SHOWS TRANSFER OF MAIN RESISTANCE FROM FEED HOLES TO DIAPHRAGM

The time of back flash and recovery of surface temperature varies considerably but in the best the whole time is about five minutes; in some cases it has reached 15 and even 20 minutes. The time of recovery varies from 3 to 12 minutes, the better diaphragms requiring the lesser time, all at pressures of $1^{1}/_{2}$ inches of water.

IV. AUXILIARY APPARATUS

Any burner or furnace intended for laboratory use where operators have sufficient skill and understanding of cause and effect, need not be supplied with any special appliances for proportioning air to gas in the mixture, or for changing the mixture pressure as service conditions require it and, therefore, any of the many standard fans and blowers may be used for compressing air alone or air and gas separately with a hand-adjusted cock in the air and the gas pipes supplying each appliance. This is by no means the case, however, with some industrial and with all domestic appliances. Where an industrial furnace operator is more or less constantly engaged in managing one furnace, he can be taught to make adjustments of hand values if provided with the ordinary water column water gauge and a small sampling burner, but this is entirely out of the question for the ordinary woman in the home or chef in a hotel, as they either cannot or will not adjust anything beyond turning the cock that regulates the heat and it must be confessed, sometimes not even this. For domestic service, including that of hotels and restaurants, it may reasonably be expected that they operate a single cock for each burner to regulate the heat, but maintenance of mixture proportions essential to surface combustion processes must be automatic and fool-proof. This at first, like some of the other questions taken up, looked like a difficult problem yet it seems to be working out in a thoroughly satisfactory way.

AUTOMATIC MIXTURE PROPORTIONING

Automatic mixture proportioning has been accomplished by two devices which working together carry out the fundamental method; *i. e.*, proportioning by equal pressure drop on an air and a gas orifice, having areas in the desired proportion. Regulation of air pressure to an equality with that of the gas supply available at the appliance will bring them to a control cock having two ports with areas in the desired proportion and by suitably large pipes or small port openings; these ports determine the flow to a common mixture outlet, and the proportions will remain constant so long as the principal resistance to the flow of both

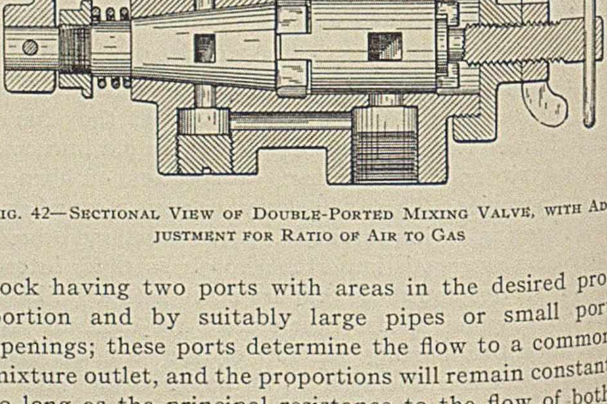


FIG. 42—SECTIONAL VIEW OF DOUBLE-PORTED MIXING VALVE, WITH ADJUSTMENT FOR RATIO OF AIR TO GAS

is in the cock ports. This is accomplished, first, by sufficiently large supply pipes but it is necessary also that the ports bear a suitable relation to the burner opening so that while the pressure drop through the burner is large enough to establish the desired velocities for localizing the combustion zone, there is also some drop of pressure through the ports themselves. In other words, the combined area of the ports in the wide open position must never be so large as to build up in the mixture chamber a pressure equal to that in the air and gas supply pipes. This does not involve any serious drop through the ports; two- or three-tenths of an inch of water is ample, and less will do if necessary, but the more there is the more definite the proportioning and incidentally the smaller the valve needed. To permit of an adjustment to changes of gas quality one port may be made of fixed size with the other adjustable, but in opening and closing both must vary in constant ratio. It is not expected that users will make this quality adjustment, but rather the gas men who make installations and, of course, in any one district a setting will be found good for the average air requirement of the sort of gas supplied, the variation in which is never large enough to seriously interfere with the operation on this mean setting. Wherever the gas is uniform or substantially so, in air requirements, this gas quality adjustment can be eliminated and the ports fixed at the proper value, once for all. One successful cock of this sort is sketched in Fig. 42 and shown photographically in Fig. 43, complete on the right and in various stages of dissection at the left. This has two plugs, keyed together so as to rotate together, but otherwise free; one, carrying the small gas port, is tapered and spring seated for tightness, while the other, carrying the air port, is cylindrical, and has an axial adjustment for length of effective opening to adjust for gas quality. Both plug ports are aligned with the casing ports so as to absolutely open and close together. With this cock, the user regulates the burner exactly as has been the case with common burners, controlled by single ported cocks.

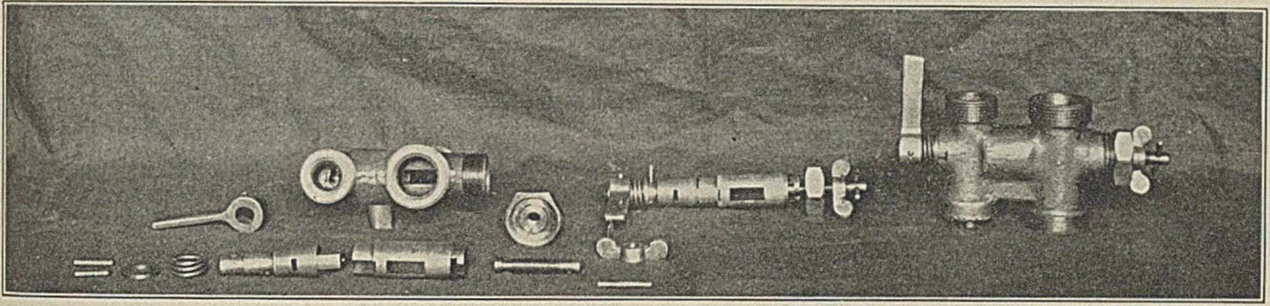


Fig. 43—Double Ported Adjustable Mixing Valve; Complete at the Right and in Various States of Assembly at Other Points

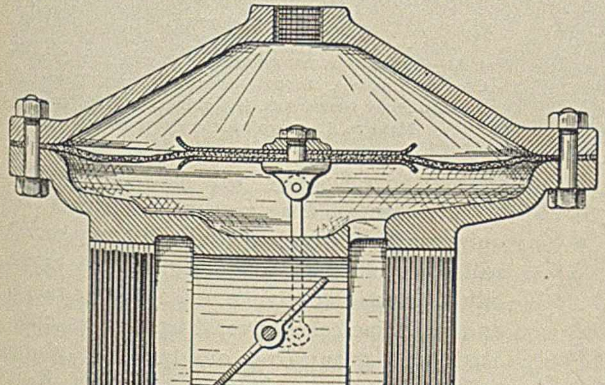


Fig. 44—Sectional View of Air Pressure Regulator for Maintaining Air Pressure Equal to that of Gas

CONTROL OF PRESSURES

It is necessary, however, for the satisfactory working of any form of double ported cock, intended to maintain constant proportions of air and gas while controlling the total quantity of flow from zero to a maximum, that the air and gas approach at equal pressures so that the drop in pressure to the common mixture pressure be equal; this may be accomplished by regulating the air pressure to that of the gas, or conversely. The former has been used as most satisfactory, and in accordance with it, the air delivered by the fan is passed through a diaphragm regulator carrying a damper valve in the main air passage. This damper is rotated by a crank and connecting rod, fixed to the meter leather diaphragm, the weight of which is balanced by a spring or dead weight, if horizontal, but is

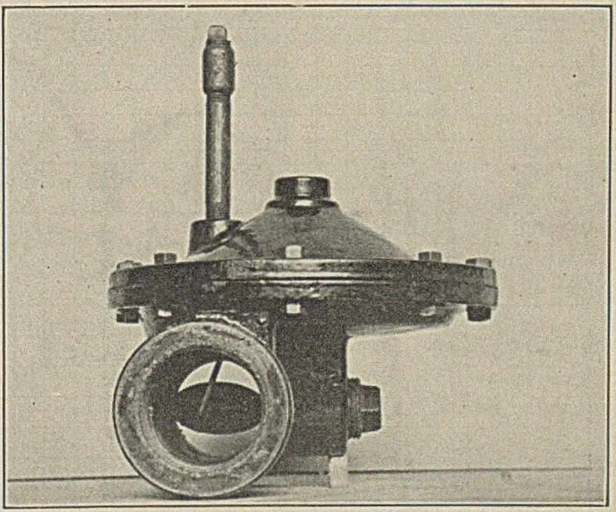


Fig. 45—View of Regulator Complete; Control Damper Held Open by a Knife

to be neglected if operated in a vertical plane. The delivered air pressure is caused to act on the bottom of the diaphragm while the local gas pressure acts above; both sides, being dead ends, that is, not swept by any current, there is little tendency to dry the leather. All changes of gas pressure vary the diaphragm load and move the damper to the position for re-equalization promptly and positively so that no matter how local gas pressures may vary, the air automatically follows and the mixture quality remains what it should be. The construction of this regulator is shown by the sketch, Fig. 44, and the two photographs, Fig. 45 showing one size of regulator complete, and Fig. 46 showing it partly dissected.

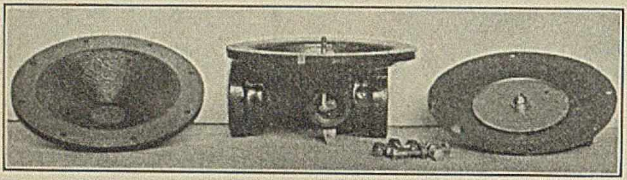


Fig. 46—Air Pressure Regulator Partly Assembled, Showing at the Center Connecting Rod and Crank for Actuating the Damper by the Diaphragm Movement

AIR PRESSURE NECESSARY

Air under pressure is always necessary for the operation of these surface combustion appliances but the pressure need be no more than is necessary for good regulator action, for which about 1 inch water drop is desirable. Air pressures of this order of magnitude are easily obtainable by fans and are preferably, though not necessarily, electrically driven. If the full available gas pressure is used, and this be three inches, then the fan should deliver at four inches of water, but very satisfactory operation can be secured at mixture pressures as low as 1.5 inches, for full capacity, which would require less than two inches of gas pressure and less than three inches fan delivery. At such pressures the power requirements of the fans for ordinary appliances are very small, as may be easily calculated. For quick reference, the results of such a calculation are given in chart in Fig. 47 for a wide range of capacities and pressures, to which is added a scale for reading motor horse power for any fan efficiency and electrical input horse power for any electric motor efficiency. For small sets the fan efficiency will probably be between 30 and 50 per cent, while the motor efficiency will perhaps average 50 per cent. The power and current requirements are so low that any lamp socket will have electrical capacity enough to run any domestic appliance, even a large range, and in some cases several appliances operated as a group from one fan.

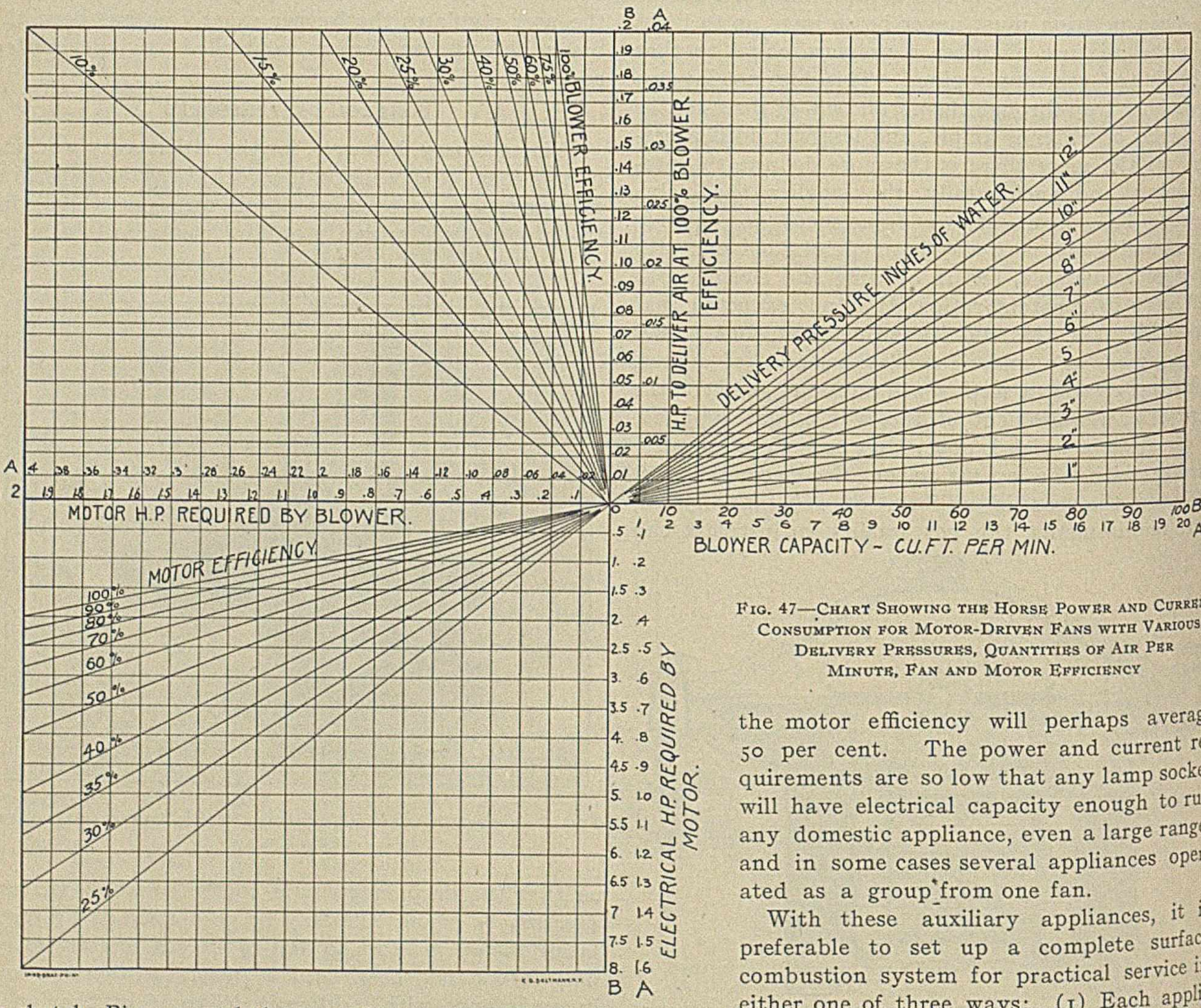


Fig. 47—Chart Showing the Horse Power and Current Consumption for Motor-Driven Fans with Various Delivery Pressures, Quantities of Air Per Minute, Fan and Motor Efficiency

With these auxiliary appliances, it is preferable to set up a complete surface combustion system for practical service in either one of three ways: (1) Each appliance with its own fan and regulator and so completely independent except for connection to gas and electric service mains. (2) A central fan with distributing air pipes to each appliance with its own regulator. (3) Combinations of appliances in groups.

It is comparatively easy to see how central or group systems would work out for large installations suitable, for example, for hotel kitchens, but it is a matter of some interest to examine the independent domestic unit.

FIRST SURFACE COMBUSTION RANGE

The first of these ever constructed was made by converting one of the standard side cabinet ranges now on the market, using mixing valves that had been used elsewhere and a fan taken from a vacuum cleaner, in the absence of one of suitable capacity as to volume and pressure. The fan used was that of the Regina cleaner in one casing with a G. E. motor and had an air volume capacity about four times what was needed, delivering at about 11 inches of water where four or five would have been sufficient; it consumed 90 watts with all burners in operation. These things are stated to explain the somewhat crude appearance of some parts of this, the first self-contained surface combustion range ever constructed and put into service in a home kitchen. In Figs. 48 and 49 all parts are clearly shown, except the check valve between fan delivery and regulator to prevent gas escape from the fan, should a burner be turned on when the fan is not in operation; this was not at first provided. It will be noted that the mixing valves or double ported cocks are fitted with graduates to guide the operator in adjustment, as the absence of visible flame, the ordinary guide, here demands a substitute. All auxiliary or secondary air openings into the oven are closed as now unnecessary and if left tending to reduce efficiency by the air so drawn in and discharged hot to the flue. For the same reason the chimney vent is made smaller. The oven flue linings were not changed but should have been to provide for the flow of a smaller volume of gases at higher temperatures with the surface combustion burners than with the original Bunsen burners.

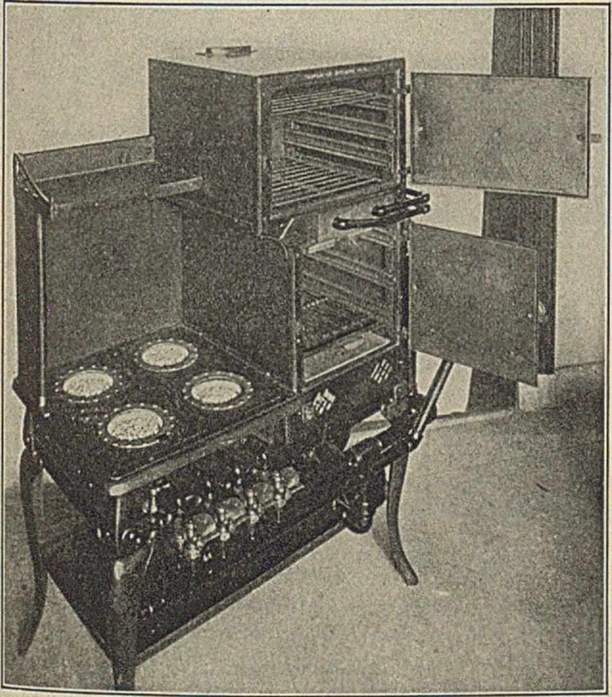


Fig. 48—Diagonal Top View of First Domestic Range; Solid Cast Iron Top, with Four Top Burners; Refractory in Place but Burner Grid Removed

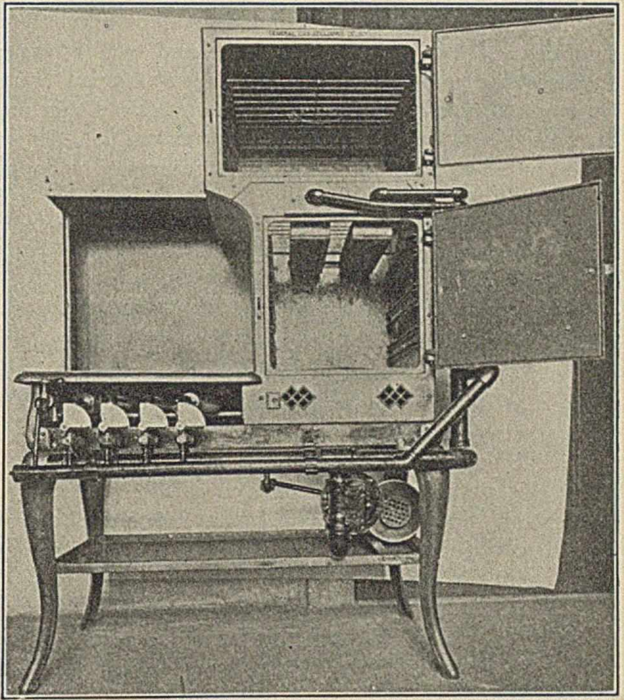


Fig. 49—Front View of First Complete Domestic Range, with Oven Doors Open. Broiler and Oven Burners are Visible, Each being Rectangular, Mixture Supplied to Holes Drilled in Ribs between Mixture Chamber and Hearth. Burners are Suspended from Front and Back Walls. The Closing of the Openings for Secondary Air is also Visible on the Lower Door, no Secondary Air Being Needed for the Surface Combustion Process

V. EFFICIENCY OF SURFACE COMBUSTION APPLIANCES COMPARED WITH BUNSEN

As in other cases, it is here found that the absolute and relative efficiency of surface combustion and Bunsen burner appliances is not a constant thing but varies with conditions and, therefore, any discussion must be more or less limited in scope to give a correct impression. For this reason the figures obtained from tests will be confined to domestic appliances operating on city gas, such as cook stove top burners, broilers, oven, room and water heaters, all made by removing Bunsen burners from standard appliances and substituting the new ones. Top burners were tested by taking the consumption and time to raise a weighed body of water to 200° F., from an initial low temperature; the same or identical vessels always open were used in all comparative tests.

From a large mass of tests conducted with various bed materials and thicknesses, different sizes, shapes and materials of vessels, different distances between bed or flame and the vessel, at all sorts of gas or mixture pressures at various positions of the cocks and with various stove, top or burner ring construction, the figures themselves vary so much as to be at first perplexing to one seeking some definite, general conclusion on the relative value of the two systems. Careful analysis, however, reveals some order from which conclusions follow relating results to conditions. The first of these is that with identical conditions or as nearly so as the differences in the systems permit, the surface combustion burners always do an equal amount of heating of the water with less gas than the Bunsen but how much less seems to be dependent on the construction of burner, stove frame and water vessel. Perhaps the most important of these external conditions is the vessel itself, and however queer this may at first seem, an explanation is available. If the vessel be large, of good conducting material, like copper or aluminum, and containing a large amount of cold water, it would approximate the heat absorber of a gas calorimeter and could take up a very large amount of the heat being generated at a given rate. On the other hand, if the vessel has a small heat-absorbing surface in proportion to the rate of combustion and be made of poor conducting material then there is less chance of heat being taken up by the water, other things being equal. Size and material of vessel placed over a burner developing heat at a given rate do, therefore, determine, to some extent, the rate of heat absorption, but also the rate of heat dissipation from its sides, both the submerged and exposed part, and the water surface. This last factor is also more or less influenced by the extent to which the vessel is filled and the air drafts blowing on it. It thus appears that a great deal depends on the vessel and its filling, but as many detailed figures are always confusing the results of two vessels only are given in this connection.

One of these is a cylindrical tinned iron sauce pan, about 8 inches in diameter and of equal height and the other a smaller tapered pressed steel enameled sauce pan, about $6^1/_2$ inches in diameter, both tested on New York City gas, over burners consuming 15 cu. ft. per hour, the Bunsen burner being of the Crane construction and the surface combustion having a $4^3/_8$ inch hearth with $^{20}/_{64}$ to $^{24}/_{64}$ inch material, $^1/_2$ inch deep and covered at the edges by a cast iron ring with vents between it and the vessel $^1/_8$ inch wide. For equal amounts of heat taken up by the water the relative consumption was as follows:

Bunsen burner consumption = 1.44 × surface combustion burner consumption with large iron pot; 1.66 × surface combustion burner consumption with smaller enameled pot. These two burners turned down to a simmer, using the enameled pot and keeping the water just below the boiling point as nearly as could be judged by the eye, the consumptions were: Bunsen 5.2 cu. ft. per hour and surface 2.42 cu. ft., giving the ratio of 2.15.

The average of the two other series with enameled vessels on Westchester, N. Y. gas, a thick silica bed surface combustion stove, grid top, 15 cu. ft. per hour, with a G. G. A. Co. Bunsen burner, gave consumption ratios of 1.71 and 1.75. A different surface combustion burner, that designed for quick metal heating becoming normal in less than one minute, as compared with three or four minutes for the above burners, and illustrated in Fig. 38, gave a ratio on N. Y. C. gas of 1.80. This last was also fitted with a grid top, the enameled vessel being held about $^1/_2$ inch above the bed.

These are high values and indicate a large fuel consumption as may be seen from the following figures: Assuming a Bunsen burner to be consuming 15 cu. ft. per hour, then to give the same heating effect in a cooking vessel, the surface combustion burner for consumption ratios of 1.8, 1.7, 1.6, 1.5, 1.4, and 1.3 would require 8.3, 8.8, 9.4, 10.0, 10.7 and 11.5 cu. ft. per hour, saving 6.7, 6.2, 5.6, 5.0, 4.3 and 3.5 cu. ft. gas per hour while doing the same work. The high ratio above reported as actually attained may not be under favorable conditions and low values have frequently been found; in one case lower efficiency with a certain surface combustion burner and top construction than with the Bunsen; but this fact pointed out the mistake in construction which, when corrected, resulted in high ratios. As has already been pointed out, the size of vessel is important but so also is the heat dissipation from the top. In one case a solid stove top was used with circular openings to take the burners and quite low efficiencies were obtained, as low as 1.2, but it shortly appeared that most of the hot gases were escaping along the underside of the cold top instead of rising around the vessel, due to bad construction. A simple substitution of a grid that allowed the gases to rise with no other change raised the ratio from 1.2 to 1.68.

GAS SAVED BY NEW PROCESS

It may easily happen that service conditions will arise that will demand constructions that are not highly efficient as, for example, cold cast iron tops for intermittent service, in the interest of cleanliness, so that a commercial stove construction will probably be a compromise. The best judgment that can now be made is that, taking into consideration all these conditions, there may be expected a consumption ratio of about 1.55 Bunsen to flameless, or 0.65 flameless to Bunsen, which indicates a saving of about 35 per cent of what is now being used though it is possible according to actual tests that it may be as high as 45 per cent.

EFFECT OF EXCESS AIR

It has previously been stated that the expected savings from the surface combustion process were to be derived first from the elimination of the excess air now required of all Bunsen burners, and second by the superior penetrating power of radiant heat in warming bodies from the fire. The influence of these two together is well shown in all the preceding relative consumptions but perhaps nowhere quite so well as in the case of the simmering test where two fifteen-foot burners were turned down to keep the water just at the boil for about one hour, which raised the consumption ratio from 1.66 to 2.15. This is a splendid demonstration because in the turned down condition very much more cold air rises with the hot flame gases to the pot bottom in Bunsen burners than when they are on full while there is no change, whatever, in this respect with the surface combustion burner. The difference above is, moreover, largely due to excess air because at the turned down condition the surface combustion burner bed was only faintly radiant.

The minimum effect of this excess air influence is perhaps best obtainable from a comparison of two water heater tests made on identical coils of the Vulcan heater, one as constructed with standard Bunsen burners and the other with a surface combustion burner substituted, but without other change. Both were operated to heat the water in a standard forty-gallon copper tank, equipped with thermometry and the results are uncorrected for radiation from it or pipes. On an assumed calorific value for the gas, the Bunsen burner gave an efficiency of 70.4 per cent, while the surface combustion burner gave 82.3 per cent, a ratio of 1.17, the flue gas temperature of the Bunsen being 248° F. against 309° F. or 61° higher, for the surface with its excess of 12.3 per cent efficiency. Of course, a properly constructed surface combustion heater can easily be made to yield as close to 100 per cent efficiency as may be desired; these figures are given not to show what may be expected of such, but purely as a measure of the excess air influence when it is reduced to its lowest value in the Bunsen equipment; this condition is entirely eliminated by surface combustion.

Another measure of excess air influence is given by the figures for a comparative top oven test in which an upper oven was heated by burners below, intended primarily for a broiler oven below, Figs. 48 and 49. As originally equipped with Bunsen burners this top oven required 19 cu. ft. of gas per hour to maintain at its center a temperature of 480° F., as against 13.5 cu. ft., a ratio of 1.4, when surface combustion burners were substituted, with no other change than the closing of the secondary air openings, linings which should have been changed being left in place.

VALUE OF RADIANT HEAT

The direct value of the radiant heat developed by surface combustion burners is shown most clearly in test of such apparatus as a broiler, or a radiant room heater, Fig. 31. Tests have been made in such broilers by taking the consumption for the proper cooking of steak and chops, both thick and thin, chicken, squab, fish, lobster, and toast, under the direction of competent chefs, and comparing with that required for the same carefully measured and weighed in Bunsen burner broilers. For this purpose was selected the Crane Bunsen burner broiler with cast iron fingers heated to a dull red by the flame, thus giving more radiant heat than other types not so provided though more commonly used. This was done to provide the most vigorous Bunsen burner competition available as a basis of comparison for the surface combustion burner and the results varied in specific instances, the general average being very close to a consumption ratio of 2. This means that surface combustion broiling can be done with about half the gas now required on the Bunsen burner type with feeble radiation and less than half on others. The quality of the work done is uniformly better though it must be confessed that opinion differs somewhat here, never going so far, however, as to charge the surface combustion broiler with inferior work. The intense radiant heat which, of course, is under control, permits the thing being cooked to be placed from 6 inches to 10 inches away from the burner, promptly sears the outside, prevents the escape of flavoring juices and makes the side that is cooking not only clearly visible but illuminates it so well that the operation can be perfectly carried on in a dark room.

This gas saving of 50 per cent or better for radiant operations like the broiling reported above, is confirmed almost identically by the tests on the radiant room heater, also compared with the Vulcan which carries a perforated cast iron plate attaining a dull to bright red by the heat of a Bunsen bar burner below. Heat was here measured by the temperature rise of a measured body of water in a flat sheet metal box placed in front, far enough away to escape contact with any hot gases. The consumption for equal amounts of heat thus thrown out is almost exactly twice for the Bunsen compared with the surface combustion.

It may be said, therefore, that surface combustion domestic appliances can save in all directly radiant operations about half the gas required by Bunsen appliances and in other cases like top burners and ovens an average of about 35 per cent in round numbers derived from actual tests in laboratory and kitchen. These figures are for continuous operation and are reduced in some cases by intermittent work such as involves the lighting of a burner for a few minutes and then turning it out almost as soon as it gets warm. For such service as this, efficiency is not so important as a quick heat and if less time than one minute be available one present type burner can be retained in each stove for it, reserving for the surface combustion burners the large gas consumption work where gas savings are equivalent to appreciable sums of money.

INSTALLATION OF NEW APPARATUS

At this point the question naturally arises as to when the saving of gas becomes large enough to pay for the electric current consumed by the fan and in what time the net saving will pay for the increased cost of surface combustion appliances over Bunsen. The answer to the last question is to be found only when it is known how much the appliance will be used as the fixed charges per hour of use depend on the number of service hours per year; in this respect the case is similar to plant operation. If a domestic range is to be used one week per year it matters little how efficient it may be and the cheapest thing available in first cost is the thing to buy. On the other hand it will take a very short time to pay for the extra cost of an appliance that is used every day and doubly so if operated many hours per day, especially if the service requires considerable gas. Calculations could be given for all sorts of hypothetical cases but as any one can make them for conditions that are important to him they are here omitted; however, one case is included for illustration.

Suppose a domestic range with a full capacity consumption of 100 cu. ft. per hour were operated three hours per day and three hundred days or 900 operating hours per year at an average rate of 50 cu. ft. per hour with such distribution of various burner service as corresponds to an average saving of 40 per cent of what a corresponding Bunsen range would require. It may also be assumed that the latter would cost the consumer \$35 and the former \$50 and that gas costs \$1.00 per 1000 cu. ft. and electric current 10 cents per K. W. hour. The surface combustion range would consume per year $50 \times 3 \times 300 = 45{,}000$ cu. ft. of gas, while the corresponding Bunsen would consume $45{,}000 \div (1.0 - 0.4) = 75{,}000$ cu. ft. so that the saving of the former over the latter is 30,000 cu. ft., worth \$30 per year. From this is to be subtracted the cost of 900 hours of electrical supply, which must be estimated. This can be calculated from the power charts given, and it will be found that for even low efficiencies of fan and motor not over 0.5 ampere at 110 volts or 55 watts should be ample. In fact actual measurement of the Regina vacuum cleaner set, illustrated on the first range, Figs. 48 and 49, which had a delivery pressure twice and an air volume about four times what was required, required 92 watts with all burners in operation and 90 with none, proving the excess capacity and the probability of operating with fans and motors designed for the service on less than half an ampere.

Assuming that at the start no efficient fan and motor be available and that the absurdly high consumption of 90 watts would be required for the necessary 10 cu. ft. of air per minute at 4–5 inches water pressure, the electrical cost of operation would be $10 \times 90/1000 = 0.1$ cent per hour, in round numbers, or \$9.00 per year. This makes the net saving in operation \$30.000 — \$9.00 = \$21.00 per year, and as the excess of first cost was assumed to be \$15.00 it would be paid off completely in 600 hours of operation, or if uniformly distributed in $8^1/_2$ months.

One short way of disposing of the electrical cost is to consider that the gas saved by a single top burner will more than pay for the electric current to operate the entire range so that for all burners in operation in excess of one the electrical current costs nothing. That this statement is justified is indicated by the following, assuming the inefficient fan and motor to be used that costs 0.1 cent per hour to operate. If the service of a standard 15 cu. ft. Bunsen top burner is preferred by a 10 ft. surface combustion burner (ratio 1.5) the gas saving is 5 cu. ft. per hour, which is worth $5 \times 1000/100 = 0.5$ cent per hour, a net saving of 0.4 cent per hour. This shows how conservative is the general estimate above, that other gas saving at one burner will more than defray the expense for current for the entire range, for under the conditions named the gas saving at one burner is five times the cost of current for all of them.

Gas Saving Necessary to Just Pay Cost of Electric Current Expended for Fan Operating Surface Combustion Appliances

Electric H.P. required by fan	Equivalents watts	Equivalent Amperes at 110 volts	220 volts	Current at 10 c. per K. W. hour	Cu. ft. gas per hr. costing same as electric current at \$1.00 per 1000 cu. ft. gas
0.01	7.46	0.06782	0.03391	0.0746	0.75
0.02	14.92	0.13564	0.06782	0.1492	1.49
0.03	22.38	0.20346	0.10173	0.2238	2.24
0.04	29.84	0.27128	0.13564	0.2984	2.98
0.05	37.30	0.33910	0.16955	0.3730	3.73
0.06	44.76	0.40692	0.20346	0.4476	4.48
0.07	52.22	0.47474	0.23737	0.5222	5.22
0.08	59.68	0.54256	0.27128	0.5968	5.97
0.09	67.14	0.61038	0.30519	0.6714	6.71
0.10	74.60	0.67820	0.33910	0.7460	7.46
0.11	82.06	0.74602	0.37301	0.8206	8.21
0.12	89.52	0.81384	0.40692	0.8952	8.95
0.13	96.98	0.88166	0.44083	0.9698	9.70
0.14	104.44	0.94948	0.47474	1.044	10.44

In the preceding table there is given a series of equivalents in gas saving, cu. ft. per hour, the value of which just balances various values of electrical horse power requirements of fan.

CONCLUSION

It is hoped that this review of the development of surface combustion will show that it is now possible to design rather than merely invent apparatus, and that such apparatus as commercial conditions may require may now be produced in no more time than is necessary to decide on the models to be manufactured and the production of an initial stock. However, there is no intention of leaving the impression that the work of development is finished for it is only just fairly started, and should be continued with corresponding improvement in appliances for the next half century.

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METHODS FOR THE EXAMINATION OF NATURAL GAS FOR THE PRODUCTION OF GASOLINE

By E. S. Merriam and J. A. Birchby

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The production of natural gas gasoline from the casing head gas of the oil fields, by compression and cooling, has, within the last five years, grown to be a very important industry. Through the failure of many plants to obtain gasoline in paying quantities, it was early recognized that a preliminary examination of any proposed gas should always be made, and naturally the problem was put up to the analytical chemist. Any one at all familiar with the literature on natural gas will realize that positive statements in regard to the presence and quantities of the higher paraffines occurring in natural gas are not numerous. Ethane, propane, and butane were early found in natural gas, but no reliable figures could be given as to their amounts. In fact from combustion data alone only the total quantity of paraffin vapors present can be determined, and not which ones.[1] Generally the results are recorded on the assumption that methane and ethane alone are present.

The exact analysis of a mixture of five hydrocarbon gases does not seem possible, with the means available in an ordinary laboratory. Fractional distillation at —190° C. and —120° C. seems to have given Lebeau and Damiens[2] good results. The use of high pressures in connection with the critical temperature of the vapors believed to be present might lead to a more or less correct result, though the solubility of a gas in a liquid hydrocarbon must be taken into account.

[1] G. A. Burrell, Bur. of Mines, *Bull.* **15**, 67.

[2] *Compt. rend.*, **156**, 144–7 and 325–7; *Chem. Abstracts*, **7**, 1338.

Even if we had methods whereby the percentage of butanes and pentanes could be determined in a given gas, it would still be a difficult matter to calculate how much of each could be condensed to liquid at any given temperature and pressure, and when it is found that the various makes of compressors and condensers are not equally efficient, it can readily be seen that the chemist should be extremely conservative and cautious in his reports.

In view of these facts it is evident that the most logical method to pursue is to obtain gases from plants where the production is known, and to examine these gases by methods which will respond to the presence of the more readily condensible hydrocarbons. In this way empirical relations between certain physical and chemical properties of the gases and the yields in actual practice can be established, and a probable yield for any unknown gas can be predicted.

A second method is to construct a small compressor so that any gas may be subjected to any desired pressure or any degree of cooling. We have proceeded along both these lines, and the object of this article is to describe the methods which we have found most suitable.

It may be of interest to describe first some methods which we tried and discarded.

First.—By passing the gas through absolute alcohol it was believed that the heavier hydrocarbons would be partially dissolved. If this alcohol be then diluted with water, the hydrocarbons, being insoluble in and lighter than water, would separate and their volume could be determined. This method was used by Bunsen in showing the presence of benzene in illuminating gas (Hempel-Dennis, "Gas Analysis"). In the case of natural gas, however, owing to the rapid escape of the lighter constituents, such brisk effervescence occurred on diluting that the heavier hydrocarbons were carried off. Even with ice water and in a closed vessel no reliable results could be obtained.

Table I

No.	D	Per cent air	D′	A	B	A/B	Olive oil absorption	M	Yield	Pressure	Remarks
26	1.305	25.0	1.406	13.6	6.0	2.27	15.8	67	5.0	80	"Gas pump gas"
27	1.276	38.5	1.383	11.1	5.4	2.06	13.2	66	5.0	90	"Gas pump gas"
30	1.41	0.0	...	19.0	6.8	2.79	26.2	65	8.0	80	"Gas pump gas"
33*a*	1.24	44.0	1.429	11.2	5.7	1.97	14.5	60	5.0	80	"Gas pump gas"
33*b*	1.12	..	...	6.6	1.9	3.48	9.2	58	..	...	33*a* after compression
77	1.244	0.0	...	12.9	4.3	3.0	19.0	58	4.0	...	Taken from well under 50 lbs. pressure
80	1.202	61.0	1.515	6.8	3.2	2.12	8.8	69	..	...	Yield 6 to 7 after eliminating air at 225 lbs.
84	1.004	34.0	1.005	2.4	1.1	2.18	5.2	73	0.75	100	
85	0.931	27.5	0.905	3.7	0.4	9.2	4.7	48	0.0	250	This gas had been through a plant at 250 lbs.
96	0.799	0.0	...	4.0	1.1	3.63	5.8	58	0.50	250	Unsuccessful plant
99	0.795	0.0	...	3.4	1.1	3.1	4.7	69	0.25	200	Unsuccessful plant
117	1.087	0.0	...	6.9	1.4	4.92	10.6	52	0.0	180	Gas had been through at 180 lbs.
125	1.398	26.5	1.542	16.0	7.1	2.25	21.4	60	5.0	110	
135	1.31	0.0	...	14.0	4.4	3.18	16.8	57.5	4.0	not known	
136	1.142	17.0	1.171	8.8	2.9	3.04	9.0	61	2.5	...	

Second.—By treating the gas with a suitable high boiling oil, such as lubricating oil, to absorb the vapors, and then distilling the mixture, it was sought to regain the vapors. The hydrocarbons thus obtained could not be condensed satisfactorily.

Third.—By combustion. This method as mentioned above gives the total paraffins only, and while a rich gas can easily be distinguished from a poor one, the method did not seem to respond with sufficient delicacy to the presence of the heavier hydrocarbons.

The first method which showed promise was to determine the solubility of the gas in absolute alcohol.[1] The following solubilities are given in Watts' dictionary:

1 volume of alcohol dissolves 0.523 vol. CH_4 at 0° C.
1 volume of alcohol dissolves 1.5 vols. C_2H_6.
1 volume of alcohol dissolves 6.0 vols. C_3H_8.
1 volume of alcohol dissolves 18.0 vols. C_4H_{10}.

The process used was simply that of Hempel for determining benzene vapors in illuminating gas: 1 cc. of absolute alcohol was placed in a Hempel explosion pipette over mercury, 100 cc. of gas introduced and the decrease in volume noted after three minutes shaking. This decrease will be due to a slight extent to methane, and in an increasingly greater measure to ethane, propane, etc. The 1 cc. of alcohol will be completely saturated with CH_4, probably nearly saturated with C_2H_6, but will in general not be saturated with the heavier constituents which are present in smaller amounts and which have a far higher solubility. If, then, a second quantity of 100 cc. of fresh gas is shaken with this same 1 cc. of alcohol, the decrease in volume this time will be due mainly to the heavier vapors present. Since alcohol has an appreciable vapor tension, is also an oxygen-containing body, and should therefore be a poorer solvent for hydrocarbons than another hydrocarbon, we soon discarded its use and used 1 cc. of kerosene instead. The results obtained by the use of kerosene have proven of great value.

In Table I, the figures under A denote the number of cc. of gas absorbed by 1 cc. of kerosene, under B the absorption when a second 100 cc. of gas is shaken with the same 1 cc. of kerosene. B is, of course, in every case, smaller than A, and is proportional to the heavier constituents present. We have found that the value of B approximately represents the yield of gasoline in gallons per 1000 cu. ft. of gas. When B is small it will exceed the yield; when high it will fall below the yield. The ratio of A to B is also of significance, as can be expected from general principles. If the hydrocarbons causing B are of high molecular weight they should be more readily condensible and show a higher solubility. The first 100 cc. of gas

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[1] G. A. Burrell, *loc. cit.*

therefore will not come so near to saturating the 1 cc. of kerosene, and B will be greater than would be the case if more volatile constituents were present. The ratio of A to B should show something about the condensibility of the vapors and the pressure needed to liquefy them. The determination of A and B should, of course, be made at a fixed temperature; the figures given refer to 20° C.

Further information in regard to the nature of the hydrocarbons can be gained very simply. It is easy to determine the mean molecular weight of the vapors which have dissolved in any solvent. All we need to know is their volume and weight under the temperature and pressure prevailing. For this determination we have used a small vessel of the shape shown in Fig. 1. This contains some glass beads to increase the surface, and is charged with 5 cc. of olive oil. We have used olive oil rather than a mineral oil since it has practically an unvarying constitution, is non-volatile and does not foam. The olive oil is first saturated with our city gas, which, from combustion data, appears to consist of about 75 per cent methane and 25 per cent ethane; the gas in the upper part of the bulbs is driven out by aspirating through a small amount of air, and the whole is weighed. The bulbs are then connected between a gas burette and Hempel pipette filled with water, and 100 cc. of gas are slowly passed back and forth a dozen times or more, or until no further gas is absorbed. The decrease in volume is noted and the increase in weight of the absorption bulbs. Readings of the temperature (which we have always kept as near 20° C. as possible) and pressure then give all the necessary data for computing the molecular weight of that part of the vapor which has dissolved in the oil.

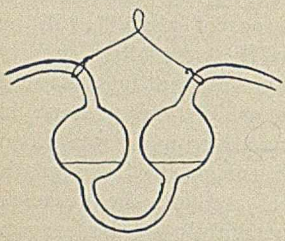
Fig. 1

An example will make the method of calculation clear. In gas No. 26 of Table I, 15.8 cc. of gas were dissolved by the olive oil, and the oil thereby gained in weight 42.9 mg. The temperature was 20° C., and the barometric pressure (corrected for the vapor tension of water) was 740 mm. At 0° and 760 mm. the 15.8 cc. reduces to 14.32 cc. The weight in milligrams of 22.4 cc. of any gas measured at 0° and 760 mm. is equal to the molecular weight M. Therefore, 14.32 : 42.9 = 22.4 : M. M is 67 in this case. The molecular weight of butane C_4H_{10} is 58, and of pentane C_5H_{12} is 72. It seems certain, therefore, that this gas contains at least 15.8 per cent of condensible hydrocarbons corresponding to butane and pentane. The absorption is, of course, by no means quantitative. It will vary for one thing with the amount of olive oil used. Using mixtures of air and gasoline vapors of known composition we have found it possible, using 5 cc. of oil, to recover from 40 to 60 per cent of the vapor present, according to the volatility of the gasoline used in preparing the mixture.

In any case the figure thus obtained for the molecular weight of the condensible vapor is of value. From it we can draw conclusions as to the pressure needed and as to the quality of the gasoline obtainable. A low molecular weight would mean a very lively condensate; a high figure would indicate a less volatile gasoline. As a rule the ratio of A to B is also consistent with the molecular-weight determination, a high M going with a low ratio. The determination of M also enables one to tell whether a gas has been subjected to pressure.

These few simple determinations together with the density of the gas and determination of the air present, when checked upon gases where the production is known, enable one to draw a fair conclusion as to the probable yield of any gas.

In Table I are given the results of examination of gases from a number of plants. D gives the density of the gas, taking air as unity. When air is present, the density of the gas itself, D′, can be calculated from the formula:

$$D' = \frac{100D - \%\ \text{air}}{100 - \%\ \text{air}}$$

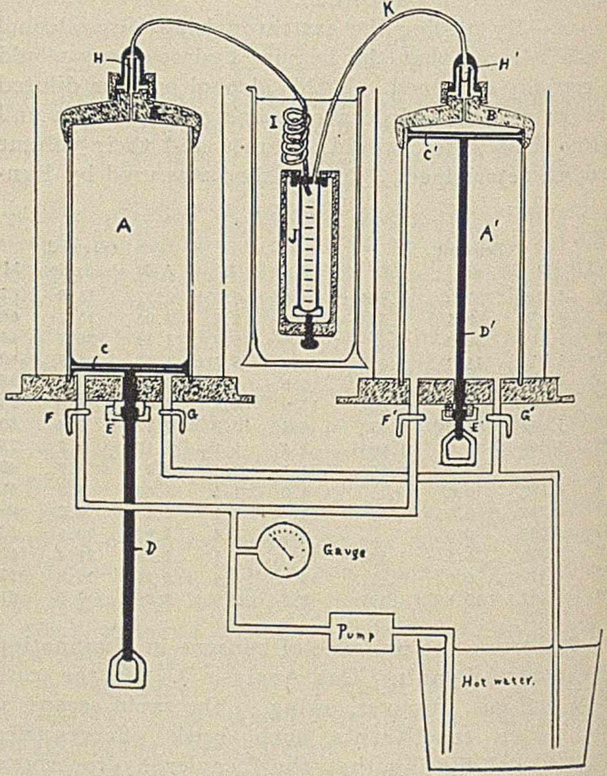

Fig. 2

Under yield is given the number of gallons of gasoline which the operators claim to be making per 1000 cu. ft. of gas. Nos. 26, 27, 30 and 33*a* are all "gas pump gas," *i. e.*, are obtained from the wells by use of a vacuum. This process favors the evaporation of the lighter constituents from the oil, and usually gives a rich gas requiring only moderate pressures: 33*b* is the same gas as 33*a* after it has been through the plant at 80 lbs. pressure. The change in the figures for A and B and their ratio is quite marked. No. 84 is from a plant which is barely making expenses. No. 85 is gas which has been through a plant at 250 lbs.

pressure. M is extremely low and A/B very high. No. 117 is gas which has been through at 180 lbs. Nos. 96 and 99 are from unsuccessful plants. No. 80 was examined by us and we reported a probable yield of 2$^1/_2$ gals., but stated that if the entrance of air could be avoided a yield of 6 gals. might be expected. The operator went over his lines finding numerous leaks which he repaired, and is now making 6 to 7 gals. per 1000 cu. ft.

For further tests we have constructed a small compressor by which the exact yield under any working conditions can be obtained. The results obtained in this way are free from any uncertainty, and the approximations of the analytical methods and personal equation of the analyst are done away with.

In the accompanying Fig. 2, A and A′ are 2 cylinders of polished brass tubing 4″ × 10″, each fitted with a bronze cap B, B′, screwed and soldered on. Each cylinder is provided with a piston C, C′, with close fitting leather cups above and below, and a piston rod, D, D′, provided with a stuffing box, E, E′. Each cylinder is provided with a water jacket which can be filled with hot water. In the base of the cylinders are two openings, F, F′ and G, G′, which serve for the entrance and exit of the hot water used for exerting the pressure. By the use of a small boiler testing pump any pressure up to 500 lbs. can be exerted on the gas, and the pressure can be controlled accurately by the gauge which is placed between the pump and cylinders. A nut and sleeve press the small glass tube H, H′ into a gas-tight connection on the cap of each cylinder. The sleeve is partially cut away so that the glass tube can be observed. From cylinder A leads a small capillary copper tube, the lower part of which is wound spirally and serves as the condenser I. This passes through a small brass disk against which is pressed a graduated glass tube, J, which serves to collect the condensed liquid. This glass tube is seated tightly with a rubber washer, as are also the tubes H and H′. Through this brass disk passes another tube, K, which conducts the spent gas to the other cylinder. The tube J and condenser I are set in a jar of water of any desired temperature.

The method of operation is as follows: the graduated glass tube J is removed and a little water is drawn into the cylinders on top of the pistons; the pistons are then forced up to the top of the cylinders. The excess water is thus forced out, and only enough remains to fill the space between the pistons and caps of the cylinders. Connection is now made with the gas to be tested. By opening the valves G, G′ and pressing on the stirrups the pistons are drawn down, and the cylinders filled with a measured volume of gas. The graduated glass tube J is now attached and it and the condenser I are surrounded by the cooling water. Boiling water is placed in the jackets, the valves G, G′ closed, and hot water is pumped into cylinder A′ through F′, forcing the piston up and driving the gas over into A. The rise of the water into the tube H′ shows when the gas is all out. The valve F′ is now closed. All the gas is now in A. The valve G is closed and hot water is pumped into A, compressing the gas. The gauge shows the pressure. When the desired pressure is obtained, the valve G′ is opened very carefully, allowing the right-hand piston to descend. The pump is now operated and the pressure kept constant. The gas thus passes slowly at the desired pressure through the condenser at the desired temperature, and any liquid forming in the condenser is carried down and collects in the glass tube, which is graduated so as to read directly in gallons per 1000 cu. ft. of gas.

The spent gas passes over into cylinder A′. After the gas has passed through at any pressure it can be transferred back by opening G and pumping in at F′, and put through again at a higher pressure. As many readings can be made as desired. The use of hot water in the jackets and pump prevents the condensation of gasoline in the cylinders, though it is always advisable, especially in the case of rich gases, to increase the pressure by easy stages. If the pressure were raised to 200 lbs. at the start some liquid might condense in the cylinders and not get over into the measuring tube.

We have found that all the gasoline obtainable at any pressure is thrown down by one operation, a second trip through at the same pressure not yielding any more liquid.

We have found this apparatus to work very well, and have examined a good many samples of gas by the

TABLE II

No.	D	Per cent air	D′	A	B	A/B	Olive oil absorption	M	Empirical formula from combustion data	Calculated D	Yield	Pressure Lbs.	Cooling temperature
145	0.94	0.0	...	7.3	2.5	2.92	8.8	69.0	$C_{1.66}H_{5.59}$	0.88	1.35	100	7° C.
											2.26	200	
											2.94	250	
146	1.062	7.0	1.068	8.5	3.2	2.66	10.4	63.5	$C_{1.99}H_{6.30}$	1.045	1.49	100	8° C.
											2.76	200	
											3.58	300	
147	0.957	0.0	...	6.6	2.3	2:87	7.9	68.0	$C_{1.81}H_{5.71}$	0.947	1.33	100	7° C.
											2.34	200	
											3.00	300	
148	0.802	0.0	...	3.6	0.7	5.15	4.2	105?	$C_{1.49}H_{5.31}$	0.803	0.36	100	15° C.
											0.64	200	
											0.91	300	
149	0.958	0.0	...	5.9	2.2	2.68	6.5	76.0	$C_{1.81}H_{5.87}$	0.955	1.43	100	8° C.
											2.45	250	
											3.12	350	
161	0.886	0.0	...	5.8	1.6	3.62	6.9	69.0	....	...	0.79	100	15° C.
											0.99	150	
											1.26	200	
											1.52	300	

absorption methods and the compression method.

The results of a few of these tests are given in Table II. Under yield is given the quantity of liquid condensed by use of the compressor described above. This figure is to be looked upon as an upper limit. The yield on the large scale will be less than the figure given, owing to leakage, evaporation losses, imperfect cooling, etc. The combustions were made over mercury, using oxygen and a heated platinum spiral. In almost every case the figure for hydrogen is slightly greater than that corresponding to a paraffin of the formula C_nH_{2n+2}. This is undoubtedly due to experimental error, as it is well established that natural gas does not contain free hydrogen. The density of the gas calculated from the empirical formula agrees fairly well with the observed D.

SUMMARY

I. A few simple empirical tests are given whereby the approximate quantity of gasoline obtainable from natural gas can be determined.

II. A small testing compressor is described.

III. Some typical analyses and tests are given.

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THE CHEMISTRY OF ANAESTHETICS, V.: ETHYL CHLORIDE[1]

By Charles Baskerville and W. A. Hamor

CHEMICAL HISTORY

Ethyl chloride ("sweet spirit of salt;" *aethylum chloratum; aethylis chloridum; aether chloratus; aether hydrochloricus seu muriaticus;* "hydrochloric ether;" chlorhydric ether; chloro-ethane; mono-chlorethane; chlorethyl; *chloräthyl; chlorwasserstoffäther; leichter salzather; chlorure d'ethyle; ether chlorhydrique;* "chelen" or "chelene;" "kelen" or "kelene;" "anodynone;" "antidolorin;" "ethylol;" "loco-dolor;" etc.) was first obtained in alcoholic solution by Basil Valentine (*pseudo-*).[2] "Sweet Spirit of Salt" was well known to the later chemists. Glauber, for example, referred to it in 1648.

Ludolff stated, in 1749,[3] that on heating alcohol with sulfuric acid and sodium chloride, a distillate was obtained which, when treated with lime, yielded an "ether;" but he endeavored in vain to obtain a similar compound by the action of hydrogen chloride ("muriatic gas") on alcohol. Baumé was also unsuccessful in this direction, but Woulfe[1] obtained the preparation in this way, and it was afterwards prepared and sold by an apothecary in Germany under the name of "Basse's hydrochloric ether" (1801).

HISTORY OF ITS USE AS AN ANAESTHETIC

Flourens[2] drew attention to the anaesthetic properties of ethyl chloride in 1847, and Heyfelder, in the following year, first administered the vapor for surgical purposes. Unsatisfactory symptoms often accompanied its administration at that time, these effects being attributed to imperfections in the manufacture and the consequent presence of impurities. The use of the agent as a general anaesthetic was abandoned until 1895, since which time it has rapidly gained in favor. This is principally attributable to the improved methods of administration, and to an increase in the knowledge of its properties and physiological action; and last, but not least, to improvements in its manufacture.[3]

Ethyl chloride may be regarded as ethyl alcohol (CH_3CH_2OH), in which the OH has been replaced by Cl, hence the formula CH_3CH_2Cl, which was established by Colin and Robiquet.[4]

"Alcoholic (or 'alcoholized') muriatic ether" is a solution of ethyl chloride in an equal amount of alcohol by volume. It has been used as an internal stimulant in doses of 0.6 to 1.8 cc.

USES

So far ethyl chloride has not been used technically, although Palmer[5] called attention to its advantages (and disadvantages) as an industrial refrigerating agent. In medicine it is used for (*a*) general anaesthesia (by inhalation); (*b*) local anaesthesia (by external application, in effect refrigeration); and (*c*) diagnostic and therapeutic purposes.

PREPARATION

As noted, ethyl chloride may be regarded as ethyl alcohol (C_2H_5OH), in which the hydroxyl has been replaced by chlorine. Ethyl alcohol is the raw product from which it is usually made, although ethyl chloride results in the regulated chlorination of ethane,[6] on treating acetic and other ethers with hydrogen chloride, by the action of hydrochloric acid on ether in sealed tubes,[7] and by the action of chlorine on ethyl iodide. In actual practice, ethyl alcohol is mixed

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[1] Read at the regular June meeting of the New York Section of the American Chemical Society, 1913.

[2] He described its preparation thus (*"Wiederholung des grossen Steins der uralten Weisen," ed. Petraeus*, p. 72): "This I also say that, when the spirit of common salt unites with spirit of wine, and is distilled three times, it becomes sweet and loses its sharpness." In his *Last Testament* (*"Basilius Valentinus," ed. Petraeus*, p. 786) he also says: "Take of good spirit of salt which has been well dephlegmated and contains no watery particles, one part; pour to this, half a part of the best and most concentrated *spiritus vini* which also contains no phlegma or vegetable mercury." Valentinus goes on to state that this mixture must be repeatedly distilled, and then "placed in a well-closed bottle and allowed to stand for a month or until it has all become quite sweet and has lost its acid taste. Thus is the *spiritus salis et vini* prepared and may be readily extracted."

In 1739, Johann Pott demonstrated that "sweet spirit of salt" could be obtained by the action of "butter of arsenic" or "butter of antimony" (arsenic or antimony trichloride) on spirit of wine, and other chemists found that other metallic chlorides might be employed for the same purpose. Rouelle, in 1759, found that ethyl chloride resulted from the action of sulfur chloride, phosphorus pentachloride, aluminum chloride, ferric chloride, stannic chloride, etc., on alcohol.

[3] *Die in der Medicin siegende Chemie........*, Erfurt, 1746–9.

[1] *Phil. Trans.*, **1767**, 520.

[2] Hewitt, "*Anaesthetics*," **1907**, 11.

[3] In 1880, a committee of the British Medical Society reported that ethyl chloride was not safe to employ as a general anaesthetic, owing to its liability to produce respiratory failure and convulsions. In 1898, it was stated in Sajous' *Annual*: "We would also warn against its (ethyl chloride) use for the purpose of inducing general anaesthesia, as the dangers incurred therefrom are too great." Interest in its use was revived in the same year, however, by the reports of Lotheisen, and in 1901 by McCardie, who cited a large number of successful cases in general anaesthesia. To quote Dodge [*Boston Med. Surg. J.*, **1909**, 234 (February 25)]: "It is believed that the bad results obtained earlier were due partly to impure preparation of the drug, as well as improper methods of administration.

Ware (*J. Am. Med. Assn.*, November 8, 1902) directed attention to the fact that preparations marketed in this country in 1902 contained methyl chloride to facilitate evaporation.

[4] *Ann. chim. phys.*, [2], **1**, 343.

[5] *Eng. Digest*, **5**, 262.

[6] Darling, *Ann.*, **150**, 216; Schorlemmer, *Compt. rend.*, **58**, 703.

[7] Berthelot.

with hydrogen chloride, which acts as a desiccating agent itself,[1] or dehydrating agents, as zinc chloride[2] or phosphorus pentoxide,[3] are added to remove the water produced. If these agents were not added, the reversible reaction would reach an equilibrium. This equilibrium may be avoided by increase of pressure.[4] It is also manufactured by mixing concentrated sulfuric acid (2 parts) with 96 per cent. alcohol (1 part), and, after standing, diluting with water (1/2 part), adding potassium chloride, and distilling.

IMPURITIES FROM MATERIALS USED

If pure hydrogen chloride is used, there is little danger of impurities being introduced from that source. The quality of the alcohol used, however, is very important. If denatured alcohol, especially if wood alcohol be the denaturant or one of the denaturing substances,[5] then methyl chloride will likely be produced. This gas (b. p. —23.7° C.), while very soluble in ethyl chloride, may easily be removed by rectification. Aldehydes form compounds with hydrogen chloride. Any acetic acid present is liable to form acetyl chloride, and the higher alcohols, as propyl, butyl and amyl, produce their corresponding halogen derivatives. It is desirable, therefore, to use only absolute alcohol of the highest degree of rectification.

An examination of seven different makes of ethyl chloride obtainable in London in 1905 showed that all the branded samples were pure, as was also one unbranded sample. The report of this investigation[6] states that ethyl chloride should be free from water, foreign chlorides, acids, aldehydes, ether, alcohol, and organo-metallic substances.

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[1] Ethyl chloride may be prepared by distilling ethyl alcohol (5 parts), sulfuric acid (2 parts) and sodium chloride (12 parts) together, or by passing dry hydrogen chloride into absolute alcohol; but it is said that the action of hydrochloric acid upon alcohol gives a poor yield of chloride unless zinc chloride is added to the alcohol before passing in hydrochloric acid [Groves, *J. Chem. Soc.*, **27**, 637 (1874)]. Groves found that when hydrochloric acid gas was passed into a boiling solution of zinc chloride (2 parts) in 95 per cent ethyl alcohol (3 parts), the yield was nearly theoretical. He purified the product by washing with water.

[2] Kruger (*J. prakt. Chem.*, [2], **14**, 193) recommended that a mixture of one part of zinc chloride in 82 parts of ethyl alcohol should be saturated with hydrochloric acid gas in the cold and then heated to the boiling point. Hydrochloric acid gas being conducted into the mixture during distillation, as the process is carried out, a reflux condenser prevents the alcohol vapor from coming over and the zinc chloride is said to act by abstracting water from the alcohol, the nascent ethylene combining with hydrogen chloride to form ethyl chloride, according to Schorlemmer (*J. Chem. Soc.*, **1875**, 308). On the action of hydrochloric acid on alcohol, alone and in the presence of zinc chloride, see also Robiquet and Colin, *Ann. chim. phys.*, [2], **1**, 343; Regnault, *Ibid.*, [2], **71**, 355; Kuhlmann, *Ann.*, **33**, 108; and Lowig, *Pogg. Ann.*, **45**, 346. On velocity of the reaction, see Kailan, *Monatsh.*, **28**, 559 (1907). The formation of ethyl chloride in this process is partly due to the action of hydrogen chloride upon alcohol and partly to the union of this nascent ethylene with hydrogen chloride.

[3] The practice of some American manufacturers is to use phosphorus pentoxide as the dehydrating agent.

[4] The process of Mennet and Cartier (French Patent 206,574, June 23, 1890) relates to the production of ethyl chloride. An autoclave of 150 liters capacity is used, into which a mixture of 95 kg. of hydrochloric acid (21° Be.) and 34 kg. of 93–95 per cent. ethyl alcohol is maintained at 50 atmospheres pressure and at 130° C. for about 28 hours. The pressure is then diminished to 42 atmospheres and finally the autoclave is cooled. See also Hager's "*Handbuch d. Pharm. Praxis*," **1**, 189 (1910).

[5] The Commissioner of Internal Revenue ruled in 1907 that the use of alcohol would be allowed tax free in the manufacture of ethyl chloride in accordance with Section 40, Part VI, of the revised regulations, after September 1, 1907, provided the finished product contained no alcohol. The following formula was authorized for use in the manufacture of ethyl chloride: To 100 gallons of ethyl alcohol add 5 gallons of approved *wood alcohol*.

[6] *Lancet*, **1905**, ii, 1631.

PURIFICATION

Ethyl chloride is purified[1] by passing the vapor through water, dilute caustic solution and then concentrated sulfuric acid. The treatment is intended to free it from alcohol,[2] hydrogen chloride,[3] and water. Re-distillation is sometimes practised. This rectification serves to remove other alkyl chlorides, the methyl going off in the first fractions of the distillate and the higher compounds remaining in the residue.

PROPERTIES

Ethyl chloride is a colorless mobile liquid at low temperatures and is extremely volatile. It possesses a slightly saccharine taste and a penetrating and pungent, yet fragrant, "ethereal" odor. It is inflammable, burning, when ignited, with a smoky green-edged flame, producing fumes of hydrogen chloride; hence, care must be exercised in using it near an open flame or a hot cautery. It decomposes even when very close to a hot bulb or an incandescent electric light.

Ethyl chloride has a melting point of —142.5° C.; it possesses a boiling point of +12.5° C.;[4] and its specific gravity is 0.92138 at 0°,[5] 0.9176 at +8°,[6] 0.8510 at +12°,[7] and at +25°[8] the vapor has a specific gravity of 0.91708. Its vapor density is 2.22.

Water dissolves about one-fiftieth of its weight of ethyl chloride and acquires a sweetish, ethereal taste. Ethyl chloride is readily soluble in ethyl alcohol and ethyl ether, and neither solution should give a reaction with silver nitrate at ordinary temperatures. Ethyl chloride dissolves phosphorus, sulfur, fats, oils, and many resins. It combines with many metallic chlorides—for example, antimony pentachloride and ferric chloride—to form crystalline compounds. It is decomposed at a red heat into ethylene and hydrogen chloride.

STORAGE AND CONTAINERS

Owing to its extreme volatility, ethyl chloride cannot be kept in ordinary bottles, except at a temperature below +10° C., and even then the stopper must be tight-fitting and very well secured, and the bottles should preferably be stored in an inverted position. Ethyl chloride is now supplied on the market in sealed or mechanically capped glass or metal tubes of convenient forms, wherein the ethyl chloride is held under pressure. Automatic closing tubes are preferable for local anaesthesia, and there are at least five different types of these on the American market, each manufacturer using his special form of container. Ethyl chloride is also furnished by certain manufacturers in plain capped tubes.

Containers of ethyl chloride should be kept in a dark, cool place, remote from lights or fire; and no empty tubes should be refilled with a fresh lot of the compound, since such an economy may result in spreading infection.

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[1] *Pharm. J.*, [4], **15**, 694.

[2] Acetyl chloride decomposes into acetic and hydrochloric acids with water.

[3] And other bodies forming acids with water.

[4] Regnault, *Jahresber.*, **1863**, 67.

[5] Pierre, *Compt. rend.*, **27**, 213. Darling (*Jahresber.*, **21**, 328) found a density of 0.9252 at this temperature.

[6] Linnemann, *Ann.*, **160**, 195.

[7] Ramsay, *J. Chem. Soc.*, **35**, 470.

[8] Perkin, *J. prakt. Chem.*, [2], **31**, 481.

GLASS *vs.* METAL CONTAINERS

It is maintained by some that ethyl chloride decomposes when exposed to air and sunlight, hence that the drug should be kept in metal containers. It is further claimed that inasmuch as ethyl chloride is inflammable, there is less danger of breaking in accidentally dropping the metal container. In opposition to this, it may be said that in filling any container, no air remains in it on account of the great volatility of ethyl chloride. Furthermore, in drawing off a portion of the contents of a tube, pressure is produced within the tube which is constant for each temperature, it matters not how much liquid ethyl chloride is present, so long as there is some liquid there; hence no backward pressure is created, whereby air may be drawn into the tube. Undoubtedly light facilitates the decomposition of ethyl chloride by oxygen, but the authors have found that light produces no apparent change in pure ethyl chloride when oxygen is absent.[1] Assuming that the ethyl chloride is pure, there is another objection to the use of a metal container, namely, inability to tell how much of the preparation is within the tube and how much has been or is being used in the anaesthesia. This has been met by having a graduated (3 cc. capacity) dropper made of glass which may be attached to the metal container.

TABLE I—THE RESULTS OF AN EXAMINATION OF AMERICAN ETHYL CHLORIDES

Sample	Description	Odor (U. S. P. test): sulfur compounds, etc.	Residue (B. P. test)	Reaction with litmus (B. P. and P. H. tests)	Hydrochloric acid (U. S. P. test)	Metallic chlorides	Alcohol (U. S. P. test)
1........	"Antidolorin," contained in a nickel-plated tube	No foreign or unpleasant odor	None	Negative	Absent	Absent	Absent
2........	"Gebauer's Ethyl Chlorid C. P." contained in nickel-plated tube	"	"	"	"	"	"
3........	"Kelene," contained in a colorless glass tube	"	"	"	"	"	"
4........	"Ethyl Chloride Squibb," contained in colorless glass tube	"	"	"	"	"	"

IMPURITIES WHICH MAY DEVELOP IN ETHYL CHLORIDE

Uncertain results have been encountered by several who have used ethyl chloride for general anaesthesia and these have been attributed in some cases to impurities that were present and have been detected chemically.[2]

The original product must not have been properly purified, for the conditions essential for the decomposition of ethyl chloride itself involve oxygen, and, as animadverted, oxygen has no opportunity to enter the receptacles in which ethyl chloride is dispensed. The presence of small amounts of water may bring about a reverse change in ethyl chloride, with the formation of ethyl alcohol and hydrogen chloride. The latter may readily be detected by spraying some of the drug into a clear silver nitrate solution.

DETECTION OF IMPURITIES IN ETHYL CHLORIDE

The impurities likely to occur in ethyl chloride are (*a*) those which it brings with it from the manufacturer, and (*b*) those resulting through careless storage. While the exact nature of all these is unknown, yet ethyl chloride complying with the requirements of the pharmacopoeias, as given below, is entirely suitable for the purposes for which it is intended. On account of its volatility, the examination of ethyl chloride presents more difficulties than are encountered in the cases of ethyl ether and chloroform; and it is indeed fortunate that it may be easily prepared in a state of comparative chemical purity.

The *Pharmacopoeia of the United States*[1] prescribes the following tests for purity:

1. "If 10 cc. of ethyl chloride, while cold, be dissolved in alcohol, and a few drops of silver nitrate T. S. be added, no turbidity should be produced (*absence of hydrochloric acid*)."

2. "If 10 cc. of ethyl chloride be agitated with 10 cc. of cold water and the supernatant stratum of ethyl chloride be evaporated spontaneously, and if a few drops of potassium dichromate T. S. be added to the remaining aqueous liquid, followed by some diluted sulfuric acid, and the mixture be boiled, no odor of aldehyde should be developed, and a greenish or purplish color should not be produced in the liquid (*absence of alcohol*)."

3. "On allowing ethyl chloride to evaporate from clean, odorless blotting paper, which has been saturated with it, no unpleasant odor should remain upon the paper (*absence of sulfur compounds*, etc.)."

The *British Pharmacopoeia* requires that it should leave no residue on evaporation and that an aqueous or alcohol extract should have no acid reaction with blue litmus paper. The *Deutsches Arzneibuch*[2] requires also that "during evaporation, and thereafter, no garlic odor should be apparent (phosphorus compounds)." The *French Codex*,[3] while giving the incorrect specific gravity, states that it should be free from ethyl bromide and iodide. *The Pharmacopoeia Helvetica*[4] requires that when its vapors are led through water, the water must not give an acid reaction with litmus nor a reaction with silver nitrate.

All the pharmacopoeial tests seek to eliminate acids.

In the opinion of the authors, ethyl chloride intended

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[1] Five samples of "Kelene" and "Ethyl Chloride Squibb," both of which were contained in colorless glass tubes, securely capped, as delivered to the trade, were suspended, at room temperature, inside of a window having direct southern exposure for a period of 21 months, at the end of which time no apparent decomposition had occurred. The exposed samples complied in full with the various pharmacopoeial requirements (see *infra*).

Five samples of "Kelene" and "Ethyl Chloride Squibb" were also exposed, under exactly the same conditions, for a period of 8 months, and the results were the same as above. In samples from which varying amounts of ethyl chloride had been withdrawn, no decomposition occurred for the same periods.

[2] Hawley, *J. Am. Med. Assn.*, **47**, 502 (1906).

[1] *8th Decennial Revision*, p. 32.

[2] **1910**, p. 37.

[3] **1908**, p. 249.

[4] **1907**, p. 27.

for anaesthetic purposes should comply with the following requirements:

1. *Boiling Point.*—Ethyl chloride should possess a boiling point of +12.5° C.

2. *Odor.*—On allowing 30 cc. of ethyl chloride to evaporate from a filter paper 12½ cm. in diameter, no foreign or unpleasant odor, especially a garlic odor (indicating phosphorus compounds), should be apparent either during or subsequent to evaporation.

3. *Residue.*—When 60 cc. of ethyl chloride are allowed to evaporate in a platinum dish at room temperature, there should be left no weighable residue.

4. *Alcohol.*—When 10 cc. of ethyl chloride are agitated with 10 cc. of distilled water, both of which are at about 10° C., in a glass stoppered tube, and the supernatant layer of ethyl chloride is allowed to evaporate spontaneously from the opened tube at room temperature, and then 3 drops of potassium dichromate T. S. are added to the remaining water, followed by 5 drops of dilute sulfuric acid, and the mixture is then boiled, no odor of acetaldehyde should be apparent and no greenish or bluish color should be produced in the liquid.

5. *Hydrochloric Acid and Metallic Chlorides.*—On dissolving 10 cc. of ethyl chloride in 10 cc. of 95 per cent alcohol U. S. P., and then adding 3 drops of silver nitrate T. S., no turbidity, even faint, should result, and no precipitate should form.

A simple combination test for the purity of ethyl chloride consists in attaching a 30 cc. ethyl chloride container to a glass tube vial containing 35 cc. of water kept at 40° C. A slow stream of ethyl chloride is passed through the water until the container is emptied, and then 10 cc. of the water are tested with litmus paper, to which it should impart no acid reaction; 10 cc. with silver nitrate T. S., as in *test 5* above; and 10 cc. are finally tested for alcohol as in *test 4* above.

THE PURITY OF THE ETHYL CHLORIDES ON THE AMERICAN MARKET

Recently the authors examined the products of four American manufacturers, in order to ascertain whether the grades in use complied with the requirements of the various pharmacopoeias above cited. The results are presented in Table I. It will be seen that all the samples examined were of official grade. American manufacturers appear to take the necessary simple precautions to guard against the presence of organic impurities.

College of the City of New York

A RAPID VOLUMETRIC METHOD FOR DETERMINING *o*- *m*- AND *p*-CRESOLS, THYMOL AND PHENOL

By L. V. Redman, A. J. Weith and F. P. Brock

Received July 14, 1913

This method determines by one titration rapidly and accurately:

A. Ortho-, meta- and para-cresols or phenol.

B. The meta-cresol in the presence of *o*- and *p*-cresol.

C. Phenol in the presence of *o*- and *p*-cresol.

D. The meta-cresol, the phenol and the sum of the *o*- and *p*-cresols in any mixture of these compounds.

Three methods have been proposed for determining the cresols separately: (1) gravimetric,[1] weighing the ortho- and para-cresol as the dibrom-cresol-bromide, the meta-cresol as tribrom-cresol-bromide; (2) volumetric,[1] by Koppeschaar's solution, titrating back the unabsorbed bromine; (3) volumetric, by using a solution of iodine[2] in sodium acetate and titrating back the unabsorbed iodine with thiosulfate. This latter method does not serve for the quantitative determination of *m*-cresol.

A special method has been devised for determining *m*-cresol[3,4] in the presence of ortho- and para-cresol, by weighing the *m*-cresol as trinitro-*m*-cresol. The *o*- and *p*-cresol are oxidized away by strong nitric acid and trinitro-phenol is soluble if present in small amounts, *i. e.*, up to 10 per cent. The method, therefore, is reliable in the presence of *o*- and *p*-cresol and less than 10 per cent of phenol. H. Ditz[5] has given the following equations whereby the *m*-cresol present in a mixture consisting only of the three *o*-cresols may be determined

$$x + y = a \qquad (1)$$

$$\frac{3\text{Br}.x + 2\text{Br}.y}{108.064} = b \qquad (2)$$

x = meta-cresol.
y = *o*- and *p*-cresol.
a = Wt. of mixture of cresols taken.
b = Wt. of Br disappearing.
Br = 79.97 grams.

The same equations will apply to a mixture of the *o*- or *p*-cresols and phenol. The equation (2) is modified for the formula weight of the phenol[6] as follows:

$$\frac{3\text{Br}.x}{94.048} + \frac{2\text{Br}.y}{108.064} = b \qquad (3)$$

x = the amount of phenol in the mixture taken.

Siegfried and Zimmermann[7] have criticized H. Ditz and Cedivoda's method and have shown that variable results from 2–20 per cent are obtained by brominating the cresols in an acid bromine solution. Their method varies from that of Koppeschaar's for determining phenol, only in the fact that one hour's time is allowed after the KI is added before the thiosulfate is run into the solution. F. Russig and G. Fortmann[4] have also criticized Ditz and Cedivoda's method adversely. Ditz replied[8] to their objections and H. Ditz and F. Bardach[9] have published results at variance with Russig and Fortmann's conclusions.

Recently Pence[10] has shown that Koppeschaar's solution in an acid menstruum will determine quanti-

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[1] Ditz and Cedivoda, *Z. angew. Chem.*, **12**, 1873 (1899). Ditz and Bardach, *Biochem. Z.*, **37**, 272 (1911). Siegfried and Zimmermann. *Biochem. Z.*, **29**, 368 (1910).

[2] Pence, This Journal, **4**, 518 (1912).

[3] F. Raschig, *Z. angew. Chem.*, **13**, 759 (1900).

[4] F. Russig and G. Fortmann, *Ibid.*, **14**, 157 (1901).

[5] H. Ditz, *Ibid.*, **13**, 1050 (1900). H. Ditz and F. Bardach, *Biochem. Z.*, **37**, 272 (1911).

[6] Siegfried and Zimmermann, *Biochem. Z.*, **29**, 368 (1910).

[7] *Biochem. Z.*, **37**, 272 (1911).

[8] *Z. angew. Chem.*, **13**, 1050 (1900).

[9] *Biochem. Z.*, **37**, 272 (1911).

[10] This Journal, **4**, 518 (1912).

tatively the meta-cresol as tribrom-meta-cresol. But the ortho- and para-cresols could not be determined either as the dibrom-cresols or the dibrom-cresol bromide, since the amount of bromine absorbed varied between the amounts required to form the dibrom-cresol and the dibrom-cresol bromide. Phenol, *o*-, *m*- and *p*-cresols all form the bromides in the presence of excess bromine, and if the precipitates are filtered off before the KI is added the reaction is nearly quantitative,[1] according to the following equations:

$$C_6H_5OH + 4Br = C_6H_2Br_3OBr,$$

$$2\text{-}CH_3.C_6H_4OH + 4Br = 2\text{-}CH_3.C_6H.Br_3.OBr$$

$$\text{and 1- or 3-}CH_3.C_6H_4OH + 3Br = \text{1- or 3-}CH_3C_6H_2Br_2OBr$$

The methyl group of the cresols will be slowly replaced by Br if left in contact with excess Br for several days. This has been shown by Autenrieth and Beuttel.[2] However, if the KI be added while the precipitate is present in the acid solution the free hydriodic acid reduces the bromide as follows:

$$C_6H_2Br_3OBr + HI = C_6H_2Br_3OH + Br + I$$

This reduction is complete for phenol[3] and meta-cresol;[4] consequently they may be determined accurately by adding bromide bromate to their acid solution, later adding KI and titrating back with thiosulfate. For the *o*- and *p*-cresol the case is somewhat different. The hydriodic acid does not reduce the bromide completely in a reasonable length of time, and as a consequence, all the results of the different investigators show that by this method more than 2 mols of bromine are absorbed for each mol of *o*- or *p*-cresol present. The authors of this paper have brominated the *o*- and *p*-cresols by the same method as described by Koppeschaar and modified[5] later for determining phenol, and the results have shown in every experiment that the bromine in the hydroxyl is gradually replaced by the hydrogen of the hydriodic acid, but the reaction is so slow that after an hour's time 6 to 40 per cent of the bromine still remains in the hydroxyl. For rapid and accurate work then, the acid bromine menstruum is not satisfactory in determining *o*- and *p*-cresols.

Recently a method was devised by Wilkie,[6] using a sodium bicarbonate and iodine solution for determining phenol. The authors of this paper have found the method quite accurate and when modified by diluting and continuous shaking[1] the phenol may be determined to an accuracy of two parts in a thousand with a reaction period of only one minute. No subsequent filtering off of the precipitate is needed as in Wilkie's method. The short reaction period does not redden the precipitate enough to obscure the end point. Wilkie's method is a modification of Messenger and Vortmann's,[7] who used caustic soda in place of sodium bicarbonate. Messenger and Vortmann's results are not very satisfactory. Gardner[1] and Hodgson have modified Messenger and Vortmann's method so that only one iodine is absorbed by each mol of phenol.

Pence[2] has used an iodine solution for determining *o*- and *p*-cresol in the presence of sodium acetate. He found that this method would work satisfactorily for *o*- and *p*-cresol but not for the meta-cresol. The present authors have found iodine in sodium acetate too slow for a reaction period of one minute. (Pence recommends one hour.)

The authors of this paper have not tested the gravimetric method for determining the cresols as dibrom-*o*- and *p*-cresol bromides and tri-brom-*m*-cresol bromide as the gravimetric is tedious and slow in the drying of the precipitates; the precipitate gives off the odor of bromine during drying and is at best not accurate within 1–2 per cent.[3]

Problem.—There remains then to discover a rapid and accurate volumetric method, which will serve equally well for the determination of each of the three cresols and phenol. If such a method can be found, it will be possible to determine by a single titration (1) the amount of *m*-cresol in a mixture of the three cresols, (2) the amount of phenol in a mixture of *o*-, *p*-cresol and phenol, (3) the amount of phenol and meta-cresol and the sum of the *o*- and *p*-cresols in a mixture of all four.

The Method.—Such a method has been found by determining the cresols in very dilute[4] solution, $N/100$, using an $N/30$ solution of iodine[5] dissolved in KI, adding the sodium bicarbonate[6] until the mixture is about $^1/_2$ normal, shaking continuously the reacting mixture for one minute, acidifying and titrating back the excess iodine with thiosulfate.

EXPERIMENTAL

Apparatus.—The only appliances needed are (1) standardized burettes, (2) ground stoppered $^1/_2$ liter bottles, (3) 25 and 50 cc. pipettes and a shaking machine. The authors found that continuous shaking by hand of the bottles was as convenient as using the shaking machine when the "reaction period" was of only one minute's duration.

Solutions.—The solutions consisted of $N/30$ iodine, solutions containing $^1/_{60}$ formula weight of each of the three cresols and phenol, $N/10$ thiosulfate, N sodium bicarbonate, 2 N sulfuric acid. The $N/30$ iodine was made up by dissolving 4.2 grams of resublimed iodine in a saturated solution of 15 grams KI, and making up to 1 liter. The standardization of the iodine solution was by arsenious acid. The thiosulfate solution was prepared by dissolving 125 grams of sodium thiosulfate ($Na_2S_2O_3.5H_2O$) in 5 liters of water, allowing the solution to stand for one week and then standardizing it against the iodine.

The three cresol solutions were made up in each case by taking 1.801 grams of redistilled cresol and

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[1] Ditz and Cedivoda, *Z. angew. Chem.*, **12**, 1873 (1899). Autenrieth and Beuttel, *Arch. Pharm.*, **248**, 112 (1910). A. Seidell, *Am. Chem. J.*, **47**, 523 (1912).

[2] W. Autenrieth and F. Beuttel, *Archiv. der Pharm.*, **248**, 112 (1910).

[3] Rhodes and Redman, This Journal, **4**, 655 (1912).

[4] Pence, This Journal, **4**, 518 (1912).

[5] *Ibid.*, **4**, 655 (1912); **5**, 389 (1913).

[6] Wilkie, *J. S. C. I.*, **30**, 398 (1911).

[7] Messenger and Vortmann, *Ber. d. chem. Ges.*, **23**, 2753.

[1] W. M. Gardner and H. H. Hodgson, *J. Chem. Soc.*, **95**, 1819 (1909).

[2] Pence, This Journal, **4**, 518 (1912).

[3] Siegfried and Zimmermann, *Biochem. Z.*, **29**, 368 (1910).

[4] Redman and Rhodes, This Journal, **4**, 655 (1912).

[5] Messenger and Vortmann, *Ber.*, **23**, 2753.

[6] Wilkie, *J. S. C. I.*, **30**, 398 (1911).

making it up to 1 liter. The cresols were from "Merck's highest purity" and were weighed out very carefully after redistilling.

Care was taken to exclude moisture and the samples were weighed out and made up accurately to volume. The *N* sodium bicarbonate solution was made by dissolving 84.1 grams of $NaHCO_3$ in 1 liter of water, the 2 *N* sulfuric acid by adding 56 cc. of concentrated bottle acid (sp. gr. 1.84) to about $^1/_2$ liter distilled water, and making the total volume up to one liter. The two latter solutions need be only approximate.

Brominating the Cresols.—At the beginning of the research a bromide-bromate solution was used and acid added as in determining phenol. The bromination method was found to work quite satisfactorily for phenol and meta-cresol, but the amount of bromine absorbed by the *o*- and *p*-cresol at the end of the thiosulfate titration depends upon three factors:

(1) The excess of free bromine present.

(2) The length of time the bromine has acted upon the cresol solution.

(3) The time allowed for the hydriodic acid to act upon the brominated product, reducing the dibromcresol bromide to the dibrom-cresol.

If enough bromine be added the reaction is complete and dibrom-cresol bromide is formed and may be weighed as such.[1] But if the reaction in the presence of excess bromine proceeds for only one minute, the reaction is not complete. After allowing the hydriodic acid to reduce it for one minute and titrating back the excess iodine, 6 to 10 per cent of the hydroxyl still remains filled by bromine, giving an error in the determination of 3 to 5 per cent. The longer the hydriodic acid acts upon the product, the less bromine is left in the hydroxyl until after one hour's time the reduction has proceeded within 4 per cent of completion. The difficulty seems to be one of delayed diffusion. The precipitate, which is at first flocculent and fills the whole solution, condenses into a few small, solid waxlike particles which do not allow the hydriodic acid free access to the unreduced bromide. The precipitate which originally occupied a space of $^1/_4$ liter shrinks (with partial solution) to a volume of less than 1 cubic millimeter, and when the colorless point is reached with the thiosulfate, one can see a continuous column of blue rising from the little granules at the bottom of the liquid, showing that the hydriodic acid is reducing (but very slowly) the dibrom-cresol bromide. Siegfried and Zimmermann[2] tried to hasten the reduction by warming the solution, but their attempts were unsuccessful. They recommend diluting the solution to 0.025 *N* and allowing 15 minutes for the "reaction period" without continuous shaking, then adding the KI, thoroughly shaking and titrating with thiosulfate. Their results show that the cresols may be determined by this method within 1 to 3 per cent. Our experiments confirmed their results. One difference was observed; if the shaking was continuous, the precipitate decreased in volume as described above and the determination was not accurate.

The bromine-acid method was abandoned in favor of the alkaline iodine method as the results are too dependent upon the dexterity and patience of the individual experimenters. Time was also a factor. The bromine method could not be hastened by shaking as in the case of phenol and meta-cresol, for the precipitates of dibrom *o*- and *p*-cresol bromide coagulated into such small dimensions that rapid diffusion through it of the hydriodic acid was quite impossible. Allowing a reaction period of fifteen minutes and a reduction period for the bromide of one hour after the KI is added, the method requires about one and one-half hours for determinations which are accurate only to 1 to 3 per cent. When this method is applied to a mixture of phenol and *o*- or *p*-cresol the error is aggravated and amounts to 3 to 21 per cent, according to Siegfried and Zimmermann.[1]

DETERMINATION OF *o*-, *m*- AND *p*-CRESOLS SEPARATELY

Each of the cresols was determined separately, according to the following method: About 50 cc. *N* sodium bicarbonate were poured into a $^1/_2$ liter ground stoppered bottle, 100 cc. of water added, 15 or 20 cc. of the *N*/10 cresol were then run in from a standardized burette, and the volume was very carefully read. Enough *N*/30 iodine (40–70 cc.) to color the solution a permanent alkaline iodine color was then added. A reaction period of 1 minute was allowed, during which time the solution was shaken continuously, by hand or in the machine. Then 50 cc. 2 *N* sulfuric acid were added and after shaking thoroughly the excess iodine was titrated back with thiosulfate.

Tables I, II and III show the results for the three cresols.

TABLE I—DETERMINATION OF META-CRESOL

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	*N*/10 *m*-cresol Cc.	*N*/30 iodine Cc.	Reaction period Min.	2 *N* acid added Cc.	Thio Cc.	Per cent found of *m*-cresol
1......	20	100	20.00	70	10	25	4.20	100.0
2......	20	100	20.00	70	10	25	4.20	100.0
3......	20	100	15.00	50	10	25	2.26	100.0
4......	30	100	14.97	50	5	20	2.26	99.9
5......	50	50	15.02	50	5	30	2.20	100.0
6......	100	...	15.00	50	5	30	2.25	99.8
7......	(*a*)	...	15.00	50	5	15	3.20	93.4
8......	(*a*)	...	15.00	50	5	55	3.30	92.7
9......	50	100	15.00	50	1	30	2.20	100.2

(*a*) 100 cc. *N* sodium acetate were added in place of the bicarbonate.

For solutions, etc., see Table III.

Experiments 1 and 2 show that 20 per cent excess iodine and 10 minutes' "reaction period" do not increase the absorption of iodine over the 1 minute's reaction and 14 per cent excess free iodine in Experiment 9.

Experiments 3 and 6 show that an increase of sodium bicarbonate from $^1/_6$ *N* to normal does not increase the iodine absorption.

Sodium acetate was substituted for sodium bicarbonate in Experiments 7 and 8 which confirm Pence's[2] results that the *m*-cresol does not go over completely to tribrom-*m*-cresol in a short time in the presence of sodium acetate.

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[1] Ditz and Cedivoda, *Z. angew. Chem.*, **12**, 1873 (1899).

[2] Siegfried and Zimmermann, *Biochem. Z.*, **29**, 368 (1910).

[1] Siegfried and Zimmermann, *Biochem. Z.*, **29**, 387 (1910).

[2] Pence, THIS JOURNAL, **4**, 518 (1912).

TABLE II—DETERMINATION OF ORTHO-CRESOL

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	$N/10$ *m*-cresol	$N/30$ iodine Cc.	Reaction period Min.	2 N acid added Cc.	Thio Cc.	Per cent found of *m*-cresol
10....	100	..	15.00	35.0	5	55	1.70	100.0
11....	50	50	15.00	39.9	5	30	3.37	99.96
12....	50	50	20.03	50.0	1	30	3.33	99.60
13....	50	50	20.00	50.0	1	30	3.41	99.90
14....	50	50	15.00	40.0	1	30	3.14	100.30

For solutions, etc., see Table III.

Experiments 10 and 11 show that the results are not affected by increasing the excess of free iodine from 11 to 22 per cent and Experiments 12, 13 and 14 show the absorption to be complete in 1 minute's time.

TABLE III—DETERMINATION OF PARA-CRESOL

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	$N/10$ *m*-cresol Cc.	$N/30$ iodine Cc.	Reaction period Min.	2 N acid added Cc.	Thio Cc.	Per cent found of *m*-cresol
15....	50	50	20.00	50.3	1	30.	3.55	99.7
16....	50	50	15.00	50.0	1	30	6.80	100.0
17....	50	50	15.00	40.0	1	30	3.29	100.0
18....	50	50	15.00	40.0	1	30	3.22	100.0

Thiosulphate = 0.0982 N. Sulfuric acid = 2 N. $NaHCO_3 = N$.
Iodine = 0.0340 N. Temperature = 23° C.

Experiments 15, 16, 17 and 18 show that uniform results are obtained by making the solution $^1/_2$ N with sodium bicarbonate, allowing only 1 minute for the "reaction period." Excess of iodine (50 per cent in Experiment 16) did not increase the iodine absorption. It was consequently considered unnecessary to determine the effects of increased "reaction period."

It may be mentioned that the tri-iodo-meta- and di-iodo-para-cresols are precipitated as white flocculent masses before the solution is acidified. The di-iodo-ortho-cresols is precipitated as a red, more or less granular substance. On the other hand, iodo-phenol is not precipitated in $N/2$ sodium bicarbonate and the precipitate forms only on the addition of the acid. In $N/10$ sodium bicarbonate the precipitate forms and is not so red as the precipitate from the stronger carbonate solution.

TABLE IV—DETERMINATION OF PHENOL BY IODINE-SODIUM-BICARBONATE SOLUTION

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	Phenol sol. Cc.	Iodine Cc.	Reaction period. Min.	2 N acid added Cc.	Thio Cc.	Per cent found phenol.
19..........	10	90	15	50	1	20	5.00	85.5
20..........	10	90	15	50	1	25	3.70	94.9
21..........	10	90	15	50	15	25	3.20	98.6
22..........	25	75	15	50	1	25	3.00	100.0
23..........	50	50	15	50	1	30	3.00	100.0
24..........	50	50	15	50	1	30	3.00	100.0
25..........	50	50	15	50	25	25	3.05	99.7
26..........	50	50	10	50	25			

Iodine sol. = 0.03306 N. Others as in Table III.

Table IV gives the determination of phenol by the same method as used for determining the cresols. The method does not vary from Wilkie's, except that the concentrations of the reagents are so chosen that with continuous shaking for one minute the reaction is complete. This rapid reaction leaves the precipitate a flocculent, white or pinkish mass and does not obscure the iodine-starch color, requiring thereby no filtering off of the precipitate as in Wilkie's method, which allows ten minutes for the "reaction period" and as a consequence a filtering off of the dark red precipitate is required. In Experiment 26, the 25 minutes' shaking had made the precipitate so dark that the determination could not be made without filtering.

Experiments 19 and 20 show that $N/10$ sodium bicarbonate is not sufficient to complete the reaction in 1 minute. Fifteen minutes are required for its completion under these conditions (Expt. 21). Sodium bicarbonate $N/4$ was used in Expt. 22 and was found to be sufficient with one minute's reaction period. One minute is sufficient time to complete the reaction with $N/2$ bicarbonate and when 25 minutes was allowed for the reaction no further absorption of iodine took place. The precipitate was a lilac-pink. With less phenol and the same amount of iodine (Experiment 26); the precipitate was a dark wine color and obscured the end point in titrating back with thiosulfate for excess iodine. A precipitate appeared in Experiments 19 to 21, but no precipitates formed in Experiments 23 to 26 until the acid was added.

DETERMINATION OF A MIXTURE OF *o*-, *m*- AND *p*-CRESOL

A solution was made up by taking one-third by weight of each of the cresols and diluting until the strength of the solution contained (108.064/60) grams cresols per liter. The results are given in Table V. In the second last column is given the amount of iodine absorbed by the cresols and the last column represents the amount of iodine which should have been absorbed, calculated for the amount of cresols in the solution (reckoning the ortho- and para-cresols as di-iodo-cresols and the meta-cresol as the tri-iodo-cresol). The error in each case is 0.2 per cent and reckoned as an error for any one of the three cresols represents a loss of 0.6 per cent, since they are each present in equal amounts, or if the error be distributed over each of the three ingredients, it is an error in each of 0.2 per cent.

TABLE V—DETERMINATION OF MIXTURES OF *o*-, *m*- AND *p*-CRESOLS

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	Cresol mixtures Cc.	Iodine Cc.	Reaction period Min.	2 N acid added Cc.	Thio Cc.	$N/10$ iodine absorbed Cc.	Calculated iodine absorption Cc.
27.....	25	75	15	40	1	25	1.5	11.75	11.73
28.....	25	75	15	40	1	25	1.5	11.75	11.73
29.....	25	75	14	40	1	25	2.3	10.97	10.95

For solutions, etc., see Table VI.

A MIXTURE OF PHENOL, *o*-, *m*- AND *p*-CRESOL

The equation of Ditz to determine the amounts of *m*-cresol in the presence of *o*- or *p*-cresol, and modified later by Siegfried and Zimmermann for determining phenol in the presence of *p*-cresol may be extended to include the determination of phenol, *o*-, *m*- and *p*-cresol in the presence of all four compounds and with these equations, if there be known (1) the weight of the mixture present; (2) the total amount of iodine absorbed; the following determinations may be made from a single titration.

(1) The meta-cresol present.

(2) The phenol present.

(3) The sum of the *o*- and *p*-cresols present.

If x = weight of (phenol + *m*-cresol).
y = weight of (*o*- and *p*-cresol).
m = Total weight taken of the mixture.
e = effective formula weight of phenol and *m*-cresol.

a = weight of phenol present.
b = amount of *m*-cresol.
n = number of mols of iodine disappearing.

Then

$$x + y = m \qquad (1)$$

$$\frac{3x}{e} + \frac{2y}{108.064} = \frac{n}{2} \qquad (2)$$

$$a + b = x \qquad (3)$$

$$\frac{a}{94.048} + \frac{b}{108.064} = \frac{x}{e} \qquad (4)$$

$$\frac{108.064 - e}{e - 94.048} = \frac{108.064\,a}{94.048\,b} \qquad (5)$$

Of the above quantities, n is known and is the amount of iodine disappearing or absorbed:

m is known and is the amount of the mixture of cresols and phenol weighed out into the solution.

x, y, e, a, b are five unknowns, and with the five independent equations given, they may be obtained.

This method is limited since the amount of the mixture m is obtained by weighing, and no impurity can be present without affecting the results. Further, it can be seen from the nature of the equations containing e that small variations in the determination of e affect the value of a and b considerably. However, if the dried precipitate of the iodo compounds were weighed after the titration with the thiosulfate a different value for m would be obtained; m would then represent the weight of the halogenated mixture, not the mixture itself. Equation (1) will become

$$x + y + (127.96)\ N/2 - (1.008)\ N/2 = m.$$

The equation is useful for analyzing mixtures containing water and other compounds which do not halogenate and which prevent the weighing of the mixture before precipitation with the iodine. The determination by the iodine and sodium bicarbonate is as accurate as the operator chooses to make it. Using large volumes of solutions (50 cc.) and allowing at least 8 minutes for the solution to run out of the 50 cc. burettes, very accurate results can be obtained.

TABLE VI—DETERMINATION OF MIXTURES OF PHENOL, ORTHO-, META- AND PARA-CRESOL

Ex. No.	$NaHCO_3$ Cc.	Water Cc.	Cresol mixtures Cc.	Iodine Cc.	Reaction period Min	2 N acid added Cc.	Thio Cc.	[illegible] ne Cc.	Calculated iodine absorption Cc.
30...	25	75	20	60.0	1	25	4.02	15.88	15.99
31...	25	75	20	60.0	1	25	3.83	16.08	15.99
32...	25	75	20	60.0	1	25	3.95	15.96	15.99

Thiosulfate = 0.0982 N. Sulfuric acid = 2 N. Temperature = 23° C.
Iodine = 0.03306 N. Sodium bicarbonate = N.

Table VI gives the results of three successive titrations of a mixture composed of equal volumes of solutions of phenol, *o*-, *m*- and *p*-cresol having the following strengths:

Phenol = 0.09060 N.
o-Cresol = 0.06800 N.
p-Cresol = 0.06800 N.
m-Cresol = 0.09850 N.

The second last column gives the amount of iodine absorbed by the mixture. The last column gives the amount which should have been absorbed calculated from the amount of materials added to the mixture. The error varies from 2 parts to 5 parts per thousand. If the discrepancy be calculated over the four ingredients the error is 0.2 to 0.5 per cent. If the error be calculated as due to one single substance present the determinations vary by 0.8 to 2.0 per cent, since the substances are present in equal amounts by weight.

DETERMINATION OF THYMOL

The assumption is very general in the literature that time is an important factor in the halogenation of aromatic compounds. This is especially true for the more highly substituted phenolic bodies. Fifteen minutes to one hour is recommended as the time for complete halogenation. The assumption that this rate of reaction is comparatively slow seemed untenable. If complete diffusion be effected by continuous shaking the reaction should be complete in a very short time. To test this, the determination of thymol (3-methyl-6-isopropyl phenol) was undertaken.

The iodine-sodium bicarbonate method was applied to the determination of thymol and the results are given in Table VII. The calculations are made for the thymol strength, assuming that two iodines enter the ring giving di-iodo-thymol.

TABLE VII—DETERMINATION OF THYMOL

Ex. No.	H_2O Cc.	$NaHCO_3$ Cc.	Thymol Cc.	Iodine Cc.	Reaction period Min.	H_2SO_4 Cc.	20 per cent KI Cc.	Thiosulfate Cc.	Per cent of thymol found
33....	100	25	15	27.4	2	25	..	1.72	100.0
34....	100	25	10	18.0	1	25	..	1.07	100.0
35....	100	25	5	32.25	1	25	..	7.79	122.6
36....	100	25	15	32.0	1	25	..	3.20	100.8
								3.30(*a*)	99.6
37....	100	25	15	30.0	1	25	5	2.58	100.2

Iodine = 0.03306 N. Sulfuric acid = 2 N.
Thio = 0.0982 N. Sodium bicarbonate = N.
Thymol = 0.0491 N. Temperature = 23° C.

(*a*) This result was obtained by titrating the blue color, which returned after the first titration. The time allowed for the blue to return was 10 minutes. The blue did not return in one-half hour after the second titration.

Experiments 33 and 34 show that the iodination is complete in one minute. Seidell[1] states that one-half hour must be allowed for thymol to be brominated. This is true only in case the diffusion is incomplete. If the free iodine is in excess (300 per cent), as in Experiment 35, the hydroxyl is partly filled with iodine and gives a determination 22 per cent too high, calculated as the di-iodo-thymol. Experiment 36 indicates that the iodine which is absorbed in the hydroxyl will be freed in a few minutes if the precipitate is left in

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[1] *Am. Chem. J.*, **47**, 519 (1912).

contact with the small amount of hydriodic acid, which has been formed in the solution. The reduction can be seen in the rapid return of the blue color. This return of the blue continues only until the iodine in the hydroxyl has been completely liberated. An addition of 5 cc. of 20 per cent KI reduced the di-iodo-thymol bromide in one minute to the di-iodo-thymol and the blue color does not return rapidly (*i. e.*, within one hour).

In working with the cresols and phenol the blue did not return except in the case of the ortho-cresol. The reading was taken after the blue ceased to return (5 to 10 minutes). No KI was added. However, it is advisable to use KI if the experiments show a tendency for the blue color to return within five or ten minutes. The free hydriodic acid produced in the acid solution by this addition reduces[1] the thymol iodide completely, with one minute's shaking. Wilkie states that his determinations were all high ($1^1/_2$ per cent). The explanation lies probably in the fact that the iodine is partly absorbed into the hydroxyl and as the iodo precipitate is filtered off in his method, there is no possibility of its reduction.

DIRECTIONS FOR DETERMINING PHENOLIC COMPOUNDS

First. Solutions required: 0.1 *N* sodium thiosulfate, 24.8 grams per liter; 0.03 *N* iodine solution, 12.7 grams per liter; *N* sodium bicarbonate; 2 *N* sulfuric acid; 0.5 per cent starch solution.

Second. Into a 500 cc. ground stoppered bottle, put 50 cc. water and 50 cc. of approximate *N* sodium bicarbonate, add 15 cc. of the unknown solution of the phenolic compound which has been previously diluted to approximately 0.1 *N*.

Run in the iodine solution until the mixture in the bottle remains a permanent brown iodine color; 20 per cent excess is recommended. Stopper the bottle firmly and shake it well for one minute.

Third. Add carefully, at first, to prevent excessive bubbling, 50 cc. of 2 *N* sulfuric acid. Shake well and titrate the excess iodine with the thiosulfate, using starch as indicator. Occasionally blue color returns rapidly after the end point has been first reached. For such determinations it is best to add 5 cc. of 20 per cent KI to hasten the freeing of the iodine which is held in the hydroxyl. The final end point after the blue ceases to return is the correct reading for the thiosulfate. All the solutions should be at 20°–25° C.

SUMMARY

I. Rapid and accurate determinations of *o*-, *m*-, and *p*-cresol, phenol and thymol have been effected by the use of iodine solutions in the presence of sodium bicarbonate.

II. The method is equally rapid and accurate for all five compounds, the error for each compound being within 0.2 per cent.

III. The "reaction period" for these determinations is one minute, when the shaking is continuous.

IV. The sum of the cresols present in a mixture may be determined within a total error of 0.2 per cent.; the *m*-cresol may be determined in the presence of *o*- and *p*-cresol by this method.

V. A series of simple equations are given which will permit the determination of phenol, meta-cresol and the sum of the ortho- and para-cresols in the presence of each other in any combination or proportion if two quantities be known.

(*a*) The weight of the mixtures taken.

(*b*) The amount of iodine absorbed.

VI. Results of experiments are given which show that these four compounds can be determined in the presence of each other by this method within an error of 0.2 to 0.62 per cent, calculated on the sum of the materials present.

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AN APPARATUS AND METHOD FOR DETERMINING HYDROGEN SULFIDE IN ILLUMINATING GAS[1]

By E. P. Harding and Einer Johnson

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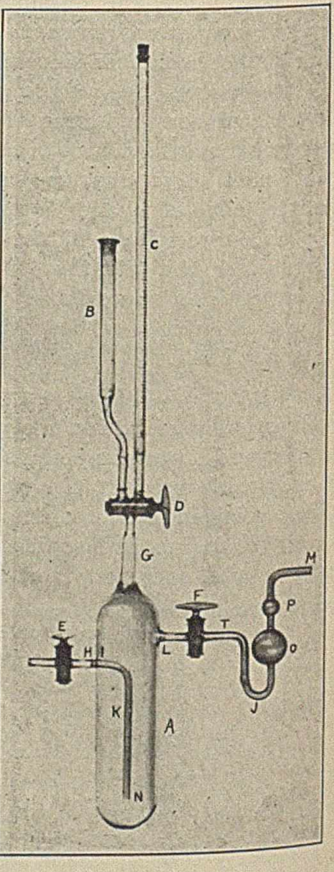
The apparatus herein described was designed as a means of testing the efficiency of a set of gas purifiers such as are used in the manufacture of coal gas or carburetted water gas for illuminating purposes. It combines the accuracy of the gravimetric cadmium chloride method and the rapidity of the Tutwiler method.[2]



The apparatus consists of a bulb, A, of 300 cc. capacity about 18 cm. long and 5 cm. in diameter, sealed at the lower end and contracted at the top to 13 mm. To the contracted end is fused the tube G, terminating in a Greiner and Friedrichs stopcock, D, to which is fused burettes B and C, each having a capacity of 10 cc. Burette B is 20 cm. long and 13 mm. in diameter calibrated in the middle portion. C is 34 cm. long and 10 mm. in diameter graduated into 10 cc. and reading to tenths of one cc. Both B and C are fitted with stoppers. To one side of bulb A at L, 14 cm. from the base of A, is attached tube T 7 mm.

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[1] Werner *Jahresber.*, 633 (1886). Lloyd, *J. Am. Chem. Soc.*, **27**, 16 (1905).

[1] Published in abstract in Proceedings of the 8th International Congress.

[2] *J. Am. Chem. Soc.*, **23**, 173.

in diameter and terminating at M bearing a stopcock, F, 25 mm. from L, a U tube, J, a bulb, O, of 10 cc. capacity and a bulb, P, 2 cc. in capacity. To the opposite side of bulb A at H, 12 cm. from the base of A, is fused tube K 7 mm. in diameter beginning at I and extending into the bulb and terminating at N, 20 mm. from its base. K bears the stopcock E, 30 mm. from H. S is a clamp which supports the apparatus. When passing gas through the apparatus it is supported by placing it in a hole in a block of wood.

In making a determination, from 100 to 150 cc. of a strong solution of cadmium chloride are run into bulb A, stopcock F being open and E closed. The apparatus is then tilted in such a position that 5 or 6 cc. of the solution pass into bulb O which acts as a seal and indicator preventing traces of hydrogen sulfide from escaping unabsorbed and indicating when the cadmium chloride solution in A is nearly spent. Bulb P prevents traces of solution in O from being carried from the apparatus.

Burette C is filled with a standard solution of iodine, two solutions of different iodine strengths being used, one containing 4.828 grams of iodine per liter and another one-tenth as strong. The strong solution is of such a strength that 1 cc. is equivalent to 10 grains of hydrogen sulfide per 100 cubic feet when one-tenth of a cubic foot of gas is used in the determination and is used in testing the crude gas while the weaker solution is used in testing partially purified gas. Stopcock D is closed and A is connected at M with the meter and at I with the gas supply cock by means of rubber tubing. The meter is read, E is opened and the flow of gas so regulated that from 1 to 1.5 cubic feet pass through the apparatus per hour. When a color appears in bulb O, the gas is shut off by closing stopcock E and the meter reading taken. In testing partially purified gas when no color has appeared in O after one-tenth cubic foot of gas has passed but when a perceptible precipitate has formed in A, the gas supply is cut off. If a perceptible precipitate has not appeared in A after one-tenth cubic foot has passed, the flow is continued until one does appear.

The apparatus is disconnected from the meter and gas supply, removed from its support, D opened and then so tilted that the solution in O runs back into A. Wash water is drawn in through M by applying suction at top of B and through K by opening E, closing F and applying suction at top of B. The gas above the solution in A is removed by opening F and applying suction at top of B. D is closed and fresh starch solution run into B, then D is opened and the starch solution run into A. E and F are closed and the air in A placed under diminished pressure by applying suction at top of B. D is then closed and B is filled with concentrated hydrochloric acid which is allowed to pass slowly into A until the precipitate of cadmium sulfide is completely dissolved. A little excess of hydrochloric acid is then run in and D closed. The hydrogen sulfide thus liberated in A under diminished pressure and out of contact with air is titrated with the iodine solution. Burette C is read and the iodine solution introduced intermittently by carefully opening D, the apparatus being shaken after each addition. When the starch-iodo blue color persists for one-half minute, the end point in the titration has been reached. (The pink or violet color which first appears in the solution must be distinguished from the starch-iodo blue which is the correct end point.) C is then read. The apparatus is then emptied, rinsed with water and a blank test run to determine the amount of iodine solution necessary to produce the permanent starch-iodo blue color. In making this test the same amount of starch solution and the same volume of water as is used in the determination is used and the whole acidified with hydrochloric acid. From the amount of gas and the volume of iodine solution used in the determination and in the blank, the number of grains of hydrogen sulfide per 100 cubic feet of gas is calculated. For control work the volume of gas used need not be reduced to its corresponding volume at standard conditions of temperature and pressure.

Comparative determinations of hydrogen sulfide were made by the gravimetric cadmium chloride, the Tutwiler and the volumetric cadmium chloride methods. In these determinations the meters used were dry meters checked against each other, the samples were taken simultaneously and the volume of gas used reduced to corresponding volume at standard conditions of temperature and pressure by means of the following formulae:

$$V = v \cdot \frac{17.64\,(h—a)}{460 + t} \cdot n = \frac{17.64\,(h—a)}{460 + t}.$$

$V = vn$ where
V = volume of gas at 60° F. and 30″ pressure.
v = observed volume.
t = observed temperature in Fahrenheit degrees.
h = observed barometric pressure.
a = tension of aqueous vapor at t.
n = correction factor for t and h.

The following results in grains, cadmium chloride, $CdCl_2$, per 100 cubic feet were obtained:

Grav.	Vol.	Tutwiler	Grav.	Vol.	Tutwiler	Grav.	Vol.	Tutwiler
Coal gas.						Water gas		
2.72	2.93	31	1.81	1.72	27	0.59	0.55	16
0.53	0.46	22	0.88	0.84	18	0.26	0.23	8
0.89	0.79	27	4.86	4.76	110	0.40	0.36	11
1.58	1.54	38	2.73	2.69	65	0.15	0.13	5
1.00	0.92	24	1.22	1.18	25	0.34	0.31	12
2.68	2.65	30	2.72	2.61	28	Crude coal gas		
1.31	1.25	23	1.65	1.59	30	225.0	220.0	360.0
2.35	2.26	29	1.30	1.26	26	190.0	188.0	310
			1.09	1.04	24			

The uniformly higher results obtained by the gravimetric method may be due to the absorption of other sulfur compounds than hydrogen sulfide, a much larger volume of gas and cadmium chloride solution being used in the gravimetric method than in the volumetric method.

The principal advantage of Tutwiler's method is its rapidity. A test can be made in about three minutes. Its chief disadvantage is its inaccuracy. The results obtained are only approximate especially on the partially purified gas, the error varying from 1000 to 4000 per cent as shown by the comparative tests above. This error is due to the titration of the gas with the iodine solution, the unsaturated hydrocarbons, cyclopentadiene[1] and probably sulfur compounds other than hydrogen sulfide reacting with the iodine. Results on the crude gas are less inaccurate, the error amounting to about 15 per cent. This is of course due to the much greater ratio between the amount of hydrogen sulfide present and the other compounds with which the iodine reacts. McMillar states in the original publication of Tutwiler's method that 15 grains of hydrogen sulfide per 100 cubic feet of gas could escape detection. In the writers' experiments, in no case did the Tutwiler show less than 10 grains per 100 cubic feet on clean coal gas nor less than 4 grains per 100 cubic feet on clean water gas.

The gravimetric cadmium chloride method is the most accurate in use at the present time. The great objection to this method, however, in control work is the length of time required to make a determination. The purifying boxes foul quite rapidly and in determining their efficiency tests should be made rapidly and as nearly simultaneously at inlet and outlet of purifier as possible. A method which requires hours for a test becomes impracticable. The large bulk of cadmium chloride solution used allows absorption of other sulfur compounds than hydrogen sulfide, which when oxidized with the bromine give too high results. Another objection is the large amount of cadmium sulfide precipitate required to produce an amount of barium sulfate which can be readily and accurately weighed. When a sample of 0.1 cubic foot of gas is taken, each milligram of $BaSO_4$ is equivalent to 2.252 grains of sulfur per 100 cubic feet. Thus for partially purified gas containing but a fraction of one grain of hydrogen sulfide per 100 cubic feet, a number of cubic feet of gas must be used in order to obtain a weighable precipitate.

The volumetric cadmium chloride method has several advantages over the gravimetric method. Accurate results are obtained on a much smaller volume of gas; a smaller volume of cadmium chloride solution causes less absorption of sulfur compounds other than hydrogen sulfide; the method is much more rapid, requiring for a determination instead of hours, from seven to ten minutes, depending upon the purity of the gas.

The advantages of the volumetric cadmium chloride method over the Tutwiler are several. Twenty-eight times as much gas is used in the average determination as is used in the Tutwiler; the burette readings are one-tenth those of the Tutwiler and much more accurate results on gas of low hydrogen sulfide content are obtained. A test can be made in from seven to ten minutes.

Instead of a meter, a graduated cubic foot bottle may be employed for measuring the volume of gas used.

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[1] *London Journal of Gas Lighting*, 4/5/10, p. 41; 4/12/10, p. 18.

A METHOD FOR THE DETERMINATION OF PHOSPHORUS IN VANADIUM STEEL AND FERRO-VANADIUM

By C. F. Sidener and P. M. Skartvedt

Received July 21, 1913

This paper embodies the adaptation of some well-known reactions to the determination of phosphorus in vanadium steel and ferro-vanadium, together with results obtained by the method, which is as follows: The sample is dissolved in dilute nitric acid. If an insoluble metallic residue remains, a little hydrochloric acid is also added. The solution thus obtained is evaporated to dryness and baked until the nitrate of iron is decomposed. The residue is dissolved in concentrated hydrochloric acid and about 0.02 gram of aluminium in the form of aluminium chloride is added. The solution is nearly neutralized with ammonia, heated almost to boiling, and the iron reduced by the gradual addition of a concentrated ammonium bisulfite solution with stirring. The reduction is best accomplished by keeping the solution slightly acid until nearly reduced, and then adding ammonia until a slight permanent precipitate of iron hydroxide remains after vigorous stirring, finally dissolving the precipitate with a few drops of ammonium bisulfite. To the solution, now smelling quite strongly of sulfur dioxide, one or two cc. of phenylhydrazine[1] are added drop by drop with stirring. If no precipitate appears, a few drops of ammonia are added until a slight permanent precipitate is formed. Then a few drops more of phenylhydrazine are added to complete the precipitation. The solution is boiled about two minutes, allowed to settle and filtered.

This precipitate consists of aluminium phosphate, aluminium hydroxide and more or less of the vanadium. After washing with hot water until the washings show no cloudiness when tested with mercuric chloride, the precipitate is dissolved off the filter into the original beaker with dilute nitric acid.

In the nitric acid solution containing the phosphorus and vanadium, the latter is oxidized by the addition of a little hydrogen peroxide, and then a slight excess of sodium carbonate is added. The solution is boiled for about five minutes and the phosphorus precipitated as aluminium phosphate by gradually adding dilute nitric acid until the solution no longer gives an immediate brown tinge to turmeric paper.[2] It is important that this point be very carefully noted. The precipitate is filtered off and washed with a 1 per cent solution of ammonium nitrate. It is then dissolved off the filter into an Erlenmeyer flask with dilute nitric acid and a little hydrogen peroxide added, which will produce a deep red color if much vanadium is present and a pinkish yellow if but a trace is present. If this test shows the presence of even a trace of vanadium, another precipitation with sodium carbonate and nitric acid is necessary. The number of precipitations required to separate the phosphorus from the vanadium depends upon the amount of vanadium in the sample. For those containing up to 1 per cent, a single precipitation is sufficient; 1 to 5 per cent, two precipita-

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[1] Hess and Campbell, *J. Am. Chem. Soc.*, **21**, 776.

[2] C. M. Johnson, "Chemical Analysis of Special Steels," p. 26.

tions; and from 5 to 30 per cent, two and often three.

To the nitric acid solution is now added ammonium molybdate to precipitate the phosphorus which is determined by the permanganate oxidation method in the usual manner. If the vanadium has not been completely separated from the phosphorus it will be indicated by the orange color of the ammonium phosphomolybdate precipitate which is quite characteristic; also by the tendency of the precipitate to form quickly and adhere to the glass.

Results obtained by this method are given in the following tables: Table I shows the results obtained from a mixture of standard solutions containing iron, phosphorus and vanadium in proportions approximately those found in vanadium steels.

TABLE I

Iron taken, 1 gram; vanadium, 6.75 mg. in first 11 and 27 mg. in last four experiments; phosphorus, 2 mg. The actual weight of phosphorus varied from 1.38 mg. to 2.40 mg., but for convenience of comparison all were calculated to a 2 mg. basis.

Milligrams of phosphorus found				
2.01	1.98	2.01	2.07	1.97
2.03	2.13	2.00	2.01	1.99
2.03	1.95	1.97	2.08	1.98

TABLE II—RESULTS ON A BUREAU OF STANDARDS VANADIUM STEEL CONTAINING 0.15 PER CENT VANADIUM AND 0.035 PER CENT PHOSPHORUS

No.	Grams steel taken	Percentage phosphorus found
1	1.2377	0.0353
2	0.8329	0.0352
3	2.9114	0.0340
4	2.5538	0.0350
5	3.5430	0.0347
6	3.9635	0.0356

TABLE III—RESULTS ON TWO BUREAU OF STANDARD STEELS TO WHICH WAS ADDED VANADIUM IN VARIED AMOUNTS FROM 0.5 PER CENT UP TO 30 PER CENT OF THE WHOLE WEIGHT TAKEN

	Steel taken Grams	Percentage vanadium added	Percentage phosphorus in the steel	Percentage phosphorus found
1	1.4102	0.5	0.093	0.096
2	1.5759	0.5	0.093	0.092
3	1.4749	0.5	0.093	0.0917
4	1.5297	0.5	0.093	0.094
5	1.5090	0.5	0.093	0.101
6	1.5015	0.5	0.093	0.108
7	1.5022	0.5	0.093	0.097
8	1.5019	0.5	0.093	0.089
9	1.0462	1	0.112	0.110
10	1.0088	1	0.112	0.113
11	1.2064	1	0.112	0.111
12	1.1623	1	0.112	0.109
13	1.0244	5	0.112	0.107
14	1.0469	5	0.112	0.119
15	0.9995	5	0.112	0.113
16	1.0092	20	0.112	0.116
17	1.0055	20	0.112	0.111
18	1.0040	20	0.112	0.111
19	1.0077	30	0.112	0.102
20	1.0095	30	0.112	0.103
21	1.0107	30	0.112	0.106
22	1.0092	30	0.112	0.114

Although some of the results in the above tables are not as concordant as might be desired, yet it is believed that they may be taken as satisfactory for so troublesome a determination.

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MINNEAPOLIS

A FUSION METHOD FOR THE DETERMINATION OF SULFUR IN IRON AND STEEL

By FREDERICK H. FRANKLIN[1]

Received June 6, 1913

The accurate determination of sulfur in iron and steel presents many difficulties, owing to the extremely variable and complex nature of the iron-carbon alloys. It has been shown that sulfur combines with manganese in preference to iron.[2] Therefore, in most commercial iron and steel alloys we have to deal with the former sulfide. It has been found that the insoluble residue left on dissolving iron for the sulfur determination usually contains some sulfur and this must be determined in accurate work. It is also well known that when much cementite is present volatile compounds of sulfur and carbon are formed which are difficult to oxidize and so escape estimation. It may readily be seen therefore that the method employed should be capable of giving a correct measure of the total sulfur no matter whether it exists in one or all of the above combinations.

For the purposes of this paper it will be sufficient to describe briefly one representative from each of the two principal classes into which the sulfur methods may be divided.

The volumetric or evolution method is in very general use and is usually modified by its advocates to meet the existing conditions. The gravimetric or oxidation method possesses some advantages over the former and is believed to be the most accurate method now in use. Both of these methods have a multitude of modifications and the mere statement that sulfur was determined by the volumetric or by the gravimetric method is no proof that the figures reported are the most accurate obtainable by the class chosen.

The Volumetric or Evolution Method.—In its simplest form this method consists of dissolving the metal in 1.1 sp. gr. hydrochloric acid and passing the evolved gases through an ammoniacal solution of cadmium chloride. The mixture of cadmium sulfide and dilute ammonia is acidified with hydrochloric acid and titrated with a solution of iodine that has been standardized either against sodium thiosulfate or iron of known sulfur content. The chief advantages of this method lie in its rapidity and the index of the amount of sulfur afforded by the precipitated sulfide. For most irons and steels this method when properly carried out gives results that agree fairly well with those obtained by the gravimetric method.

To overcome the shortcomings of the method some authors propose annealing the drillings which by changing cementite, martensite, etc., into pearlite, prevents loss of sulfur as volatile compounds. It is also claimed by other writers that by passing the evolved gases through a red hot tube, the carbon-sulfur compounds are broken down to hydrogen sulfide.

A German Commission,[3] appointed by the Verein Deutscher Eisenhüttenleute to investigate the de-

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[1] Cf. Saunders and Franklin, Official chemists for the New England Foundrymen's Association.

[2] Carnot and Goutal, *Compt. rend.*, **1897**, 125; *J. C. S.*, **1897**, 72.

[3] Schwefelbestimmung in Eisen u. Stahl, *Stahl. u. Eisen*, 28 Jahr., Nr. 8.

termination of sulfur in iron and steel, considered the use of hydrochloric acid of 1.19 sp. gr. absolutely necessary and that when used, the passage of the evolved gases through a red hot tube can be dispensed with.

T. Gifford Elliot,[1] in the *Journal of the Iron and Steel Institute*, combines the annealing and strong hydrochloric acid modifications and when titrating runs in an excess of standard iodine solution and titrates back with sodium thiosulfate.

The Gravimetric or Oxidation Method.—This is usually executed by dissolving the iron or steel in strong nitric acid. The solution is evaporated to dryness, baked, redissolved in strong hydrochloric acid, diluted, filtered and the sulfur precipitated as barium sulfate. This method is also modified at several stages,[2] the most important of which are solution in nitric acid and removal of excess acid before precipitation of barium sulfate.

Potassium bromide and chlorate are used by Noyes to prevent loss of sulfur during solution and the same author separates the iron by ammonia before precipitating the barium sulfate. In nearly all methods, however, the barium sulfate is formed in the presence of a large amount of ferric chloride and no attention is paid to the iron retained by the barium sulfate.

That the oxidation method has many failings is indicated by the numerous attempts to overcome them by modifications. This is one of the principal reasons that led to the development of the new method which is called the Fusion Method and is the result of a search for a method capable of giving accurate results with any kind of iron. It was desired that solution of the iron be effected without the use of acids and that the sulfur be precipitated as barium sulfate without the presence of iron salts.

Having observed that the carbonaceous residue obtained by the solution of iron in copper-potassium chloride solution contained sulfur, an experiment was carried out to learn how much of the total sulfur it contained.

A few grams of cupola iron (pig iron remelted in the cupola) were dissolved in a solution of copper-potassium chloride and filtered through asbestos. The carbonaceous residue was mixed with sodium carbonate, sodium peroxide and a little sugar, then ignited by a hot wire. The aqueous solution of the fusion was acidified with hydrochloric acid heated to boiling and the sulfur precipitated by barium chloride. The results were surprising, giving a greater percentage of sulfur than was obtained by the volumetric method.

A large number of experiments were carried out and all results agreed closely with the gravimetric figures. A search through the literature on sulfur was made and the nearest approach to this method was found in an article by C. Meineke in *Zeitschrift für angewandte Chemie.*[3] The author dissolves the iron by boiling with a solution of copper-ammonium chloride, acidified with hydrochloric acid, and then after filtering off the insoluble, dissolves it in an oxidizing acid and, after evaporating to dehydrate silica, filters and precipitates sulfur as barium sulfate.

THE FUSION METHOD

This method is given with considerable detail, not because this is necessary for accurate results but because of a desire to assist those who are not familiar with the technique of the operations involved.

The sample should be prepared with care and should be moderately fine; drillings made slowly with a rather dull drill are best.

SOLUTIONS, ETC., REQUIRED FOR THE FUSION METHOD

Copper-Potassium-Barium Chloride Solution.—Dissolve 600 grams of copper-potassium chloride in warm water, add 30 cc. of hydrochloric acid, 30 cc. of barium chloride solution, and dilute to 1600 cc. After standing 24 hours, filter through asbestos.

Sodium Peroxide is practically free from sulfur.

Anhydrous Sodium Carbonate is free from sulfur.

Barium Chloride Solution of 20 per cent strength.

Hydrochloric Acid, C. P., has a density of about 1.19.

Dilute Hydrochloric Acid.—Add 100 cc. of hydrochloric acid to 900 cc. of distilled water.

Asbestos Suspension.—The acid-washed fiber is ignited and again washed with dilute hydrochloric acid and kept suspended in water.

Dissolve 3 grams of sample in about 120 cc. of copper-potassium chloride solution containing barium chloride, by means of a suitable stirring device. A Juno motor in series with an incandescent lamp gave excellent service. Allow the solution to stand about thirty minutes, then decant upon an asbestos pad formed in a porcelain Gooch crucible, using suction to hasten filtration. Wash the residue into the crucible by means of a fine stream of dilute hydrochloric acid, using as little as possible. After acid has run through, add just enough fine asbestos suspension to cover the carbonaceous residue. Finish washing with 15 to 20 cc. of warm water.

After all has passed through, wash down the sides of the crucible with a few drops of alcohol. Remove the pad and residue with tweezers, an operation easily accomplished if the crucible has a removable bottom. Separate the asbestos as completely as possible and dry the black residue at a temperature slightly under 100° C. for about 15 minutes.

Weigh 3 grams of anhydrous sodium carbonate and mix with it the dried residue by means of a small glass mortar and pestle.

Transfer to a nickel crucible of 20 cc. capacity and incorporate 3 grams of sodium peroxide. Place the covered crucible over a small flame and heat till the gentle oxidation is completed and the melt is quiet and homogeneous. This operation requires only about 2 or 3 minutes and should not be continued longer or much nickel will be dissolved.

While the melt is solidifying, cause it to cover the sides of the crucible. Rinse off the outside of the crucible and place in a small beaker containing 50 cc. of hot water and warm until the fused mass is de-

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[1] "The Volumetric Estimation of Sulfur in Iron and Steel," *J. I. S. I.*, **1911**, No. 1.

[2] Bamber, *J. I. S. I.*, **1**, 319 (1894).

[3] Abstract in *Chem. News*, March 1, 1889.

tached. After removing and rinsing the crucible, add 15 cc. of hydrochloric acid, using precautions to prevent loss.

After boiling this solution until clear, evaporate to dryness in platinum and heat in oven at 130°–135° C. to dehydrate silicic acid. Dissolve the residue in 50 cc. of distilled water containing 1 cc. of hydrochloric acid, filter and wash until a filtrate of about 90 cc. is obtained. Heat to near the boiling point and add 7 cc. of hot 20 per cent barium chloride solution, drop by drop, keeping the temperature near the boiling point. A Schuster dropping flask (shaped like a tiny retort) is convenient for this purpose. Keep the beaker with the precipitate warm for some time and allow to stand over night or about 15 hours. Collect the barium sulfate on an asbestos pad in a platinum Gooch crucible, wash, ignite and weigh.

With steels and low silicon irons the method may be shortened by omitting the evaporation to remove silica, if the amount of asbestos fused with the residue is not large. Should a slight precipitate of manganese dioxide appear it may be dissolved by the addition of a minute crystal of tartaric acid, which usually produces a sparkling light green solution.

In the following table of results, those obtained by the volumetric method are marked *v*, and those by the gravimetric, *g*:

TABLE OF RESULTS

		Percentages sulfur	
Sample Bureau of Standards	Percentage Sulfur	Fusion method	Other methods
C renewal	0.035	0.039	0.032 *g*
B	0.039	0.038	0.042 *g*
B	0.039	0.044	0.036 *v*
B	0.039	0.041	...
C 2nd	0.034	0.032	...
C 2nd	0.034	0.036	...
C 2nd	0.034	0.043	...
D 3rd	0.035	0.036	0.041 *g*
D 3rd	0.035	0.041	0.036 *v*
0.4 Bes. steel	0.118	0.124	0.115 *g*
Amer. Fdy. Assn., A	0.056	0.057	
	Number		
Cupola iron	38676	0.177	0.155 *v*
	21678	0.123	0.113 *v*
	37485	0.108	0.105 *v*
	39991	0.102	0.097 *v*
	39345	0.160	0.130 *v*
	34345	0.116	0.101 *v*
	40103	0.165	0.147 *v*
	16519	0.128	0.105 *v*
	16450	0.124	0.107 *v*
	16419	0.126	0.119 *g*
	30253	0.095	0.092 *v*
	16519	0.128	0.116 *g*
	41173	0.131	0.096 *v*
	39345	0.170	0.130 *v*
Pig irons	(Cu = 0.76%)	0.054	0.054 *g*
	30402	0.053	0.040 *v*
	29765	0.075	0.074 *g*
	29949	0.047	0.047 *v*
	29949	0.051	...
	2789	0.095	0.084 *g*
	18169	0.049	0.044 *g*
White irons			
Chilled roll	...	0.170	0.160 *g*
Malleable, as cast	41652	0.148	0.095 *v*
Malleable, as cast	41780	0.168	0.128 *v*
Low sulfur steel	...	0.014	0.010 *g*

Numerous blank tests were run, using regular amounts of reagents under the same conditions as the analyses themselves and the average amount of sulfur found was 0.0013 per cent.

EXPERIMENTAL

It was thought at first that all the sulfur would not be obtained in the carbonaceous residue but my earliest experiments always gave results that agreed well with the analyses of the Bureau of Standard samples. Carnot and Goutal[1] have shown that "When iron or steel is heated with dilute acids, almost all the sulfur is converted into hydrogen sulfide but when the solvent is a neutral or faintly acid solution of copper-potassium chloride all of the sulfur remains in the residue, partly as ferrous sulfide, but often mainly as cupric sulfide. Direct examination shows that the copper solution has no effect on ferrous sulfide and it follows that the sulfur is partly present in the metal as some other sulfide. Direct examination also shows that the sulfur in combination with copper in the residue is equivalent to the manganese in the iron or steel. Hence part of the sulfur is in combination with manganese as manganous sulfide."

Should any sulfur pass into solution it will immediately form barium sulfate with the excess of barium chloride present in the solvent. Moreover, the solvent is saturated with barium sulfate so that precipitation is immediate.

A few experiments in support of these views and some others which show the effect of free hydrochloric acid on the solubility of barium sulfate are given below:

Barium Sulphate is Carried Down by Carbon

I—4 cc. of $BaCl_2$ solution were added to a 1 gram sample of shot iron while dissolving in copper-potassium chloride solution. After filtering as usual, 2 grams of granular zinc were added and the solution rotated rapidly till clear. No precipitate was found in hours.

II—Sample treated as in preceding experiment but 2 cc. of $N/20$ H_2SO_4 were added before filtering. Copper was removed by granular zinc but no precipitate found.

III—To the last test (II), 2 cc. $N/20$ H_2SO_4 were added and a precipitate formed immediately.

Barium Sulfate is Insoluble in the Ferrous-Cuprous Solution

IV—2 grams of pig iron dissolved in CuKBaCl solution gave 0.096 per cent S or 0.0140 gram $BaSO_4$.

V—2 grams of pig iron dissolved as before and 2 cc. of $N/20$ H_2SO_4 added, stirred 5 minutes longer and allowed to settle forty-five minutes on oven. $BaSO_4$ precipitate could be distinctly seen. The iron contained the equivalent of 0.0140 gram of $BaSO_4$ and 0.0116 gram was added giving a total of 0.0256 gram and 0.0245 gram was found. Results but 0.001 gram low, showing practically no loss of $BaSO_4$.

Barium Sulfate is Precipitated Immediately and Completely

VI—2 grams of high sulfur iron (S = 0.27 per cent) were dissolved in CuKBaCl solution. Remained on oven one hour and filtered. The filtrate divided into two portions.

A—Placed in long Nessler tube and kept on oven 24 hours. No precipitate visible. After filtering through Gooch, no gain in weight. Absence of $BaSO_4$.

B—Placed in long Nessler tube and 1 cc. of H_2SO_4 (= 0.006 gram of $BaSO_4$) added. After standing on oven 2 hours, precipitate of $BaSO_4$ was distinctly visible. After 24 hours, filtered on Gooch and weighed 0.007 gram. The residue was tinged with iron oxide.

To Learn if $BaSO_4$ Separates from High Sulfur Samples on Long Standing

VII—3 samples of cast iron, 47006–47007–47008, were carried

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[1] Loc. cit.

through for sulfur, using CuKBaCl solution and gave:

	Percentages sulfur	
No.	Fusion method	Vol. method
47006	0.136	0.114
47007	0.121	0.109
47008	lost	0.106

The filtrates from above stood on the oven for 4 days, then were filtered through paper and carefully washed with dilute HCl and water.

They weighed as follows:

47006	0.0014 gram
47007	0.0050 gram
47008	0.0025 gram

These tests deposited basic salts while standing on oven, to dissolve which they were treated twice with 2 cc. of HCl, but this did not prevent appearance of basic salts. On filtering no indication of $BaSO_4$ was noted and only an iron stain remained on paper. The 3 filter papers were ignited and weighed separately, then combined and fused with Na_2CO_3, the solution made faintly acid with HCl and evaporated to crystals. The residue was dissolved in 10 cc. of water and only a slight flocculent precipitate was visible (SiO_2?).

Effect of Hydrochloric Acid on the Solubility of Barium Sulfate

VIII—Four solutions were prepared, each containing 3 grams of sodium carbonate and sodium peroxide, made just acid to methyl orange with HCl. 5 cc. $N/20$ H_2SO_4 were added to each (=0.0294 gram $BaSO_4$).

HCl was added in increasing amounts to each test as follows:

	1	2	3	4
HCl	0.25 cc.	0.50 cc.	1.00 cc.	2.00 cc.

Tests were heated to boiling and slowly precipitated with 7 cc. hot $BaCl_2$ solution, using a Schuster bottle. Volume = 100 cc. All precipitates were granular and settled rapidly. All precipitates were collected on a carefully prepared asbestos pad and the following results were obtained:

	1	2	3	4
Gram $BaSO_4$	0.0303	0.0304	0.0290	0.0312

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THE ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY AND COPPER

By D. J. Demorest

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The following method of analysis has been devised after making hundreds of determinations on alloys and mixtures of metals. The earlier results were inaccurate but they showed the sources of error and ways for improvement in the manipulation until the method as here presented is, in the writer's opinion, the best method for obtaining quick and fairly accurate results in the analysis of the alloys of the above named metals.

The results obtained are reliable to within 0.2 per cent for lead, tin and antimony and 0.1 per cent for copper.

When fine shavings of an alloy containing any or all of the metals lead, tin, antimony, and copper are digested at a boiling heat with concentrated sulfuric acid, the lead is left insoluble as $PbSO_4$ while the tin goes into solution as $Sn(SO_4)_2$, copper as $CuSO_4$, and antimony as $Sb_2(SO_4)_3$. The lead sulfate is filtered off and weighed and the antimony in the filtrate is titrated with standard permanganate solution according to the reaction:

$$5Sb_2(SO_4)_3 + 4KMnO_4 + 24H_2O = 10H_3SbO_4 + 4MnSO_4 + 2K_2SO_4 + 9H_2SO_4$$

After the antimony is titrated, the tin is reduced with iron in the presence of precipitated antimony and the stannous iron is titrated by standard iodine solution.

In another sample the lead is separated as above, and from the filtrate from the lead sulfate the copper is precipitated as CuCNS either with or without a previous titration of the antimony as the chemist may prefer. The CuCNS is then titrated with $KMnO_4$ or the copper is determined by the very accurate iodide method.

The new things about this method are: *First*, the titration of the antimony by permanganate in a sulfuric acid solution free from HCl; *second*, the combination of these four methods for lead, antimony, tin, and copper; and *third*, the manipulation necessary for the combination. A great many determinations were made before the manipulation necessary to obtain accurate results was worked out. It is necessary that the details as here given be strictly adhered to, but this is easily done.

Procedure.—Place 1 gram of fine shavings or drillings in a Kjeldahl flask with a short neck, and add 20 cc. of concentrated sulfuric acid. Heat nearly to boiling and continue the heating until the sample is nearly decomposed and the lead sulfate is white. This may take one-half hour. Finally boil for several minutes. Cool the solution and then add 50 cc. of water while the solution in the flask is kept agitated. Heat the liquid to boiling and keep boiling for several minutes. This is necessary to get the antimony sulfate completely into solution, as it crystallizes out from a cold concentrated sulfuric acid solution. Allow the lead sulfate to settle out for about five minutes or until the solution is clear, but do not allow the temperature of the liquid to fall below about 60° C. The liquid above the $PbSO_4$ should become clear quickly. If it does not, it should be heated longer. After the liquid has become clear, pour it through a weighed Gooch crucible with an asbestos mat. Pour the solution off as completely as possible without allowing more than a very small amount of the $PbSO_4$ to go over into the crucible.

Now introduce 10 cc. more of concentrated sulfuric acid into the Kjeldahl and heat to boiling and keep boiling several minutes, cool, add 30 cc. of water, heat to boiling for a few minutes, allow the solution to cool to about 50° C. and pour it and the precipitate of lead sulfate into the Gooch crucible. Wash the crucible and precipitate six or eight times with distilled water, taking care to keep the volume of the filtrate down to 125–150 cc. Ignite the $PbSO_4$ at a dull red heat, preferably in a muffle furnace, for fifteen minutes or more, cool and weigh. It contains 68.3 per cent lead.

Pour the filtrate from the $PbSO_4$ into a 450 cc. Erlenmeyer flask, heat to 60°–80° C. and titrate the antimony with standard permanganate of about

N/10 strength. After some permanganate has been run in, the solution takes on a pink tinge but the addition of the permanganate is continued until the color becomes a deep permanganate; then two or three cc. more of permanganate are added. Stir the solution for a minute then titrate the excess permanganate with a standard ferrous sulfate solution until the pink just disappears. This is the end point and it is quite sharp.

The permanganate should be standardized by dissolving 0.2 gram of pure antimony in 30 cc. of boiling concentrated sulfuric acid and, after diluting to 150 cc., titrating with permanganate at 70° C. Fairly close results may be obtained by calculating the antimony strength of permanganate from its iron value by multiplying the iron value by 1.076, but it is much better to standardize against pure antimony.

After the antimony is titrated, the tin is determined according to the method of Low improved by Patrick and Wilsnack.[1] Add to the solution 50 cc. of hydrochloric acid and about 0.15 gram of antimony dissolved in 5 cc. of concentrated sulfuric acid unless there is already that amount of antimony present, in which case no antimony need be added. Insert into the neck of the flask a three-hole rubber stopper. Through one hole pass a glass tube which reaches to the bottom of the flask. Between the stopper and the flask and opposite the other holes, pass a platinum wire on the end of which is a sheet of pure iron (such as ingot iron) about two inches long and one-half inch wide, which rests on the bottom of the flask. Pass CO_2 or hydrogen or natural gas (which has bubbled through NaOH solution to remove H_2S) through the glass tube, and heat the solution to slow boiling; continue the boiling and the stream of gas for thirty minutes after the solution has become colorless. The antimony precipitates out and with the iron reduces the tin to the divalent condition. Cool the solution while a rapid stream of the gas is kept passing through the flask to keep out air. When cold add through a funnel in one of the holes in the stopper 100 cc. of cold, recently boiled, distilled water containing several cc. of starch solution. Pull the iron sheet up out of the solution by means of the platinum wire. Remove the funnel and while a slow current of gas is passing, insert the tip of a burette through one of the holes and titrate the tin with a *N*/10 iodine solution until a blue color is obtained. The end point is very sharp but will fade after several minutes. The results are quite accurate.

At the same time that the above sample is being analyzed, another sample should be similarly treated up to or *through* the antimony titration, if the chemist desires duplicate results on the lead and antimony. To the sulfuric acid solution add three grams of tartaric acid, next ammonia until the solution is slightly alkaline, and then two cc. of sulfuric acid; heat nearly to boiling. Add two grams of sodium sulfite and when it is all dissolved add a gram of KCNS dissolved in 10 cc. of water. Shake the flask well and allow the CuCNS to settle for fifteen minutes while the solution is kept hot. Filter through an asbestos mat, wash well with water, and determine the copper in the precipitate by either the sulfocyanate-permanganate method or by the iodide method after igniting the precipitate and dissolving the copper oxide in nitric acid.

NOTES ON THE PROCESS

1. When an alloy containing lead or tin is dissolved in hot sulfuric acid, there is considerable free sulfur liberated. This does no harm.

2. The alloy must be digested with the sulfuric acid at a boiling heat for several minutes in order to dissolve it completely and to oxidize all the tin to the "ic" form. There is no tendency for the antimony to be oxidized further than to the trivalent state.

3. It is necessary that the lead sulfate be ignited at a dull red heat for some time since it seems to hold excess sulfuric acid very tenaciously. Even then the results tend to run a little high.

4. In the antimony titration it is necessary to employ a large excess of permanganate in order to complete the oxidation. Often the solution will become turbid during the titration, but this does not affect the results. When the titration is made thus, in a solution free from HCl, the end point is not evanescent.

The following are some results obtained by the above method:

Grams Lead		Grams Antimony		Grams Tin		Grams Copper	
Taken	Found	Taken	Found	Taken	Found	Taken	Found
0.600	0.602	0.200	0.200	0.200	0.201	0.0460	0.0450
0.600	0.599	0.200	0.201	0.200	0.201	0.0440	0.0440
0.600	0.602	0.200	0.199	...	...	0.1350	0.1340
1.000	1.001	0.200	0.200	0.200	0.200	0.0430	0.0425
0.500	0.502	0.250	0.250	0.250	0.252	0.0890	0.0894
...	...	0.200	0.200	0.200	0.917	0.0500	0.0500
0.700	0.703	0.300	0.301	0.150	0.149	0.2500	0.2510
0.500	0.500	0.250	0.249	0.250	0.250	0.0500	0.0500
0.700	0.701	...	...	0.150	0.148	0.0500	0.0490
0.600	0.601	0.200	0.200	0.200	0.200	0.0255	0.0250
0.600	0.600	0.200	0.200	0.200	0.200	0.0255	0.0254
...	...	...	...	...	...	0.0255	0.0240
...	...	...	...	...	...	0.0255	0.0256

The copper in the above experiments was determined by the sulfocyanate-permanganate method.[1]

The purity of the metals used was ascertained by determining the most likely impurities in them. The weights taken in the above experiments were such as to give the amounts recorded.

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A RAPID AND ACCURATE GRAVIMETRIC METHOD FOR DETERMINING FAT IN ICE CREAMS, CEREALS AND CHOCOLATE

By E. P. Harding and Guy Parkin

Received July 14, 1913

In This Journal, 5, 131, the authors of this paper described a method for determining milk-fat in evaporated milk and milk powders at the conclusion of which they stated that the method was at that time being tried out on various ice creams, on cheese, cereals, flours and various other products.

The present paper is a continuation of that work

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[1] This Journal, 4, 597.

[1] This Journal, 5, 215.

and as the amount of the substance used in an analysis, its nature and fat content differ from those of the milk products, the method will be given again somewhat in detail.

A. THE DETERMINATION OF FAT IN ICE CREAM

The reagents used are acetic acid, 25 per cent by volume; carbon tetrachloride, redistilled; 95 per cent ethyl alcohol, redistilled; and redistilled petroleum ether with boiling point 50° C. to 70° C.

The apparatus used is a 100 cc. Nessler jar or any convenient 100 cc. extraction tube with two rubber stoppers, one unperforated and used while shaking, the other doubly perforated carrying blow-off tubes, similar to the Werner-Schmidt blow-off tubes but with a double bulbed rubber air-pressure pump for forcing the ether layer out of the extraction jar. A 11 cm. filter paper, funnel and stand, wide-mouthed flasks of 50 to 75 cc. capacity for weighing the fat, a small evaporating dish for holding wash petroleum ether, a petroleum ether wash bottle, a condenser, and a drying oven.

The process in detail is as follows: The ice cream is melted by warming to 50° C. and well mixed, without churning, to form a uniform sample. Five grams of this mixture are weighed into the 100 cc. extraction jar, 5 cc. of 25 per cent acetic acid added, and the contents warmed to about 50° C. by cautiously rotating the jar over a low flame or by placing it in a water bath at that temperature. When the protein has dissolved, 12 cc. of carbon tetrachloride are added and the jar vigorously shaken for two minutes. Ten cc. of alcohol are added, the jar again vigorously shaken, then 35 cc. of petroleum ether are added and the vigorous shaking continued one minute. The jar is then allowed to stand from one to two minutes when the separation will be complete. (If an emulsion forms it can be broken up with a few drops of alcohol.) The blow-off tube is then inserted and the ether layer cautiously blown onto the filter which filters through onto the tared flask. (In blowing off the ether layer, care must be taken that none of the carbon tetrachloride layer is blown off which may happen if a too close separation of the two layers is attempted. This may be avoided with reasonable care in the manipulation.) Five cc. of carbon tetrachloride are then added to the contents of the jar which is thoroughly shaken, then 30 cc. of petroleum ether are added, the jar again thoroughly shaken, one minute allowed for separation and the ether layer blown off with the necessary precautions as above stated. Another addition of 5 cc. of carbon tetrachloride and 30 cc. of petroleum ether is made with thorough shaking after each addition, and the separation of the ether layer after one minute standing is repeated as in the first blow off. Five cc. of petroleum ether are then placed in the small evaporating dish and gently drawn into the jar by sucking on the blow-off tube; after a few seconds this ether which has mixed with the thin ether layer in the jar is blown off through the filter. The filter paper is then well washed with small portions of petroleum ether, about 15 cc. in all, the flask connected with the condenser, the ether distilled off, and the flask heated for one hour (to constant weight) at 100° C. in the drying oven, then weighed.

During the process while the jar is being prepared for the second and third blow offs, the weighing flask is connected with the condenser and most of the ether distilled off. This shortens the process to about one and one-half hours and permits the use of a 50 to 75 cc. flask for weighing the fat.

Table I—Results Showing that a Fourth Blow Off is Not Necessary

Sample No.	1st, 2d and 3d Blow offs Grams weight	Per cent fat	4th Blow off Grams weight	Per cent fat
I...........	0.3909	13.03	0.0003	0.01
II...........	0.3303	11.02	0.0012	0.04
III...........	0.3378	11.29	0.0009	0.03
IV...........	0.3601	12.00	0.0003	0.01
V...........	0.2741	9.14	0.0006	0.02

Table II—Results Obtained on Vanilla Ice Creams.[1]

The Roese-Gottlieb Method as given in Circular 66 and the Babcock Method as given in Leach were used as comparison methods.

	Harding-Parkin			Roese-Gottlieb			
Sample No.	Sample weight Grams	Grams fat	Per cent fat	Sample weight Grams	Grams fat	Per cent fat	Modified Babcock Per cent fat
389	3.00	0.3375	11.25	3.00	0.3387	11.29	10.00
389	3.00	0.3363	11.21	3.00	0.3312	11.04	10.00
389	3.00	0.3378	11.29	....	......	.....	....
395	3.00	0.3307	11.02	3.00	0.3303	11.01	10.00
218	3.00	0.3601	12.00	3.00	0.3540	11.80	11.00
218	3.00	0.3612	12.04	3.00	0.3580	11.93	11.00
219	3.00	0.2741	9.14	3.00	0.2755	9.18	8.00
233	3.00	0.2804	9.34	3.00	0.2787	9.29	....
231(a)	3.00	0.2897	9.65	3.00	0.2850	9.50	7.00
X	3.00	0.2251	7.50	3.00	0.2250	7.50	6.00
Y	3.00	0.2338	7.79	3.00	0.2261	7.53	....
Z	3.00	0.2404	8.01	3.00	0.2350	7.83	....
I	3.00	0.2438	8.12	3.00	0.2415	8.05	....
II	3.00	0.2493	8.31	3.00	0.2419	8.06	....
III	3.00	0.2379	7.99	3.00	0.2394	7.98	....

(a) Determination was made on a soured sample.

Table III.—Results Illustrating Change in Butter-Fat Contents of Various Parts of an Ice-Cream Packer after Standing

The samples were two gallon packers which were well filled and in a fresh frozen condition when first sampled. The second sampling was made after the packer had stood twenty-four hours without disturbing at room temperature.

	Fresh frozen condition			After standing 24 hours		
Sample No.	Top Per cent fat	Middle Per cent fat	Bottom Per cent fat	Top Per cent fat	Middle Per cent fat	Bottom Per cent fat
I.....	12.17	12.19	12.05	12.38	12.21	12.12
II.....	12.66	12.34	12.63	12.61	12.57	12.41

CONCLUSION

The method is recommended for determining fat in ice cream because:

I. It is a short, practical gravimetric method readily adapted to commercial control work, requiring from one to one and one-half hours for a complete determination.

II. It gives a pure fat.

III. It gives a larger per cent of fat when compared with standard methods.

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[1] See also results obtained on chocolate ice creams, This Journal, 5, 134.

IV. It will give accurate results without a close adherence to the amounts of reagents used.

B. THE DETERMINATION OF FAT IN CEREALS, COMPOUND CEREALS, FERTILIZERS AND CHOCOLATES

The method used in the determination of oil in cereals, compound cereals and fertilizers with one exception was the same as that applied to ice creams. It was found that acetic acid would not cut the fiber and liberate the oil quantitatively. The same volume of hydrochloric acid with a specific gravity of 1.12 was substituted for the acetic acid with quantitative results.

The method as applied to chocolate was the same as that applied to cereals with the exception that it was necessary to centrifuge two minutes in obtaining the first separation. The following data will show that the Bigelow and Albrech method gives higher results but the extract upon evaporation contained fibrous material which it was impossible to filter off and therefore weighed as oil.

Table I—Results Obtained on Graham Flour, Buckwheat Flour, Compound Cereals and Fertilizers

The sixteen-hour ether extraction method as given in Food Inspection and Analysis by Leach was used as a comparison method.

	Harding-Parkin			16-hour ether extract		
Sample No.	Flour Grams	Oil Gram	Oil Per cent	Flour Grams	Oil Gram	Oil Per cent
I	2	0.0518	2.59		......	....
I	2	0.0521	2.60		......	....
I	2	0.0529	2.64		......	....
I	2	0.0535	2.67		......	....
II	2	0.0422	2.11	2	0.0410	2.05
III	2	0.0311	1.56	2	0.0300	1.50
III	2	0.0310	1.55			....
IV	2	0.0492	2.46	2	0.0482	2.41
IV	2	0.0476	2.38	2	0.0475	2.37
IV	2	0.0505	2.52		......	....
IV	2	0.0493	2.46		......	....
IV	2	0.0494	2.47		......	....
IV	2	0.0490	2.45		......	....
IV	2	0.0477	2.38		......	....
IV	2	0.0498	2.49		......	....
IV	2	0.0510	2.55		......	....
IV	2	0.0497	2.48		......	....
V	2	0.0490	2.45	2	0.0478	2.39
V	2	0.0492	2.46		......	....
VI	2	0.0372	1.86	2	0.0385	1.92
VI	2	0.0361	1.80		......	....
VII(a)	2	0.0630	3.15	2	0.0590	2.95
VIII(a)	2	0.0504	2.52	2	0.0500	2.50
VIII(a)	2	0.0516	2.58		......	....
IX(a)	2	0.0540	2.70	2	0.0533	2.66
X(b)	2	0.0760	3.80	2	0.0774	3.87
X(b)	2	0.0744	3.72		......	....
X(b)	2	0.0740	3.70		......	....
XI(c)	2	0.2128	10.64	2	0.2127	10.63
XI(c)	2	0.2371	11.85	2	0.3360	11.80

(a) Determination on buckwheat flour.
(b) Determination on compounded cereals.
(c) Determination on fertilizers.

Table II

The following data were obtained showing a fourth blow off to be unnecessary.

	1st, 2d, 3d Blow offs		4th Blow off	
Sample No.	Oil Gram	Oil Per cent	Oil Gram	Oil Per cent
207	0.0422	2.11	0.0012	0.06
203	0.0630	3.15	0.0008	0.04
211	0.0516	2.58	0.0006	0.03

Table III

The following results were obtained on chocolate. The Bigelow and Albrech Method as given in the Proceedings of A. C. A. C. Bull. No. 137, pp. 102–3, was used as a comparison method.

	Harding-Parkin			Bigelow-Albrech		
Sample No.	Chocolate Grams	Cocoa Butter Grams	Cocoa Butter Per cent	Chocolate Grams	Cocoa Butter Grams	Cocoa Butter Per cent
173	2.00	1.0393	51.96	2.00	1.0720	53.60(a)
173	2.00	1.0341	51.70(b)	2.00	1.0680	53.40(a)

(a) This cocoa butter had a dirty appearance and contained chocolate fiber.
(b) The refractive index of this fat was found to be 1.4575 as 40° C.

CONCLUSION

I. The method extracts all the oil from cereals and fertilizers and requires but two hours for a complete determination. Other reliable methods require sixteen hours of extraction.

II. It extracts from chocolate all the oil in a pure, fibrous-free condition.

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PROPOSED METHOD FOR DETECTING ADULTERATION OF CIDER VINEGAR WITH DISTILLED VINEGAR

By S. L. Crawford

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At the present time it is only possible to determine whether a cider vinegar has been adulterated with an appreciable amount of distilled vinegar, providing the different constituents have not been raised to cover up the addition of the distilled vinegar. The glycerine determination, for example, is only valuable providing a sufficient amount of glycerine has not been added to the vinegar to make up for the lowering of the glycerine content caused by the addition of distilled vinegar. Therefore, in looking for a way of determining whether cider vinegar contains added distilled vinegar, our principal aim has been to find some difference between cider vinegar and distilled vinegar, which could not be affected by additions made to the vinegar.

It has been known for some time that there was in cider vinegar a volatile constituent which had a reducing effect on Fehling's solution, and in order to get the true amount of reducing sugars in vinegar, it is necessary to evaporate several times after the addition of water. What this substance is, has not yet been determined, but what we found was that while distilled vinegar or pyroligneous acid does not contain any appreciable amount of this volatile substance, all cider vinegar shows its presence in sufficient amount to make it a valuable constant in determining the purity of a vinegar.

The proposed method is to take 50 cc. of sample, dilute to 250 cc. and distil over 200 cc. into a 250 cc. flask. Neutralize and make up to the mark. Take 50 cc. of this distillate and determine sugars by the method given in Bureau of Chemistry, *Bulletin* 107. The result is given as invert sugar according to Munson and Walker's tables.

In Table I are shown results determined on seven different samples of distilled vinegar obtained from different sources, and of varying age running from one month to one year. It will be seen from the figures given in Table I that distilled vinegar when reduced to 4 per cent acid strength contains from a trace to 0.0026 gram per 100 cc. of this volatile substance, which is practically negligible.

In Table II is given the amount found in a fully fermented dry refined cider six months old, and a completely fermented first pressing juice, which has not been refined, also six months old. As only traces were found in these samples, it goes to show that the volatile substance is produced during the acetification of the apple juice.

Table III shows the amount found in four samples of cider vinegar made from first pressings, having an average of 0.162 gram on a 4 per cent basis.

TABLE I

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent basis
1	Distilled vinegar....	10.0	0.0065	0.0026
2	Distilled vinegar....	9.44	Trace	Trace
3	Distilled vinegar....	10.67	Trace	Trace
4	Distilled vinegar....	9.01	0.0005	0.0002
5	Distilled vinegar....	10.46	0.0045	0.0017
6	Distilled vinegar....	9.61	0.0010	0.0004
7	Distilled vinegar....	10.38	Trace	Trace

TABLE II

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.
8	Dry refined cider.........	0.36	Trace
9	1st pressing..............	0.75	Trace

TABLE III

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent acid basis
10	1st press............	4.70	0.2232	0.190
11	1st press............	4.70	0.2051	0.174
12	1st press............	4.50	0.1664	0.148
13	1st press............	4.20	0.1424	0.136

TABLE IV

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent acid basis
14	2nd press..........	5.53	0.2244	0.162
15	2nd press..........	4.62	0.2092	0.181
16	2nd press..........	4.20	0.1784	0.170

TABLE V

	Percentage composition				
Sample	1st press	2d press	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent acid basis
17......	75	25	4.98	0.1824	0.147
18......	66.7	33.3	4.48	0.1405	0.125
19......	75	25	4.72	0.1752	0.149
20......	75	25	4.86	0.1621	0.133
21......	85	15	4.96	0.1384	0.111
22......	66.7	33.3	4.72	0.1562	0.133
23......	75	25	4.82	0.1520	0.126
24......	50	50	5.52	0.1700	0.123
25......	50	50	5.69	0.1840	0.129

In Table IV are the amounts found in three samples of cider vinegar made from second pressings, all kept different lengths of time before repressing. Sample No. 14 was repressed the second time one hour after the first pressing; No. 15 nineteen hours after the first pressing; and No. 16 was repressed five days after the first pressing.

As these figures are fairly constant, it does not appear to make any appreciable difference in the amount of volatile reducing substance present, how long the pomace is kept before repressing.

Table V shows nine samples of cider vinegar composed of varying amounts of first and second pressings, and it will be seen that the amount of volatile substance found is fairly constant when reduced to a 4 per cent basis, running from 0.111 to 0.149.

All of the above samples are of known purity and all comparatively new vinegars, none of them being more than one year old.

While the above figures are not sufficient evidence upon which to determine the purity of a cider vinegar, it would seem from the work done, that if a large number of vinegars of varying composition and age were examined, a maximum or minimum content for cider vinegar could be found, which would, in addition to the known glycerine content and other constants, be of considerable aid in determining whether a cider vinegar has been adulterated with distilled vinegar or pyroligneous acid.

If desired, it can be readily determined whether the adulteration is due to the presence of distilled vinegar or pyroligneous acid, owing to the fact that if pyroligneous acid has been used, the vinegar will contain more than 0.007 gram per 100 cc. of formic acid, while if distilled vinegar has been used, the amount of formic acid present will be below 0.007 gram per 100 cc., depending upon the amount of cider vinegar present in the mixture. A pure cider vinegar when subjected to the formic acid test will show from a trace to 0.007 gram per 100 cc. of a substance which is calculated in this determination as formic acid.

We give below the analysis of a vinegar actually made from distillery slop and distilled vinegar. It will be seen that if this vinegar was branded "reduced with water" to take care of the low non-sugars and ash, it would be impossible for any chemist to prove that it was not a pure cider vinegar.

Specific gravity at 20° C................	1.0145
Acetic acid, grams per 100 cc.............	4.86
Solids, grams per 100 cc..................	1.97
Reducing sugars before inversion, grams per 100 cc..............................	0.70
Ash, grams per 100 cc.....................	0.209
Alkalinity of ash, cc. $N/10$ acid...........	29.60
Phosphoric acid soluble, mgms. per 100 cc..	6.98
Phosphoric acid insoluble, mgms. per 100 cc.	17.38
Polarization degrees Ventzke..............	—1.6
Formic acid, grams per 100 cc............	Absent
Glycerine, grams per 100 cc..............	0.292
Volatile reducing substance, grams per 100 cc................................	Absent
Lead precipitate.........................	Good
Artificial color.........................	None detected
Non-sugars, grams per 100 cc............	1.27
Per cent of solids reducing sugars........	35.50
Ratio of ash to non-sugars................	1.6

One form of adulteration which the above method would be useful in detecting is when the slop or residue from an apple brandy still is mixed with a weak solution of alcohol and run over the generators, or distilled vinegar is added direct, artificially colored and sold as cider vinegar.

As practically every constituent of the apple is left unchanged in the still after distillation, it is almost impossible to detect this form of adulteration by any of the regular methods of analysis, for nothing has been taken away from the original apple juice except the alcohol, and that is replaced either with other alcohol or its equivalent of acetic acid. A vinegar of this kind, however, contains either no volatile reducing substance or only a trace, due to the small amount present in the distilled vinegar, as the original apple juice has never undergone the acetic fermentation, at which stage the volatile reducing substance is formed. For this reason the adulteration can be readily detected.

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CHEMICAL STUDIES ON THE LIME SULFUR-LEAD ARSENATE SPRAY MIXTURE

By W. E. Ruth

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PREVIOUS WORK

Much experimental work has been done with arsenicals of various kinds in the way of spraying tests and methods of preparation; most of this, however, has been carried on by horticulturalists and entomologists. Some work has been done with lime sulfur, with a view to methods of preparation and the forms of combination in which the sulfur is present in solution. More of the latter work has been performed by chemists.

As far as known at present, Bradley[1] and Tartar[2] have made the only studies of lime sulfur and lead arsenate mixtures from a chemical standpoint. Their work consisted of comparing the neutral with the acid lead arsenate when mixed with lime sulfur. They compared the total sulfur and calcium content of the lime sulfur but made no study of the various forms of sulfur in solution before and after mixing.

EXPERIMENTAL

COLOR CHANGES.—To every one who has handled lime sulfur and lead arsenate in a mixture for one spraying, it is a well known fact that a change occurs in the appearance of lead arsenate. The white lead arsenate very soon becomes black in presence of lime sulfur solution. If a solution of lead acetate be added to a solution of sodium thioarsenate a precipitate when first formed has a reddish yellow color which very soon gives way to a darker brown and this in turn to a very dark gray—almost black.

Several drops of concentrated lime sulfur solution added to a small quantity of fine particles of lead arsenate suspended in water will result in the lead arsenate undergoing the same color changes described above in the precipitation of the lead thioarsenate. With the addition of the first lime sulfur solution the particles of lead arsenate turn to the reddish yellow color and in the presence of more lime sulfur it turns darker and finally black in the excess of lime sulfur.

Again if the lime sulfur be added to the lead arsenate in the water in small diluted portions, up to a certain point the sulfur will be precipitated so as to decolorize completely the solution and beyond that point the color of further additions of lime sulfur apparently is not affected.

EFFECT ON LEAD ARSENATE OF MIXING WITH LIME SULFUR SOLUTION

At first it was attempted to mix small definite quantities of lead arsenate with accurately measured portions of lime sulfur solution so that definite quantities of lead and arsenate could be accounted for after mixing with lime sulfur. This, however, was abandoned, because it was found impractical to separate the black lead-arsenate-sulfur residue quantitatively from the filter upon which it was separated and washed from the lime sulfur.

To avoid this difficulty, quantities of approximately one hundred grams of lead arsenate were mixed with lime sulfur. (Lime sulfur concentrate 32.5° B., diluted 1 to 40, about the concentration recommended for summer spray.) The mixture was prepared from Grasselli commercial lime sulfur and Sherwin Williams "New Process" lead arsenate which was slightly acid to litmus. The latter showed the following analysis, dry basis:

Total lead (Pb) Per cent	Total arsenic oxide oxide (As_2O_5) Per cent	Water-soluble As_2O_5 Per cent
64.18	26.42	0.42
64.28	26.52	0.46

The lime sulfur was used in large excess in an attempt to simulate conditions that obtain in spraying. The mixture was very frequently stirred to prevent the caking that is so common with lead arsenate in lime sulfur. After standing several hours the lead-arsenic-sulfur residue was filtered with suction and washed with previously boiled and cooled water to the complete disappearance of color of lime sulfur solution, and then with several hundred cc. more of water to insure complete removal of lime sulfur. The residue was dried in an oven not over 40° C. and kept in a vacuum desiccator until ready for analysis.

One-gram samples were digested with 100 cc. of approximately 10 per cent nitric acid solution on the steam bath for several hours; filtered, washed and the digestion repeated. The solution contained the lead arsenic and calcium. It was transferred to a 300 cc. volumetric flask, diluted to the mark and aliquots used for determining the lead and arsenic. The lead was determined from the solution by the chromate method and the arsenic by the modified Gooch and Browning method.

One preparation of the mixture gave the following results for lead and arsenic oxide:

	Lead (Pb) Per cent	Arsenic oxide (As_2O_5) Per cent
1..........................	42.61	8.87
2..........................	42.17	9.06
3..........................	42.24	8.86
4..........................	42.28	8.89

A second preparation gave the following by the same method:

	Lead (Pb) Per cent	Arsenic oxide (As_2O_5) Per cent
1..........................	45.52	9.09
2..........................	45.72	9.09

The total sulfur, free sulfur and calcium were also

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[1] This Journal, **1**, 606.

[2] *Ibid.*, **2**, 271, 328.

determined in the second preparation, showing the following:

	Total sulfur Per cent	Free sulfur Per cent	Total calcium Per cent
1	22.51	19.32	5.14
2	22.52	19.56	5.02

Total sulfur was determined by the Fresenius[1] method, the arsenic being removed from the hydrochloric acid solution with H_2S. The calcium was determined by the Rose[2] method of decomposition with chlorine and separation of lead and arsenic by hydrogen sulfide. Free sulfur was determined by carbon disulfide extraction.

The decrease in percentages of lead and arsenic from those of the original lead arsenate to the percentages in the mixture is very marked. The decrease is apparently due to the addition of sulfur and calcium to the mixture. But the results of analyses do not total a hundred per cent, as shown below:

Pb	45.62
Total S	22.51
Ca	5.08
As_2O_5	9.09
	82.30

This evident loss caused the writer to try some method of examining the mixture for the presence of oxygen compounds of sulfur such as sulfates, sulfites or thiosulfates. Accordingly, one-gram samples were placed in the shaker bottles with about 800 cc. of previously boiled and cooled distilled water, shaken for four hours and filtered. These solutions were made up in liter flasks and aliquots used in analyses. Solutions gave strong tests for calcium with ammonium oxalate, as well as a test for thiosulfate, but no evidence of sulfide, sulfites or sulfates.

The solutions decolorized iodine solution but when bleached again with stannous chloride gave no precipitates with barium chloride in hydrochloric acid solution (even after long standing), thus eliminating presence of sulfites or sulfates. A portion of the solution boiled with hydrochloric acid became cloudy in appearance, due to free sulfur precipitating from the decomposition of thiosulfate. Other portions of the solutions mixed with chlorine water and allowed to stand over night, then boiled and acidified with hydrochloric acid, gave liberal precipitates of barium sulfate indicating the thiosulfate.

Quantitative determinations of sulfur by the latter described method and calculated for the whole solutions gave the following results:

No.	Free sulfur Gram	Calculated equivalent of CaS_2O_3 Gram
1	0.0188	0.03324
2	0.0185	0.04255
3	0.0176	0.04048
4	0.0194	0.04462
5	0.0162	0.03726
6	0.0159	0.03657
7	0.0162	0.03726
8	0.0172	0.03956

The amounts of calcium thiosulfate shown here calculated to the original weight of the sample show from three and three-tenths to four and four-tenths per cent thiosulfate present. The solutions showed only traces of arsenic, so that very small quantities of calcium arsenate could possibly be present.

The Cornell Station[1] has shown that mixing lead arsenate with lime sulfur increases the fungicidal value of lime sulfur. Haywood[2] in his work on lime sulfur says: "It is a well known fact that sulfites act as antiseptic agents. There is reason to believe that they would also act as insecticides. From the decomposition of the wash there are obtained sulfur in a very finely divided form, thiosulfate for a time, and sulfite which is gradually set free. The writer (Haywood) is of the opinion that these are the active agents in killing insects." Haywood shows by reaction how the thiosulfates are formed from the polysulfides. If it is true, as he supposes, that the fungicidal properties of lime sulfur are largely due to the formation of thiosulfates and sulfites with liberation of free sulfur, here then is an explanation, partially at least, for the increase of the fungicidal properties of the lime sulfur solution when mixed with lead arsenate.

Bradley and Tartar[3] state that no sulfides of arsenic are formed since they would be soluble in the alkaline lime sulfur solution, but none were found in the solution. The writer also failed to find any sulfide of arsenic in the lime-sulfur solution.

If a portion of the lead arsenate-sulfur residue be covered with a 10 per cent sodium hydroxide solution, then warmed on the steam bath for a short time and allowed to settle, some of the supernatant liquid when acidified with hydrochloric acid will be shown to contain arsenic sulfide. A small quantity will be thrown out of solution. A part of the residue remaining after extraction for free sulfur was treated with the alkali, but the solution gave no precipitate of arsenic sulfide when acidified.

A second portion of the residue which had been extracted until free from sulfur was warmed with sodium polysulfide. After standing several hours on the steam bath the liquid gave quite a heavy precipitate of arsenic sulfide when acidified with hydrochloric acid. Arsenic in the arsenic sulfide precipitates was verified by boiling with hydrochloric acid and potassium chlorate and precipitating as magnesium ammonium arsenate.

EFFECT OF MIXING ON LIME SULFUR

To observe the effect of mixing on the lime sulfur solution approximately one-gram samples of the lead arsenate dried free from moisture were mixed with accurately measured quantities of the lime sulfur solution (concentrate 32.5° B. used in different dilutions). The mixtures were made in small ground glass stoppered flasks that were filled by the quantities of lime sulfur used so as to exclude all air possible. The lime sulfur was separated from the lead arsenate residues by means of Gooch filters. Aliquot parts of 10 cc. were immediately drawn off, and the de-

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[1] Treadwell and Hall, p. 357, Vol. II, 3rd ed.

[2] *Ibid.*, p. 359.

[1] Wallace, Blodgett and Hesler, Cornell Sta., *Bull.* **290**.

[2] Haywood, Bureau of Chem., U. S. D. A., *Bull.* **101**.

[3] *Loc. cit.*

termination of total sulfur made from one, and total sulfides, thiosulfate, sulfite and sulfate all made from a second part.

The monosulfide sulfur was not determined but total sulfide sulfur was precipitated by iodine solution, determined as barium sulfate and the iodine titration continued for thiosulfate as described by Harris.[1]

As comparative results were sought in the lime sulfur before and after mixing with lead arsenate the above method was found very satisfactory and quick for precipitating the sulfide sulfur.

After the thiosulfate titration the sulfide sulfur was filtered off, and sulfites, now oxidized to sulfates, along with any sulfates originally present, were precipitated as barium sulfate in the cold hydrochloric acid solution by standing at least twelve hours.

The results of analyses of lime sulfur mixed with lead arsenate as described above are shown below in Tables I and III. Those shown in Table I are for mixtures standing one hour and Table III shows results for mixtures standing overnight. Tables II and IV show the differences in the various forms of sulfur, being more or less, as the case may be, than in the original lime sulfur solution before mixing with lead arsenate.

Tables II and IV show losses of sulfide sulfur and calcium from solutions and increases of thiosulfate and sulfate (including sulfites) in every case. Mixtures Nos. 1, 2, 3, in both Tables I and III were made at the same time from the same diluted lime sulfur solution with approximately the same weights of lead arsenate as shown in the tables. The results in the first three mixtures, Table I, show that the thiosulfate in solution is increased in the lime sulfur by mixing as well as the sulfate (including sulfites), but upon further examination of 1, 2, 3, Table III, it will be seen that the oxidation has continued—the thiosulfates having decreased and sulfates increased. It must be borne in mind that the flasks were full to exclusion of air, and any oxidation could come only from the lead arsenate, also that the water used in dilution of lime sulfur concentrate had been previously boiled to free it from air and carbon dioxide.

Nos. 5 to 14, Table III, are mixtures made with smaller quantities of a more diluted lime sulfur to observe, if possible, the effect of lesser concentration on the mixture. In Table IV it will be noticed that the amount of sulfide sulfur lost from the weaker solution approaches very closely the amount lost from solution in the more concentrated form. The sulfide sulfur loss is due to precipitation in some form by the lead arsenate as well as the formation of thiosulfates and sulfates from the sulfides.

The loss of calcium from the solution apparently is due to only partial solubility of the calcium thiosulfate in the lime sulfur, as well as due to any small quantities of calcium arsenate that may be formed, the latter being mostly insoluble in the excess of lime sulfur solution.

In columns 4 and 5, Tables I and III, are given the total sulfurs in the lime sulfur solutions. The total sulfur as calculated (shown in column 4) is found by summing up the three forms of sulfur in solution.

The total sulfur shown in column 5 is that determined directly on a separate portion of the solutions. Columns

TABLE I—ANALYSES OF LIME SULFUR SOLUTION WITH LEAD ARSENATE STANDING ONE HOUR. WEIGHTS OF VARIOUS FORMS OF SULFUR IN GRAMS

No.	1 Sulfide S	2 Sulfate S	3 Thiosulfate S	4 Total S calculated	5 Total S determined	6 Weight of lead arsenate used	7 Weight of Ca in sol.
1...	0.31200	0.00281	0.03477	0.34958	0.32964	1.0006	0.09539
2...	0.30066	0.00309	0.03635	0.34010	0.32031	0.9997	0.09333
3...	0.29922	0.00295	0.03635	0.33852	0.32243	1.0013	Lost
Blank (a) 4...	0.42132	0.00116	0.01738	0.43986	0.43735	None	0.12116
5...	0.23245	0.00178	0.03984	0.27407	0.24525	0.0128	0.07817
6...	0.20834	0.00178	0.03824	0.24836	0.22105	1.0015	0.08141
7...	0.21020	0.00178	0.03984	0.25182	0.22222	1.0013	0.07434
8...	0.20607	0.00175	0.03984	0.24766	0.22002	0.9996	0.07640
9...	0.21844	0.00179	0.03984	0.25907	0.23478	1.0203	0.07537
10...	0.21246	0.00178	0.03824	0.25248	0.22846	1.0088	0.07611
Blank (a) 11...	0.38680	0.00104	0.02231	0.41015	0.38859	None	0.11791

(a) The "blank" determination before mixing is for the same quantity of the same lime sulfur solution used in the mixtures given immediately above.

TABLE II—DIFFERENCES IN GRAMS IN TABLE I FOR WHOLE AMOUNT OF LIME SULFUR USED BEFORE AND AFTER MIXING (1 HOUR)

No.	1 Sulfide S Loss	2 Sulfate S Gain	3 Thiosulfate S Gain	4 Difference between total S determined and total S calculated. Gain	5 Weight of lead arsenate used	6 Ca loss from solution
1.......	0.10932	0.00165	0.01739	0.01994	1.0006	0.02577
2.......	0.12066	0.00193	0.01897	0.01979	0.9997	0.02783
3.......	0.12210	0.00179	0.01897	0.01609	1.0013	Lost
5.......	0.15435	0.00074	0.01753	0.02882	1.0128	0.03974
6.......	0.17846	0.00074	0.01593	0.02731	1.0015	0.03650
7.......	0.17660	0.00074	0.01753	0.02960	1.0013	0.04357
8.......	0.18073	0.00071	0.01753	0.02764	0.9996	0.04151
9.......	0.16836	0.00075	0.01753	0.02429	1.0203	0.04254
10.......	0.17434	0.00074	0.01593	0.02402	1.0088	0.04180

TABLE III—ANALYSES OF LIME SULFUR SOLUTION WITH LEAD ARSENATE STANDING OVERNIGHT. WEIGHTS OF VARIOUS FORMS OF SULFUR IN GRAMS

No.	1 Sulfide S	2 Sulfate S	3 Thiosulfate S	4 Total S calculated	5 Total S determined	6 Weight of lead arsenate used	7 Ca in solution
1...	0.21782	0.00350	0.02687	0.24819	0.25052	1.0024	0.07537
2...	0.21391	0.00419	0.02529	0.24339	0.23925	1.0017	0.07493
3...	0.23390	0.00391	0.02055	0.25836	0.26198	1.0021	0.08067
Blank (a) 4...	0.42132	0.00116	0.01738	0.43986	0.43735	None	0.12116
5...	0.0364	0.0024	0.0231	0.0619	0.0797	1.0125	....
6...	0.0362	0.0020	0.0231	0.0613	0.0770	1.0194	....
7...	0.0352	0.0022	0.0245	0.0619	0.0782	1.0122	....
8...	0.0352	0.0021	0.0191	0.0564	0.0669	1.0065	....
Blank (a) 9...	0.2162	0.0010	0.0127	0.2299	0.2269	None	....
10...	0.0607	0.0031	0.0167	0.0805	0.0860	1.0007	....
11...	0.0688	0.0029	0.0175	0.0892	0.0946	0.9994	....
12...	0.0739	0.0031	0.0159	0.0929	0.0969	1.0072	....
13...	0.0648	0.0032	0.0159	0.0839	0.0917	1.0289	....
Blank (a) 14...	0.2448	0.0010	0.0155	0.2613	0.2680	None	

(a) The "blank" determination before mixing is for the same quantity of the same lime sulfur solution used in the mixtures given immediately above.

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[1] Mich. Sta., Tech., *Bull.* 6.

4, Tables II and IV, show the differences between the two results for total sulfur.

The difference shown in Table II is indicated as a gain, that is, the calculated total shows a gain when compared with total sulfur by determination. This difference was at first thought to be due to analytical error but when the same comparisons were made for the mixtures standing overnight, with only one exception as indicated, the calculated totals show a loss as compared with the total sulfur as determined direct.

TABLE IV—DIFFERENCES IN GRAMS IN TABLE III FOR THE WHOLE AMOUNT OF LIME SULFUR USED BEFORE AND AFTER MIXING (12 HOURS OR MORE)

No.	1 Sulfide S Loss	2 Sulfate S Gain	3 Thiosulfate S Gain	4 Difference between total S determined and total S calculated Loss	5 Weight of lead arsenate	6 Ca loss from solution
1...	0.20350	0.00234	0.00949	0.0033	1.0024	0.04579
2...	0.20741	0.00303	0.00791	0.00414[a]	1.0017	0.04623
3...	0.18742	0.00275	0.00317	0.00362	1.0021	0.04049
5...	0.1798	0.0014	0.0104	0.0178—	1.0125	......
6...	0.1800	0.0010	0.0104	0.0157	1.0194	......
7...	0.1810	0.0012	0.0118	0.0163	1.0122	......
8...	0.1810	0.0011	0.0064	0.0105	1.0065	......
10...	0.1841	0.0021	0.0012	0.0055	1.0007	......
11...	0.1760	0.0019	0.0020	0.0054	0.9994	......
12...	0.1709	0.0021	0.0004	0.0040	1.0072	......
13...	0.1800	0.0022	0.0004	0.0078	1.0289	......

(a) No. 2 is the only exception in the table where the total sulfur as calculated by summing up the three forms of sulfur showed a gain over the total sulfur as determined.

Whether the gain as shown by the calculated total at the end of an hour is due to analytical error and the loss shown by the calculated total of mixtures after long standing is due to formation of a form of sulfur not included by the present analytical methods, or whether they are both due to analytical error, is not understood and no explanation is offered for it at this time.

DISCUSSION OF RESULTS

As stated before, the writer failed to find any arsenic sulfide in the lime sulfur. But the evidence presented leads the writer to believe that a small amount of the arsenic oxide is converted into the sulfide or that it forms a thioarsenate possibly with lead which would hold it insoluble in the weaker alkaline lime sulfur solution. The close analogy of the color changes undergone by precipitating lead thioarsenate and that of mixing lead arsenate and lime sulfur led the writer to look for the formation of arsenic sulfide.

The results show that the mixing of lead arsenate and lime sulfur increases the thiosulfates and sulfites in the residue. If Haywood[1] is correct in his view that the fungicidal value of lime sulfur is due to the presence of thiosulfate and sulfites, this increase of thiosulfate in lime sulfur upon mixing it with lead arsenate probably explains the increased fungicidal value of the lime sulfur and lead arsenate mixture.

In conclusion, the writer wishes to acknowledge his indebtedness to Dr. A. W. Dox, of this Station, at whose instigation the above work was undertaken.

AGRICULTURAL EXPERIMENT STATION
IOWA STATE COLLEGE
AMES

SPONGES AS A FERTILIZER

By JOSEPH G. SMITH

Received Aug. 13, 1913

Loggerhead sponge is used with "wonderful results" by the farmers of the Florida Keys who "hardly ever use chemical fertilizers" and it "grows in countless thousands in shallow water where it is easy to procure" as well as to "an enormous size," according to Mr. Thomas E. Reedy of Key West. Its use for the same purpose by the citrus fruit growers of the mainland is attested by Dr. H. F. Moore, of the U. S. Bureau of Fisheries, and has been seen by him growing in such quantities in the salt waters of southern Florida that he has "long thought it should be exploited."

The claims for it as a fertilizer are verified by analyses of samples from Key West submitted by Mr. Reedy, the approximate results on air-dry material being 4 per cent of nitrogen, 3/4 of 1 per cent each of potash (K_2O) and phosphoric acid (P_2O_5), 5 per cent of lime (CaOMgO, mainly CaO) and 40 per cent organic matter. Mr. T. C. Trescott, Chief of the Nitrogen Division of the Bureau of Chemistry, very kindly made the nitrogen determinations. Mr. C. F. Miller, of this Bureau, made the others, duplicating them by repetition, and they were verified in part by the writer.

Analyses of other non-commercial species and of other samples of the Loggerhead are desirable although it is not likely that they differ materially from one another in composition since they all have the same general characteristics and are developed under practically identical conditions.

It is evident from the composition of this material and from its demonstrated efficiency as a fertilizer that it has considerable value to coast and island farmers and fruit growers having easy access to it wherever it is found.

With a view to determining the feasibility of extending its use, further investigations are in progress and contemplated.

BUREAU OF SOILS
DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

LABORATORY AND PLANT

THE CHEMICAL LABORATORY OF THE PICHER LEAD CO.

By JOHN A. SCHAEFFER

Received August 18, 1913

The completion of the new chemical laboratory of the Picher Lead Company, located at Joplin, Missouri, marks another advance in the construction of industrial laboratories, again showing the value of the highest type of equipment for scientific investigation which is so essential in the control of manufacturing opera-

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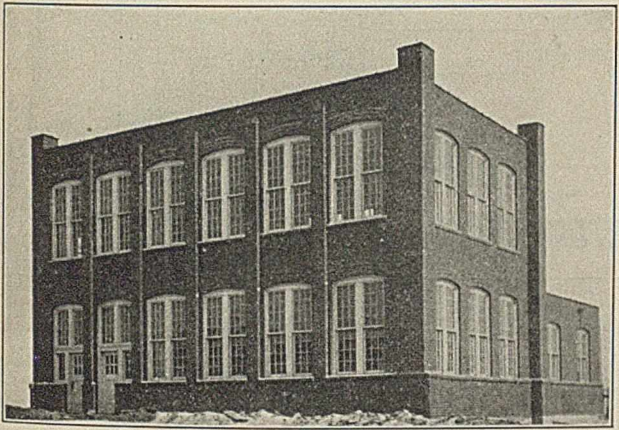
[1] *Loc. cit.*

tions, in the study of new processes and in the research work which must necessarily be conducted along all lines in which the manufactured products are utilized. The many new features incorporated in this laboratory will be of undoubted value to chemists and chemical engineers and a description of the laboratory is given with the hope that some points in it may be of ultimate value in the construction and equipment of other industrial laboratories.

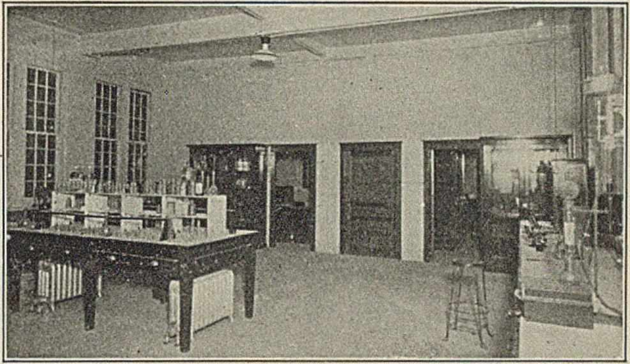
The laboratory was so designed and equipped as to fully take care of the varied work which arises in the manufacture of lead and its products. This work embraces constant analytical attention from the ore, Galena, through the smelting processes, the refining processes and thence through the various operations which lead to the finished products. It demands accurate data relative to the formulation of charges based upon analysis, correct furnace temperatures, close study of by-products and continual supervision of furnace practice. Coupled with this is the extensive research work which must be carried out on storage batteries, glass, ceramics, enamels, varnishes, rubber and paints, together with the investigation of manufacturing problems which continually arise. The scope of the work along these lines is wide and every effort was made to meet these conditions in the construction and equipment of the chemical laboratory.



EXTERIOR VIEW OF CHEMICAL LABORATORY

The building is a two-story brick and concrete structure—fireproof in every detail, the upper floor being devoted exclusively to research work. The general plan of the laboratory can be well understood by an examination of the accompanying sketches.

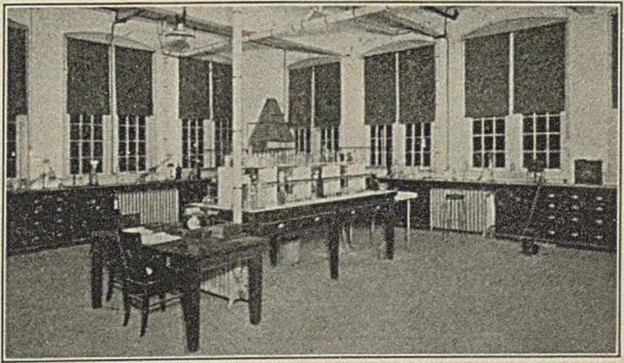
The general laboratory, which is devoted to routine work, is located on the ground floor with an eastern and southern exposure so that the best light for volumetric analysis may be obtained. This room, 30 by 32 feet in size, is sufficiently large to accommodate a full corps of chemists. The laboratory tables are of the highest type of construction, consisting of a steel shell resting upon a wood understructure. Into this steel shell a table of vitrified tile was built upon cement, being painted with white cement. The result is a white, durable, unattackable, easily cleaned laboratory table showing any trace of dust, which, in a laboratory dealing with lead products, frequently contains fine particles of lead compounds. The usual laboratory equipment is found here—such as apparatus for electrochemical work, electric hot plates, electric furnaces, drying ovens, cupellation muffles and hoods. All the tables, not only in this room but throughout the building, are equipped with electricity, gas, air, water and drains.



VIEW OF RESEARCH LABORATORY SHOWING LIBRARY AND PHOTOMICROGRAPHIC ROOM

Adjoining the general laboratory is the balance room. Here are found the analytical balances, assay balances and Westphal balance. Concrete piers sunk into the ground, and entirely separate from the building, form the base for the balances and tables. By this means no vibration from the building affects the tables, and this arrangement has resulted in showing only the very slightest vibrations in the balances themselves.

The supply room also connects directly with the general laboratory. This room is so arranged that all heavy reagents are made to syphon directly into closed containers placed upon the table in the general laboratory, thus affording a continual supply of chemicals in the general laboratory itself from the supply room, without the presence of carboys, and with no further attention or entrance into the supply room, than that which is required for the starting of the syphons when the supply in the carboys is exhausted and new ones are set in place. An unusual saving of time, space and labor has been effected by this arrangement.



A PORTION OF THE ANALYTICAL LABORATORY

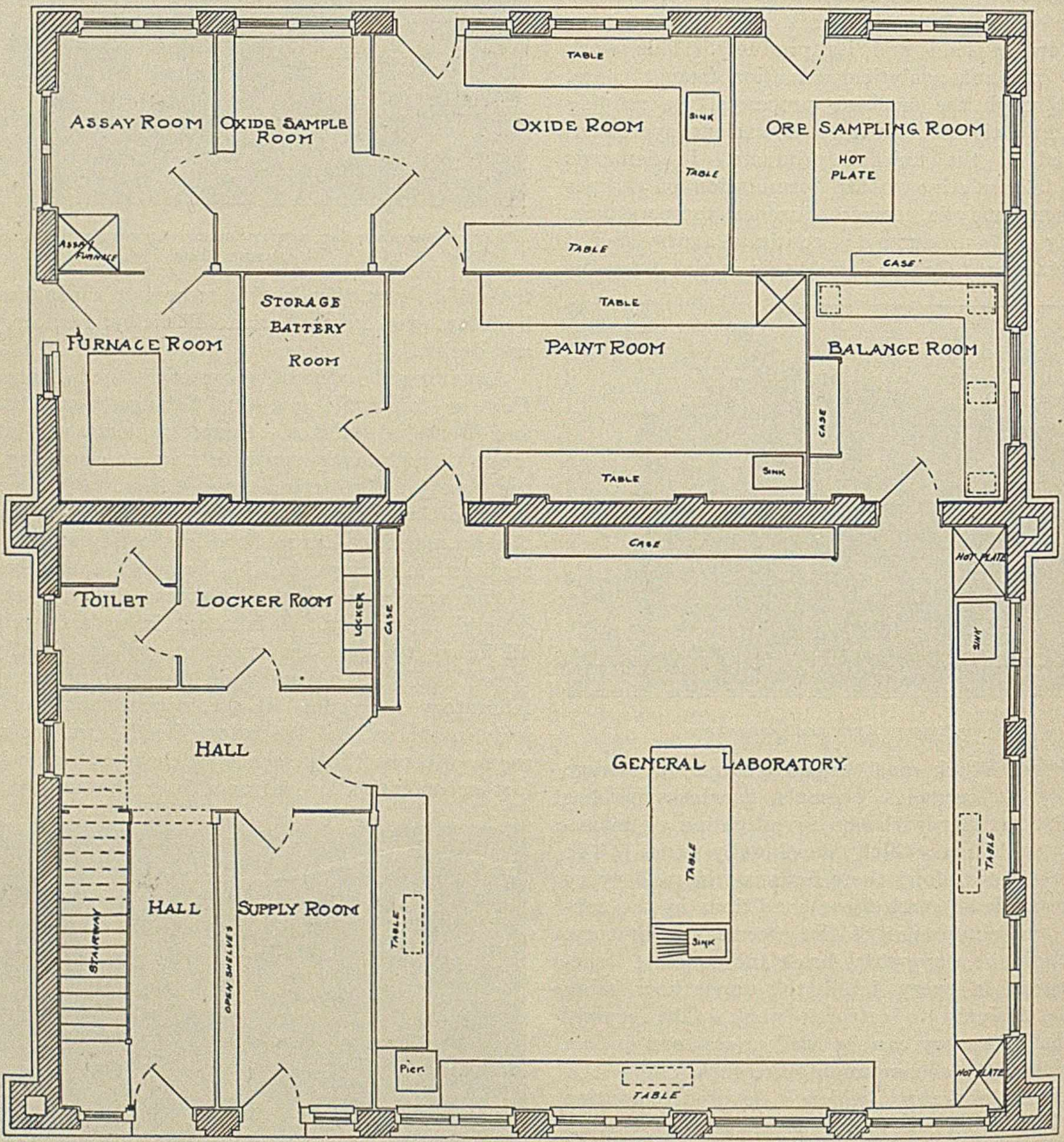
The paint room occupies the center of the ground floor. All work on the study of paints, varnishes, enamels and paint compounds is carried out here.

The room is equipped with a laboratory paint mill and mixers, electrically operated. All facilities for the striking of color batches, the grinding of experimental mixes of paints and the manufacture of varnishes have been made.

Ample opportunity for the study of storage batteries and their oxides has been given by the construction of a room devoted solely to this work. This has been so designed that constant temperatures within very narrow limits can be maintained throughout the entire year. This is of essential importance in the making of life tests on storage batteries. Here all storage battery pastes can be made, grids formed, batteries set up and life tests conducted under ideal conditions.

The ore sampling room, which plays a most important part not only in the purchasing of ores but also in the formulation of charges, occupies one corner of the rear of the building. As all ore is purchased upon an assay basis, both as regards moisture and metallic content, it is advantageous that this department be separate from the rest of the building. In consequence, the room is not in direct communication with the laboratory and care is exercised that nothing except ore samples reaches this portion of the building. The room is electrically equipped for the grinding and preparation of samples for analysis and contains a large hot plate so designed as to permit of constant temperatures being maintained for the drying of samples preparatory to grinding.

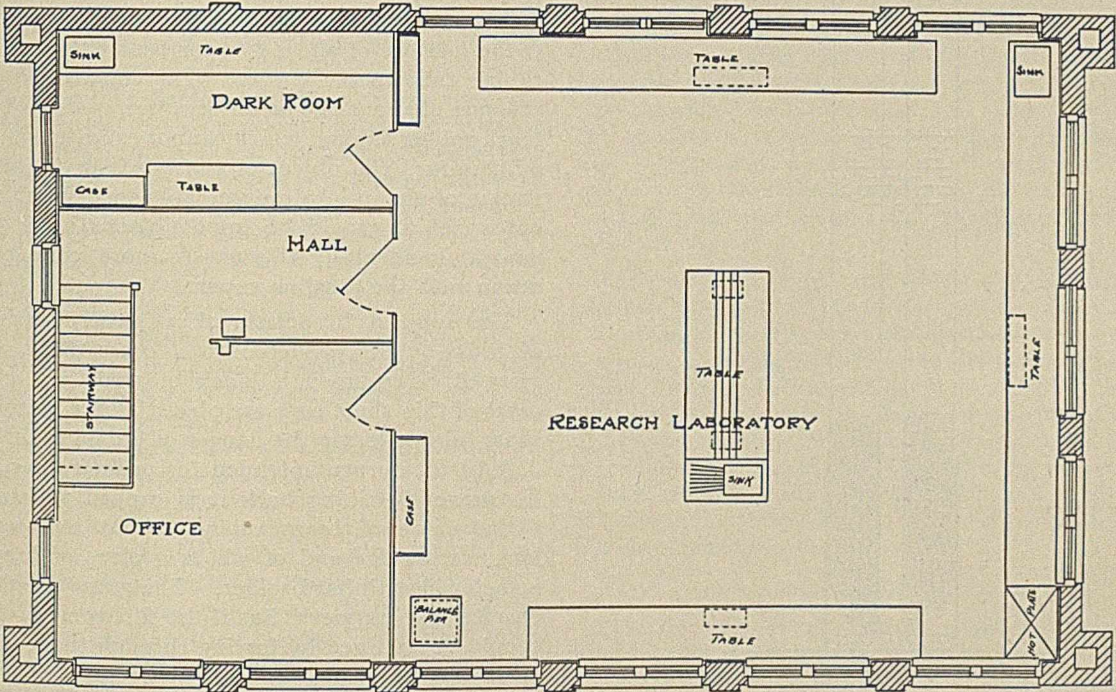
An oxide room is found in the central portion of the rear of the building. This department is a unique feature in the laboratory connected with a plant manufacturing lead products as here each barrel of oxide, either red lead or litharge, is analyzed and its history recorded for future reference. At the same time each sample is matched for color and strength, owing to



Ground Floor Plan

the many varying degrees of shade which are demanded by the trade in these products. Here are found electric stirring devices, balances, facilities for volumetric analysis and the matching of colors. Adjoining the oxide room is the sample room where samples of raw material, fuel and fluxes used in the formulation of charges, by-products and the finished products are carefully tabulated.

The assay room, equipped with muffle furnaces for the determination of gold and silver values in ores and finished products, completes the plan of the ground floor. It will be seen that every facility for general routine work in the examination of lead and its compounds has been given by the above plan.



SECOND FLOOR PLAN

On the second floor, devoted exclusively to research work, are found the research laboratory, the office, library and photomicrographic room.

The research laboratory is fully equipped for investigation work on glass, rubber, paints, varnishes, and the study of new processes together with manufacturing problems. Standard equipment of modern types is available for the investigation of any new practice on a scale which will permit of the establishment of data capable of being used directly on a commercial basis. Ample facilities are provided for the study of oils by the use of the viscosimeter and refractometer, together with the examination of the many different compounds through the spectroscope. The most improved methods for the testing of white paints for color and strength have also been installed.

The photomicrographic and microscopic study of paint films and dry pigments, which has of late years become of such importance, is fully provided for in the dark room equipped with low and high power microscopes, photomicrographic apparatus and all essential requirements for the development of negatives.

The walls throughout all the building have been plastered and painted with white laboratory enamel unaffected by gases, giving a surface easily washed and of maximum light.

The lighting system has been specially designed by the General Electric Company, the tungsten method of lighting being adopted. The heating of the building is effected by the hot water system.

The erection and equipment of this laboratory, complete in every detail, is only another instance of the stress which is laid upon research work and routine work, leading to the accurate control of manufacturing processes by the present-day manufacturer.

JOPLIN, MO.

A SIMPLE GASOLINE GAS GENERATOR FOR SULFUR DETERMINATIONS[1]

By C. E. WATERS

Received August 7, 1913

One of the recognized sources of error in the determination of sulfur as barium sulfate is the taking up of sulfur dioxide and trioxide from the products of combustion of the gas flame. The writer has repeatedly noticed drops of fairly strong sulfuric acid on the underside of platinum dishes in which solutions have been heated for a few hours by a gas flame an inch or so in height. On one occasion a watch glass filled with water was placed over the mouth of a 2-liter flask containing water. After heating over a gas flame for a comparatively short time, the water in the watch-glass gave a turbidity with barium chloride. It has also been found that the dark deposit, commonly regarded as soot, which is found on the bottom of a flask heated on iron gauze, contains a sulfide which

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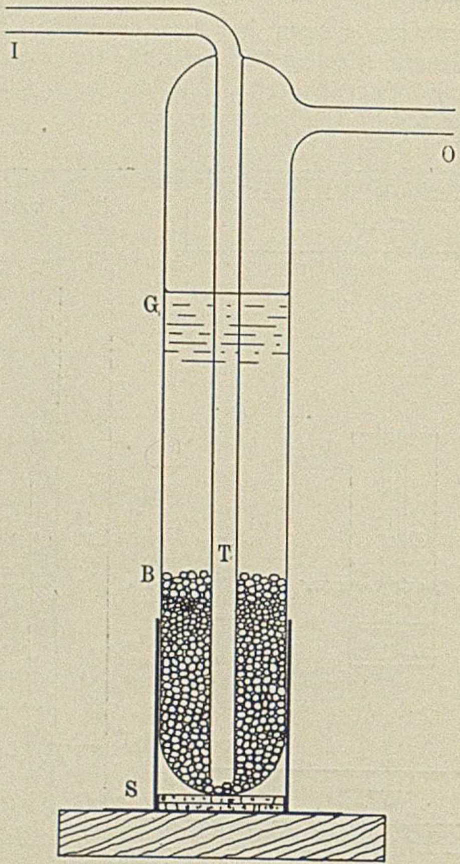
[1] Published by permission of the Director of the Bureau of Standards.

at once dissolves in dilute hydrochloric acid with evolution of hydrogen sulfide.

The amount of sulfur that would be absorbed by a solution in a covered beaker during the precipitation of barium sulfate cannot be very large and may be negligible, but this possible source of error should be eliminated in careful work. Ordinarily solutions to which barium chloride is to be added can be heated most rapidly and conveniently on the steam bath, and only a few minutes' heating over the flame is necessary to bring them to the boiling point. If, however, a fusion is required to transform the sulfur into a soluble sulfate, and especially if the melt must be stirred, the danger of contamination becomes serious. Placing the crucible in a hole in an inclined plate of asbestos board may prevent access of gases from the flame, but there is always danger that particles of gypsum from the board may get into the melt.



An ordinary alcohol lamp gives a flame which is too easily disturbed by drafts and which is not easily regulated. Barthel and other lamps depending on the Bunsen principle are also not satisfactory when a small flame is needed at the early stages of the fusion. To avoid these difficulties in determining sulfur in rubber, the writer some three or four years ago devised a simple and safe generator for gasoline gas, which is shown in the accompanying sketch.

The large glass tube, 4.5 to 5.0 cm. in diameter, and 25 cm. high, has fused into it the tube I for the admission of compressed air, which is carried down nearly to the bottom through T. It then bubbles up through the layer of beads B, and passes out at O, surcharged with the vapors of petroleum ether or of gasoline, with which the large tube is filled up to the level G. From O the mixture of air and vapor passes through a black rubber tube to the burner. The compressed air, at a pressure of about one meter of water, is also led through black rubber tubing, which cannot cause contamination with sulfur. The object of the beads is to break the stream of air up into innumerable small bubbles, without which it would be impossible to have a steady flame. Incidentally this causes more complete saturation with the gasoline vapor.

The support S consists of a loosely fitting piece of brass tubing, soldered to a brass plate, which is screwed down upon a block of wood. A couple of disks of thin sheet cork are placed at the bottom of the brass tube to lessen the danger of breaking the glass.

A Tirrill burner, intended for ordinary gas, is used. To prevent striking back it is capped with a loosely fitting piece of brass tubing, about one centimeter long, across one end of which a piece of brass gauze is fastened with hard solder. The gauze should not be coarser than 14-mesh, but if too fine some of the holes should be enlarged by forcing through them the sharpened tang of a file. A less satisfactory cap may be made by folding a piece of gauze over the end of the burner.

The compressed air is turned on full and the burner is so regulated as to give a non-luminous flame of the proper size. If the petroleum ether is too volatile, it may be mixed with gasoline. If the latter alone is used, the mixture soon becomes too poor and it is necessary to set the tube in a large beaker filled with moderately warm water. One filling of the tube furnishes gas for several hours.

After three or four years of almost constant use in this laboratory, the generator has proved entirely satisfactory and no accidents have occurred. The only precaution that may be mentioned, and even this is hardly necessary, is to extinguish the flame before turning off the supply of compressed air.

Bureau of Standards
Washington

ADDRESSES

THE PATENT EXPERT AND THE CHEMICAL MANUFACTURER[1]

By Bernhard C. Hesse

By "Patent Expert" I do not mean that professional man who is called in by a litigant only at the critical or crucial stage of a controversy long under way and most usually then in its final stages. On the contrary, I mean that professional man who is not only a highly trained and well equipped chemist, but who has also a natural or an acquired bent of mind which enables him to collect and assimilate the chemical and other facts relevant to the matter in issue, arrange them in logical

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[1] Paper presented at the 48th Annual Meeting of the American Chemical Society, Rochester, September 8–12, 1913.

order, survey them critically and prepare them for submission to legal analysis and examination by patent counsel and who makes that particular occupation his vocation in life.

There can be no question that actual patent litigation between inventors or their principals is an unhealthy and an abnormal condition and is thoroughly disadvantageous to the commercial and industrial development of chemical inventions. The energy and ingenuity consumed in litigation could be applied much more profitably to the development of the enterprise itself than to a controversy over where the rights of the one begin and the rights of the other end.

It is perfectly safe to say that the great majority of inventors and their principals are anxious and willing to respect the rights of competitors. They are, however, hampered in the practical expression of this willingness by ambiguity, uncertainty and error in the statement of supposed rights as expressed in patents. It is to the elimination of these defects that the patent expert must chiefly address his efforts and thus ultimately justify and vindicate his activities and his position in this work-a-day world.

There can be no question that the most economical and profitable employment of a patent expert is at and during the development of a chemical invention itself—not after the patent has been issued and is in litigation. His chief and most useful function is to reduce the likelihood and cost of litigation to a minimum; this he can do only by a careful and patient examination and arrangement of all the relevant facts and by their proper submission to lawyers for final judgment, *before* the application is filed in the Patent Office.

This is merely a specific application of the old adage "An ounce of prevention is worth a pound of cure." While this may seem to many an obvious and self-evident course of procedure, yet only a minority of the chemical manufacturers and inventors in this country have regarded that course as being, in the long run, the advantageous and proper one for them to follow.

Any one who has actively participated in strenuous patent litigation and has had his share of responsibilities to sustain knows the feverish excitement and dissatisfying conditions due to hard work under extreme pressure, the extraordinary and unusual demands made upon the working staff of the litigants from the highest official down and the consequent unavoidable interference with the regular occupation and operation of staff and works in many, if not all, their divisions. He is also thoroughly convinced that any and all steps taken at the inception of the cause of trouble, namely, the invention and the patents based thereon to prevent such congestion and such high-pressure work must be, in the great majority of cases, far more profitable, economical and efficient than any attempt at correction or avoidance after the trouble has begun.

It would be idle to expect or to hope that all controversies as to the beginning and ending of rights could be eliminated by such careful preparation of a patent. That the points in issue would be reduced to a minimum is certain and it is equally certain that the meritorious issues in a case would not be smothered in a mass of minor, technical or irrelevant disputes, all, or at least the great majority of them, avoidable by care, caution and patience in the draft of the specification. The smaller the number of such minor points in a patent suit, the shorter the suit and the less expensive to the litigants while the Court and all others concerned are given an opportunity to concentrate attention and effort upon the points that really are meritorious and which alone should count.

It is safe to say that in the average chemical patent suit anywhere from 25 per cent to 50 per cent of the total litigation cost could have been avoided at the outset by proper, complete and non-ambiguous drafting of the specification and its claims and careful scrutiny thereof after allowance and prior to issue of the patent. A patent conservatively drawn, complete, clear and full in its disclosure as well as clear in its claims is far more efficient as a protector against infringement of the invention involved and more certain of favorable adjudication than one not so drawn.

Chemical cases have been litigated in which a misplaced decimal point caused 8 per cent, a superfluous adverb consumed 12 per cent, an incorrect and superfluous theory used up 20 per cent of the total cost of litigation and finally, had a certain disclosure been just a little bit more explicit the litigation would not have been started at all. In still other cases had the relevant art been searched with an open and critical mind prior to patenting there never would have been any litigation. Further, the number of patents that have been rendered ineffective because of improper statement of invention, insufficient or incomplete disclosure is very great and most of these defects would or should have been avoided in the issued patent had there been suitable technical supervision and criticism such as by a patent expert. It is certainly easier and far less harrowing to examine and criticize an application even if it be your own work than to have to sustain an issued and faultily drawn patent when you have no chance for correction or alteration but must stand or fall by the document, "as is."

The pitfalls are many; there is no really dependable chart; each case must be treated on its own footing. The more careful the search, the more cautious the judgment and the fuller the knowledge of the relevant facts, the greater the fulness of disclosure, the more circumspect the phraseology and the greater the clarity of expression, the greater are the chances of success in avoiding useless points of attack, in minimizing effort and expense during litigation and the greater the protective value of the so-resulting patent to a meritorious invention. No amount of bolstering or shoring up *will* or *should* permanently help a non-meritorious invention.

THE PATENT CHEMIST—WHAT HE IS

The man whose business it is to attend to these matters I have referred to as a patent expert. This appellation is in itself something of a handicap to him in his work. There is no real reason why his expertness, real or assumed, in his special field should ordinarily be emphasized any more than in every-day life a skilled chemist is burdened with the designation of "expert." This man's real business is to be part and parcel of creative organization and machinery, not a man apart. Why not call him "patent chemist?" We have leather chemists, paper chemists, sugar chemists and the like. The patent chemist is one who specializes in the chemistry of patents, and patents in chemistry. Calling him "patent chemist" makes him on the surface at least more nearly part and parcel of the working staff than does the designation "patent expert;" the former name invites familiarity and coöperation, and suggests utility and work all of which is only helpful to those concerned, whereas there is a certain amount of aloofness or apartness, a suggestion of extraordinary and formal occasion and surroundings, of so-called "ornament," unconsciously, but none the less surely, associated with any term involving the word "expert."

THE PATENT CHEMIST—WHAT HE DOES

Now, this patent chemist, as I have called him, what does he do and how does he set about to accomplish it?

His usefulness begins with the inception of an invention and continues until the last bit of litigation is put out of the way, successfully or otherwise. He begins by getting a close understanding of the invention by careful, exhaustive and analytical study of the relevant prior art; he determines in his own way the presence of invention, defines the scope and nature of the invention, directs or requires confirmatory or exploratory work in determining and settling its scope; in other words, he formulates and "proves up" the statement of invention. Then he must see to a full and complete disclosure and finally a proper wording, classification and subdivision of the claims. His next move is to take his tentative handiwork to patent counsel to see how well or how poorly he has constructed his work; often working together they ascertain and locate weak spots and determine what shall be done to clear up, define and crystallize the situation.

THE PATENT CHEMIST, THE MANUFACTURER, THE INVENTOR AND THE LAWYER

So far, the patent chemist has acted largely as an avenue of communication between the inventor on the one hand who is a chemist and patent counsel on the other hand who is generally not a chemist. He must, in many cases, exercise great patience and ingenuity in getting the chemists' story into shape to lend itself to legal treatment, and on the other hand he must reduce the lawyer's story to such terms that the chemist understands and appreciates the situation.

More frequently than not, the patent chemist must hold the balance true as against the "fond-parent" enthusiasm, the disdain for real proofs and the airy generalizing tendencies of the inventor, the aggressiveness of the principal and the pessimism or cynicism of patent counsel, keeping his judgment calm, his reasoning sound and his facts straight throughout all this, not infrequently, very turbulent and trying period of patent-development.

The amount of labor, effort, study, investigation, reexamination, collecting of new facts or proofs and restating of positions and view points required of a patent chemist to reconcile these three elements is at times very great and difficult and always very trying, absorbing and engrossing.

To establish the usage of a certain expression in chemical publications may seem, at first blush, to be a perfectly simple matter but before the attempt to establish any particular usage has gone very far one is overwhelmed, more often than not, with a multiplicity of usages and choice becomes difficult if not impossible.

The question of what a publication, say, 40 years old meant in whole or in part to the man then writing it, to a man reading it 30 or 40 years later with all the intervening information at his disposal, is one whose correct answering may or may not interest the inventor or the principal, but patent counsel must know and the patent chemist must not only get that answer, but he must prove every part of it. The questions of analogy, homology and the like and their influence upon predication of invention are questions not always easy to answer, but whose answers patent counsel needs and the patent chemist again must supply and prove in their every part.

Practically all of the great variety of puzzling technical questions which conscientious, capable and competent patent counsel will propound in the course of developing a patent for a chemical invention resolve themselves into one or the other of the three above given and the road to the answer is not unusually long, hard and rocky.

Then comes the question of the accuracy, completeness, fullness, conciseness and clearness of one's own disclosure, the arguing back and forth over this expression and that expression, this or that sequence of ideas and so forth; the same is repeated on the statement of invention and finally it all has to be gone over again when the claims are taken up.

This kind of work is no occupation for a real chemist nor an inventor nor a principal. It is too slow for any of them; their entire mental attitude and habit of thought would have to be changed from an enthusiastic, creative state of mind based upon an abundance of relevant information to a cold, impersonal, analytic mental attitude based upon information, much of it not wholly relevant, but seemingly wholly foreign to the case; from the joyous and impetuous contemplation of his own creation the inventor would have to drop down to a very chill criticism of his own work as if it were the work of a total stranger. That is for most inventors a practical impossibility, and it is only natural that it should be so.

Essentially the inventor in the usual course of his occupation must take chances—otherwise he would not be an inventor; essentially, those concerned in securing by patent what the inventor has achieved must take no chances and must be sure that no chances are being taken. It would certainly be extraordinary if both functions were to be successfully united in one and the same individual. Moreover, it as frequently as not takes more labor and effort to get a satisfactory specification together, than it takes to make and operate the invention. Very often, things on paper look very different from the real thing, but it is a most difficult operation to reduce those differences to comprehensible and concise written language. The average inventor would rather follow up the practical realization of his invention, or start something new and fresh than be obliged to go over and over the same old trail straining his eyes for something he does not care to see, and which does not hold nor grip his interest. His particular work is done; it is up to others now—the patent chemist and the patent counsel. They must dig into the relevant chemistry and the relevant court decisions, write and rewrite the specification and claims until, in their judgment, all foreseeable contingencies are provided for and taken care of.

THE PATENT CHEMIST AND THE PATENT OFFICE

At last, the specification is filed in the Patent Office and quite as often as not, the first Office Letter will show the patent chemist that he did not provide for all chemical contingencies and the patent lawyer that he did not provide for all law contingencies, or in the event they have done both they evidently did not succeed in saying so in a manner that *could not* and *would not* be misunderstood. Then the work must be taken up anew; explanatory letters must be written and many times these are not sufficient and personal interviews are needed to uncover the cause of the misunderstanding. Here again the patent chemist must take up the technical side of the case, which, as a rule, he can present conclusively far better than the patent lawyer just as the patent lawyer is far better able to present conclusively the law involved. Experience has shown, however, that law points are then far less frequently involved than are technical points.

If now the application, when in allowable shape, is put into interference it is the patent chemist who must in the last resort decide if the proposed interfering claims are, or are not such that his case can properly make; then the details of the interference proceeding and the preparation of the technical testimony direct and cross, for and against, should all pass the patent chemist's scrutiny. The quality and amount of work required of the patent chemist in such proceedings is dependent almost wholly upon the caution and alertness exercised by him during the development of the application.

When finally a patent is issued and negotiations for acquisition of rights thereunder are taken up it is the patent chemist who must expound the technical aspects of the subject to counsel for the other side and must again and again defend his work.

THE PATENT CHEMIST AND LITIGATION

However, the work of the patent chemist so far is a mere prologue to his work when a suit for infringement of patent is under way. Here is where he at times becomes actually the right hand of counsel and the real test of his ability and preparedness takes place. He must sift and test the evidence of infringement, he must scrutinize and forecast all possible and probable positions of his opponents, must have the entire mass of facts and data at his tongue's end; in fact, he must be a walking and living dictionary, guide book and cyclopaedia not only through the particular art and case involved, but into the most refined and subtle distinctions in any and every branch of chemistry which even remotely touches the subject involved. The patent chemist frequently has the fate of the entire case entrusted to his keeping and his success depends not only upon how carefully he has prepared his case, but also upon the celerity with which he can produce his proofs and his alertness in anticipating or forecasting the moves, near or remote, of his opponents and preparing for them betimes. He must be able to do his work quickly and surely not only in the quiet of his laboratory or study, but more often under the strain of proceedings actually in progress and in the presence of his opponents. Not a single phase of the entire case must escape his attention and scrutiny. In one litigated case there was a total of 408 different chemical statements for each of which all the relevant facts had to be collated from the literature and the relevant testimony on both sides tabulated for use as the case progressed; the subject matter was relatively simple. What would have happened had that subject matter been really complex is wholly a matter of conjecture and fearful to contemplate. Other and more complicated cases have entailed quite as much if not more diffuse and wide-spread labor. Certainly no inventor wants to be pestered with such, for him, dry-as-dust details.

If the crucial test of a patent be its ability to withstand onslaught in the courts then the crucial test of the utility of a patent chemist is his ability to handle the vast amount of chemical facts involved with alertness, celerity and accuracy on such occasions. This will be rendered more certain and of a higher degree of efficiency the greater the familiarity of the patent chemist with the subject-matter and generally this familiarity is the greater, the longer the patent chemist has been associated with the subject. The same is true of the patent lawyer. Upon this assumption it further follows that the only wise policy is to commit the drafting of the specification and its prosecution in the Patent Office from the very start to that patent chemist and to that patent lawyer to whom the defense of the patent in the courts is to be finally entrusted. Let these men select the ground on which a dispute, if any, is to be conducted while they have an opportunity of so doing; let them shape the course and form of the document over which a struggle is expected and the results will be far more satisfactory than if those who are finally called upon to defend have no choice in the matter but must take things as they find them.

It is true that only a very small fraction of the issued patents is ever brought to the supreme test, and it would be a very wasteful policy indeed to expend upon patents of obviously little intrinsic value the same amount of labor that would be called for by a very valuable patent or set of patents. But as to a patent or patents of value there can be no two opinions as to the best general course to pursue, let those who must ultimately do the defending select their own ground while they may.

Many suits for infringement of patents are started or are proposed to be started, many more than actually find their way to trial in the Courts. In the preparation of the technical matter (both offensive and defensive) in such cases the patent chemist must clear up and maintain clarity in the technical questions involved because in such informal proceedings success demands completeness, celerity and alertness to almost the same extent and degree that the more formal court proceedings do. Many a contemplated litigation has not been started because of precisely such proper preparation of material prior to and during negotiations looking to amicable adjustment.

It is not only natural but inevitable that the state of known facts changes and shifts and becomes fuller as the inventive idea and the patent pass through the different stages just outlined and therefore judgment and opinion must frequently be tested and re-examined; these constitute the real cause for keeping the patent chemist in very close touch, in the majority of cases, with the growth and development of the invention as well as with the business and all other similar conditions surrounding it.

THE PATENT CHEMIST AND THE CHEMICAL FACTORY

From this sketchy outline of the patent chemist, his field, his mode of operation and his relation to the manufacturer, it is no doubt clear that he is a man who must look at his chemistry not only with the eye and the mind of a chemist and of a manufacturer, but through the spectacles of a lawyer as well; he must look at patent law with the eyes of a chemist and the mental attitude of a lawyer and translate the law into chemical terms; he must know how to get convincing and correct answers to questions of great variety and scope, many of them seemingly trivial and simple, but at times of the utmost importance. He is neither a producer nor a creator of things; he is perhaps nothing more, in the final analysis, than a catalyst—a catalyst enabling two or more different agencies to operate in harmony and in complete understanding with each other and thus to increase the speed with which the object aimed at is achieved and with generally beneficial effect upon the quality of the final product. He may also be regarded as a foster-parent to the children of the brains of others and his function is to aid in their protection while in development. He is perhaps nothing more than an additional insurance against error in making plans for the future and his value grows with the value of those plans. He is not a lawyer, nor is he a real chemist, but he must be primarily and fundamentally a chemist with a chemist's instinct and a chemist's sympathies; he must have a working knowledge and an appreciation of all business conditions likely to influence the course of development of any and all of the inventions with which he is brought into contact; he is a mixture of chemist, manufacturer and lawyer and he must have an instinct and judgment for determining the correct time for, and the proper men to whom special questions must be submitted for final treatment. He must be especially alive to his own limitations and to those of others; he must not be unalterably wedded to his own opinions; he must be able, on occasion, to obliterate his own personality and to pocket his pride.

Now this brings me to the question of the status of the patent chemist in the organization or staff of a chemical factory. There can be no question that he must be in the confidence of the concern much more than the routine or works chemist; he must have greater freedom of action, greater radius of activity and his information should be first-hand wherever and whenever possible. He can make himself useful not only as above outlined, but also by keeping systematic track of what competitors at home and abroad are doing as foreshadowed in the technical press, patent applications and issued patents in all countries thus anticipating attempts to blanket or forestall his friends, but he may very often also be able to call to the attention of his principals new fields of endeavor and ways and means of entering them, which but for his watchfulness might escape notice. He should be made use of at every new manufacturing or operating step of his principals.

As to his position, should he be definitely inside or outside the organization, the answer is that it depends upon circumstances. In Europe, in some of the chemical branches, the patent chemists are fixed members of the organization, while in others the patent chemists are in business on their own account. Just how each or any organization shall handle that question involves the same questions as does the acquiring of any other commodity or service—by exclusive contract, by provisional contract or in the open market. Each concern must choose and decide for itself.

To put it in a very few words, the chief function of the patent chemist is to apply Davy Crockett's rule "Be sure you are right, then go ahead" to chemical inventions—a task not always interesting nor pleasant, but always useful and bubbling over with worth-while work.

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THE THEORY OF THE REMOVAL OF SUSPENDED MATTER FROM GASES

By W. W. Strong

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At the present time several processes are being used for removing suspended solid and liquid particles from gases, but no method has been indicated as to how the relative efficiencies of these methods can be compared. Indeed it is not well known what forces must be employed to secure the desired results. No accurate methods are in use whereby measurements can be made to indicate the amount of the suspended matter that has been removed from the gases. The purpose of the following paper is that of putting the whole subject upon a more exact and scientific basis.

"CLEARANCE" AND "PRECIPITATION"

In general, two methods are employed to express changes in the density of suspended matter in gases. If the suspended matter is of little value as is the case with coal smoke, copper fumes, etc., the density is usually measured by a photometric method. The Ringelmann scale is an example in point. The light employed is ordinary daylight. Probably the standard light for these purposes should be a light source possessing the same intensity curve as the sensibility curve of the average eye. The "clearance" of suspended matter by any process is the difference in the percentage of light transmitted by a unit volume of the smoke or fumes before and after the process was applied. Smoke of unit thickness absorbing 98 per cent of the white light of a parallel beam is subjected to washing. If it then absorbs 7 per cent of the light, the "clearance" would be 91.

Several difficulties are met in applying this method. The suspended matter may show a selective absorption of the light and thus color effects are introduced. The coefficient of absorption of light may not obey a law like that of Beers', *i. e.*, the absorption may not depend entirely upon the quantity of suspended matter in the beam of light but may also depend upon the density of the suspended matter. Each kind of suspended matter probably shows small variations of the above two types and these variations should be carefully considered.

The second standard method of measuring the amount of suspended matter in gases is that of filtering out the suspended matter from a known volume of the gas and weighing the filtered material. Unfortunately, there is no convenient and quick filtering apparatus of this kind available. (Probably the process of electrical precipitation is as practical as any and the writer is designing apparatus for this purpose.) This method is always used when the suspended matter is of value. The change in the amount of suspended matter per unit of volume due to any filtering or cleaning process will be called the "precipitation." Suppose the weight of zinc oxide per unit of volume of gas is 1.00. The dust is subjected to filtering by a bag and then contains a weight, 0.01 of zinc oxide per unit volume. The "precipitation" is then 99.

"DIFFERENTIAL" FORCES

In order to remove the particles of one substance from those of another with which they are intimately mixed, it is necessary to apply differential forces to the two sets of particles. In a gas the molecules are moving with very great velocities due to the heat motion of the gas. It is on account of this motion that gaseous substances diffuse among each other. Under ordinary experimental conditions, two gases will not separate from each other even though the masses of the molecules are quite different and the action of gravity is a differential one.

Nevertheless this separating effect of gravity does act even on the gases of the atmosphere. At great altitudes above the ground, hydrogen and the lighter gases preponderate. In the lower strata of the atmosphere the percentage of the heavier gases is much greater. The greater the difference in the masses of the two particles and the smaller their velocity of heat motion the more rapidly will gravity cause them to separate. It is partly by this means that smoke and dust is removed from the air.

The separation (which gravity produces) of gases possessing different molecular weights has been discussed by Jeans, Einstein, Perrin and others. Fine dust, fume and smoke particles can be treated like large molecules from many points of view. In the case of particles suspended in liquids, Stokes' law is found to hold for particles as small as the larger hydrocarbon molecules.

The separation may be produced in other ways. The "centrifugal," like the gravity process, causes a separation of suspended particles from gases for the reason that the two sets of particles possess different masses. In washing, the effort is made to cause the suspended particles to unite with the washing fluid. (1) In these cases the separation is due to differential "mass" forces. Sieves of wire mesh, cloth, etc., are used. These sieves catch the particles of suspended matter on account of their larger volume. The gases have to be forced through the sieves by suctional or pressure forces. The separation here may be considered as being due to the action of (2) differential "volume" forces.

It is well known that there is a region near a heated surface from which dust particles are driven. This action is somewhat similar to the pressure on radiometric planes (Crookes' radiometer) taking place at low pressures. The dust particles are subjected to a greater molecular bombardment in the direction of the heated surface and are therefore forced to move in the opposite direction. Light and heat cause a pressure somewhat similar in nature and this accounts for the repulsion of comets' tails by the sun. The "pressure" may be due to the heat motion of molecules, the radiation pressure of heat, light and electromagnetic waves or to streams of ions. This separation of particles from a medium will be considered as being due to (3) differential "radiation" forces.

The suspended particles may be subjected to the action of an electric or a magnetic field. If the particles are magnetic they will be set into motion. As few kinds of dust particles are magnetic and as this action is similar in kind to that of the electric field, it will be included under the latter action. The action of the electric field is of two kinds. The field may not be uniform. The particles may possess a different dielectric power from that of the medium and will therefore be caused to move by the non-uniformity of the electric field. In other words, the particles become polarized. Water drops can be separated from oil and gold may be separated from quartz in this manner. The separating force in this case will be called (4) the differential "force of polarization."

The suspended particles may be charged by causing them to unite with ions. If they are then subjected to the action of an electric field they are immediately set into motion with reference to the surrounding neutral particles. The method of electrical precipitation is based upon the use of streams of ions to charge the suspended particles and the above action of the electric field to remove the charged particles from the gas. The separating force here is (5) a differential "ionic" force.

THE COMPARATIVE EFFICIENCY OF THE DIFFERENTIAL FORCES

The law describing the way particles can be removed from a gas has been given by Stokes and has later been modified by Cunningham and others. The statement of the law will be given in the section on "settling due to gravity" because the verification of the law by various investigators has been made by the use of gravitational forces. Centrifugal and electrical forces will act in the same manner.

The basic law underlying the phenomena of the separation of suspended particles from fluids is of the Stokes' type, the constants of which will be a function of the density, shape, size and nature of the surface of the particles, and the pressure, viscosity, temperature, density and nature of the fluid. Assume that the particles are smoke particles, and that the fluid is a composition of air and carbon dioxide. The force that must be applied to separate a particle from the gas depends upon the Stokes law that holds for these conditions, the distance the particle must be moved and the time that is to be allowed for this movement to take place.

The efficiency of the process of removing particles from fluids can be defined in several ways. Let us assume that the efficiency of the given process is unity when the particle is caused to move with a velocity of a centimeter per second. The work done on the particle under these conditions will be represented by the force term given by a law similar to that of Stokes, since the distance over which the force has caused motion is in this case unity. If the time were made very long the applied force could be made very small. If it is required that the velocity should be greater than that given by the definition, a greater velocity may be used and the comparison of the efficiency of different precipitating agents based on this velocity.

The efficiency of any process used for removing particles from fluids will be the ratio of the energy required to cause the separation of the particles determined by a law such as that of Stokes and the amount of energy used by the given process.

Let us take a concrete example. A certain kind of smoke contains 1,000,000 particles per cu. cm., the smallest particles having a diameter of 0.0001 mm. Let us assume that the particles are all of the same size, the size of the smallest particles. Let us also assume that the separation of the particles from the gas can be made complete if the velocity of the particles is made a centimeter per second relative to the gas itself. Let it be necessary to move the particles 2 cm.; let the force required by Stokes' law to give a velocity of 1 cm. per second be F; let X cu. cm. of the smoke be treated per sec. The amount of work done per second is: 1,000,000 X 2 F = S per sec.

If the smoke is passed through a centrifuge, the differential force acting upon the smoke particles will be the centrifugal force and this should be equal to F. The energy used per second (C) to run a centrifuge that cleans X cu. ft. of smoke per second will be very largely lost in friction and windage. The efficiency of this process will be S/C.

In the method of electrical precipitation a certain wattage loss of energy (W) will represent the electrical discharges in the smoke. Some of this energy will be spent in effecting chemical reactions and in heating the gases. The efficiency of this method is S/W. A method of treatment like the above will indicate the ultimate theoretical possibilities of these various methods.

From an engineering point of view the problem is much more complicated. If large chambers are available and the volume of smoke or fumes is comparatively small, settling by gravity will probably be the best method available. If the smoke gases are cool and a large draft is available, filtering could be made quite efficient, especially if the smoke particles are large in size. Centrifugal methods can readily be used if the suspended particles are of large size. The short treatment following is theoretical. One reason for this method of treatment lies in the fact that our engineering knowledge along these lines is very incomplete and unreliable. In many cases no definite information is given of the character of the smoke or fumes to be treated.

THE DIFFERENTIAL "MASS" FORCE

One of the most important of the problems in mechanics is that related to friction or viscosity. We all know that a feather and stone fall with the same velocity in a vacuum. Why do they not do so in air? The answer is—a feather meets with resistance or friction in its course through the air. The frictional resistance due to the settling of smoke and dust particles in the atmosphere is therefore the same as the resistance which an aeroplane meets in flying: the resistance which causes shooting stars to burn and heats meteors and which causes mists and fogs to remain suspended. It is for this reason that small raindrops fall very slowly, while large drops, such as are formed during thunderstorms, fall very rapidly.

In the case of falling raindrops there is in general an equilibrium between the forces of friction and the pull downwards by gravity. The more slowly a particle falls the less resistance does it experience. A raindrop will therefore continue to be accelerated until the frictional forces which it experiences just balances the attraction of gravity.

In the upper strata of the atmosphere where the air density is very small, dust particles would fall very rapidly. In the outer portions of the solar corona dust particles would probably gravitate rapidly towards the sun, due to two causes, the great attraction exerted by the sun and the rarity of the atmosphere. In certain cases, however, the high temperature and the pressure of radiation will act so as to cause certain particles (whose size and density lie between certain ranges) to remain suspended. This pressure on the particles is exerted by the light and heat radiations striking the dust or smoke particles. If the beams of radiation are more intense in one direction (this is often the condition in certain parts of a furnace) the dust particles will be acted upon by a force in the same direction as that of the radiation. The effect of high temperature is to increase the viscosity forces.

In a very interesting paper (*Math. and Phys. Papers, Cambridge*, 3, 55), G. Stokes has discussed the effect of viscosity on the movement of a pendulum. Incidentally he took up the motion of a sphere (radius a) moving with a velocity, V, in a medium having a viscosity of $\mu\delta$. If X is the resistance to the motion of the sphere and Δ is its density and δ that of the medium, then $X = 6\pi\mu a V\delta$.

For a sphere falling under the action of gravity

$$6\pi a y V = 4/3 a^3(\Delta - \delta)g.$$

The fall of raindrops that have reached a maximum and final velocity, the settling of fumes, dust and smoke in gases, even though the particles are not perfectly spherical, follow a law such as that of Stokes. These conditions require the fluid or gas through which the particle falls to be in a state of rest.

Perrin has shown that the law of Stokes applies to particles of ultramicroscopic size even though the particles undergo the Brownian movement.

Rybczynski and later Hadamard have (*C. R.*, May, 1911) developed a slightly different formula for a sphere of density Δ_1 and viscosity y falling in a medium of density Δ and viscosity y_1.

$$(\Delta_1 - \Delta)g = 2/9\ yV/a^2y_1 + {}^2/_3 y/y^1 + y.$$

Applying this formula to water drops [$y = 1057(10)^{-5}$] falling in air [$y_1 = 18(10)^{-5}$] one finds that the velocity given by the law of Stokes should be multiplied by the factor 1.006.

In order to apply the above formulae to the settling of fumes or smoke in chambers it is necessary to know the size and density of the particles to be considered, the viscosity of the medium and the distance it is necessary for the particles to fall.

In general, gravity is not great enough to cause particles to move with sufficient velocity, especially if the particles are very small. Under these conditions particles may be caused to unite with liquid sprays or become nuclei for the condensation of vapor. This causes an increase in mass. Sound, electromagnetic radiations and an electric field may also be employed to cause an aggregation of the particles. Large differential "mass" forces may be obtained by centrifugal processes.

If a particle of mass m is caused to rotate about an axis with an angular velocity w, the distance of the particle from the axis being r, then the force that must be exerted upon the particle to keep it moving in a circular path of radius r is mrw^2.

In a centrifuge the gaseous medium should possess an angular velocity of w. The two forces that will operate on the particle when its distance r from the axis increases will be that of fricional viscosity and the centrifugal force.

The centrifuge process is frequently used when the particles to be separated from a gas possess considerable mass. Under these conditions w need not be so great. It is very doubtful if a process of this kind would be practical in the case of small smoke particles. A combination of a washing (or an electrical discharge) and a centrifugal method might be found to be better than any single method used by itself.

The efficiency of the "volume" forces depends upon the pressure required to force the gas through the sieves. The nature of the differential "radiations" have been worked out mathematically but these have no value as a practical method of removing suspended matter from gases. Neither is polarization a practical method. Probably one of the most important from the efficiency point of view is the differential ionic force.

THE DIFFERENTIAL "IONIC" FORCE

The use of electromagnetic fields for removing suspended matter from gases and liquids is practically limited to the action of the electric field. This condition is due to the fact that very few suspended particles possess any appreciable magnetism. Even nickel dust would be removed with difficulty by the action of a magnetic field. This leaves only iron and a few magnetic compounds of iron that can be acted upon by a magnetic field.

In general it may be said that the application of electric fields is restricted to a non-conducting medium, such as a gas or a dielectric liquid. There are no gases that conduct naturally. The ions or carriers in a gas must be produced artificially. Conducting liquids are electrolytes and these contain spontaneously generated ions. These liquids support only a small difference of potential and conduct by electrolysis. When electrolysis takes place gas usually accumulates at the electrodes, thus causing an added resistance to the flow of current.

The separation of suspended solid and liquid particles from a non-conducting gas or liquid is therefore dependent upon the action of electric fields possessing an intensity ranging between several hundred to several thousands of volts per centimeter. This action of an electric field is not as simple, however, as it might appear to be. The suspended particles may be caused to combine with each other (aggregation); they may be in a state of polarization and they may become charged.

In the case of suspended matter in gases the important item is that of charging the particles. The efficiency of the process depends upon the thoroughness of this charging process.

Like the other processes used for cleaning gases, the electrical process causes an expenditure of energy that is proportional to the volume of gas rather than proportional to the amount of matter suspended in the gas. No one has devised any cleaning process of the latter type although certain automatic devices promise to make the electrical process active only when there is a certain density of the suspended matter.

The writer[1] has determined the energy loss in the electrical precipitation method to be about 400 watts for treating gas at the rate of 1000 cubic feet per minute. This energy loss does not vary greatly between 0° and 200° C.; does not vary with the velocity of the gas, with the density of the suspended matter or with the composition of the gas. In order to compare this efficiency with the "perfect" efficiency given by Stokes' law it would be necessary to determine the number of particles and the average amount of energy required to remove each particle from the gas by using Stokes' formula.

A very rough calculation of the efficiency of the electrical method may be made by assuming Broghé's data for cigarette smoke. The radii of these smoke particles range between 0.1 to 0.001μ and in each cubic centimeter there are several million particles. Assume that the particles are to be given a velocity of 20 centimeters per second and that the average radius is 0.00001 centimeter:

$$F = 6\pi(0.00001)\ (\mu = 0.000178)\ (V = 20)$$

Let the particles be moved a distance of 8 centimeters and suppose there are 30,000,000 particles per cubic centimeter. Since 1000 cubic feet contain $2.8317(10)^7$ cubic centimeters, the required work in watts will be:

$$W = 8F \times 30{,}000{,}000 \times 2.8(10)^7 = \text{about 40 watts}$$

This would indicate that possibly 15 per cent of the electrical energy may be expended in cleaning the gas, this energy being converted again into heat energy through the agency of the viscosity forces.

In the above calculation it must be recognized that the data are extremely meager. It is to be hoped that theoretical investigators will take up a detailed study of these problems.

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[1] *Trans. A. I. E. E.*, June, 1913.

THE UTILIZATION OF SEWAGE[1]

By GEORGE A. SOPER[2]

It is often supposed that the discharge of sewage into rivers and harbors represents a great economic waste and many persons, among them some eminent scientists, have, in times past, proposed that cities should conserve the manurial value of their sewage. Victor Hugo was an ardent advocate of this form of conservation and Liebig, Hoffman and Crookes have raised their voices in solemn warning against the waste. Such warnings are well remembered and the question is frequently asked—Why should the sewage of our cities be discharged without any attempt being made to utilize it and return the useful ingredients to the soil?

To answer that it costs more to utilize the manurial ingredients than they are worth does not answer the question with sufficient fullness.

The principal reason why it is impracticable to utilize the manurial ingredients of sewage lies in the extremely diluted state in which the useful ingredients exist. There are few processes known to the technical arts by which such immense volumes of liquid can be successfully treated for the extraction of their valuable materials. Sewage is over fifteen times as dilute as sea water and the ammonia, phosphoric acid and nitrate in sewage are, like the gold in sea water, there unquestionably, but mingled with so much that is useless that they cannot be extracted without too great expense.

Sewage may be considered to consist of two parts of solid matter in 1,000 parts of water; and of this solid matter only a portion has any value in agriculture. Contrary to popular opinion, sewage contains relatively little excrement either liquid or solid, the explanation of this fact lying in the large amount of water used in flushing the closets and for the many objects not connected with the disposal of excrement for which the water is used. The per capita consumption of drinking water in a modern American city ranges from about 75 to over 200 gallons per 24 hours.

The City of New York and the other municipalities in the metropolitan district contained, in the year 1910, 6,019,000 inhabitants and produced over 765,000,000 gallons of sewage per 24 hours. This sewage contained over 658 tons of suspended matters, of which about one-half was nitrogenous. It has been estimated that the excrements of a mixed municipal population should be worth, on theoretical grounds, from $1.00 to $1.25 per capita per annum, from which it appears that the metropolitan district is throwing away between $6,000,000 and $7,500,000 every year.

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[1] Paper presented at the 48th meeting of the American Chemical Society, Rochester, September 8–12, 1913.

[2] President, Metropolitan Sewerage Commission of New York.

To utilize this sewage, it would be economical to build works whose running expenses, interest charges and allowance for depreciation and repairs would not exceed, say, $6,000,000. There would be clear gain in transforming the present polluted harbor into a clean and wholesome natural body of water, although this gain would not be measurable in terms of currency. Allowing 10 per cent to cover all charges, it should be good business to borrow $60,000,000, if, by so doing, works could be constructed and operated so that the value of the sewage would be completely utilized.

Sixty million dollars would not be nearly enough. In addition to the treatment works themselves, large sewers would have to be built to take the sewage to the works and carry the purified effluent away. Pumps would be necessary in order to move the sewage through the conduits. Land would have to be purchased upon which to build the plant. A large corps of employees would be required for the management and conduct of the process and for the sale of the product. Over all there would have to be a strict, sanitary supervision wielding the autocratic power which rightly belongs to public health officials in matters where life and comfort are balanced on one side against shrewd commercial enterprise on the other. And it may not be amiss to state here that desire of profit in the disposal of sewage has repeatedly been found in the past to be strongly opposed to the interests of sanitation.

It may be well to consider for a moment what has been accomplished toward the utilization of sewage. Briefly, such works are of two classes: *First*, those which provide for the direct application of untreated sewage to land; *Second*, those which provide for the extraction of the utilizable ingredients by means of suitable mechanical devices.

The application of the sewage to the soil was for many years persistently attempted in England and there are now in that country and in other lands sewage farms which afford excellent opportunities to study what it is practicable to do in this direction. The testimony of agriculturalists and economists is all of one sort. Sewage farming does not afford a satisfactory method of utilizing the useful ingredients of sewage, except under unusual circumstances, as, for example, where the contained water is needed for the crops.

With respect to the extraction of the useful ingredients nothing favorable can be said. There are no works in the world which deal with sewage of average quality from which all or nearly all the theoretically useful ingredients are extracted without costing more money than they are worth. Efforts have been made in abundance to devise plans by which commercial fertilizers could be produced; scores of patents have been taken out and many companies formed to make a business of extracting the useful materials, but these ventures have proved disastrous.

The search for a profitable method of extracting the useful ingredients of sewage is rendered especially difficult by reason of the physical and chemical condition of the sewage. Coarse materials, if floating, can readily be removed by screens and, if heavy, they will promptly subside in settling basins. But a large part of the materials characteristic of sewage is in the colloid state and can neither be screened nor settled, except with much difficulty. The best settling that has been done produces sludge which contains over 95 per cent of water and persistently resists attempts at further concentration.

The sludge problem is recognized to be of central difficulty in sewage disposal, for the sludge cannot be applied to land with profit nor can its utilizable ingredients be extracted without more cost than they are worth. The sludge therefore causes embarrassment scarcely second to that produced by the sewage from which it is obtained. Apparently, there are but few things that can be done with sludge even if the sole object is to get rid of it without nuisance. It can be fermented with the production of large volumes of methane and other gases of small value and a humus-like residue from which the liquid readily drains off.

This sludge, when drained and dried, can be burnt. Sludge can be dug into the ground and, if not applied in too large quantity, in course of time it will disappear. The most usual method of dealing with sewage sludge is to transport it by pumping, cartage or tank steamer to some remote point where it can be dumped, simply with the object of getting rid of it.

The outlook for the future need not be discouraging because of the failures of the past. There may yet be found some method for the production of dense sludge and the extraction of its utilizable ingredients. If the physical state of the colloid particles could be altered so that they would part with the large amount of water which they contain, these particles should settle rapidly and dense sludge be produced. If the sludge could be further concentrated either by centrifugal action or otherwise, considerable advantages would be gained.

An inviting field lies open for the inventor of a successful process for the utilization of sewage, for there are hundreds of cities, and among them the largest in the world, which will give the raw material without imposing any other obligation than that reasonable sanitary requirements shall be observed. The City of London has for years advertised that its sewage was ready for anyone who wanted it, but the nearest approach to an acceptance of this offer was from a company which, after many promising arrangements, went out of business without taking a gallon of sewage away.

A process for the utilization of sewage may be of value even if it does not recover sufficient of the useful ingredients to completely meet the cost of obtaining them. If the cost of treating the sewage can be reduced by half or even less, the economic return may be sufficient to warrant a wide employment of the scheme, it being remembered that the prime object in installing sewage disposal plants is to get rid of the sewage without offense.

The recent contributions of science to the art of sewage disposal have been directed almost exclusively to the disposal of the wastes in such a way as to be permanent and sanitary and as inexpensive as possible. In nearly all works constructed within the last few years, the point of view has been that sewage was a thing to be gotten rid of and in getting rid of it there was no prospect of any useful return.

17 Battery Place, New York

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

THE STATUS OF THE CEMENT INDUSTRY

The total production of the cement mills in the United States in June, 1913, was 2 per cent less than in June, 1912, and on July 1, of this year, less than 60 per cent of the cement kilns in the country were in operation; this was attributed to the prevailing hesitancy in the undertaking of constructive enterprises on a large scale. However, owing to the accumulation of orders received at an earlier period, the June shipments continued large, approximating 8,000,000 barrels—about 1,000,000 barrels in excess of the actual output. The surplus stocks at the mills on July 1 totaled 10,000,000 barrels, an increase of 6 per cent over last year.

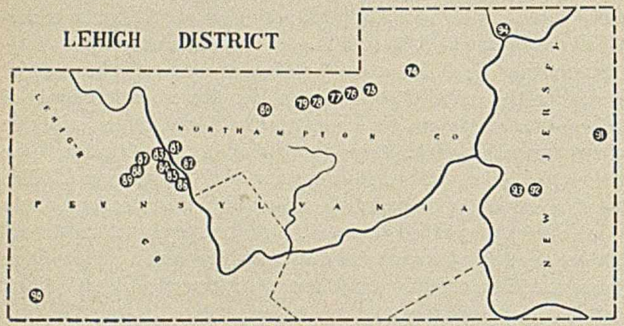
According to *The Journal of Commerce*, the significance of the cut in production may be better realized from the fact that for

LEHIGH DISTRICT CEMENT PLANTS

No.	Name	Location	Railroad	Capacity in bbls. per day
74	Northampton Portland Cement Co.	Stockerton, Pa.	Lehigh & New England	1,800
75	Nazareth Cement Co.	Nazareth, Pa.	Lehigh & New England	3,300
76	Phoenix Cement Co.	Nazareth, Pa.	Lehigh & New England	1,000
77	Dexter Portland Cement Co.	Nazareth, Pa.	Lehigh & New England	2,400
78	Penn-Allen Portland Cement Co.	Nazareth, Pa.	Lehigh & New England	2,000
79	Pennsylvania Cement Co.	Bath, Pa.	Lehigh & New England	3,000
80	Bath Portland Cement Co.	Bath, Pa.	Lehigh & New England	3,000
81	Lawrence Cement Co. of Pennsylvania	Siegfried, Pa	Central of New Jersey	3,500
82	Atlas Portland Cement Co.	Northampton, Pa.	Central of New Jersey	46,600
83	Whitehall Portland Cement Co.	Cementon, Pa.	Lehigh Valley	1,250,000
84	Atlas Portland Cement Co.	Coplay, Pa.	Lehigh Valley	46,600
85	Lehigh Portland Cement Co.	West Coplay, Pa.	Lehigh Valley	36,600
86	Coplay Cement Manufacturing Co.	Coplay, Pa.	Lehigh Valley	5,000
87	American Cement Co. of New Jersey	Egypt, Pa.	Lehigh Valley	6,500
88	American Cement Co. of New Jersey	Lesley, Pa.	Lehigh Valley	6,500
89	Lehigh Portland Cement Co.	Ormrod, Pa.	Lehigh Valley	36,600
90	Lehigh Portland Cement Co.	Fogelsville, Pa.	Phila. & Reading	36,600
91	Edison Portland Cement Co.	New Village, N. J.	D., L. & W.	8,000
92	Vulcanite Portland Cement Co.	Vulcanite, N. J.	Central of New Jersey	5,500
93	Alpha Portland Cement Co.	Alpha, N. J.	Lehigh Valley	18,000
94	Alpha Portland Cement Co.	Martin's Creek, Pa.	Pennsylvania	18,000

the first six months of the year the production of 39,000,000 barrels was nearly 25 per cent ahead of last year, while shipments were 14 per cent larger than for the first half of 1912. Surplus stocks increased nearly 3,000,000 barrels in the half year.

The Lehigh district, a map of which is presented herewith, seems to be following the trend of orders more closely than a few years ago, when market conditions were quite chaotic; this district supplies about one-third of the American cement production. The Lehigh production fell 10 per cent in June, while shipments increased 3 per cent as compared with those of June, 1912. Seventy-five per cent of the Lehigh kilns were active on July 1, 1913, but the surplus stocks at the mills on that date, amounting to 3,000,000 barrels, were only 4 per cent larger than last year. Producers in the Lehigh district have taken steps to prevent market demoralization by reducing their output; as a result of this policy, prices are being fairly well maintained.



THE BECKTON GAS LIGHT AND COKE COMPANY OF LONDON, ENGLAND

The Beckton Gas Light and Coke Company, which supplies gas for two-thirds of the British metropolis, is described in the *American Gas Light Journal*, **99**, 34.

At the river pier some 1,750,000 tons of coal are unloaded per annum, the hydraulically operated grabs being capable of handling 700 tons per day. The retort houses are 14 in number, and extend about half a mile, in double line. Some are electrically operated, others have the aid of compressed air, and a third variety is provided with hydraulic machinery. Jointly the retorts are capable of producing 61,000,000 cubic feet of gas per day, and of carbonizing 5,000 tons of coal. In addition, there is a carbureted water-gas plant capable of producing 27,000,000 cubic feet of gas per day. The plant is stated to be the most complete in existence, all the operations of gas-making and recuperation being controlled by hydraulic power operated by levers from a central stand. The blowing plant for this installation consists of four 110-horse power turbine-driven fans. The carbureted water gas, after being tested, is mixed with the coal gas at the inlet of the gasholders, of which the storage capacity totals 19,000,000 cubic feet, the largest gasholders holding 8,000,000 cubic feet.

A pumping plant capable of pumping 4,100,000 cubic feet of gas per hour delivers the gas to the storage holders or for use in London. There are extensive repair workshops, including the boiler shop for the repair of all stationary and locomotive boilers, and other work of a similar nature. There is a foundry capable of producing some 50 tons per week, with a pattern-making shop in connection therewith. The private locomotive sheds of the works provide accommodation for 31 locomotives, and these are engaged upon 45 miles of single track.

In the tar works are stills for the distillation of 18 million gallons of tar per annum, with underground storage for 4,000,000 gallons. The five pitch beds adjoining the stills have a capacity of 30,000 tons. For the refining of the light oils the naphtha stills and washing plant prepare the distillate which, in the benzol house, yields benzol, toluol, and solvent naphtha amounting to 120,000 gallons yearly. Naphthaline is refined by means of 12 stills, and is manufactured into salable forms in a house close by. Another battery of stills serves for the purification of carbolic acid, up to the standard required for surgical purposes. A series of large tanks contains the stores of creosote used for timber preserving, very large quantities being produced. In another quarter is the house in which anthracene is purified.

The liquor works contains stills and saturators producing 24,000 tons of sulfate of ammonia per annum. Beside it stand a sulfuric acid plant in which sulfuric acid is manufactured from the spent oxide resulting from gas purification; the furnaces are of modern mechanical type. Ammonia gas is also purified for the manufacture of aqueous ammonia and for the production on a large scale of anhydrous ammonia (for refrigerating plant). In the cyanogen plant crude cyanogen liquor is converted into crystalline prussiates of soda and potash, and provides material for the manufacture of Prussian blue and for the cyanides of potassium and sodium.

THE MODERN BY-PRODUCT COKE OVEN

In the *Monthly Bulletin of the American Iron and Steel Institute*, **1**, No. 5, are published several papers relating to the present status of the by-product coke oven in the United States.

Meissner expressed the opinion that when located at points suitable to its requirements, the by-product coke oven was the most satisfactory and economical yet known for the manufacture of metallurgical coke. In the last six months of 1912 coke was produced at the rate of 2,900,000 tons per year at the Gary, Ind. by-product coke oven plant, on a mixture of 76.4 per cent Pocahontas and 23.6 per cent high volatile coals. The conservation of coal through producing this amount of coke in by-product ovens instead of bee-hive ovens amounts to about 1,190,000 tons per year. It has been found by the United States Steel Corporation that the coke produced in by-product ovens, when properly made, is fully equal in quality to that obtained in bee-hive ovens; and that it is possible to utilize a larger variety of coals, when properly selected and mixed, including coals which up to the present time have been practically regarded as "non-coking," and make a highly satisfactory metallurgical coke. The by-product plant can be erected near the blast furnaces and it is practicable to ship to it coking coals from any radius within favorable freight rate; this, however, is not the case with the bee-hive ovens, which, in most cases, are placed near the coal mine which supplies the coal, and, when the mine is exhausted, the bee-hive plant has to be abandoned.

Blauvelt pointed out that the first ovens in this country coked 4.4 tons of coal per oven per 24 hours, and that 25 ovens, with a carbonizing capacity of 110 tons a day, were regarded as the proper unit for one crew of men. "The oven of to-day is carbonizing 20 tons per day, and practically the same crew of men, with the help of modern machinery, will handle 50 ovens or more, carbonizing 1,000 tons per day." He stated that from 40,000,000 to 50,000,000 feet per day of illuminating gas from coke ovens are now produced and sold in the United States. The following points were indicated by Blauvelt as important to a well-designed oven: Largest yield of surplus gas; ability to substitute producer gas for oven fuel gas; maximum yield of by-products; maximun yield of good coke; shortest coking time; lowest cost of operation and repairs; simple and strong, with weight properly distributed.

Atwater called attention to the fact that the recovery oven has achieved a definite place as a part of the steel-making process, and that it presents economies and advantages with which the present-day steel manufacturers must reckon. Meissner had referred to the employment of benzol as a motor fuel; Atwater cited the case of a truck engaged in general city delivery work. On a six months' test with benzol alone as a fuel, a gallon of benzol yielded 15 per cent more work than a gallon of gasolene; based on an equal number of heat units supplied the efficiency was about the same.

"NERADOL D", A SYNTHETIC TANNIN

Stiasny, in the course of a paper on artificial tannins,[1] gives an account of the production of "syntans" (synthetic tannins), one of which products has been placed on the market by the Badische Company, Ltd., under the name of "Neradol D." Syntans are condensation products which may be produced either by heating phenols with formaldehyde in a slightly acid solution and solubilizing the resinous products thus obtained by means of sulfuric acid, or they can be made by first sulfonating the phenols and then condensing them with formaldehyde under such conditions that only soluble products are formed.

"Neradol D" resembles, in its appearance, a vegetable tannin extract of bright color. The analogy between this product and natural tannins is shown by the following behavior of "Neradol D:" Its water solution is of a semi-colloidal character, passing a semi-permeable membrane only slowly and giving a precipitate with gelatine solution. Iron salts produce a deep bluish violet coloration, and a 10 per cent solution of iron alum is a suitable means of controlling the course of "Neradol D" tannage; this is done by placing a few drops of the iron solution on the fresh cut of a half-tanned hide, when the tanned layers are colored deep blue. Lead acetate as well as aniline hydrochloride give precipitates with "Neradol D." Stiasny makes special mention of the very bright color of solutions of "Neradol D" and of the complete solubility in cold water—distinct advantages over the ordinary tannin extracts.

It is said that the real character of "Neradol D" is that of a light leather tannin, and that sumach and gambier are those natural tannins whose effects have the greatest resemblance to that of "Neradol D." It may be used as a bleaching agent of dark-colored leather; in this case the retanning action of this artificial tannin prevents loss of weight, which accompanies most of the usual methods of bleaching heavy leathers.

THE CAUSES AND PREVENTION OF SEWER PIPE FAILURES

It has been stated that, with the inclusion of cement pipe and the cost of labor and materials, it is probable that $75,000,000 are spent annually in this country in the construction of sewers and drains. This expenditure has been largely based upon a visual examination of the pipe or tile, and a conjectural inference as to the loads which it may be expected to carry safely. With a view of developing a correct method of calculating the loads on pipe and of preparing adequate standard specifications for the quality of drain tile and sewer pipe, the Engineering Experiment Station of Iowa State College has conducted a series of experiments, the results of which are reported by *Engineering Record*, 68, 46; these are presented at some length on account of their interest to the ceramic and sanitary engineer.

The following general conclusions reached as to the failure of drain tile and sewer pipe in ditches are based on extensive data obtained from drainage engineers:

1. There have been a large number of failures of drain tile and sewer pipe by cracking in ditches, and there is a wide prevalence of cracked pipe in existing sewers and drains. The cracking is generally confined to pipe larger than 14 in. in diameter. Engineers have not properly appreciated either the extent or the importance, nor have they fully understood the causes, of cracking of drain tile and sewer pipe in ditches.

2. The principal cause of the cracking of the drain tile and sewer pipe in ditches is simply that, as at present manufactured, sizes larger than 15 in. in diameter are very generally too weak to carry the weight resting upon them from more than a few feet depth of ditch filling.

3. In very many cases it is entirely impossible to prevent cracking in ditches of drain tile and sewer pipe as at present manufactured by any possible reasonable amount of care in bedding and laying the pipe and refilling the ditches. A material difference in the carrying power of the pipe, however, can be made by proper care in bedding and laying.

4. Drain tile and sewer pipe crack more readily in ditches with hard bottoms than when laid on slightly yielding soils.

5. It is reasonable, advantageous and necessary to require the pipe-laying contractor carefully to shape the bottom of the ditch to fit the under half of the pipe surface, and to bed the pipe carefully for this distance in sand or granular soil, so as to secure a firm, uniform bearing.

6. Drain tile and sewer pipe are so rigid and crack from such slight distortions, as compared with the yielding of the most solidly tamped earth filling, that it is not feasible to prevent cracking by tamping the ditch filling on each side of the pipe at the midheight. Such side tamping, however, should always be required, and thoroughly done, for it is of great value in preventing the collapse of pipe after it is cracked.

7. Where the pipe is found to crack in spite of faithful observance of the specifications stated in 5 and 6 above, the only effective remedy, other than using stronger pipe, is to bed the pipe in concrete up to the midheight. Such concrete can be lean, and need not be thick if the soil is firm, but must thoroughly fill all spaces between the lower half of the pipe and the bottom and sides of the ditch.

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[1] *Chem. World*, 2, No. 7, 216. See also THIS JOURNAL, 5, 705.

8. The width of the ditch at the level of the pipe makes a great difference in the weight of filling resting on the pipe, this weight being greater the wider the ditch. Moreover, the narrower the ditch at the midheight of the pipe, the more effective is the side support against the collapsing of cracked pipe.

9. Where the ditch filling over the pipe is rammed in layers during refilling, there is serious danger of cracking large drain tile and sewer pipe by using too heavy rammers and too thin a layer just above the pipe.

10. While large amounts of cracked drain tile and sewer pipe are standing without collapsing in existing drains and sewers, the stability of cracked pipe must be considered precarious, as has been demonstrated by numerous collapses.

11. Cracked pipe is especially dangerous in tile drains and storm sewers, for the reason that, in the best engineering practice, it is not found practicable to make the capacity of drains and sewers equal to the most exceptional floods. Hence they are certain eventually to be overcharged, and to run under pressure, and the collapse of cracked pipe is likely to result at such times from the softening of the soil by water escaping through the joints and cracks.

The general principles of the theory of loads on pipes in ditches, which were borne out by a long series of laboratory and field tests, may be in part summarized as follows:

1. The weight of the filling in a drainage or sewerage ditch, at the time of maximum load on the pipe, is carried partly by the pipe, and partly by friction against the sides of the ditch. Cohesion greatly reduces the loads carried by the pipe at ordinary times, after the ditch is refilled and partly consolidated, except in the case of clean sand, or gravel filling, but does not appreciably affect the maximum loads.

2. The maximum loads on pipes in ditches, due to the weight of ditch-filling materials, will usually occur at the time of the first very thorough surface flooding of the ditch filling after construction, when there is a large settlement of the refill, but there is possibility of their occurring later, at the time of extreme saturation of the ditch filling by surface flooding of the ditch and by overcharging of the drain or sewer. The maximum loads may even be postponed for many years in some cases, as is frequently shown by settlement of the filling in old ditches during paving construction.

3. Safe values of the ordinary maximum loads on pipes in ditches, due to the weight of ditch-filling materials, can be computed by the formula $W = CwB^2$, using the values of C given where W = load on pipe in ditches, in pounds per linear foot; C = coefficient of loads on pipes in ditches; w = weight of ditch filling material, from 90 to 120 lb. per cubic foot; B = breadth of ditch at top of pipe, in feet; and H = height of fill, above top of pipe, in feet.

A NEW DESIGN IN BOILER SETTINGS

A modification of the usual horizontal tubular boiler setting is described in a recent bulletin issued by the Travelers' Indemnity Company, of Hartford, Conn.

The two distinctive features of the setting are the furnace arch *A A*, and the air duct *B B*, admitting secondary air through the bridge wall. In the ordinary form of setting for horizontal tubular boilers, the fire sheet of the shell, relatively very much cooler than the burning gases in contact with it, acts as a check upon combustion by its chilling effect and is itself subject to destructive strains. The deflecting arch, as shown by the sections, ends immediately back of the bridge wall, and the faces of fire brick are staggered to form projecting rings on its surface. This arch facilitates more staisfactory combustion of the furnace gases, and, in addition, distributes over the shell and tube surfaces the excess of work usually put upon the fire sheet. Both of these increase the efficiency of the boiler as well as add to its life. The arch must be carefully laid, with good blocks for the end thrust, and segmental brick of the proper radius, with thin points of fire clay. If thus constructed, it will stand up under the high heat to which it is subjected.

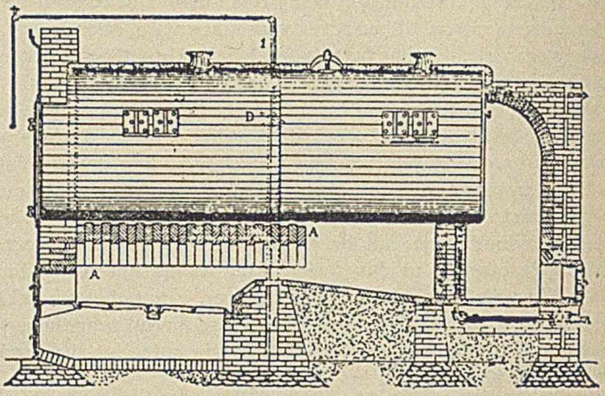


Fig. 1—Vertical Longitudinal Section through Boiler Setting

The auxiliary air supply to the hollow bridge wall enters through the duct *B B*, controlled by the damper *D*; to the transverse passage *C*, which has a clean-out door; and then up and out through $^1/_4$-inch spaces between the fire brick in the crown of the bridge wall. The air is warmed by passage through the ducts, and is then introduced to the burning gases at what has been experimentally determined to be the best point for its addition.

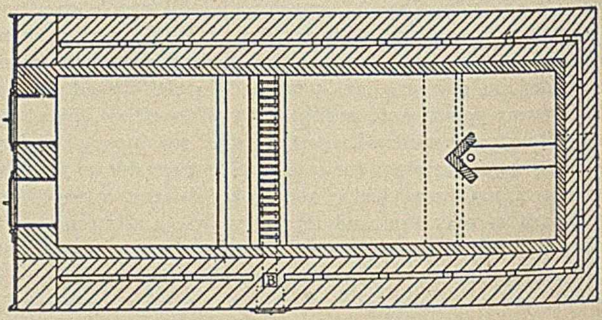


Fig. 2—Horizontal Section through Boiler Setting

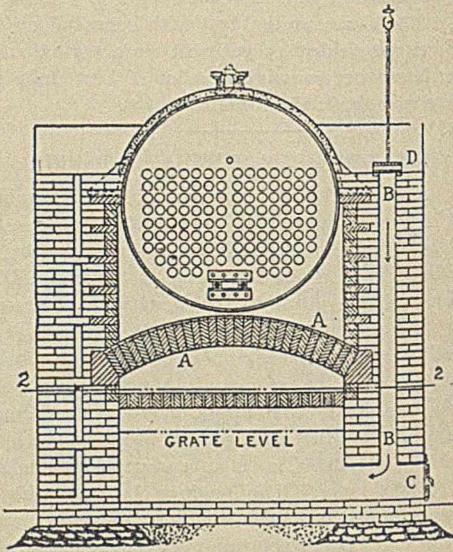
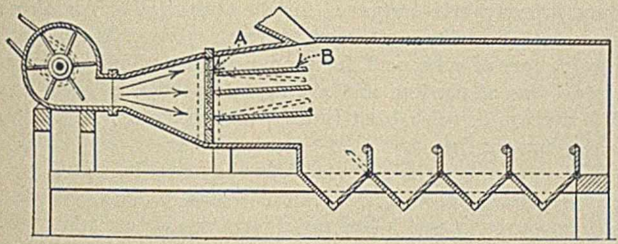


Fig. 3—Section through Ignition Arch

A SEPARATOR FOR DRY MATERIAL

F. O. Stromberg, of Seattle, Wash., has devised an apparatus for the dry separation of ground ore, etc., which consists of a fan or other means of introducing an air blast, which passes through a conical-shaped connection into a box, the bottom of which is divided into separate cone-bottomed receptacles. A screen is placed at the entrance of the box, shown at *A* in the drawing, for the purpose of creating eddies which will permit the greater part of the material to pass through the central slot formed by the movable partitions *B*. These partitions are adjustable and removable, and both the front and rear edges of each partition may be vertically independently adjusted. The arrows in the sketch show that the wind delivered from the fan passes into the inlet of the box and then expands slightly into strata or currents, the central one of which will pass along into and through the inlet without obstruction. Those currents which flow along the top and bottom of the box will set up eddies, as indicated by the fine arrows, and it is the purpose of these partitions to check the tendency to the formation of eddies and to deliver the blasts of air into the box in several strata moving horizontally, and at equal speed. If these screen-panels are used with different meshes, an important bearing will be had upon the amount of air admitted through the slot or opening covered by that particular screen.



Power is applied to the fan which sets up a blast of air through the trunk and screen partition and throughout the length of the box to its outlet end. The material fed into the air-current encounters various strata of air which move at different velocities, according as the partitions have been set, and according to the mesh of the screen at the various openings; the larger pieces naturally offer more resistance to blasts of air than the smaller ones, and, therefore, the larger pieces will fall into the hopper nearest to the entrance of the long box, while the finer particles will fall into successive hoppers further along until the finest are discharged at the end of the box in the form of dust.

ABSORPTION AND REACTION TOWERS FOR CHEMICAL WORKS

Rudolf Heinz,[1] after reminding the reader that the main requirements for good absorption are greatest possible surface per cubic foot of filling, good mixing of gas, and the correct proportioning of the ratio between the section of the tower and the net section free for the passage of the gases, points out that the intending purchaser has a large variety of tower packings to select from. The days of coke as a filling material, except in certain very special cases, are numbered, and it has long been established that a small tower with good packing will accomplish the same amount of work as a large coke tower. Plain acid-proof bricks, prism-shaped bricks, triangular, rhombohedral, and trough-shaped bricks, and rings of various kinds, have all been tried in practice, and all have been found to have a common defect, namely, that they occupy a large percentage of the volume of the tower and leave insufficient "absorption space" for the gases.

Heinz states that the most successful tower packing of recent years were the "Guttmann" hollow balls; the success of these was due to their very high "free space" (the percentage of the cubic capacity of a tower which remains free for gases). Millions of these balls were sold, but they could not come into general use on account of their high cost and because they were unsuitable for large towers and gases containing dust.

The latest type of filling material, "Guttmann" cells, are stated to be superior to even hollow balls, not only in regard to efficiency, but also because the cells are cheaper and possess a very high "free space." As shown in the illustrations (Figs. 1 and 2), these cells, when built up in a tower, form in section a regular honeycomb structure, each four cells enclosing a reaction space corresponding to an additional cell. The whole of the tower is thus symmetrically divided up into a number of equal reaction spaces, and in such a manner that both the outer and inner surfaces of the cells are wetted, and must be traversed by the gases which are ascending and diffusing through the tower filling. The formation of separate streams of liquids or gases cannot occur when these cells are used. Fig. 1 shows diagrammatically four cells arranged in the same manner as if they were stacked in a tower, the path of the liquid being indicated by plain arrows and the probable course of the gases by means of circled arrows. Slots (*a*) are made in the top and bottom walls of the cells; the gases entering from below expand in the interior of the cell, and pass out through the slots at the top. Each cell is provided at the sides with a number of projections (*b*), which rest against corresponding projections on the neighboring cells, and, at the same time, form the slots for the reaction space formed by four adjacent cells. The side walls of the cells being very steep, render it practically impossible, Heinz claims, for solid matter to collect on them, while, if necessary, the cells may be readily and quickly flushed down and cleaned. For extremely dusty gases—such, for example, as pass through a Glover tower—the lower third of the tower may be filled with large slabs or bricks in the usual way. The "active surface" of the large cells is 15 square feet per cubic foot, and of the small cells 30 square feet per cubic foot, and they are said to be designed and proportioned in every way to give the best results.

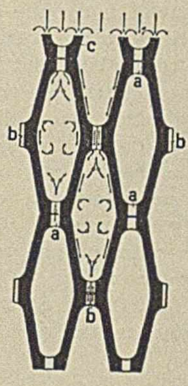


FIG. 1

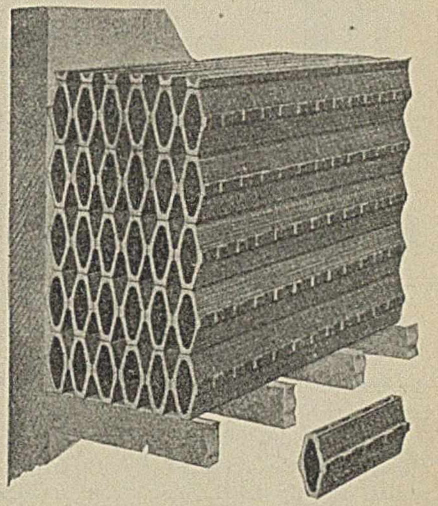


FIG. 2

THE ROTAMETER

The "Rotameter" is a new instrument which indicates the volume of gas or liquid consumed per hour. It does not, however, measure absolute quantities like an ordinary gas meter or voltmeter, but gives the force of the gas current. It is based upon the following principle: The gas current which is to be measured flows through a vertical glass tube, the inside diameter of which increases continuously from the bottom to the top. Inside the glass tube is a conical float which rises to a certain height when gas is flowing through the former. The lift of the float depends upon the velocity of the gas or upon the volume of gas going through the tube in an hour, minute or second. On the float is a notched cylindrical rim. The gas, shooting through these notches, rotates the float like a Segner waterwheel, and

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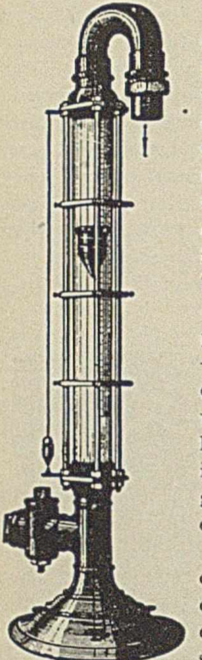
[1] *Z. angew. Chem.*, **26**, No. 57, 419; see also *Chem. Trade J.*, **53**, 75.

this rotation always keeps it in a vertical position and pre [illegible] friction on the wall of the tube. On the body of the float is a white, spiral line, which makes visible its quick rotation, and thus one can note if the meter is working or not.



The glass tube is graduated on the outside, and the calibration is obtained empirically, since its interior cannot be made with absolutely uniform slope. The scale on the glass tube may be made to read directly in cubic feet per hour (minutes or seconds) or in millimeters. In the latter case, tables are furnished with the meter for the determination of the exact volume of gas in cubic feet flowing through the meter. The instrument works as follows:

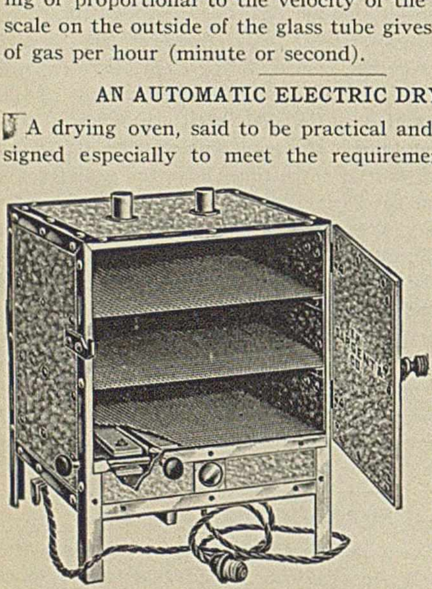
The float is lifted by the gas until the power which forces the gas current past it —*i. e.*, the loss of pressure at that point—is equal to the weight of the float; or, in other words, the float is lifted so high that it leaves an opening between itself and the inside wall of the tube which allows the gas to flow through with a drop in pressure equal to the weight of the float.

The reading of the meter depends, of course, upon the density of the gas, as a denser gas, for the like loss in pressure requires a larger area for the passing of the same amount of gas. It, therefore, lifts the float higher and gives an apparently larger reading than a lighter gas.

Rotameters are adapted to measure, regulate and control the quantity (or the velocity) of gases in pipe lines. They are installed directly in the line. The smallest current will, it is claimed, lift the float at once and hold it at a height corresponding or proportional to the velocity of the gas in the line. The scale on the outside of the glass tube gives directly the quantity of gas per hour (minute or second).

AN AUTOMATIC ELECTRIC DRYING OVEN

A drying oven, said to be practical and inexpensive, and designed especially to meet the requirements of the industrial chemist, is being marketed by Messrs. E. H. Sargent & Co., of Chicago, Ill. It is shown in the accompanying illustration.



Electrically heated and automatically controlled, the claim is made that the oven may be set for any desired heat above room temperature and under 160° C. Under proper conditions, the manufacturers state, it will maintain that temperature within 1° C.

The oven has as much working space as the ordinary 10-inch × 12-inch single copper wall oven, it does not occupy any more space, and it may be easily moved from place to place. It has a working space 10 inches high, 12 inches wide and 10 inches deep, and is provided with 2 shelves. The heating device with the thermostatic control is located in the base of the oven, a locking device is provided to insure against an accidental movement of the control mill-head on the outside, and there is a peep-hole for observing the heating coils. The manufacturers state that each unit of the heating element is easily accessible and replaceable n case of injury, without the employment of tools or the dismounting of the whole heating element. Adjustible ventilation is provided to facilitate drying. The current consumption is very small, and the oven may be operated from an ordinary lamp socket.

A number of these ovens, which are constructed of asbestos composition bound with metal, have been installed for practical trial; the manufacturers report that no complaint has been received.

THE MINERAL PRODUCTION OF SWEDEN

The official report of the Swedish mineral output for 1912 shows the following (*Eng. Min. J.*, **96**, 507, 510):

There were 6,700,556 metric tons of iron ore produced. Of this amount, 5,945,394 tons were considered first-class. The Swedish iron works consumed for the entire production of iron 43,219,576 hectoliters of wood charcoal; 359,584 tons of coal, 136,472 tons of coke; and, for the production of ingots, 337,321 metric tons of pig iron and 212,143 metric tons of scrap iron. The average Swedish blast furnace produces 20.07 metric tons of pig iron per day.

There were also mined the following ores in metric tons: zinc, 50,036; silver-lead, 2,877; iron pyrites, 31,835; manganese, 5,101; copper, 3,059. The metal production, excluding iron, was as follows: copper, 3,957 metric tons; zinc, 3,228; lead, 1,072 metric tons; silver, 961 kg.; gold, 30 kg. Other products and by-products of the mineral industry were: zinc sulfide, 33,522 metric tons; copper sulfate, 870; feldspar, 34,305; quartz, 22,365; alum, 144; ferrous sulfate, 335; graphite, 79; and powdered pyrolusite, 62 metric tons. All figures are arranged in the order of descending value.

THE PRODUCTION OF CALCIUM CARBIDE

It is reported that the world's production of calcium carbide is increasing. According to statistics published in *Chemical News*, **108**, 106, it reached 300,000 tons in 1912. In Europe, Germany is the principal consumer of carbide. In 1911, 37,000 tons were imported, and in 1912 the importations amounted to 48,000 tons; no exportations were reported. Sweden produces the largest quantity of calcium carbide and consumes the least. The factories at Odda are capable of producing 80,000 tons per annum. In 1912, Switzerland exported calcium carbide valued at $1,000,000; Austria-Hungary exports about 11,000 tons per year; England imports only between 14,000 and 18,000 tons; while France imported 3,302 tons and exported 6,225 tons in 1912. It is especially the development of lighting by acetylene in the French colonies which has increased so regularly the exports of carbide.

PROGRESS OF THE ELECTRIC STEEL INDUSTRY

A list of electric furnaces in operation by steel manufacturers in the United States is given in *Iron Age*, July 10, 1913.

Seven of these furnaces are of the Héroult design and include that of the Halcomb Steel Co., Syracuse, N. Y., a five-ton furnace producing tool steel; the Firth-Sterling Steel Co.'s furnace at McKeesport, Penn., of the same size and producing the same material; another belonging to the same company and at the same place, $2^{1}/_{2}$-ton size, also producing tool steel; the Illinois Steel Co., Chicago, Ill., 15-ton capacity, producing rails; the American Steel & Wire Co., Worcester, Mass., 16-ton, producing wire rods; National Malleable Castings Co., Sharon, Penn., 3-ton capacity, producing castings; Treadwell Engineering Co., Easton, Penn., 2-ton capacity, also producing castings.

Of the Girod design there is the one-ton tool-steel furnace of the Simonds Manufacturing Co., Lockport, N. Y.; the Bethlehem Steel Co., South Bethlehem, Penn., a 10-ton tool-steel furnace; the 3-ton furnace, producing castings, of the Washington Iron Works, Seattle, Wash., and the 5-ton castings furnace of the

Portland Bronze & Crucible Steel Foundry, Portland, Ore. The Hering design includes the $^1/_2$-ton castings furnace of the Niagara Steel Castings Co., Buffalo, N. Y., and the $^1/_2$-ton tool-steel furnace of the Firth-Sterling Steel Co., McKeesport, Penn. The 2-ton castings furnace of the Crucible Steel Castings Co., Lansdowne, Penn., is of the Roechling-Rodenhauser design, while the $^3/_4$-ton castings furnace of Deere & Co., of Moline, Ill., is of the Kjellin type. The $1^1/_2$-ton castings furnace of the Buchanan Electric Steel Co., Buchanan, Mich., is of the modified Stassano design, and the $1^1/_2$-ton furnace of the Crucible Steel Castings Co., Milwaukee, Wis., together with the $1^1/_2$-ton castings furnace of the Chicago Electric Castings Co., are designed by the Metallurgical Engineering Co., Chicago, Ill. The 1-ton special steel furnace of the Harrow Spring Co., Kalamazoo, Mich., is of the Greene induction type. The accompanying table shows the installations of electric furnaces by countries.

ELECTRIC FURNACES BY COUNTRIES

Countries	Number	Countries	Number
Germany	34	Spain	1
Italy	20	Mexico	4
England	16	Canada	3
France	13	Japan	1
Austria	10	Brazil	1
Sweden	6		—
Russia	4	Total, foreign	121
Belgium	3	United States	19
Norway	3		—
Switzerland	2	Grand total	140

IRON CASTINGS TO RESIST CORROSION

The Canadian Engineer, July 17, 1913, states that some practical rules laid down by the American Foundrymen's Association for obtaining castings resistant to corrosion are the following: (1) Use white iron if possible (white irons are especially useful where any acidity is to be encountered); (2) if it is not practicable to use white iron castings, chill those surfaces which are to be in contact with corrosive solutions; (3) if gray iron must be used, obtain dense, close-grained castings through the use of steel scrap or otherwise; (4) avoid oxidized metal, using pig irons of good quality, together with good cupola practice; and (5) keep the sulfur as low as possible. If possible, use deoxidizing agents, such as titanium or vanadium.

THE PRODUCTION OF FINISHED STEEL IN 1912

The Bureau of Statistics of the American Iron and Steel Institute in a special bulletin issued August 7th, announced complete statistics of the production of iron and steel merchant bars, concrete bars, skelp, nail plate, hoops, bands and cotton-ties, sheet piling, etc., in the United States in 1912; also statistics of the production of all kinds of finished rolled forms.

PRODUCTION OF FINISHED ROLLED IRON AND STEEL BY STATES

(Gross tons)

STATE AND SUBDIVISIONS	1912	1911
Maine, Mass	193,401	157,448
R. I., Conn	81,410	73,788
New York	1,034,071	768,763
New Jersey	175,143	154,563
Pennsylvania	12,254,040	9,426,827
Del., Virginia	32,888	30,487
Maryland	284,617	264,222
West Va	591,333	472,177
Ky., Tenn., N. C., Ga., Tex	192,737	187,149
Alabama	532,247	356,609
Ohio	4,330,487	3,382,063
Indiana	1,873,906	1,156,411
Illinois	2,253,664	1,939,350
Mich., Wis	246,991	148,285
Missouri	82,883	68,961
Kan., Colo., Wash	438,622	407,314
Ore., Cal	58,401	44,754
Total	24,656,841	19,039,171

The bulletin shows the following totals for 1912 of all kinds of finished rolled forms of iron and steel, etc., with the production of similar articles in 1911, in gross tons:

ROLLED IRON AND STEEL	1911	1912
Rails	2,822,790	3,327,915
Plates and sheets	4,488,049	5,875,080
Nail and spike plate	48,522	45,331
Wire rods	2,450,453	2,653,553
Structural shapes	1,912,367	2,846,487
Merchant bars	3,047,362	3,697,114
Bars for concrete work	258,741	274,332
Skelp, flue, etc	1,980,673	2,446,816
Long angle splice bars, etc	(*a*)	571,772
Hoops	225,074	270,007
Bands and cotton ties	342,810	587,395
Sheet piling	22,827	22,276
Railroad ties	39,197	41,396
All other finished rolled	1,169,191	1,187,108
Rolled forg. blms. and billets	231,115	462,476
Exports blooms, billets, etc	(*a*)	347,783
Total	19,039,171	24,656,841

(*a*) Statistics not collected in 1911.

THE COMPOSITION OF WATER GAS

Vignon (*Compt. rend.*, 156, 1995) confirms the observation of Clement and Desormes and of Langlois that water gas always contains some methane. Investigation has shown that the formation of the methane is due to the presence of calcium oxide in the coke used. Experiments on the action of steam at 1000° on mixtures of coke and lime showed that the percentage of methane in the water gas increased with increasing proportions of lime. The formation of the methane is considered by Vignon to be due to the following reactions:

$$4CO + 2H_2O = 3CO_2 + CH_4,\ 2CO + 2H_2 = CO_2 + CH_4 \text{ and}$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

The lime is said to act as a catalyst in these reactions.

THE PAPER INDUSTRY OF AUSTRIA-HUNGARY

Paper, September 10, 1913, reports that new features have marked the close of the business year of the Austro-Hungarian paper industry.

This is particularly the case as regards the arrangements for uniform prices and terms. In this matter the example of the German Association seems to have been followed.

The Balkan troubles seem to have exercised a special effect upon the Austrian paper industry, of which the Balkan territory had long been special outlet. Among the measures of a social-political order, to which the attention of the association has been directed, was the question of resting from work on Sundays and the prohibition of juvenile night work. The question of the increased cost of wood and other raw materials had engaged the attention of the Government in connection with the augmented difficulty of procuring supplies. The proposed imposition of an export duty on rags had also been much discussed on the same lines as have marked that proposal in Germany. Another question of importance has been the revision of commercial treaties with foreign nations.

According to the statistics of production issued by Herr Franz Kramany the figures show in 1912:

	Tons
Paper of all kinds	424,785
Board of all kinds	49,521
Wood pulp	258,036
Cellulose	292,195
Bleached straw pulp	2,762
Total, 1912	1,027,299
Total, 1911	981,740
Total, 1910	954,036
Total, 1909	893,856

SCIENTIFIC SOCIETIES

AMERICAN CHEMICAL SOCIETY—FORTY-EIGHTH MEETING, ROCHESTER, SEPTEMBER 8–12, 1913

PROGRAM OF PAPERS

GENERAL MEETINGS

Industrial Research in America. President's Address. A. D. Little.

Copper Covered Steel: Properties and Uses of the Composite Metal Made by Welding together Copper and Steel. (Illustrated.) James O. Handy.

The Physical Chemistry of Photographic Development. C. E. Kenneth Mees.

The Patent Expert and the Chemical Manufacturer. Bernhard C. Hesse.

The Utilization of Sewage. George A. Soper.

In Commemoration of the Centennial of the Publication of the Berzelian System of Symbols. Henry Leffmann.

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

H. E. Barnard, *Chairman* Glen F. Mason, *Secretary*

1. **Bouillon Cubes: Their Composition and Food Value.** Frank C. Cook.

2. **A Refractometer for Sugar Determinations.** H. E. Howe.

3. **Hydrolysis of Starch.** Edward Gudeman.

4. **Lime Sulfur-Lead Arsenate Spray Mixture.** W. E. Ruth.

5. **The Commercial Utilization of Glucose and Glycerine in Modern Breads.** O. G. Marckworth.

6. **Sulfur Dioxide in Gelatine.** (Illustrated.) Paul Poetschke.

7. **Solubility of Casein in Dilute Acids.** L. L. Van Slyke.

8. **The Effect of Rain on the Value of Hay.** J. A. Le Clerc.

9. **The Acid Content of Fruits.** (Illustrated.) P. B. Dunbar and W. D. Bigelow.

10. **Estimation of the Lime Requirements of Soil.** J. A. Bizzell and T. L. Lyon.

11. **The Valuation of the Lime-Sulfur Spray as an Insecticide.** H. V. Tartar.

12. **The Effects of Raw Materials on the Chemical Composition of American Beer.** L. M. Tolman and J. G. Riley.

13. **Food Standards and their Effect upon Food Law Enforcement.** Floyd W. Robison.

14. **The Analysis of Maple Products. II. A Comparative Study of the Delicacy of Methods.** J. F. Snell and J. M. Scott.

BIOLOGICAL CHEMISTRY SECTION

Carl L. Alsberg, *Chairman* I. K. Phelps, *Secretary*

1. **The Presence of Histidine-like Bodies in the Pituitary Gland (Posterior Lobe).** (Preliminary Communication.) T. B. Aldrich.

2. **The Mutual Action of Pepsin and Trypsin.** J. H. Long.

3. **A Further Study of the Well Water of Delaware, Ohio.** G. O. Higley.

4. **Comparison of the Observed and Computed Heat Production of Cattle.** H. P. Armsby.

5. **On the Distribution of Mercury Following Acute Bichloride of Mercury Poisoning.** Jacob Rosenbloom.

6. **The Non-interference of Ptomaines with Certain Tests for Morphine.** Jacob Rosenbloom and S. Roy Mills.

7. **Notes on the Result of the Electrolysis of Witt's Peptone and Whole Protein.** James P. Atkinson.

8. **The Non-Development of Cytolytic Sera Following the Intravenous Injection of Mold Spores.** R. A. Gortner and A. F. Blakeslee.

9. **The Occurrence of a Toxin in the Bread Mold,** *Rhizopus nigricans.* R. A. Gortner and A. F. Blakeslee.

10. **The Effect of Acids upon the Catalase of Taka-Diastase.** Ray E. Neidig.

11. **Polyatomic Alcohols as Sources of Carbon for Molds.** Ray E. Neidig.

12. **Cleavage of Benzoylalanine by Mold Enzymes.** Arthur W. Dox and W. E. Ruth.

13. **The Importance of Food Accessories as Shown by Rat Feeding Experiments.** Frank C. Cook.

14. **The Influence of Various Organic Substances upon the Secretion of Diastase by Certain Fungi.** C. F. Chapman and W. C. Etheridge.

15. **The Role of Oxidases in the Curly Dwarf Disease of Potatoes.** H. H. Bunzel.

16. **A Time Recorder for Kymograph Tracings.** Oliver E. Closson.

17. **Apparatus for Studying Oxidases.** Oliver E. Closson.

18. **A Method for Studying Slight Degrees of Glycosuria, Adapted from Macleod and S. R. Benedict.** Amos W. Peters and Mary E. Turnbull.

19. **A Method of Estimating Fat in Infant Stools.** W. S. Hubbard and D. M. Corvie.

20. **Nature of Humus and its Relation to Plant Life.** S. L. Jodidi.

21. **The Estimation of Protein, Amino and Nucleic Acids in Potable Waters.** Philip Adolph Kober.

22. **Surface Tension in Muscle Contraction.** Wm. M. Berg.

23. **The Estimation of Raffinose by a Modified Biological Method.** C. S. Hudson and T. S. Harding.

24. **The Elimination of Zinc.** Wm. Salant and John B. Rieger.

25. **The Absorption and Fate of Tin in the Body.** Wm. Salant and Ernest L. P. Treuthardt.

26. **The Fate of Protein Digestion Products in the Body.** D. D. Van Slyke.

27. **The Configuration of Some Heptoses.** George Pierce.

28. **Vanillin in Wheat, and its Relation to Soil.** M. X. Sullivan.

29. **Some Organic Constituents of the Culture Solution and the Mycelium of Molds from Soil.** M. X. Sullivan.

30. **A Method for the Determination of Small Amounts of Fat.** W. R. Bloor.

31. **Nitrogenous Hydrolysis Products of Several Phosphatids.** C. G. MacArthur.

32. **Fatty Acids from Kephalin.** L. V. Burton and C. G. MacArthur.

33. **A Metabolism Experiment with Swine:** (*a*) **Mineral Requirements and Paths of Excretion;** (*b*) **The Balance of Acids and Bases;** (*c*) **The Relation of Magnesium and Calcium Metabolism;** (*d*) **Creatinine Excretion by Swine;** (*e*) **Anomalies in Digestion Coefficients.** E. B. Forbes.

34. **The Fate of Creatine and Creatinine when Administered to Rabbits.** V. C. Myers and M. S. Fine.

35. **Studies in the Comparative Physiology of Purine Metabolism.** Andrew Hunter, M. H. Givens and C. M. Guion.

36. **Estimation of Protein, Amino and Nucleic Acids in Potable Waters.** P. O. Kober.

37. **The Acidity of the Urine.** H. D. Haskins.

38. **Metabolism Studies of Five Cases of Endarteritis Obliterans.** Max Kahn.

39. **Calcium Content of Tuberculous Lungs.** Max Kahn.

40. **Metabolism Studies of Two Cases of Amaurotic Idiocy.** Max Kahn and A. Hymanson.

41. **Further Studies of Edema.** T. L. Harkey.

42. **A Study on the Influence of External Hemorrhages on the Partition of Urinary Nitrogen.** Olive G. Patterson.

43. **Biochemical Studies of Selenium.** Victor E. Levine.

44. **Pigments Produced from Thymol by Ammonium Hydroxide.** Benjamin Horowitz and W. J. Gies.

45. **A Differential Stain for Mucine and Mucoids.** Louis Berman and W. J. Gies.

46. **The Origin and Significance of Salivary Sulfocyanate.** Max Kahn and W. J. Gies.

47. **Biochemical Studies of Dental Caries.** A. P. Lothrop and W. J. Gies.

48. **Further Studies of the Permeability of Lipin-Collodion Membranes.** W. J. Gies.

49. **The Physical and Chemical Constants of a Number of Monarda Fistulosa Oil.** E. N. Daane and Edward Kremers.

50. **The Water and Volatile Oil Content of the Leaves of Monarda Fistulosa.** Nellie Wakeman and Edward Kremers.

51. **Light and Health.** W. D. Bancroft.

FERTILIZER CHEMISTRY DIVISION

Paul Rudnick, *Chairman* J. E. Breckenridge, *Secretary*

1. **Chairman's Address. Fertilizer Chemistry. A Report of Progress.** Paul Rudnick.

2. **On the Use of Alundum Crucibles in the Determination of Phosphoric Acid.** L. A. Watt and W. T. Latshaw.

3. **The Analysis of Complete Fertilizers Containing Cyanamid.** H. W. Hill and W. S. Landis.

4. **On the Preparation of Neutral Ammonium Citrate Solution.** Paul Rudnick and W. L. Latshaw.

Report of Committees

Committee on Nitrogen. Paul Rudnick.
Committee on Phosphoric Acid. G. A. Farnham.
Committee on Potash. J. E. Breckenridge.
Committee on Phosphate Rock. F. B. Carpenter.
Committee on Fertilizer Legislation. F. B. Carpenter.

INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

G. D. Rosengarten, *Chairman* S. H. Salisbury, Jr., *Secretary*

Geo. P. Adamson, *Vice-Chairman, Presiding*

1. **The Protection of Iron and Steel by Paint Films.** Norman A. Dubois.

2. **Some Tests of Paints for Steel Subjected to Alternate Exposure to Air and Fresh Water.** (Illustrated.) Percy H. Walker and S. S. Voorhees.

3. **The Effect of Resene on Soap Solutions.** Charles H. Herty and C. W. Williard.

4. **Isoprene from Commercial Turpentine.** Charles H. Herty and J. O. Graham.

5. **The Milling of Wheat and Testing of Flour.** Harry McCormack.

6. **A New Design of Coke Oven and a New Method of Coking.** Harry McCormack.

7. **The Electrolytic Reduction of Iron for Permanganate Titration.** H. C. Allen.

8. **A Method for the Determination of Magnesium in Calcium Salts.** J. C. Hostetter.

9. **Methods for the Examination of Natural Gas for the Production of Gasoline.** E. S. Merriam.

10. **The Condensation of Gasoline from Natural Gas.** George A. Burrell and Frank M. Seibert.

11. **Some Experiments on the Conversion of Long Leaf Pine to Paper Pulp by the Soda and Sulfate Processes.** Sidney D. Wells.

12. **Jerusalem Self-burning Limestone.** Charles P. Fox.

13. **Improved Burner for Laboratory Use.** Charles P. Fox.

14. **The Correlation of Chemical, Structural, and Thermal Analyses of Steels.** J. Culver Hartzell.

15. **If the Chemist Manufactured Cotton-seed Meal.** E. L. Johnson.

16. **The American Petroleum Society.** Irving C. Allen.

17. **Flash Testing.** Irving C. Allen.

18. **Alum Specification Report.** W. M. Booth.

Report of the Committee on Coal Analysis and Discussion. Led by W. A. Noyes.

ORGANIC CHEMISTRY DIVISION

Treat B. Johnson, *Chairman* William J. Hale, *Secretary*

1. **The Structure of Urushiol, a Component of Japanese Lac.** E. Kohmann and Treat B. Johnson.

2. **The Reactions of Both the Ions and the Non-ionized Forms of Acids, Bases and Salts.** S. F. Acree.

3. **The Existence of Mandelic Aldehyde in Aqueous Solution.** William Lloyd Evans and C. R. Parkinson.

4. **The Mechanism of the Rearrangements of Dihydro-β-Naphthoic Acids.** C. G. Derick and O. Kamm.

5. **Researches on Purines. xii: 2-Oxy-6-methyl-9-ethylpurine; 2-Oxy-6,8-Dimethyl-9-ethylpurine; 2-Oxy-6-methyl-8-thio-9-ethylpurine; 2-Methylmercapto-6-oxy-8-thiopurine; 2-Oxy-6-methyl-9-ethylpurine-8-thioglycollic Acid.** Carl O. Johns and Emil J. Baumann.

6. **Researches on Purines. xiii: 2,8-Dioxy-1,6-dimethylpurine; 2,6-Dioxy-3,4-dimethyl-5-nitropyrimidine (α-Dimethyl-nitrouracil).** Carl O. Johns and Emil G. Baumann.

7. **Acyl Derivatives of *o*-Aminophenol.** J. H. Ransom and A. Nelson.

8. **Diacetyl: A Study in Structural Chemistry.** W. M. Blanchard.

9. **The Determination of Phenol in the Presence of Formaldehyde and Hexamethylenetetramine.** L. V. Redman, A. J. Weith and F. P. Brock.

10. **The Rate of Reaction between Hexamethylenetetramine and Phenol.** L. V. Redman, A. J. Weith and F. P. Brock.

11. **Synthetic Resins in Lacquers and Varnishes.** L. V. Redman, A. J. Weith and F. P. Brock.

12. **A New Synthetic Resin.** L. V. Redman, A. J. Weith and F. P. Brock.

13. **Synthetic Resins Produced by the Anhydrous Reaction between Phenols and Hexamethylenetetramine.** L. V. Redman, A. J. Weith and F. P. Brock.

14. **Chairman's Address. The Practical Utility of Hinsberg's Reaction.** Treat B. Johnson.

15. **An Anomalous Reaction of Resorcinol.** Edwin F. Hicks.

16. **The Action of Phthalic Anhydride on Benzene in Presence of Aluminium Chloride.** F. B. Allan and C. R. Rubidge.

17. ***o*-Benzoyl-benzoyl Chloride and *o*-Benzoyl-benzoyl Cyanide.** F. B. Allan and H. C. Martin.

18. **The Oleoresins of Jeffry and Singleleaf Pines.** A. W. Schorger.

19. **The Leaf Oil of Douglas Fir.** A. W. Schorger.

20. **The Condensation of Thiourea with Acetylacetone.** William J. Hale.

PHARMACEUTICAL CHEMISTRY DIVISION

B. L. Murray, *Chairman* F. R. Eldred, *Secretary*

1. **Chairman's Address. Legislation Affecting Pharmaceutica Chemistry.** B. L. Murray.

2. **The Determination of Mercuric Iodide in Tablets.** A. W. Bender.

3. **The Insecticidal Value of Fluid Extract of Larkspur Seed.** J. B. Williams.

4. **The Ferric Alum Estimation of Casein.** H. V. Arny and H. H. Schaefer.

5. **Some Physico-chemical Considerations in Reference to Inhalation Anaesthetics.** Charles Baskerville.

6. **Amyl Nitrite, its Preparation, Purity and Tests.** F. O. Taylor.

7. **The Chemico-legal Interpretation of the U. S. Pharmacopoeia.** Louis Hogrefe.

8. **The Chemistry and Properties of Glycerophosphates.** Gaston DuBois.

9. **Purity of Chemicals and Quality of Vegetable Drugs during 1912.** A. R. L. Dohme and H. Engelhardt.

10. **Spirit of Nitrous Ether.** H. Engelhardt and O. E. Winters.

11. **The Composition of the Fruit of the Virginia Creeper.** *Ampelopsis quinquifolia.* Geo. O. Beal and Edw. A. Glenz.

PHYSICAL AND INORGANIC CHEMISTRY DIVISION

S. L. Bigelow, *Chairman* R. C. Wells, *Secretary*

1. **Observations on the Electrochemical Behavior of Minerals.** R. C. Wells.

2. **Fluidity and the Law of Mass Action.** Eugene C. Bingham.

3. **The Solubility of Water in Hydrocarbons.** E. C. McKelvy and F. A. Wertz.

4. **Electrolysis of Solutions of the Rare Earths.** (Illustrated.) L. M. Dennis and B. J. Lemon.

5. **Action of Light on Copper Sulfate Solution.** Wilder D. Bancroft.

6. **Catalysis of Acetic Acid.** Wilder D. Bancroft.

7. **The Critical Solution Temperature and its Use in the Estimation of Moisture.** E. C. McKelvy.

8. **The Analysis of Basic Lead Sulfates.** George A. Perley and G. F. Lane.

9. **Variations in the Compositions of Minerals.** Edgar T. Wherry.

10. **The Increase in the Oxidizing Potential of Dichromate Ion on Platinum Caused by Certain Reducing Agents: An Improved Method for the Electrometric Titration of Ferrous Salts.** George Shannon Forbes and Edward P. Bartlett.

11. **Equilibrium in the System Pyridine, Silver Nitrate and Water.** W. S. Hubbard.

12. **New Precipitants for Copper.** Philip Adolph Kober.

13. **The Electrochemical Equivalent of Iodine and the Value of the Faraday.** E. W. Washburn and S. J. Bates.

14. **The Reduction of Chromium Chloride.** H. C. P. Weber.

15. **Electrolysis of Solutions of Sodium Hydrazide in Anhydrous Hydrazine.** T. W. B. Welsh.

16. **Anhydrous Hydrazine as a Solvent.** T. W. B. Welsh and H. J. Broderson.

17. **Chemical Reactions in Anhydrous Hydrazine.** T. W. B. Welsh and H. J. Broderson.

18. **Electrolysis of Silver Trinitride in Liquid Ammonia.** A. R. Hitch.

19. **Thermal Decomposition of Various Trinitrides.** A. R. Hitch.

20. **The System Hydrazine Trinitride, Hydrazine.** H. E. Riegger.

21. **Action of Various Oxidizing Agents upon Hydrazine in Liquid Ammonia Solution.** W. J. Marsh.

22. **Critical Phenomena in Binary Systems.** Fritz Friedrichs.

23. **The System Ammonium Sulfate, Ammonia.** Fritz Friedrichs, A. E. Houlehan and L. J. Ulrich.

24. **The System Mercuric Chloride, Ammonia.** Fritz Friedrichs.

25. **The System Ammonium Iodide, Ammonia.** L. J. Ulrich.

26. **The System Ammonium Chloride, Ammonia.** G. J. Fink.

27. **The System Copper Sulfate, Ammonia.** G. J. Fink.

28. **The System Silver Trinitride, Ammonia.** A. S. Yount.

29. **The Structure of the Trinitride Radicle.** J. W. Turrentine.

SYMPOSIUM ON PHOTOGRAPHIC CHEMISTRY

30. **Direct Photographic Positives.** Geo. E. Perley.

31. **Practical Sensitometry.** P. G. Nutting.

32. **Some Applications of Quantitative Absorption Spectroscopy in Chemistry.** S. E. Sheppard.

33. **The Latent Image.** W. D. Bancroft.

34. **Theory of Developer.** W. D. Bancroft.

35. **Some Notes on the Cylindrical Acetylene Flame as a Standard of Light.** L. A. Jones.

36. **The Sensitiveness Curves of Photographic Plates Exposed to X-Rays.** Orim Tugman.

37. **The Theory of the Acid Fixing Bath.** A. C. McDaniel.

RUBBER CHEMISTRY SECTION.

D. A. Cutler, *Chairman* Dorris Whipple, *Secretary*

1. **Chairman's Address. Crude Rubber.** D. A. Cutler.

2. **Some Refinements of the Ignition Method for the Determination of Rubber in Vulcanized Goods.** G. H. Savage.

Discussion of Committee Reports.

WATER, SEWERAGE AND SANITATION SECTION

Edward Bartow, *Chairman* H. P. Corson, *Secretary*

1. **Manganese in Illinois Waters.** Edward Bartow and H. P. Corson.

2. **The Comparative Value of Pure Calcium and Magnesium-calcium Lime for Water Softening.** Edward Bartow and Clarence Scholl.

3. **Ventilation of the Schools of New York City.** (Illustrated.) Charles Baskerville.

4. **Winkler's Method for the Determination of Oxygen in Water: the Effect of Nitrite and its Prevention.** Frank E. Hale and W. Melia.

5. **The Determination of Sulfur in Certain Culture Media.** H. W. Redfield and C. Huckle.

6. **A Comparative Study of Methods for Determining Sulfur in Peptone.** H. W. Redfield and C. Huckle.

7. **The Value of Testing for Hydrogen Sulfide Production in the Bacteriological Examination of Potable Waters.** E. M. Chamot.

8. **A Study of the Best Conditions for Hydrogen Sulfide Production in Peptone Media.** E. M. Chamot and H. W. Redfield.

9. **The Influence of the Composition of Carbohydrate Culture Media on the Amount and Character of the Gases Formed by Fecal Organisms.** E. M. Chamot and R. C. Lowary.

10. **A Study of the Stokes Neutral Red Reaction.** E. M. Chamot and C. M. Sherwood.

11. **Further Notes on Standards of Potable Waters.** J. Culver Hartzell.

12. **The Determination of Minute Amounts of Sulfur Dioxide in Air.** A. Seidell and P. W. Meserve.

13. **The Quantitative Use of the Spectroscope in Water Analysis.** W. W. Skinner and W. D. Collins.

14. **Comparison of Methods for the Determination of Dissolved Oxygen.** W. W. Skinner and J. W. Sale.

15. **Longevity of B. Typhosus in Water.** F. L. Rector.

AMERICAN ELECTROCHEMICAL SOCIETY. DENVER MEETING

The Twenty-fourth General Meeting of the American Electrochemical Society took place at Denver, Colorado, September 9–11, 1913.

PROGRAM OF PAPERS

1. **The Shape Factor.** Irving Langmuir.

2. **Simultaneous Determination of Copper and Lead, with the Rotating Anode.** A. J. White.

3. **Rapid Refining of Copper with a Rotating Cathode.** C. W. Bennett and C. O. Brown.

4. **The Heat Resistivity of Graphite and Carbon.** J. W. Richards.

5. **Effect of Light on Decomposition Voltage.** Alan Leighton.

6. **The Art of Electric Zinc Smelting.** W. McA. Johnson.

7. **Possible Applications of the Electric Furnace to Western Metallurgy.** D. A. Lyon and R. M. Keeney.

8. **The Transformation of Radiant into Chemical Energy.** S. C. Lind.

9. **Electric Smelting of Chromium, Tungsten, Molybdenum and Vanadium Ores.** R. M. Keeney.

10. **The Carnotite Industry.** Siegfried Fischer.

11. **Some Aspects of Heat Flow.** E. F. Northrup.

12. **The Electrolysis of Cyanide Solutions.** E. F. Kern.

13. **The Electrolysis of Aqueous Solutions of the Simple Alkaline Cyanides.** G. H. Clevenger and M. L. Hall.

14. **Some Observations on Base Metal Thermocouples.** O. L. Kowalke.

15. **Osmium-Platinum.** F. Zimmerman.

16. **The Electric Zinc Furnace.** P. E. Peterson.

17. **Solid Thick Deposits of Lead from Lead Acetate Solutions.** F. C. Mathers.

18. **Progress in Electrostatic Ore Dressing.** F. S. MacGregor.

Sessions for the reading and discussion of papers were held at the Shirley Hotel, Denver; the University of Colorado, Boulder; the Colorado School of Mines, Golden; and on the top of Pike's Peak.

Trips to various points of interest, both technical and geographic, were included in the program. Among the plants visited were the following:

Sutton, Steele & Steele Co.: Experimental mill and testing plant. Dry process of ore concentration; electrostatic separation of sulfide minerals.

Western Chemical Manufacturing Co.: Manufacture of acids, anhydrous ammonia, and liquid carbonic acid, concentration of mixed sulfide ores, magnetic separation, producer-gas power plant.

Henry E. Wood Ore Testing Co.: General testing of ores, concentration, flotation, cyanidation, magnetic separation.

United States Mint: Electrolytic refining of gold.

American Zinc Ore Separating Co.: Testing plant, electrostatic, separation, dry jigging, separation of complex ores.

American Smelting & Refining Co.: Lead smelting, Huntington-Heberlein and Dwight-Lloyd sinter roasting, bag-house recovery of smelter fume.

Screenless Sizer Co.: McKesson-Rice screenless sizing of ores, crushed rock and coal.

THE CHEMICAL SOCIETIES IN NEW YORK CITY

PROGRAM OF MEETINGS FOR THE SEASON 1913–1914. SESSIONS IN RUMFORD HALL, CHEMISTS' CLUB

American Chemical Society, October 10, 1913.
Society of Chemical Industry, October 24, 1913.
American Chemical Society, November 7, 1913.
Society of Chemical Industry, November 21, 1913.
Joint Meeting, American Chemical Society, December 12, 1913.
American Chemical Society, January 9, 1914.
Society of Chemical Industry (Perkin Medal), January 23, 1914.
Joint Meeting, American Electrochemical Society, February 6, 1914.
American Chemical Society (Nichols Medal), March 6, 1914.
Society of Chemical Industry, March 27, 1914.
Society of Chemical Industry, April 24, 1914.
American Chemical Society, May 8, 1914.
Joint Meeting, Society of Chemical Industry, May 29, 1914.
American Chemical Society, June 5, 1914.

OBITUARY—EUGENE A. BYRNES

The death of Dr. Eugene A. Byrnes occurred on August 1st, at Haven, Maine, where he had gone for a vacation.

Dr. Byrnes was born in New York State in 1862. He had graduated from the University of Michigan, and in 1884 became a teacher in the Central High School, Washington, D. C. Subsequently he entered the Examining Corps of the United States Patent Office, and rapidly rose to the position of Chief of a Division. In the meanwhile he graduated from the Law School of Columbian University, and was admitted to the Bar. He also took a post-graduate course leading to the degree of Ph.D. in Electro-chemistry and Physics. In 1901 he resigned his official position and entered upon the practice of law with Mr. C. P. Townsend as a partner. Later Mr. J. H. Brickenstein entered the firm, the three constituting the well-known firm of patent lawyers, Brynes, Townsend and Brickenstein.

Dr. Byrnes was a member of the American Chemical Society, American Electro-Chemical Society, American Institute of Electrical Engineers, Chemists' Club of New York City, Society of Chemical Industry, Patent Law Association of Washington, and of the Cosmos and Chevy Chase Clubs of Washington.

OBITUARY—F. H. DANIELS

Fred H. Daniels, Chairman of the Board of Engineers of the United States Steel Corporation, Chief Engineer of the American Steel and Wire Company, and President of the Washburn and Moen Company, died at his home in Worcester, Mass., on August 31, 1913, after a long illness.

Mr. Daniels, who was born in 1853, had been very prominently identified with the development of the iron and steel industries for 40 years, and over 150 patents, a number of which revolutionized processes of manufacture, indicate his activity.

Mr. Daniels supervised the erection of plants for the American Steel and Wire Company at Waukegan, Ill., Cleveland, O., San Francisco, Cal., and Birmingham, Ala. He was one of the board of consulting engineers who designed the United States Steel Corporation's plant at Gary, Ind., and served in a similar capacity at the time of the erection of the Duluth mills of the Minnesota Steel Company.

In 1900, the Paris Exposition Jury of Awards bestowed a gold medal on Mr. Daniels as "celebrateur," and in 1909, he was decorated by King Oscar of Sweden.

W. A. Hamor

NOTES AND CORRESPONDENCE

ON METHODS OF ANALYSIS OF CRUDE GLYCERINE

Editor of the Journal of Industrial and Engineering Chemistry:

From the recital of difficulties given by E. A. Ray in This Journal, 5, 784, it is evident that there is some confusion existing as to the exact procedure of the International Standard Method for glycerine analysis.

The glycerine sub-committee of the American Chemical Society met at London in 1910, with the British Expert Committee and representatives from Germany and France and agreed on the following: (see report of the American Committee, This Journal, 3, 679). The British report is identical.

INSTRUCTIONS FOR CALCULATING THE ACTUAL GLYCERINE CONTENT

(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylizable impurities if present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol.

This is the official method at present in use in the United States. Nothing is said about any allowance nor is there a limit set at 2.5 per cent organic residue at which or below which the chemist is prohibited from making a correction for acetylizable impurities.

The British *Executive* Committee, a committee of British Soap Manufacturers, appended a recommendation to the report of the Expert Committee as follows:

RECOMMENDATIONS BY EXECUTIVE COMMITTEE

If the non-volatile organic residue at 160° C. in the case of a soap lye crude be *over* 2.5 per cent, then the residue shall be examined by the acetin method and any excess of glycerol found over 0.5 per cent shall be deducted from the acetin figure.

This recommendation was not signed by the British Experts and was rejected by the American Committee as being arbitrary and unscientific. Residues of 2.5 per cent and below often give very material corrections for impurities. Even if this correction is small there is no reason why it should not be made nor is there any clear reason why the limit should be set at 2.5 per cent rather than at 1, 2 or 3 per cent. It is the chemist's task to determine the actual glycerine present to the best of his ability and leave all questions of allowance and limits to others.

English crudes purchased under these conditions of sale as laid down by British manufacturers will of course be tested with these limitations, but there has been no such custom with regard to American crudes, which have been bought and sold on the basis of the American Chemical Society report.

Referring to the instructions for calculating the glycerine content it will be seen from (2) that the determination of the organic residue is not required. It may be obtained by determining the ash and deducting this from the total residue. This determination is not needed when glycerine alone is being looked for and the chemist who has been asked to analyze a sample for glycerine by the International method is within his rights in declining to state the per cent of organic residue or ash unless he receives additional compensation therefor. There would seem to be little excuse, however, for a chemist to refuse to state the total residue and the correction as found, these determinations being necessary before the true per cent of glycerol can be ascertained.

The difference between the tests of the referee and seller amounting to 1.38 per cent might easily be due to the presence of solid salt in the samples or to the deposition of salt after the crude had left the seller's factory. The accurate sampling of crude glycerine if salt has separated is next to impossible and chemists may differ 5 per cent and more on very salty crudes.

Doubtless the crude referred to by Dr. Ray is free from solid salt or he would have called attention to its presence. It is a fact, however, that it is the exception rather than the rule to find a delivery of American soap lye crude entirely free from deposited salt. If manufacturers of crude would give their product ample opportunity to cool and settle in tanks before filling out into drums the fundamental cause for most of the dissatisfaction with glycerine analysis would be removed.

A. C. Langmuir

Chairman Sub-Committee on Glycerine Analysis

September 8, 1913

WHAT'S THE MATTER WITH THE AMERICAN CHEMIST?

Editor of the Journal of Industrial and Engineering Chemistry:

Judging from the answers one reads to the above question, Mr. Chemist is fast arriving. Some of the answers are amusing, some dramatic, and there are lamentation and pathos in others. The plaintiffs seem to be actuated by disposition, by training, by fitness, or by sarcasm. Surely, Mr. Chemist will come out of the crucible thoroughly refined at the end of the heat; but it seems to me that we are losing sight of viewpoints and are failing to differentiate between pure science and applied science.

Science is the study and correlation of phenomena and their interpretation, together with the formulation of laws. We have abstract science and we have concrete science. The former is not concerned primarily with matter; but the latter is. Chemistry lies between the two, and might be termed an abstract-concrete subject. Then we have pure chemistry and applied chemistry, and at the foundation of all work in chemistry we find *analysis*. All chemists are analysts of greater or less degree, depending upon the extent of their training, experience, and innate qualities. To speak in disparaging language of the *analyst* or the *analytical chemist* is to reproach the great and good men in the profession of chemistry, past and present. Such terms as "has-been" and "would-be" need no comment, except to say that it is far better to be a "good-old-has-been" than "a never-was" or "a never-will-be."

Then there is the term *research*. What does it mean? Is it a going after a nebular something floating about in the cosmos of chemistry? Some seem to think so, and such chemists I should term research chemists devoting their time and ability to pure chemistry *per se*. We shall always need such men; but these men must have private fortunes, or must be provided with funds by others. We need patrons of recluses. The work of the recluse is invaluable, and should be encouraged; but he must not forget the Latin phrase *per aspera ad astra*.

However, there is another meaning to *research*. Perhaps the word *inquiry* defines it. With this definition in mind, I should say that there is the research chemist who is searching along synthetical lines by means of analytical methods for the purpose of producing a given product, which product he has produced by abstract reasoning, for a given purpose. That is to say, the *end product to be* is predetermined, and its measure of value when found is *applicability*.

Research men fall naturally into one of the above categories; but some are so endowed as to fit either. Then again some fit one or the other by adaptability, an extremely valuable asset. Hence, we have two genera and four species of research chemists.

In considering the industrial phase of research chemistry, we are confronted with the fact that the manufacturer is not engaged in business as a recreation or as a philanthropic enterprise, but for the purpose of producing remunerative products. The German manufacturer does not employ a research chemist from *per se* motives; but for what he will or hopes to get from *results*. There is no lack of money in Europe or America or Canada or Mexico for the research man who can "deliver the goods;" but everybody fights shy, financially, of him who cannot present a reasonable demonstration of his ability to *find out* by *inquiry* through *research* some method to reduce cost or increase production or both, just as he fights shy of the novitiate in chemistry. High ambition and lofty ideals are right and just and commendable; but they are by no means confined to the research chemist in pure science *per se*. This type of chemist might and may bring about the results desired by the manufacturer, and we wish him every success and encouragement; but he is too great a risk for the manufacturer who is looking for an industrial research chemist. If the industrial research chemist is treated as a hireling, he is himself largely a fault, and the thing for him to do is to stop "kicking against the pricks" if he wishes to occupy a higher plane, *and there are many up there to-day*.

Perhaps I have been unfortunate in my professional dealings with research men and various enterprises for the past twenty odd years, and perhaps I "see through a glass darkly;" but I am convinced that "by their works ye shall know them," the research men in industrial chemistry.

J. CULVER HARTZELL

BLUE ASH, OHIO
September 11, 1913

ON CALCULATING THE FAT-FREE RESIDUE OF MILK

Editor of the Journal of Industrial and Engineering Chemistry:

In *Chem. Abst.*, 7, 2444, under "Foods," there is given a formula proposed by H. M. Höyberg for "Calculating the Fat-free Residue of Milk" [$(V + F)/4$ = fat-free dry residue], *Skand. Vet. Tidskrift*, 1912, 259–62; *Deutch. tierärztl. Woch.*, 21, 253.

It appears that the above formula was first suggested by Dr. S. M. Babcock as long ago as 1891 in the Eighth Annual Report of the Wisconsin Experiment Station for the year ending June 30, 1891, page 298. Dr. Babcock writes the formula $(L + F)/4$ = solids-not-fat, in which L = the Quevenne lactometer reading.

The Quevenne lactometer reading = V in Höyberg's formula since both = "a figure obtained by subtracting unity from the specific gravity and placing the decimal point after the first two numerals (neglecting O)."

During the year 1907, while comparing the per cent of solids of a very large number of chemical analysis of milk with the results secured by using different formulas for calculating the solids-not-fat after determining the Quevenne lactometer reading and the per cent of fat by the Babcock method, I noticed that when the per cent of fat was added to the Quevenne reading and the sum secured was divided by 4, the quotient equaled very closely the per cent of solids-not-fat secured by the chemical method. Then I developed the formula $(L + F)/4$ = the per cent of solids-not-fat. Before going further, I looked up the work done by others along this line and found that the formula was suggested by Dr. Babcock as stated above.

In 1909, along with other formulas commonly used, this one was published in the book: "Questions and Answers on Milk and Milk Testing," p. 68, by C. A. Publow and H. C. Troy, Orange Judd Company.

The formula is very simple and easy to apply and since three different chemists, working independently, have developed it and find it to give accurate results, it appears that it should have a permanent place in practical milk inspection and factory work where it is necessary to secure an approximately correct composition in the shortest possible time.

HUGH C. TROY

N. Y. STATE COLLEGE OF AGRICULTURE
CORNELL UNIVERSITY, ITHACA
September 18, 1913

NOTE ON COLORIMETRIC METHOD FOR TITANIUM IN IRON AND STEEL

In describing the procedure for determining titanium in steel when less than 0.02 per cent is present (THIS JOURNAL, 5, 735), I referred to the importance of conducting the ether separation so as to have small and nearly constant amounts of iron in the acid solutions. This essential condition is best attained by carrying out the ether separation in the following manner:

Cool the concentrated ferric chloride solution, pour into the separatory funnel, and wash with hydrochloric acid (2 parts strong acid : 1 part water) until the volume amounts to 25 cc. Add 50 cc. alcohol-free ether, agitate thoroughly, and allow to stand for five minutes after the two solutions have separated. Draw off the acid solution, avoiding the ether solution entirely even though a slight loss of acid solution may be necessary to do so. These precautions insure a greatly reduced and practically constant amount of iron in the acid solution.

CHAS. R. MCCABE

LIMA, OHIO
Sept. 19, 1913

PETROLEUM PRODUCTION IN 1912

GAIN OF TWO MILLION BARRELS

The great production of petroleum in 1911, which was 220,449,391 barrels, was equaled and passed in 1912, when the total reached 222,538,604 barrels. Higher prices were the rule in 1912 except in California, and even in that State there was no material decline. The total value therefore increased markedly, reaching $164,087,342, or 22.41 per cent above the value for 1911.

The greatest increase in quantity was in California, where the total advanced from 81,134,391 to 86,450,767 barrels, a gain of 5,316,376 barrels, or 6.55 per cent. Wyoming showed the remarkable gain of 742 per cent, from 186,695 barrels to 1,572,306 barrels, owing to the increased activity of the Mid-West Oil Co. and the Wyoming Oil Fields Co. Operations in northern Texas also more than offset the usual decline in the Gulf region and resulted in a significant gain for the State.

INCREASED EXPORTS

The volume of crude oil and of all the usual products exported from the United States increased, owing to the fact that foreign conditions were much more favorable to American exporters. Meanwhile the importation of gasoline from the East Indies was a favorable element in relieving the growing demand for this product on the Pacific coast.

DECREASED STOCKS

The improved conditions in the export trade and the increased capacity of the refiners to take care of the great yield of crude oil resulted in a marked decline in stocks in all fields except California, and even there the storage of petroleum was checked by an increase in consumption.

The total stocks of all crude oils at the beginning of 1912 aggregated 138,000,000 barrels. By the close of the year they had declined to 125,000,000 barrels, a decrease of about 10 per cent. The decline was greatest in the fields east of the Rocky Mountains, where on January 1, 1912, the stocks aggregated 94,000,000 barrels; they were reduced during the year to 79,000,000 barrels, a decrease of about 16 per cent.

This decline at once brought out a marked stimulation of prices all over the East, with a view to increasing the activity of drilling. Its effect was so marked, that the natural decline of the older fields was checked. Even Ohio showed a slight increase in production in 1912, for the first time in 12 years.

The total production by States is given below:

Quantity and Value of Petroleum Produced in the United States and the Average Price per Barrel in 1912

State	Quantity (barrels)	Value	Average price per barrel
California	86,450,767	$ 39,213,588	$0.454
Colorado	206,052	199,661	0.973
Illinois	28,601,308	24,332,605	0.851
Indiana	970,009	885,975	0.913
Kansas	1,592,796	1,095,698	0.688
Kentucky	484,368	424,842	0.877
Louisiana	9,263,439	7,023,827	0.758
New York	874,128	1,401,880	1.604
Ohio and Michigan	8,969,007	12,085,998	1.347
Oklahoma	51,852,457	34,957,612	0.674
Pennsylvania	7,837,948	12,886,752	1.644
Texas	11,735,057	8,852,713	0.754
Utah Wyoming	1,572,306	798,470	0.507
West Virginia	12,128,962	19,927,721	1.643
Total for 1912	222,538,604	164,087,342	0.737
Total for 1911	220,449,391	134,044,752	0.608

GOVERNMENT CONTROL OF CHILEAN MINERAL DEPOSITS

Consul Alfred A. Winslow, Valparaiso, reports that much interest is taken in the law just passed by both branches of the Chilean Congress which suspends the old mining code indefinitely, and which really means much for the future of Chile, since the mineral resources are its greatest attraction for foreign capital. It is understood that this is a result of heavy investments of American capital in copper and iron ore properties during 1912 and 1913, which will represent an expenditure of $15,000,000 to $20,000,000 when the respective plants have been completed. The new law provides that: (1) During the time the right of individuals to denounce iron mines is suspended, the State shall be authorized to make the necessary declaration and inscription of such deposits. (2) Such claims to have the superficial dimensions decreed by the President of the Republic, and possession to be taken in the usual way provided in case of individuals by the mining code, though the State shall not be obliged to start work within the term laid down in such cases. (3) The rights thus acquired by the State shall be in perpetuity, and no license or other rates shall be paid. (4) The mensuration and establishment of titles to be undertaken by the mining section of the Direction of Public Works. (5) All iron mines the property of individuals, the rights to which shall lapse through non-payment of the necessary taxes, shall revert directly to the State and shall not be sold by auction as provided in the mining code. (6) The President of the Republic is authorized to establish the regulations necessary for carrying out this law.

The *South Pacific Mail*, of Valparaiso, states the case quite clearly from the viewpoint of the Chilean: "The present mining code considers all metals wherever found as the property of the State, but grants the privilege of denouncing and staking out claims to individuals. The recent discoveries of rich extensive deposits of iron ores suitable for export in their primitive form led to the filing of many claims, in the hope of being able to pass them on later to foreign capitalists. As large tracts of valuable State lands were thus being taken possession of by individuals who had no intention of themselves working the mines, but merely wished to clear a commission on their sale, the right of denouncing and staking out claims as regards iron ores was indefinitely suspended.

It is understood that Government surveyors have already determined the existence of vast deposits of iron ore. These deposits will now definitely become State property on the payment in the usual terms of the surface value of the ground in cases where the land is privately owned. Government will, therefore, be in position either of reserving these supplies against the time when smelting works have been established in this country, or of treating directly with foreign syndicates for working the ore; and in either case the treasury will reap the benefit formerly accruing to the person who first denounced the claims, a solution which must be considered a just one, in view of the fact that the surveys are being carried on at Government expense."

One American company has acquired extensive deposits of rich iron ore that it is proposed to ship to the United States in large quantities, beginning with the opening of the Panama Canal, which will place a large tonnage at the disposal of American interests who are after business in this part of the world.

SCOTTISH OIL FUEL FOR BRITISH NAVY

Winston Churchill, the British Lord of Admiralty, estimates a probable annual output of 400,000 to 500,000 tons of oil fuel from Scottish shale fields for 150 years to come, if necessary. It is announced that the present output is about 250,000 tons. An Edinburgh writer states that "Scottish shale oil has proved, by repeated and prolonged tests, to be highly suitable for the purposes of the Admiralty, which in turn has shown a lively appreciation of the importance of having a reliable supply of the new fuel within easy reach."

PROGRESS OF ARTIFICIAL-SILK INDUSTRY

Consul William H. Hunt, St. Etienne, France, reports that processes for producing artificial silk continue to multiply. New means of rendering the silk strong, supple, and brilliant are constantly being discovered, and the industry has now attained a high degree of perfection.

The dry-weaving process, by which the solid thread is directly obtained, has replaced the use of coagulating liquids. In spite of this, nitrocellulose silk is disappearing from the market because it can not enter into competition with other artificial silks obtained by a simpler process and which are cheaper and more solid.

The first of these rival productions was obtained by dissolving cellulose in cupro-ammoniacal liquor. The difficulties encountered in this operation brought about the discovery of cellite, an acetyl cellulose, soluble in acetone, which might be employed for cinematograph films, being incombustible, were it not for its too great suppleness; it can be used for coating wood and metals for it does not crack. Another substance of the same nature is sericose, which is used for printing on calico.

The solidity of all artificial silks may be increased by treating them with formaldehyde, which operation is called "stheriosage."

The report just issued by La Soie Artificielle, Givet, discloses a net profit of $201,100, against $144,500 the previous year. The capital is $289,500.

CLAY PRODUCTS INDUSTRIES IN THE UNITED STATES IN 1912

The great magnitude of the clay-working industry of the United States is shown in a chart just issued by the United States Geological Survey. It shows a total value for 1912 of $172,811,275, an increase of $10,575,094 over 1911. These products include the several varieties of brick, drain and other tile, sewer pipe, terra cotta, pottery, fire brick, and other clay products, the various building bricks representing the greatest value, with a total of $73,425,819. The number of building bricks manufactured was 10,281,114,000.

Ohio led the States in the value of her clay products with an output amounting to $34,811,508, or over one-fifth the total production for the United States. Pennsylvania was second, with a production valued at $21,537,221; New Jersey third, with $19,838,533; and Illinois fourth, with $15,210,990. Eight states produced clay products in 1912 to a value exceeding $5,000,000 and 26 states to a value exceeding $1,000,000.

During 1912, pottery was produced to the value of $36,504,164, the increased value of the output for 1912 over 1911 being almost $2,000,000. Ohio was by far the largest producer in 1912, being credited with $15,508,735, and New Jersey was next, with over $8,000,000. Six states produced pottery to the value of more than $1,000,000.

BOOK REVIEWS

Iron and Steel, an introductory text-book for engineers and metallurgists. By O. F. Hudson, with a section on corrosion. By Guy D. Bengough. New York: D. Van Nostrand Co. 173 pp., 8vo, illustrated. $2 net.

This volume is one of a series entitled "Outlines of Industrial Chemistry," text-books, introductory to the chemistry of the national industries, edited by Guy D. Bengough, lecturer in metallurgy, Liverpool University. In the preface the author, who is lecturer in metallography, Birmingham University, states that the object has been to give the more important principles of the metallurgy of iron and steel in as short a manner as possible, omitting almost entirely the practical details of methods of production in order to lay more stress on the constitution of steel and cast iron and the effect of mechanical and heat treatment, corrosion being taken up in a special section. And the author has accomplished what he set out to do in a clear and concise manner, producing a very readable and interesting book for beginners.

The first chapter deals with the testing of iron and steel, stress being put on English methods; under impact tests, the Fremont machine might have been mentioned and under Hardness, the Shore scleroscope referred to.

The chapter on smelting of iron ores is rather short, the section on iron ores being poor; the magnetites of the Lake Superior district are emphasized, while the hematite deposits from the same locality are not mentioned. The description of the blast-furnace is rather too brief, and while the reactions in the upper part of the furnace are given at length, those of silicon, phosphorus, manganese and sulfur in the smelting zone are not given.

The brief description of the properties of cast iron is good, though the use of the word "eutectic" without a definition when describing the effect of phosphorus is probably an oversight.

The chapters on Foundry Practice, Malleable Cast Iron, Puddling, the Crucible, Bessemer and Open Hearth Processes are concise and clear. The statements that coke-fired crucible furnaces are most commonly used, that mild steel is not used for the charge, undoubtedly refer to English practice, for in this country the regenerative furnace is almost exclusively used and "melting bar" forms the basis of most charges. The same applies to the statement that the basic open hearth is used principally for mild steel. The Duplex process seems worthy of description.

The section on the mechanical treatment of steel is also short and clear, as is that on the impurities in steel, though the statement that since iron sulfide is fluid at ordinary rolling temperatures, it gives rise to red-shortness, even in small quantities, will not be accepted by all.

The chapter on the Constitution of Iron Carbon Alloys is specially well written and illustrated by excellent photographs, while that on heat treatment is also good. Annealing and refining are not distinguished.

The description of special steels is very clear and well written. The space devoted to analyses of high-speed tool steels, however, might better be used for a page of analyses of alloy steels in general.

The chapters on Steel Castings and Case-hardening and Welding are also good.

Section II, eighteen pages of material dealing with the corrosion of iron and steel, is clearly written and very interesting, but could have been much condensed and yet brought within the scope of the rest of the book. A critical discussion of the relative corrosion of wrought iron and steel would have been very timely.

Taken as a whole, the book is a good one, is well written in a clear, concise manner, and while it is in places written from the British point of view, it contains the main principles of interest to the general reader who is beginning the study of Iron and Steel from the standpoint of the engineer. The make-up of the book, paper, printing, etc., are good, the reproductions of the photomicrographs being exceptionally clear and sharp.

Wm. Campbell

Metallic Alloys: Their Structure and Constitution. By G. H. Gulliver. Second edition, revised, largely rewritten and greatly enlarged, 409 pages, 310 illustrations, 8vo. Price,

$3.25 net. London: Chas. Griffin & Co., Ltd. Philadelphia: J. B. Lippincott Co.

This is a very decided improvement on the first edition which made its appearance in 1908, and contained but 254 pages and 104 illustrations.

To quote from the preface: "The book obviously is not intended as a guide to the practical manufacturer of alloys, except in so far as a knowledge of the equilibrium conditions, and the unstable conditions of mixtures is of assistance in regulating their composition and heat treatment. It is addressed mainly to engineers and to students of engineering who desire some knowledge of the minute structure of metals and alloys, and of the manner in which the structure develops and changes."

The contents are: methods of investigation, physico-chemical equilibrium of mixed subst nces; binary alloys in which no definite chemical compounds are formed; binary alloys which show evidence of the formation of definite chemical compounds; transformations which take place in completely solid metals and alloys; equilibrium conditions in metallic mixtures; the structure of metals and alloys; the bronze, the brasses, and other alloys of copper; steel and other alloys of iron; alloys of more than two metals; the microscope in engineering practise; 245 references to the literature, and a rather complete index.

After showing that alloys are solutions and discussing the various theoretical considerations of equilibrium, by reference to typical curves and diagrams, the author proceeds to the classification of binary alloys, treating each class first theoretically and then by means of existing cases. Considerable space is devoted to recrystallization.

The reviewer was pleased to note the author's treatment of imperfect equilibrium, especially the diagram. To quote: "The simpler conditions of imperfect equilibrium are of very frequent occurrence, and are of considerable practical importance, though difficult to investigate with any degree of exactness, because the constitution of the mixture must be always somewhat indeterminate." Textbooks usually omit careful reference to the condition so often noticed in rapidly cooled alloys, a good illustration of which is the changes in the positions of the vertical or nearly vertical boundary lines between the different fields of the commercial brasses.

The discussion of chilling, annealing and vibration is interesting. In this connection the very important subject of *pouring temperature* is touched upon. "In castings which are allowed to cool gradually in the mould, the length of time occupied in solidification depends upon the pouring temperature of the metal, and the material of which the mould is made. A low pouring temperature and a mould of high heat conductivity means a chilled casting, while a high pouring temperature and a mould of low conducting power will allow of only slow solidification, followed by a more or less effective annealing; heating the mould is equivalent to decreasing its conductivity." This is an extremely important phase of alloy work and it is unfortunate that so little work has been done along this line, due, of course, to the lack of suitable pyrometers. The author has not, however, entirely covered the literature on the subject.

The chapter on "steel, and other alloys of iron" is much more complete than is usual in elementary books of this kind.

The final chapter on "The Microscope in Engineering Practise" is of considerable interest and importance, particularly to an engineer.

In the discussion of methods of investigation one would have liked to see more space given to the subject of pyrometers and particularly to furnaces, which is dismissed with one short paragraph.

On page 194 we read "the addition of lead to brass reduces the size of the crystals," with a reference to "The Tensile Strength of Copper-tin Alloys" by Shepherd and Upton, published in the *Journal of Physical Chemistry*, June, 1905. After a careful perusal of this reference the reviewer fails to find such a statement. Indeed the statement is in error, as lead up to about 1 per cent has very little effect upon brass, while in greater quantities it segregates in tiny globules, diminishing, of course, both the strength and ductility of the metal. If it reduced the size of the crystals the strength would thereby be increased, which is not the case.

On page 281 in the section on copper-aluminum alloys we read: "The only alloys of this series which have a commercial value are those containing more than 89 and less than 5 per cent of copper." And again on page 283, "it is not advisable to use more than 5 per cent of copper." These statements do not accord exactly with the facts, in actual practise, particularly in automobile work. While a copper-aluminum alloy, containing but 5 per cent of copper is used where a lower elastic limit is required, in crank cases requiring considerably more strength, an alloy containing 8 per cent copper is regularly used.

The book is clearly printed on good paper, the diagrams are clear and possess an excellent feature in that wherever several persons have worked upon a system, the results of all are plotted. The micrographs, the greater number of which have been prepared especially for this book, are very clear.

The references are assembled at the ends of the various chapters. This arrangement, the reviewer believes, is objectionable to the reader, unless he be unusually well acquainted with the book.

However, this book is an excellent elementary treatise and would make a very good addition to a library of one interested in alloys.

J. M. LOHR

Service Chemistry. By VIVIAN B. LEWIS AND J. S. S. BRAME. Fourth edition. London: Arnold; New York: Longmans. 1913, 8vo. Pp. 576 + xvi. Price, $4.20 net.

This is essentially a work on industrial and engineering chemistry. It differs from the standard books of that class in two ways. It pays little or no attention to matters not coming under the professional notice of officers of the army or navy. On the other hand, it does not appear to assume previous knowledge of the principles of the science, for it includes an introduction to the principles, and brief conventional accounts of the common elements and their compounds are scattered through the book.

The industrial material seems to be well selected, and in many instances the topic is discussed in much more detail than we should expect in a single volume. Thus combustion (17 pp.) deals at length with charcoal and coal, their state of division, their tendencies to spontaneous ignition, adsorptive powers, and so forth. The impurities in water and boiler incrustation each occupy a whole chapter. The chapter on fuel (36 pp.) discusses calorific values and the ways of measuring them, liquid fuel and machinery for its injection by steam, pressure alone, and air; internal combustion engines, the various fuels they use and the relative efficiencies of these fuels. Nitric acid, niter, and explosives, their manufacture and behavior, receive much detailed attention (100 pp.). Iron and steel, in relation to their uses in the services, occupy a long chapter (50 pp.). Alloys are discussed in two chapters, and excellent diagrams make the theory clear in each case. Corrosion and the means of preventing it, and a descriptive list of pigments close the volume.

As a condensed treatise on certain branches of applied chemistry, the book is up to date and practical, and the discussion is critical and instructive. The many suggestive remarks, and valuable and appropriate bits of information that are continually encountered, show that the authors have given much thought to the needs of students preparing for naval or military service.

It cannot be said that the authors are so successful in handling the fundamental matters which lead up to these applications. A chapter on galvanic batteries immediately following that on hydrogen necessarily involves the mention of many substances and reactions which have not yet been reached. There is evidence that the authors understand how to apply modern views to chemical problems, but they are not pedagogically very successful in introducing those views in the systematic portions of the book. The modern ideas are introduced, but the discarded views remain side by side with them, in a way that must confuse the student-reader very much. Molecules repel each other (p. 9) although the kinetic theory is correctly used a little later. Nascent hydrogen seems to infest all kinds of galvanic cells alike, although the ionic theory is used in the same connection. The electromotive series of the metallic elements appears correctly, except for the omission of hydrogen. The bald rule of precipitation makes its appearance, but the equilibrium between ionogens in solution is given without any cross-connection in the next paragraph.

The whole discussion of molecular weight is vitiated by an old fallacy—that an atomic weight in grams of "any gaseous element" occupies 11.16 liters at 0° and 160 mm. What about the five inert gases, not to speak of ozone, and the vapors of phosphorus, mercury and many other elements?

The section headed "chemical behavior" of hydrogen says that "its chemical behavior is such that it is often theoretically looked upon as being the vapor of a metal." This whole section should be clarified.

"The metallic elements end in *um*," not their names. Split infinitives are too frequent.

Saturation, water of crystallization, and efflorescence require more than two sentences among them, for the sake of clarity. The next section, that on "water of hydration" should be redistributed. It is composed of one statement about the union of the oxides of metallic elements with water. one on the transition points of ice, water, and steam, one on the influence of water on climate, and one on the high specific heat of water.

The book could be used for reference in high schools and colleges. The more interested pupils would find in it much information on practical subjects, which are barely touched upon in the ordinary text books. The book is well printed and copiously illustrated.

Alexander Smith

Liquid Air—Oxygen—Nitrogen. By Georges Claude. Translated by Henry E. P. Cottrell, with an afterword by the translator, and a preface by Dr. d'Arsonval. 418 pp. Published by Blakiston's Son & Co., Philadelphia. Price, $1.50

Georges Claude is the enthusiastic experimenter who refused to let any difficulties, particularly the great one of lubrication of cylinders at low temperatures, keep him from accomplishing the production of liquid air by expansion of compressed air behind the piston. The story of his persistent endeavor to develop this process, as opposed to the Hampson and the Linde processes, and his final success in making it the most efficient one for producing liquid air, is told in this book. Notable as was this achievement, in Claude's mind it was only one step toward the cheaper separation of oxygen and nitrogen from the air and the development of their use in chemical industry, so the book tells also the advances made by the author in the separation of oxygen from air by partial condensation and in methods of rectification of liquid oxygen.

While the presentation of the author's own accomplishments in their proper scientific and historical setting is the main theme of the volume, the whole subject of the liquefaction of gases and the separation of mixed gases by liquefaction and evaporation is quite fully set forth. The contents are in four parts: Part I on the elementary physics of the general subject and the historical steps from Faraday to the victory of Kamerlingh-Onnes over helium. This leads naturally into Part II, on the commercial liquefaction of air, in which both the theory and the practice are treated, particularly as to the relative advantages of the Linde process of expansion by simple outflow without useful work, on the one hand, and the Claude method of expansion with recoverable external work, on the other hand. Part III is an entertaining trio of chapters on the preservation and properties of liquid air. Part IV is on the separation of air into its elements, which is the commercially important process to which liquefaction is preliminary.

A detailed discussion of the various rectification processes of Linde, Levy, Heilbronner and Claude is given. For his latest machines, as manufactured by the *Societe l'Air Liquide*, the author claims the possibility of separating 1.5 cu. m. of oxygen per horse-power hour.

Interesting throughout, Parts II and IV contain most valuable information for all who need to keep up with the progress of the liquid air and oxygen industry. It is to be regretted that there could not have been in the same volume a treatment of the remarkable accomplishment of Claude in the recovery by refrigeration of the vapors of volatile liquids which otherwise go to waste in many manufacturing operations.

The book, except in the more theoretical parts, is written in the style of the popular lecture, which has made it all the more difficult for the translator to conceal the fact that the book was written in French, rather than in English. Errors that appear in the text are amusing, rather than important.

George B. Pegram

Disinfection and Disinfectants. By M. Christian. Physician in Chief, Royal Institute for Infectious Diseases, Berlin. Translated from the German by Charles Salter with eighteen illustrations. London: Scott, Greenwood and Son, 8 Broadway, Ludgate, E. C. 1913.

Any attempt to cover all aspects of the subject of disinfection and disinfectants within the compass of 100 pages would, of course, be a hopeless task, and the author of this little work has not made any such attempt. The volume confines itself substantially to a review of the fundamental principles underlying disinfection, together with a brief résumé of disinfectants in common use and apparatus used in their connection. A rather disproportionate amount of space is given to detailed descriptions of specific forms of the latter.

The book is divided into four chapters, the first of an introductory character, giving a general review of the methods of transmission of disease. The second chapter describes the principles and methods of disinfection by physical means, including dry heat, steam, hot liquids, light and other rays, and electricity. Chapter three takes up the subject of chemical disinfection, while Chapter four concludes with descriptions of combinations of systems of disinfection, together with illustrations and descriptions of specific apparatus.

The book being originally a German work which has been translated and published in England, the apparatus and methods described differ in many respects from those in use in this country. The whole work is elementary in its character and does not make any attempt to go deeply into the scientific aspects of the subject. The matter of testing the potency of disinfectants by laboratory tests is barely touched upon, the one method given being rather primitive in its character.

The book should prove a useful and interesting little manual for those whose work requires some knowledge of disinfection, but who have not the time or inclination to make a special study of the subject. The text is clear and free from typographical errors.

J. A. Deghuée

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Sulfite Digesting Liquor, Tests for. By Goesta von Zweigbergk. *Paper*, Vol. 12, 1913, No. 13, pp. 15–17.

Sulfur Trioxide, Determination of, in Sulfur and Pyrite Roasting Furnaces. By E. Richter. *Pulp and Paper Magazine of Canada*, Vol. 11, 1913, No. 13, pp. 445–447.

Water, Lime Sterilization of. By Charles P. Hoover and Russell D. Scott. *Engineering Record*, Vol. 68, 1913, No. 10, pp. 257–259.

Water Purification. By George W. Fuller, *et al.* *Engineering Record*, Vol. 68, 1913, No. 11, pp. 293–294.

Wood, The Preservation of, by Cyanization. By Friedrich Moll. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 67, pp. 459–463.

RECENT INVENTIONS

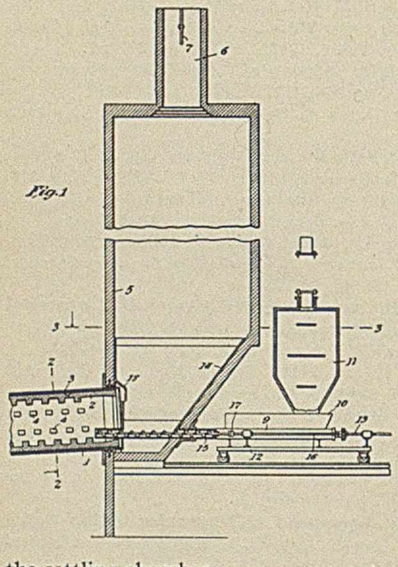
By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Manufacture of Oxalates. L. W. Andrews, June 24, 1913. U. S. Pat. 1,065,577. A mixture of sawdust and alkali is placed in a closed vessel. Superheated steam under low pressure is introduced into the vessel and heat is applied to the exterior of the vessel.

Purifying Vanadium. W. F. Bleecher, June 24, 1913. U. S. Pat. 1,065,582. A lead salt is added to an acid solution containing vanadium and impurities. An alkaline carbonate is then added until lead vanadate is precipitated. This is treated with sulfuric acid, producing lead sulfate and an acid solution of vanadium free from impurities.

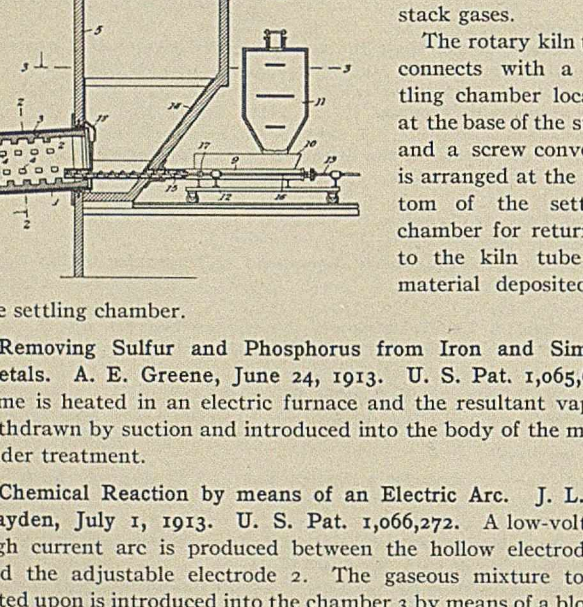
Cement-burning Kiln. T. A. Edison, June 24, 1913. U. S. Pat. 1,065,597. The furnace is designed to effect economics in the fuel burned by reducing the temperature of the stack gases and to reduce the loss due to the carrying off of unburned material in the stack gases.

The rotary kiln tube connects with a settling chamber located at the base of the stack and a screw conveyor is arranged at the bottom of the settling chamber for returning to the kiln tube the material deposited in the settling chamber.

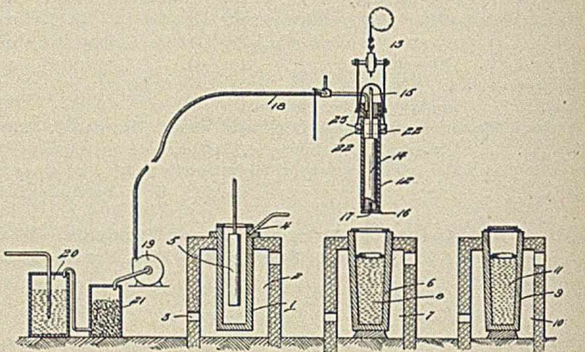


Removing Sulfur and Phosphorus from Iron and Similar Metals. A. E. Greene, June 24, 1913. U. S. Pat. 1,065,605. Lime is heated in an electric furnace and the resultant vapors withdrawn by suction and introduced into the body of the metal under treatment.

Chemical Reaction by means of an Electric Arc. J. L. R. Hayden, July 1, 1913. U. S. Pat. 1,066,272. A low-voltage high current arc is produced between the hollow electrode 1 and the adjustable electrode 2. The gaseous mixture to be acted upon is introduced into the chamber 3 by means of a blower at a sufficient pressure to produce a high velocity gaseous current through the copper tube 6. The gases are acted upon while passing through the arc and are immediately cooled below the dissociation point of the product of the reaction by contact with the walls of the tube 6.



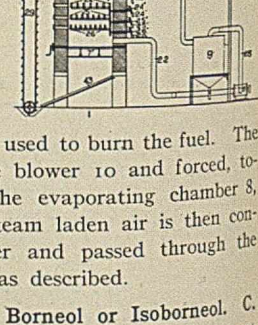
Producing Clad Metals. W. M. Page, July 1, 1913. U. S. Pat. 1,066,312. A billet of steel is first treated to give it a clean surface and then heated in an atmosphere of steam to produce a thin layer of oxid. The billet is then dipped into molten copper which causes the oxid and underlying carbon to react to produce pure iron with which the copper can unite. The billet with cohering film of copper is then removed, the manipulation being conducted in an atmosphere of producer gas freed from carbon dioxid and oxygen.



Producing Citric Acid. B. Zahorski, July 1, 1913. U. S. Pat. 1,066,358. A culture of fungus *Sterigmatocystis nagra* is cultivated in a culture medium containing about 15 per cent of citric acid and a sugar solution is inoculated with the culture, the growth of the fungus being allowed to proceed in the solution to produce citric acid therein.

Producing Soluble Albumin Powder. R. Bass, July 1, 1913. U. S. Pat. 1,066,364. Cooked meat is hydrolyzed with ammonia and water at a temperature of 102° to 107° C. The temperature is reduced to 45° C. and calcium hydroxid is added. The temperature is then raised to 90° to 100° C. and soda lye is added after which the soda is neutralized with hydrochloric acid.

Hydrating Lime and Utilizing Heat of Hydration. H. L. Doherty, July 8, 1913. U. S. Pat. 1,066,719. In this process limestone is charged into the top of the kiln and the lime produced passes into the hydrating chamber 5, where it is subjected to the action of current of air mixed with sufficient steam to hydrate the lime. The air, heated by the heat developed by the reaction, is divided into two currents, one passing up through the kiln in contact with the hot lime in the cooler 3, where it is further heated and then into the combustion zone 2, where it is used to burn the fuel. The other current is withdrawn by the blower 10 and forced, together with fresh air, through the evaporating chamber 8, where it takes up water. The steam laden air is then conducted into the hydrating chamber and passed through the lime, where the steam is utilized as described.



Manufacture of Camphor from Borneol or Isoborneol. C. Ruder, July 8, 1913. U. S. Pat. 1,066,758. A neutral solvent is added to a mixture of borneol and chromic acid in quantities such that the temperature does not rise above 25° to 30° C.

Refining Shellac, Etc. H. Cassard, July 8, 1913. U. S. Pat. 1,066,794. Shellac is subjected to the dissolving action of alcohol. There is then added a hydrocarbon solvent for the wax and the two solutions mixed homogeneously at a temperature above the melting point of the wax. The two solutions are allowed to settle in layers at this temperature and separated.

Smelting Iron Ores. F. M. McClenahan, July 8, 1913. U. S. Pat. 1,066,833. Aluminiferous iron ore is smelted in the presence of sodium chlorid as the fixing agent.

Producing Carbon or Lampblack. G. Fernekes, July 8, 1913. U. S. Pat. 1,066,894. A stream of methane is passed into a zone of sufficient temperature (above 1300° C.) to immediately dissociate the gas into carbon and hydrogen.

Making Fertilizer. O. K. Slater, July 8, 1913. U. S. Pat. 1,067,224. A mixture of slag and phosphatic minerals is softened and disintegrated by subjecting it to the action of steam under pressure. It is treated with sulfurous fumes while still moist and then acted upon by ammonia gas.

Varnishes. L. Meunier, July 15, 1913. U. S. Pat. 1,067,536. A concentrated solution of tannin in water is mixed with neutral sulforicinate of soda and highly rectified turpentine.

Manufacture of Formaldehyde. M. J. Kusnezow, July 15, 1913. U. S. Pat. 1,067,665. A mixture of methyl alcohol vapor and air is passed over heated metallic silver.

Non-Inflammable Cellulose Compound. W. G. Lindsay, July 15, 1913. U. S. Pat. 1,067,785. The composition contains acetyl cellulose in acetone, urea, triphenylphosphate and acetone.

Hydrogenated Fatty Food Product. C. Ellis, July 22, 1913. U. S. Pat. 1,067,978. This is a composition of lard-like consistency comprising hydrogenated corn oil of viscous consistency and an edible fatty material which may be hydrogenated cottonseed oil.

Manufacture of Malt. R. Wahl, July 22, 1913. U. S. Pat. 1,068,028. Lactic acid is added to malt during its manufacture.

Decomposition of Fats and Oils. B. E. Reuter, July 22, 1913. U S. Pat. 1,068,079. Glycerides are decomposed into glycerin and acids by successively heating emulsions of the charge with different restricted portions of a sulfo-fatty acid catalyzer, each portion being insufficient to effect complete decomposition, and removing the aqueous solution of glycerin and spent reagent.

Treating Carbon and Apparatus Therefor. W. A. Smith, July 29, 1913. U. S. Pat. 1,068,707. The body of carbon or carbonaceous material to be treated is moved progressively through a heating zone established by causing induced currents of electricity of suitable amperage to traverse the body of the charge or an appropriate resistor in contact with the charge, but not necessarily in a direction transverse to the direction of movement of the charge.

Fig. 1

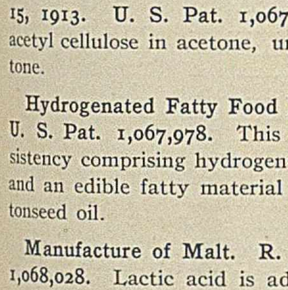
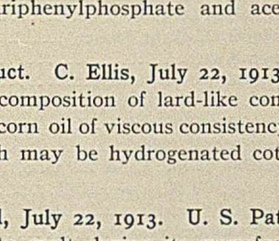


Fig. 2



Roasting Ores and Recovering Zinc. C. J. Reed, Aug. 5, 1913. U. S. Pat. 1,069,178. Zinc sulfid ore is mixed with a previously oxidized portion of the same material and heated in an oxidizing atmosphere. The soluble zinc compounds are dissolved and the zinc recovered from the solution.

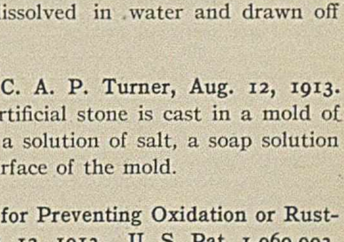
Electrolytically Refining Copper. G. D. Van Arsdale, Aug. 5, 1913. U. S. Pat. 1,069,305. Metallic copper is dissolved from an anode thereof in an electrolyte containing soluble cuprous sulfite and deposited upon a cathode.

Steel Process. J. Churchward, Aug. 5, 1913. U. S. Pat. 1,069,387. This process is based upon the idea that carbon has an astringent effect upon steel, tending to make the particles or fibers of the metal assume a globular form, in consequence of which certain valuable characteristics of the steel are diminished, and that this astringent capacity of carbon may be removed by maintaining it at 3100° F. for a certain time. Steel subjected to this temperature for from twenty-five to forty minutes is stated to have a compact, integral, fibrous structure resembling that of wood.

Treating Sulfid Ores. Titus and Barenscheer, Aug. 5, 1913. U. S. Pat. 1,069,498. Sulfid ores of metals whose chlorids are readily fusible such as zinc sulfid, are mixed with sodium chlorid, heated and exposed to the action of chlorin.

Manufacture of India-Rubber Goods. W. E. Windsor-Richards, Aug. 5, 1913. U. S. Pat. 1,069,508. Cellulose is mixed with india-rubber at a temperature of about 200° C. and the mixture vulcanized.

Separating Barytes from Ores. C. J. Greenstreet, Aug. 5, 1913. U. S. Pat. 1,069,545. Barytes is separated from zinc and barytes ores by mixing sodium chlorid therewith and heating in a crucible to a sufficient heat to melt the sodium chlorid. The melted sodium chlorid dissolves the barytes and rises to the top of the crucible from which it may be drawn off. The sodium chlorid is then dissolved in water and drawn off from the insoluble barytes.



Making Artificial Stone. C. A. P. Turner, Aug. 12, 1913. U. S. Pat. 1,069,832. The artificial stone is cast in a mold of sand previously treated with a solution of salt, a soap solution having been applied to the surface of the mold.

Treatment of Iron or Steel for Preventing Oxidation or Rusting. F. R. G. Richards, Aug. 12, 1913. U. S. Pat. 1,069,903. A rust-preventing deposit of manganese and iron phosphate is formed by subjecting the iron or steel to the action of manganese dioxid and phosphoric acid.

Therapeutic Compound and Process of Making the same. E. Hug, Aug. 12, 1913. U. S. Pat. 1,069,951. Erythrene is heated under pressure until a caoutchouc-like substance is produced.

Process of Obtaining Thorium. M. Koss, Aug. 12, 1913. U. S. Pat. 1,069,959. Thorium is obtained by acting upon monazite with sulfuric acid and treating the product with hypophosphoric acid.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF SEPTEMBER, 1913

ORGANIC CHEMICALS

Acetanilid	Lb.	21	@	23
Acetic Acid (28 per cent)	C.	2.00	@	2.15
Acetone (drums)	Lb.	15¾	@	16¾
Alcohol, denatured (180 proof)	Gal.	36	@	39
Alcohol, grain (188 proof)	Gal.	2.48	@	2.50
Alcohol, wood (95 per cent)	Gal.	45	@	47
Amyl Acetate	Gal.	2.20	@	2.30
Aniline Oil	Lb.	10⅛	@	10⅝
Benzoic Acid	Lb.	23	@	27
Benzol (90 per cent)	Gal.	21	@	23
Camphor (refined in bulk)	Lb.	42½	@	44
Carbolic Acid (drums)	Lb.	9	@	11½
Carbon Bisulfide	Lb.	6½	@	8
Carbon Tetrachloride (drums)	Lb.	7¾	@	8¼
Chloroform	Lb.	25	@	35
Citric Acid (domestic), crystals	Lb.	52	@	52½
Dextrine (corn)	C.	3.12	@	4.00
Dextrine (imported potato)	Lb.	6	@	7
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	19½	@	20
Oxalic Acid	Lb.	7⅞	@	8
Pyrogallic Acid (bulk)	Lb.	1.20	@	1.40
Salicylic Acid	Lb.	28	@	30
Starch (cassava)	Lb.	3¼	@	4
Starch (corn)	C.	2.34	@	3.00
Starch (potato)	Lb.	4½	@	5
Starch (rice)	Lb.	8	@	9
Starch (sago)	Lb.	2⅜	@	2¾
Starch (wheat)	Lb.	5¼	@	6½
Tannic Acid (commercial)	Lb.	35	@	36
Tartaric Acid, crystals	Lb.	30¼	@	31¾

INORGANIC CHEMICALS

Acetate of Lead (brown, broken)	Lb.	7¾	@	8
Acetate of Lime (gray)	C.	2.50	@	2.60
Alum (lump)	C.	1.75	@	2.00
Aluminum Sulfate (high-grade)	C.	1.25	@	1.75
Ammonium Carbonate, domestic	Lb.	8	@	8½
Ammonium Chloride, gray	Lb.	5⅞	@	6⅛
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	3.17½	@	3.50
Barium Chloride	C.	1.60	@	1.80
Barium Nitrate	Lb.	5¼	@	5½
Barytes (prime white, foreign)	Ton	19.00	@	23.50
Bleaching Powder (35 per cent)	C.	1.25	@	1.30
Blue Vitriol	Lb.	5⅛	@	5½
Borax, crystals (bags)	Lb.	3¾	@	4¼
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Bromine, bulk	Lb.	30	@	35
Calcium Chloride, fused	C.	85	@	1.10
Chalk (light precipitated)	Lb.	4	@	4½
China Clay (imported)	Ton	nominal		
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign	Ton	16.00	@	17.00
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.55	@	3.60
Lead Nitrate	Lb.	8⅜	@	8⅝
Litharge (American)	Lb.	6¾	@	7
Lithium Carbonate	Lb.	65	@	70
Magnesia (powdered)	Lb.	5½	@	6
Magnesite (raw)	Ton	30.00	@	35.00
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphoric Acid (sp. gr. 1.75)	Lb.	21½	@	25½
Phosphorus	Lb.	45	@	1.00
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°	Lb.	6¾	@	7
Potassium Bromide	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%	C.	3.40	@	3.65
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Cyanide (bulk), 98–99%	Lb.	19	@	24
Potassium Hydroxide	C.	4.75	@	5.25
Potassium Iodide (bulk)	Lb.	2.95	@	3.00
Potassium Nitrate (crude)	Lb.	4¾	@	5
Potassium Permanganate (bulk)	Lb.	9¾	@	10
Quicksilver, Flask (75 lbs.)		40.00	@	—
Red Lead (American)	Lb.	7	@	7⅛
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	38	@	40
Soapstone in bags	Ton	10.00	@	12.00
Soda Ash (48 per cent)	C.	55	@	65
Sodium Acetate	Lb.	4	@	4½
Sodium Bicarbonate (domestic)	C.	1.00	@	1.10
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	4½	@	5
Sodium Carbonate (dry)	C.	60	@	80
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Hydroxide, 60 per cent	C.	1.47½	@	1.52½
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot	C.	2.40	@	2.45
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
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.	11¾	@	12
Tin Oxide	Lb.	46	@	48
White Lead (American, dry)	Lb.	5¾	@	6
Zinc Carbonate	Lb.	9	@	10
Zinc Chloride (granulated)	Lb.	4½	@	5
Zinc Oxide (American process)	Lb.	5⅜	@	6⅜
Zinc Sulfate	Lb.	2½	@	3

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	42	@	45
Black Mineral Oil, 29 gravity	Gal.	13½	@	14
Castor Oil (No. 3)	Lb.	8⅞	@	10
Ceresin (yellow)	Lb.	12	@	22
Corn Oil	C.	6.65	@	6.70
Cottonseed Oil (crude), f. o. b. mill	Gal.	43	@	43½
Cottonseed Oil (p. s. y.)	Lb.	7½	@	8
Cylinder Oil (light, filtered)	Gal.	21½	@	32
Japan Wax	Lb.	9	@	9½
Lard Oil (prime winter)	Gal.	95	@	97
Linseed Oil (double-boiled)	Gal.	50	@	51
Menhaden Oil (crude)	Gal.	31	@	35
Neatsfoot Oil (20°)	Gal.	98	@	1.10
Paraffine (crude, 120 & 122 m. p.)	Lb.	3½	@	3¾
Paraffine Oil (high viscosity)	Gal.	26	@	28
Rosin ("F" grade)	Bbl.	4.30	@	4.35
Rosin Oil (first run)	Gal.	27	@	31
Shellac, T. N.	Lb.	23½	@	24
Spermaceti (cake)	Lb.	30	@	35
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Spindle Oil, No. 200	Gal.	18	@	19
Stearic Acid (double-pressed)	Lb.	8½	@	10½
Tallow (acidless)	Gal.	63	@	65
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	42	@	42½

METALS

Aluminum (No. 1 ingots)	Lb.	22½	@	23
Antimony (Hallet's)	Lb.	7¾	@	8½
Bismuth (New York)	Lb.	2.05	@	2.10
Bronze powder	Lb.	50	@	3.00
Copper (electrolytic)	Lb.	16⅔	@	—
Copper (lake)	Lb.	16⅞	@	—
Lead, N. Y.	Lb.	4.75	@	—
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	43.50	@	44.50
Silver	Oz.	61	@	62
Tin	C.	42.00	@	43.00
Zinc	C.	5.80	@	5.90

FERTILIZER MATERIALS

Ammonium Sulfate	C.	3.05	@	3.10
Blood, dried	Unit	2.85	@	—
Bone, 4½ and 50, ground, raw	Ton	27.50	@	28.00
Calcium Nitrate (Norwegian)	C.	2.05	@	2.10
Castor meal	Unit		3.10	
Fish Scrap, domestic, dried	Unit	3.00	&	10
Mowrah meal	Ton	nominal		
Phosphate, acid, 16 per cent bulk	Ton	—	@	6.75
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	3.00	@	3.25
Tennessee, 70–80 per cent	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent	Ton	38.55	@	—
Pyrites, furnace size, imported	Unit		0.13⅛	
Tankage, high-grade	Unit	2.72½	@	2.75 & 10