

## REVIEWS.

### RECENT PROGRESS IN INDUSTRIAL CHEMISTRY.<sup>1</sup>

BY JOHN D. PENNOCK.

Received July 9, 1906.

IN his address delivered before the Congress of Applied Chemistry, held in Berlin in 1903, Mr. Ernest Solvay drew a striking picture of the fall of the LeBlanc soda process before the more economical ammonia soda process, showing year by year from 1870 to the present the constant lessening of one and the constant progression of the other, until in 1903 the world's production by the ammonia soda process was 1,610,000 tons, and 150,000 tons by the LeBlanc, while in 1873, twenty years before, there were produced by the LeBlanc process 447,000 tons, and only 2,600 tons represented the yearly production of ammonia soda.

Though the production of soda ash was then greatly curtailed, the LeBlanc works by no means had to close their doors, for while by the ammonia process, soda ash could be produced at a much less cost than by the LeBlanc process, there was not so great a difference in the cost of caustic soda as made by the two processes, and while the chlorine, combined with the sodium, the fundamental reagent in both processes, appeared in the LeBlanc process as a decidedly valuable by-product in the form of bleaching-powder, in the ammonia process it appears as calcium chloride, a practically waste product.

Naturally there are many uses to which calcium chloride may be put and for which a small financial return may be obtained, such as a drying agent for air, for refrigerating purposes in the place of brine, for cooking solution in the canning industry, for wall plaster in the Cappon process, and the seasoning of Portland cement, etc., but the sum of all these uses amounts to but a very small percentage of the total calcium chloride produced.

Therefore the mainstay, the prop that has kept the LeBlanc works from utter ruin, is the by-product chlorine, available and salable at a good price in the form of hydrochloric acid or bleaching-powder.

While the ammonia soda process has completely captured the soda ash market, it was expected that electrolytic methods would soon take possession of the bleach market. This assumption was not immediately realized; it required the expenditure of much capital and the failure of many companies before success was achieved, and only within the last year or two could it with certainty be said that electrolytic caustic soda and bleach have been established for all time. But the returns for last year's business indicate that there are at least two factories in England

<sup>1</sup> Read at the Ithaca Meeting of the American Chemical Society.

making a profit, namely, the Castner Kellner Alkali Co. (mercury process), which showed a profit of \$250,000 for 1905, and the Electrolytic Alkali Co. (diaphragm process), which claimed a profit of \$30,000. While the success of these two companies proves that electrolysis of sodium chloride is commercially profitable, the comparison of the returns of these two processes is also indicative of the superiority of the mercury process over the diaphragm process. This superiority is likewise shown in Europe and in the United States.

Hasenclever, at the head of the LeBlanc process in Germany, takes a pessimistic view of the future of the LeBlanc soda industry. He claims one-half the world's production of bleach, 260,000 tons, is made by electrolytic processes.

	Electrolytic. Per cent.	LeBlanc. Per cent.
Germany produces bleach.....	65	35
England.....	18	82
France.....	19	81
United States.....	100	0
Austria.....	66	34

Hasenclever says the only hope of the LeBlanc process lies in the discovery of new uses for sulphate and on the growth of the new sulphur dye industry.

Kershaw, on the other hand, when he studied the financial return of \$1,500,000 made by the United Alkali Co., of England, for 1905, puts a more rosy aspect on the future of the LeBlanc works, but he must remember that the profits of this company came not so much from soda ash, caustic and bleach as from the various other chemicals which they produce in addition to the regular products. He too, like Hasenclever, concludes that while there will be some business in soda ash and bleach, their chief profits will come from the manufacture of sulphuric acid, sodium sulphate, hyposulphite, sulphite and other sulphur salts which cannot be made by the processes of either of their rivals.

That but meagre profits are on the whole being obtained in electrolytic soda operations is indicated by the recent tendency the world over to divert the chlorine from bleach into various other lines where better prices may be obtained, such as tin crystals, pure hydrochloric acid by combustion of the chlorine and hydrogen, carbon tetrachloride, and mono- and dichlorbenzene.

The world is in search of a solvent that is cheap and at the same time non-inflammable for use in paints, rubber manufacture, wool washing, etc. Carbon tetrachloride possesses the necessary properties and consequently many investigators are at work endeavoring to devise some cheap method for producing it.

As carbon tetrachloride contains 92 per cent. of chlorine and chlorine can not be made at less than 2 cents per pound, the chlorine alone will bring the cost of carbon tetrachloride to at

least 30 cents per gallon, while the cost of the operation will be as much more.

By the Taylor electric furnace, carbon disulphide may be made in large quantities very cheaply, and with this by the old process, carbon tetrachloride may be more cheaply made than formerly.

Another outlet for electrolytic chlorine is monochlorbenzene, which is a good solvent, having a freezing-point of  $-45^{\circ}$ , boiling-point of  $132^{\circ}$ , and sp. gr. of 1.1125, and which may readily be formed according to Beilstein by passing chlorine into benzene heated to  $50-60^{\circ}$  in the presence of aluminium chloride as a catalyzer.

L. E. Andes (*Chem. Ztg. March*, 1906), on studying the properties of mono- and dichlorbenzene, finds them to have very desirable properties as solvents. Dichlorbenzene distils at  $173^{\circ}$ ; it leaves, on evaporation, no odor or residue. One hundred grams each of monochlorbenzene, dichlorbenzene and turpentine were exposed to the air for fifty hours; 14 grams of dichlor-, 80 grams of monochlorbenzene and 32 grams of turpentine had evaporated. Both mono- and dichlorbenzene can be mixed in all proportions with drying oils, and can often replace turpentine.

Carbonate saponification of fatty acids instead of caustic treatment of neutral fats is meeting with considerable favor in Europe and is quite extensively used, whereas in the United States, thus far, but little progress has been made in that line. It is undoubtedly destined some time to reduce very largely the use of caustic soda for soap-making. One inventor has recently suggested using the crude bicarbonate from the ammonia soda process before drying, but it would appear rather impracticable on account of the ammonia present in the bicarbonate, as it would require condensing apparatus to prevent ammonia loss, which the soap-maker would hardly like to undertake. But carbonate saponification has advantages, chief among them the following:

First, the glycerol need not be dragged through the entire process of boiling as in the saponification of neutral fats. Second, the yield of glycerol is larger. Third, saponification by carbonates is cheaper, as the price of carbonate of soda is much less than that of caustic soda. So far as the process of saponification is concerned, it is immaterial whether the fatty acids employed are obtained by the use of the autoclave, by high or by low pressure, or by the open-kettle methods, such as the sulphuric acid process, the Twitchell process, the fermentative fat-splitting process, or Krebitz', a lime method. The main point is that the fatty acids shall be pure and of high percentage.

The Frasch nickel ammonia process for the manufacture of caustic soda would parallel the ammonia process for carbonate of soda, but in addition to the expensive reagent ammonia, nickel is also required.

By this process nickel hydroxide is added to a saturated solution of ammonia and brine and upon agitation a nickel ammonium chloride separates out and the caustic soda is formed in solution. The double salt, after filtration, is treated with lime, the ammonia evolved and the nickel precipitated in the form of hydroxide ready for use again.

The enzymic fermentation process for the production of fatty acids, due to the work of W. Coustin and his co-workers, as carried out in a working trial in Berlin, has proved a success. The enzyme of the castor oil seed has proved most active. A mixture of 50 pounds cotton oil, 34.5 pounds castor oil seeds, 3.3 pounds water and 2.5 pounds acetic acid, at a temperature between 70° and 104°, showed after three hours 42 per cent., and in twenty-four hours 90 per cent. of fatty acids. This ready elimination of fatty acids and separation of glycerol combined with saponification with carbonates is of great importance to the soap industry.

By-product coke ovens thus far have been built horizontally, but the process of G. J. Arts, recently patented, makes use of a vertical retort. The retort is cylindrical and the heating flues encircle the retort spirally. The coal is charged in at the top and discharged continually, dropping at the bottom into a closed boiler containing water for quenching. A higher yield of by-products and a higher illuminating value for the gas is claimed for the process since the ascending gases pass through a continually cooling zone, whereas in the horizontal by-product oven the gas carrying its benzene illuminants and ammonia passes over a hot bed of coke at about 1000°, where a certain amount of the ammonia is decomposed and where benzene is broken down into naphthalene. Another important point claimed for the process is that the steam evolved from incandescent coke rising through the mass further reduces the sulphur and phosphorus in the coke and at the same time produces a certain amount of water-gas. (*J. Gas Lighting*, May 22, 1906, pp. 519.)

All England is greatly agitated at the present time over the smoke nuisance; the bringing of the offending industrial operator to the court of justice is a daily occurrence in the manufacturing districts.

The rapid development of the coke oven, the Mond and the Loomis-Pettibone producers supplying gas for gas engines and as a cheap domestic fuel, will in the future do much toward reducing the uneconomical and smoke-producing process of direct combustion fuel.

Over 150,000 boiler horse-power capacity of Loomis-Pettibone plants in connection with gas engines have been installed and are now in operation in this and foreign countries.

It is interesting to note that the Union Carbide Co., which thus far has had an entire monopoly in the carbide business, is likely to have a competitor in the Hartenstein process which is in

operation at Constantia, Michigan. By this process carbolite, the name given to the carbide of a stone or flint-like structure, is obtained, which is not objectionably porous, not so hygroscopic and does not yield the percentage of fines that the present carbide does.

The recent activity in the utilization of peat in this country has demonstrated that the briquetting of peat for fuel purposes cannot be economically done. The conversion of peat into gas in producers, and using the gas for power in gas engines, promises to be successful. Certain grades of peat are making a cheap quality of paper. At Capac, Michigan, with a plant working the patented process of C. Esser (Patents No. 690,363, December 31, 1901, and No. 771,202, September 27, 1904) satisfactory results are obtained.

Ethyl alcohol to be used in the arts may be obtained free from tax after January 1, 1907, and it will be necessary to use some sort of a denaturator. In Germany (Fifth International Congress für Angewandte Chemie, Vol. II, p. 560) denatured alcohol is classed as "complete" or "incomplete." To produce "complete" denaturation 2.5 per cent. of a solution made by 4 liters of wood alcohol and 1 liter of pyridine is added to 100 liters of alcohol. "Incomplete" denaturation is the treating of the alcohol for a certain specific use, for instance, alcohol for use in rubber goods, is treated with shellac; for celluloid with camphor, etc.

France uses wood alcohol which must contain 25 per cent. acetone and 2.5 per cent. of empyreumatic compounds. Also heavy benzene, 150° to 200°, and other substances for special purposes.

Austria uses the same denaturators as Germany.

Switzerland uses 2.9 per cent. of a solution made up of 70 per cent. acetone, 10 per cent. pyridine, 10 per cent. solvent naphtha and 10 per cent. of the last runnings of wood alcohol distillation.

The few chemical processes and problems which my limited time has permitted me to touch upon thus far dwindle into insignificance when compared with that subject which of late has occupied the attention of many investigators; namely, the "fixation of nitrogen" in a form suitable for fertilization of vegetable growths. One can with difficulty name a subject of greater importance for future generations of mankind as well as our own than that which has to do with the supplying of food for the rapidly increasing population of the world. Any process for the production of nitrogenous substances convertible into vegetable tissue when mixed with the soil, should be hailed with delight. The cost of manufacture by such a process may at the present be so great as to preclude operating in competition with the present sources of supply, but the time will certainly come, if the process is technically possible, when conditions will so change

that the costly process of to-day will be the cheap process of to-morrow. Many of the important industrial operations of to-day, founded on reactions discovered generations ago, were successfully established only after sufficient advance in engineering and the arts in general made them possible. The reaction often remains dormant until the accumulated thought and experience of patient investigators, who perhaps have failed, but nevertheless have added one link in the chain of experience, ultimately brings commercial success. Humphry Davy, seventy-five years ago, demonstrated the results of electrolysis of sodium chloride, but it was many years before the dynamo made it commercially profitable.

The rise of the ammonia soda process offers another example. The basal reaction of the process was placed by Fresnel in competition with LeBlanc's before the French Tribunal, but was rejected because at that time no method for the recovery of ammonia was known. From that time until 1863 a dozen or more investigators tried to produce a commercial process but failed, but by each succeeding failure knowledge was gained, which ultimately brought success in the Solvay process.

In creating luxuriant vegetable growths by fertilization it is impossible to say which of the constituents in a fertilizer is the most important, phosphoric acid, potassium or nitrogen. All three are perhaps equally important and at the present time available in large quantities, and for many years to come the extended areas of potash salts in Germany, and the recently discovered salts of France, will furnish the supply of potassium, and when these are consumed a process for the separation of potassium from feldspar will furnish the requirements of plant life for years after the Stassfurt or similar deposits have been exhausted. Search for potassium deposits in this country should not be abandoned. Though the Michigan company which put down a well in Wyoming in 1899 in search of potassium salts failed, further trials should be made; rather the government should drill wells, and if successful, obtain a rental of the mines as the German government is now endeavoring to do. Mr. Courtis (*Min. Ind.* 1904) claims the locations favorable for the discovery of potash salts are (1) Cady, Wyoming; (2) Magnesium Lake, Laramie Co., Wyoming; (3) Brown Springs, Cal.; (4) Death Valley, Cal.; (5) Bound Brook, N. J.; (6) Mt. Tom, Mass.

The fact that the waters of many of the alkali lakes contain 8 to 10 grams per liter of potassium chloride may indicate a deposit of soluble salts or the decomposition of insoluble silicates.

The United States, which imported from Germany 216,000,000 pounds potash in 1905, valued at \$3,551,000, should sometime have its own source of supply; for the Kingdom of Prussia, which is endeavoring to secure control of the potash salt mines, and has recently offered \$7,000,000 for one of the large mines,

will doubtless curtail the exportation and advance the price of the exported product to enable its own farmers to use larger quantities at lower prices.

No better service could be done by Congress for the good of the agricultural interests than to appropriate \$1,000,000 for the prospecting of potash salts, which are undoubtedly to be found somewhere within the boundary of the United States. There is no chemical investigation whose successful operation would bring greater financial returns than the separation of potassium from the potash feldspars which are to be found in large quantities in this country.

As for phosphoric acid, the United States has an abundant supply in the deposits of rock phosphate of the Southern States, and in apatite, which is found in many places in considerable quantities.

But as to the supply of nitrogen we are not so fortunate. The syndicate formed for prospecting in the Western States for nitrates thus far has produced no appreciable amount. The deposits on the western coast of South America will be depleted before many years, possibly within 30, and the great nitrate combine, recently formed, is continually advancing prices, and before another generation has passed we shall have to resort to some other source of nitrogen for the soil.

Briefly referring to nature's methods of securing available nitrogen, we first note that electric discharges during storms undoubtedly form oxides of nitrogen which are carried to the soil by rain and combine with alkalies in the earth to form nitrates.

Another of nature's processes of nitrogen fixation is that discovered by a German farmer, Schultz, who observed that certain plants, clover, peas, lentils, etc., greedily absorb nitrogen, and accordingly initiated the practice of turning under the early crops of these products to furnish nitrogen for the following crops. The reason for the lentil's power to thus fix nitrogen was later, in 1874, found to be due to tubercles produced on the roots of the plant by microorganisms. Other plants do not have these tubercles and hence cannot assimilate nitrogen to the same extent. That the fixation of nitrogen is thus going on is acknowledged by all biologists.

The efficacy of barnyard manures, tankage, garbage and other highly nitrogenous fertilizers is due to the ready formation of ammonia through the influence of bacteria in the soil.

It is unnecessary in this connection to dwell upon the work of these microscopic agencies, one class of which, called the ammonifiers, breaks down the organic substance forming ammonia, which is eagerly seized by the nitrifiers, producing a synthetic reaction and forming with oxygen nitric acid which is immediately taken up by an alkali forming a nitrate, in which form it is readily assimilated by the plant.

But we will pass over these natural methods and take up the application of natural inorganic and artificially produced nitrogenous substances.

In the first class we have sodium nitrate at present found in only one part of the world, Chili, and produced by a process of leaching and purification, the entire output being controlled by the nitrate kings of England.

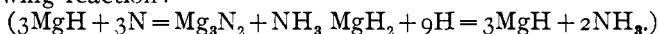
The production of this mineral is rapidly growing and it is expected that before many years the supply will be exhausted; for not only is the demand for it as a fertilizer increasing, but the production of nitric acid is constantly increasing, causing an additional drain upon the supply.

In the year 1905 the production of sodium nitrate amounted to 1,733,644 tons, three-quarters of which was used in fertilizers.

	1904. Tons.	1905. Tons.
Production of sodium nitrate.....	1,540,000	1,733,644
Shipments of sodium nitrate to Europe.....	1,179,500	1,192,120
Shipments of sodium nitrate to United States.....	265,766	353,177
Shipments of sodium nitrate to other countries...	35,042	52,605

We come now to the artificial production of nitrogen-bearing salts suitable for stimulating the growth of vegetation and will first consider those schemes for the direct fixation of the nitrogen of the air by which the nitrogenous fertilizers of the distant future will undoubtedly be supplied, and leave for later consideration the form of nitrogen salts, namely, sulphate of ammonia, the result of the dry distillation of organic substances; for undoubtedly the importance of ammonium sulphate as a fertilizer will greatly increase in the near future, gradually supplanting the waning supply of nitrates, and by reason of its much cheaper production postpone indefinitely the commercial fixation of nitrogen by electricity.

There is to-day no subject of chemical investigation of more vital importance than the fixation of nitrogen. It has already been accomplished on a small commercial scale by two different methods, but at a cost which probably is not sufficiently low to permit of successful competition with the present supply of nitrogen for fertilizer purposes, or for the manufacture of nitric acid. It was early determined by Wöhler and Deville that elementary silicon in contact with nitrogen resulted in a combination. Later it was found that boron, silicon, magnesium and titanium readily formed nitrides (convertible to ammonia with water) in an electrical furnace in an atmosphere of elementary nitrogen. Kaiser alternately leads nitrogen and hydrogen over magnesium hydride, producing ammonia, by the following reaction:

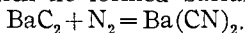


The commercial results of the experiments in these lines have been unsatisfactory.

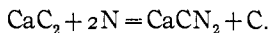


As is well-known, the only processes which have attained results approaching success, are Dr. Frank's calcium cyanamide process, and Birkeland and Eydé's process of fixation by electric discharge.

In 1903, while in Berlin, at Siemen & Halske's laboratory, it was my good fortune to see Dr. Frank's apparatus and the various products which were the result of his first work in fixation of nitrogen, calcium cyanamide, dicyanamide, etc. From that time cyanamide experimentation has continued and the beneficial effect of calcium cyanamide as a fertilizer thoroughly demonstrated; while a considerable quantity has been produced a careful study of the process would show that as at present operated calcium cyanamide could hardly be produced in competition with nitrate or ammonium sulphate. Dr. Frank's first observation, greatly to his surprise, was that when using calcium carbide and nitrogen at high temperature he got calcium cyanamide instead of calcium cyanide as he had expected from his experiments with barium carbide in which he formed barium cyanide.



With calcium carbide half the carbon was given off and he got calcium cyanamide.



Instead of first making carbide and passing nitrogen over calcium carbide at 900-1000°, the regular carbide process may be carried on in the presence of nitrogen and calcium cyanamide results. The most costly part of the process is the necessity of using nitrogen from which oxygen has been removed. This can be done only at considerable expense, either by passing over copper, or taking it from liquid air.

In arriving at a cost of calcium cyanamide which contains 16.5 per cent. available nitrogen, one must start with the cost of calcium carbide which at \$20 per horse-power year is stated to be from \$25 to \$30 per ton. To this must be added the cost of the preparation of nitrogen free from oxygen and due allowance must be made for leakage and loss of this costly nitrogen. When all expense is carefully summed up, it is quite certain the cost per unit of nitrogen in cyanamide will be in excess of the cost of nitrogen in sulphate or nitrate.

In an address before the Chemical Congress recently held at Rome, Dr. Frank stated that while one electrical horse-power year would produce the necessary carbide for the binding of 772 kilos nitrogen, still in practice only about 300 kilos were fixed as cyanamide. He reiterates the necessity for cheap electrical power and refers to the Linde process for obtaining his liquid air and further suggests that, as by action of steam at high pressure on cyanamide he obtains ammonia, he can use the oxygen of the liquid air for oxidizing the ammonia to nitric acid, thereby obtaining this product more cheaply than by the Birke-

land and Eyde process. It has also been suggested that as the fixation of nitrogen proceeds more rapidly with an excess of oxygen in the air, the cyanamide and the Birkeland and Eyde process might be located together, the former taking the nitrogen, and the latter the oxygen of Linde's liquid air.

Other chemicals of much interest have been developed out of the experiments with calcium cyanamide which will doubtless be of considerable commercial value, namely, calcium dicyanamide, dicyandiamide, guanidine and its salts.

In a letter recently received from Dr. Frank he states that a separate company has been formed for the manufacture of calcium cyanamide derivatives, and that dicyandiamide will be on the market for use in explosives and for the hardening of steel.

It is nothing new to attempt the combination of nitrogen and oxygen to form nitric acid. Over 120 years ago Cavendish observed under influence of the electrical discharge the formation of oxides of nitrogen. Since 1893 this problem has again been vigorously attacked by Crookes, Lord Rayleigh, Nernst and others in the laboratory, and by the Atmospheric Products Co., of Niagara Falls, Kowalski in Switzerland, and Birkeland and Eyde in Norway, on a commercial scale. As is well known, the only method to achieve any considerable success is that of Birkeland and Eyde.

Dr. Otto N. Witt describes a visit to the Norwegian plant at Nottoden (*Chem. Ind.*, December 1st), and says the essential feature is that an electric arc is made to continually alter its path by the alternations of a powerful magnet. The gases from the furnace, containing only 2 per cent. nitrous gas, are very hot and must be cooled before going to the absorbing apparatus which is the same as in nitric acid works. A strength of acid equal to 50 per cent. is obtained. The heat of the gases leaving the furnace is utilized in making steam under boilers and in evaporating the solution of calcium nitrate. The weak gases are absorbed in towers of granite down which milk of lime passes.

According to Dr. Witt the Norwegian plant produces 1.5 tons daily and he states the yield to be 455 kg. 100 per cent  $\text{HNO}_3$  (592 Kos.  $\text{Ca}(\text{NO}_3)_2$ ) per kilowatt year, which he figures at the ridiculously low price of \$4.00, whereas \$16.00 would be more nearly the cost of power. Guye claims the yield per kilowatt year to be 500 kg. and the *Chemical News*, 650.

At a recent conference (*L'Echo des Mines et de la Métallurgie* 33, 1776, March, 1906, p. 379) of scientific and business men called together by M. L. Grandeau, chief of the French agricultural stations, Mr. Eyde was present and stated that since May 2, 1905, three furnaces of 500 kilowatts had been in run, each using 25 cubic meters of air per minute and that their calcium nitrate product contained 13 per cent. nitrogen and he gave 112 fr. (\$22) as the cost of the power per ton of nitrate, assuming 15

fr. or \$3 as the cost of a horse-power, absurdly low. If we assume the cost of power, \$18, as attainable at Niagara Falls, the cost for power alone per kilo ton of calcium nitrate would be \$132, containing 13 per cent. available nitrogen, as against \$52 per ton for sodium nitrate containing 15 to 16 per cent. nitrogen, and \$60 for ammonium sulphate, containing 21 per cent. nitrogen. Thus, unless electrical power can be obtained for \$5 or \$6 per horse-power year calcium nitrate cannot compete with ammonium sulphate as a fertilizer.

While the cyanamide at no very distant day may be produced commercially at such few places as can furnish power cheaply, the direct oxidation of the nitrogen of air by electric discharge I consider to be a problem far from being satisfactorily solved. It is endothermic, requiring 3.7 times the power that the exothermic cyanamide process does.

The suitability of calcium nitrate for fertilizer purposes is yet untried. Calcium cyanamide, on the other hand, has been thoroughly tested by many investigators and has been found to correspond closely in value to sodium nitrate and ammonium sulphate. L. Grandeau (*J. Agr. Prat.* No. 1, pp. 8-10 (1906)), in experiments with potatoes, showed the relative effectiveness of the three fertilizers to be sodium nitrate 100, ammonium sulphate 96.5, and calcium cyanamide 93.4.

While the cyanamide process or the nitric acid process may at some quite distant date be made commercially economical, yet the immediate supply of suitable nitrogen compounds to take the place of sodium nitrate is ammonium sulphate made first and in greatest quantity by gas houses and by by-product coke ovens, second by Mond producers, third, from the destructive distillation of peat and garbage.

The relative importance of sodium nitrate and ammonium sulphate to the fertilizer industry is shown by a comparison of the figures representing the production of the two salts. In 1905, the production of sodium nitrate amounted to 1,733,000 tons, of which 1,290,000 reached the soil as fertilizer, while the production of ammonia, figured as sulphate, of Great Britain, France, Belgium, Germany, Italy, Austria, Spain and the United States amounted to 557,000 tons, of which about 80 per cent. or 445,000 tons was used in fertilizers.

It is interesting to note that of the production of 557,000 tons of ammonium sulphate per annum, 44 per cent. was produced by Great Britain, 20 per cent. by Germany, 12 per cent. by the United States and 9 per cent. by France.

Another matter of interest is that of this 244,000 tons of ammonium sulphate produced in Great Britain per annum, 60 per cent. comes from gas works, 7 per cent. from blast-furnaces, 15 per cent. from shale plants, 10 per cent. from coke ovens, and 5 per cent. from Mond gas producers.

## WORLD'S PRODUCTION OF AMMONIUM SULPHATE FOR 1905.

	Tons.
Great Britain.....	244,000
France.....	43,000
Belgium.....	39,000
Germany.....	115,000
Italy, Austria and Spain.....	48,000
United States.....	68,000

Great Britain's ammonium sulphate came from the following sources:

	1902. Tons.	1903. Tons.	1904. Tons.
Gas works.....	150,955	149,489	150,208
Blast-furnaces.....	18,801	19,199	19,568
Shale plants.....	36,931	37,352	42,486
Coke ovens.....	15,352	17,438	20,843
Gas producers.....	8,177	10,260	12,880

France's ammonium sulphate comes from:

	Tons.
Paris gas works.....	12,000
Provincial gas works.....	6,000
Paris sewage works.....	7,600
Provincial sewage works.....	3,500
Coke ovens.....	12,900
Shale.....	1,000

By what follows I hope to show that through the rapid extension of by-product coke ovens and the permanence of the industry, the waning supply of nitrogen due to the depletion of the nitrate deposits will be made good by ammonium sulphate, which is produced at the rate of 17 to 26 pounds for every ton of coal coked.

As long as coal lasts there will be a continually increasing production of ammonium sulphate. Foundries are located in large cities, blast-furnaces too are being constructed more and more in the neighborhood of cities which are not too far from the ore beds. Coke ovens will follow the blast-furnaces and in such location on the border of a large city the by-product coke oven can perform to the fullest extent its various functions.

A moment's consideration of the by-product coke oven and what it accomplishes will convince one that it is the foundation of an industry, now in its infancy, but destined to be chemically and metallurgically one of the most important and far-reaching industries in the domain of arts.

Its permanence as a source of nitrogen in a cheap form for fertilizer is assured by its underlying and fundamental importance in the operation of various industries. By it better coke, both for blast and foundry purposes, is produced than in bee-hive ovens. This is freely acknowledged by the best engineers in the country. A better price can be obtained from the foundrymen for by-product coke than for Connellsville because of its superior physical quality. This alone would insure the permanence of the

industry. But further, by it a superior quality of tar, the starting point for various industries rapidly becoming of importance, is produced in quantity varying from 60 to 100 pounds per ton of coal. The saturation of paper and felt with tar for roofing purposes is an industry of considerable importance. As a fuel in combustion engines by-product tar may be used as successfully as petroleum oil. Upon the products of the distillation of tar various industries are dependent. The utilization of pitch in the manufacture of briquettes is comparatively a new one in this country, but is destined to become of great importance, particularly to work up into valuable form the anthracite culm piles of Pennsylvania and the breeze of coke plants. Plants have recently been installed in Scranton, Detroit and Montreal for the manufacture of briquettes. Tar macadam roads, made with regular macadam foundation and an upper layer of three inches of a mixture of fine spawls and a certain grade of pitch, make a pavement perfectly impervious to moisture.

The distillate from tar has many uses, the most common being for the well-known purpose of creosoting railroad ties. Railroad men are convinced from long-continued experience that no other method of treating ties to preserve them is as satisfactory as creosoting with coal tar distillate which must have a high content of naphthalene. Large quantities are used for making lamp-black. As the consumption of pitch for briquetting purposes increases, which requires the distillation at a high temperature, anthracene will be produced in large quantities and will be shipped to Europe for alizarine manufacture, and let us hope to find a market in this country for the same purpose.

One branch of the by-product coke industry thus far very little developed, but destined to be at some future time of immense importance, is the recovery of the aromatic oils of the gas.

Of the 10,000 cu. ft. of gas produced from a ton of coal, 6,500 cu. ft. are required in the coking process. This gas contains on an average 0.75 per cent. benzene and its homologues. Now the heat value of this gas is affected only slightly by the removal of benzene. By washing gas with petroleum or coal tar oil, a benzolized oil containing 2 to 3 per cent. of benzene is produced and by distillation a crude benzene light oil is obtained.

Only slight quantities of impurities, carbon disulphide, hydrogen sulphide, thiophene and naphthalene are found to be present, and purification and redistillation furnish a benzene 100 per cent. pure and suitable for nitrifying and converting to aniline.

What does this signify—what potentiality is here contained? The raw materials for all the aniline colors now imported into the United States are valued at millions of dollars. Formerly, it it could be said that the raw materials for a color industry were lacking in this country. This is no longer true. An abundance

of benzene is now available. How long before some enterprising company will take the initiative and on a considerable scale will undertake the manufacture of colors. As deterrents against the investment of capital in the color industry are offered on every hand: (1) lack in this country of competent chemists at low salaries, and (2) high price for labor, (3) the strong entrenchment of the business in the hands of the Germans, a business for which they have been peculiarly endowed. The close coöperation of the German teachers in chemistry with the manufacturer was admitted by Ostwald in an address while in this country to be the reason for Germany's control of the color industry. Our scientific schools are turning out chemists in large numbers and no one of our teachers is willing to admit they are not as well trained as the German chemists. The superior ingenuity of the American would soon devise machinery to displace labor; the raw materials, alkali and benzene, may be obtained at a lower price in this country than in Germany; nitric and sulphuric acids can be made as cheaply here as in Europe. There is no question but that under these conditions the aniline color industry, established with ample resources, after four or five years would return ample profits to the capital invested.

It is now about ten years since Mr. Fulton's comparison of Connellsville and Semet-Solvay coke in the Buffalo blast-furnaces dispelled all fears in the minds of metallurgists as to the suitability of by-product coke. Sir Lowthian Bell's statement of the loss of carbon in the upper part of the furnace was disproved.

A similar distrust came to gas manufacturers when it was suggested to them that by the coke oven equally good gas could be produced as by the gas retort. The recent installation of 120 ovens at Chicago, now supplying 3,000,000 cu. ft. of high candle-power gas to that city, in addition to plants of equal size at Milwaukee and Detroit, which have been in successful operation for more than two years, have now dispelled all the doubts of gas-makers as to the success of the by-product gas.

There is at present in the United States over 20,000,000 cu. ft. per day of illuminating gas enriched by benzene being furnished by coke ovens. It was supposed that in cold weather and under pressure coke oven gas enriched with benzene would lose much of its candle-power. An elaborate series of experiments on coke oven gas of an initial candle-power of 13 candles showed that this gas could be enriched to 24 candle-power and stand a temperature of zero, and a pressure of 20 pounds without appreciable loss. The experiments correspond closely to what calculations by vapor-pressure showed to be expected.

When one considers the operation of the coke oven when run as a producer of illuminating gas it is evident at once that it should produce gas superior to the ordinary coal gas made in the small gas retort. In the first place the higher temperature of the gas

retort tends to break down the illuminating series, benzene, into naphthalene. In the distillation of coal the gas richest in lighting properties is evolved during the early part of the process, the gas during the later period of distillation being poor in illuminants. Now all the gas from the gas retort rich and lean making a low average, is used, whereas in a coke oven only the rich gas, only that evolved during the first six hours, or one-fourth of the distillation period, is used for illuminating purposes, while the balance after giving up its benzene to the rich gas of the first six hours to make it richer, goes back to the ovens to effect the coking of the coal. It has been proved that gas of 15 to 16 candle-power can be made from coals not considered gas coals and of very low volatile matter by this selection method, and by addition of the benzene of the lean gas to the rich gas a candle-power of 19 to 20 is obtained.

As before stated, the amount of ammonia recovered varies from 16 to 27 pounds of sulphate per ton of coal, and is directly proportional to the percentage of volatile matter in the coal, a coal of 18 per cent. volatile matter yielding 16 pounds of sulphate, and one of 37 per cent. yielding 27 pounds. But this is a small percentage of the theoretical yield from the nitrogen of the coal. If all the nitrogen were converted to ammonia and recovered as such, the yield would be 133 pounds. But we find in the coke 48 per cent. of the original nitrogen.

While experimenting with certain Illinois coals it was found that the yield of ammonia was exceptionally high, and it was accounted for by the fact that the coal contained from 2 to 3 per cent. calcium carbonate. Lime will increase the yield of ammonia 20 to 40 per cent.

While a certain coal under one form of treatment, for instance, in the coke oven, yields 24 pounds of ammonium sulphate, the same coal under another treatment in Dr. Mond's producer at lower temperature and with steam returns 75 pounds of ammonium sulphate. The rapid construction of Mond-producer plants, particularly in England, will very largely increase our supply of nitrogen for the soil. Other nitrogenous substances are destined in the near future to add to our supply of ammonia, particularly as straight distillation results in such a large yield. I refer to the distillation of peat and to the distillation of garbage and other organic refuse. Peat in dry distillation yields 40 pounds, garbage 79 pounds of ammonium sulphate to the ton.

To recapitulate, we have as features of the by-product coke oven, which have been shown to be important as working toward its permanence and consequently as furnishing a permanent source of fertilizing nitrogen; (1) the production of coke superior to bee-hive coke; (2) the production of tar which enters so extensively into the arts; (3) it is furnishing the thus far-lacking material, benzene, in large quantities for the establishment of the color industry, but used until the establishment of this industry in

enriching gas for illuminating purposes; (4) it produces illuminating gas at a lower cost and of superior quality to that made in a gas retort; (5) it furnishes cyanogen equivalent to  $1\frac{3}{4}$  pounds of potassium ferrocyanide per ton of coal; (6) as one of the by-products, it supplies the pyridine soon to be in demand for denaturing alcohol; (7) the hydrogen sulphide recoverable from the ammonia liquors when oxidized is sufficient to supply nearly one-half the sulphuric acid required in converting the ammonia into sulphate.

Therefore, let those take courage who have been predicting universal famine from lack of fertilizer nitrogen when the nitrate deposits shall be exhausted, for as long as our mines yield bituminous coal, by-product coke ovens will produce an ever-increasing amount of ammonia. As long as carbon in any form may be obtained, calcium cyanamide will carry nitrogen to the soil, and even after all carbon has been consumed, if only the rain continues to fall and rivers to produce water-power and hills give forth their limestone, and the earth is enshrouded with its nitrogenous atmospheric mantle, basic calcium nitrate, by the Birkeland process, will furnish the languishing vegetation with its necessary nitrogen.

SOLVAY PROCESS CO.,  
SYRACUSE, N. Y.

---

## A REVIEW OF THE AMERICAN PORTLAND CEMENT INDUSTRY.

BY RICHARD K. MEADE.

Received July 9, 1906.

Now that the United States ranks first of the Portland cement producing countries of the world, not only in point of the quantity manufactured but also with regard to quality, it seems fitting to take a look backward at the industry and see by what steps this success has been gained. First the enormous amount of engineering work now being done in this country has created a steady demand for Portland cement; second, the cheapening of the process of manufacture has allowed it to displace to a large extent other hydraulic cements, and also wood, stone and brick; third, the introduction of reinforced concrete, concrete building blocks, sewer pipes, etc., has widened enormously the field of concrete construction. All these causes have contributed to the wonderful growth of the Portland cement industry.

Few people realize how much concrete construction is done in the United States. If all the Portland cement made in this country last year had been used for sidewalks, these would have been equivalent to a sidewalk over 16 feet wide, reaching entirely around the world, at the equator. If this same cement