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BY-PRODUCTS IN GAS MANUFACTURE.¹

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IN dealing with the interesting topic which has been assigned me in this Centennial Celebration it seems proper, and in the interest of clearness of treatment, to deal broadly with the subject of by-products before dealing with those of the Gas Industry. I have, but a short time ago, been called on to prepare an article on this subject for the Loose Leaf Encyclopædia, and with your permission I will quote part of this article, since I feel that I have therein presented the matter to the best of my ability.

“By-products are substances or results obtained in the operation of a specific process, in addition to the substance or result

¹ Address delivered at the Celebration of the Centenary of the Introduction of Gas as an Illuminant, under the auspices of The American Philosophical Society, The Franklin Institute, The American Chemical Society, and The American Gas Institute, in the hall of the Franklin Institute, Philadelphia, on Thursday, April 18, 1912.

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primarily sought. In hunting game for food, the hides and feathers are by-products; in hunting game for hides or pelts, the carcasses are by-products; in manufacturing lumber, the sawdust and shavings are by-products; in brewing beer, the yeast is a by-product.

“In the classification of the products of manufacture, three groups are recognized—viz., *principal product*, which is that product of an establishment manufacturing more than a single product that has the largest total value; *subsidiary product*, which is a product of such an establishment having a less total value; and *by-product*. A subsidiary product may be a utilized by-product, or it may be the product of an allied industry—as, for instance, bookbinding in a printing office, or compounding fertilizers in a cottonseed-oil mill. This last example is one of many occurring in factories where the by-product of the principal industry—in this case cottonseed meal—becomes the raw material for the manufacture of a subsidiary product. The development and growth of manufactories using manufactured products as the raw material for further manufacture has not infrequently created such a change in the demand for the products of the primary establishment as to make one of its subsidiary products its primary product. A notable example of this is the Le Blanc process for the manufacture of soda products from common salt by the action upon it, in the first stage of manufacture, of sulphuric acid. In this operation, hydrochloric acid gas is given off as a by-product. At first this was wasted by being allowed to escape into the atmosphere, where it produced most devastating effects. To avoid the nuisance thus created, this gas was collected by dissolving it in water, and sold, thus becoming a subsidiary product; but with a greatly increased demand for this substance, for the manufacture of bleaching powder and other uses, through which its value was enhanced, and with the competition of electrolytic and other processes, through which the cost of the production of sodas was reduced, hydrochloric acid became in many cases the principal product of the Le Blanc factories.

“As indicated by the examples cited, the custom of utilizing by-products is a very ancient one in its origin, though frequently in the newer countries, where the raw material was abundant, or in the early development of industries, where the unit of pro-

duction was small and competition slight, the by-products have generally been wasted, and frequently have become sources of nuisances. But with the increase in density of the population, through which the necessity for abating the nuisances became urgent; with the increase in the unit of production; with a diminution in the quantity of the raw material, or the ease with which it could be obtained; and with the increase in competition, additional attention has been given to the utilization of the by-products of manufacture, until to-day they have become of great importance in all industries, and of such commercial value that the creation and maintenance of many establishments have been determined by the ability to utilize and dispose of the by-products of their processes.

"Naturally, the by-products that were first to be utilized were those which were most readily observed and whose uses were most obvious. The by-products which ran off in solution or passed away as gases, or forms of energy, such as heat, or those whose uses were remote or less readily apparent, have until very recent times been allowed to go to waste. The discovery of the first of the aniline coloring matters, mauve, in 1856, by the English chemist William Henry Perkin, and the fact that the aniline from which it is manufactured could be obtained in abundance from coal tar, gave an impetus to the utilization of the last enumerated by-product; and the rapid growth in commercial importance of the coal-tar products industry so concentrated attention on this phase of manufacture that the utilization of by-products has gone on with increasing expansion ever since."

There exists a rather widely extended popular belief that the "coal-tar colors"; many perfumes, flavors and synthetic drugs; and numerous other substances, are by-products of the gas industry, but such is not the case, for they are produced by the further manufacture of the by-products of this industry. This view limits the scope of my topic, which is, however, broadened by the modern view of the gas industry in that it embraces in its consideration not only coal gas, but all gases manufactured for the generation of light, heat or power and which are distributed for use by public service organizations. All of the processes of manufacture employed in the production of these gases depend upon the chemical transformation of the materials

used, and in all processes other products beside the gas sought are yielded.

This is particularly true in the carbonization or, using the more precise chemical term, the thermolysis, of peat, wood, resin, coal, oils, and other organic bodies, in which these bodies are subjected to widely ranging degrees of temperature and quantities of heat when enclosed in containers, such as retorts, ovens, or kilns, which more or less completely prevent access of air to these bodies during the thermolyzation process, and which are so operated that the heat, which effects the thermolysis, is conveyed to them through the walls of the containing vessel. For these bodies are complexes. The simplest of them, such as the

FIG. 1.

Coal gas tar.

FIG. 2.

Water gas tar.

resins, produced from exudates from deciduous vegetation or the thermolyzation of such exudates, and the distillates of petroleum, are still complexes. They are not elementary. They are not even single chemical compounds, but they are aggregates of chemical compounds each of which is capable, under certain conditions of temperature and pressure, of undergoing a particular kind of decomposition with the production of certain particular products, each of which, were they to remain apart, might be of such character as to form a useful product, but, being mixed, or associated with other products the tendency is that these intermediate products of thermolysis react with one another and that the final product, which may be, and usually is, a mixed

product, is a final integration of the process as it has proceeded from its initial condition, through its manifold transformations, to its end condition.

The conditions described are those which especially obtain for coal, as known in England, or bituminous coal as it is styled in the United States. This is the substance which first met with general success and which is yet to-day largely used in the manufacture of gas. It is the substance from which coal gas, so styled, has been and still is produced and though commercially regarded as, and popularly believed to be a definite and individual substance it is not so, for it not only varies in its composition, constitution and characteristics as it is obtained from different localities, but it varies by degrees as it is obtained from different geological deposits in the same geographical locality and may even vary in the deposits of the same geologic age, or, in technical parlance, of the same seam, according to the conditions to which it has been subjected. The vicissitudes to which coal forming materials are subjected in this conversion from cryptogamous vegetation, such as prevails in peat, or phenogamous vegetation in its many species, through lignite into coal, is admirably portrayed by Dr. T. E. Thorpe² and the manifest complexity and variability of the product is there well indicated. The geological significance of these transformations of vegetation are set forth by J. D. Dana in that charming, yet accurate style, of which he was a master.

Notwithstanding this recognition of complexity we have known nothing definitely as to the constitution of coal or of the nature or amount of its components. A large number of ultimate analyses, showing the percentages of carbon, hydrogen, oxygen and nitrogen present in ash-free coal, have been made and recorded in literature, as have also many proximate analyses giving the percentages of moisture volatiles, coke, or fixed carbon, and ash, with the sulphur and phosphorus contents. Such data has had and still has an economic value in gas making and coke making and in the utilization of the coal, or some of its products, in iron smelting or steel working, but it still leaves us uninformed as to what there is in the different varieties of coal or in any given coal. And we are not much further enlightened

² "Coal: Its History and Uses." Macmillan & Co., London, 1878.

by the interesting comparison made by Pennock,³ and others, of the character and composition of the tars yielded by different coals whose proximate compositions had been precisely determined, for these tars were the products of thermolysis, accompanied no doubt by metathetical changes also.

It has long been known that peat, lignite and bituminous coal, certainly, are affected by some solvents. In the early days of my professional career I devised a scheme for the classification of coal producing substances, and the different varieties of

FIG. 3.

Benzol plant.

coal, based on the character of the colors which they imparted to aqueous potassium hydroxide solutions in which the powdered material had been digested. There is some question in this case as to whether the extracted matter was identical with that in the coal or whether it had chemically reacted with the strongly alkaline reagent used. It is known, however, that we have many neutral liquids such as alcohol, benzene, ether, chloroform, acetone, carbon tetrachloride, carbon disulphide, pyridine, ligroin and other petroleum distillates, to mention but a few at com-

³ J. D. Pennock, *J. Am. Chem. Soc.*, 21, 696, 1899.

mand, which are solvents of organic substances, through which hydrocarbons and their derivatives which may be present in the coal can be extracted unchanged, while by the action of reagents of known behavior, such as nitric acid, chlorine, caustic alkalies in the molten condition and the like, derivatives of these organic substances, whose genetic relationships are known, may be obtained, and thereby, through both direct and indirect methods of approach, the constitution be ascertained.

Records of the attempts made to solve this problem of the constitution of coal, by means such as described with the results thus far obtained, have been assembled and critically reviewed in a masterly manner by Frank Wiggleworth Clarke in his "Data of Geochemistry,"⁴ and it can only be said that the results are most meager, largely because the extractives are usually tars which require further treatment for separation and identification, by slow and tedious processes and that the total yields are rarely large. It may be of interest to announce that the recently created U. S. Bureau of Mines has taken up this problem as one of its studies looking to a more complete and economic utilization of our coal and therefore to the conservation of our fuel resources, and that the results of the preliminary investigations on these lines by J. C. W. Frazer and E. J. Hoffman, of that Bureau, have been prepared for publication. I feel assured that as more definite information is acquired the character of our distillation processes, such as are now used in gas and coke making, will be profoundly modified and that the nature and yields of the by-products of the gas industry will be materially changed.

Taking the industry as it has been and now is, it may be noted that the by-products of the coal gas industry are coke, gas, carbon, tar, ammoniacal liquor and spent purifying material, either lime or oxide. In the water gas industry tar and purifying material, with a meager amount of ammoniacal liquor. In the oil gas industry lampblack, tar and spent purifying material for the new Lowe process, and "hydrocarbons" for the cracked and compressed oil gases. While in the acetylene gas industry calcium hydroxide is practically the only product incidental to the reaction other than the acetylene.

⁴ Bulletin 491 (2d ed.) U. S. Geological Survey, pp. 705-731, 1911.

From the outset the commercial and economic value of certain of the collateral products obtained from the chemical reactions which yield coal gas were recognized, and to such an extent that the original organization, whose parliamentary recognition we now celebrate as a significant event in the evolution of chemical industries, was styled the "Chartered Gaslight and Coke Company"; the production of coke, by the distillation process employed apparently being regarded by Winsor and his associates, as of equal, or nearly equal industrial importance to that of coal gas. We know that in the last quarter century the rela-

FIG 4.

Blow case.

tive economic importance of the gas and coke obtained from bituminous coal by distillation processes has been, and to-day still is, in many localities or under certain industrial conditions, reversed, and that where by-product coke ovens are employed the coke is the principal product and coal gas is one of the subsidiary by-products. In by-product coke making, particularly where gas is supplied to public service corporations, for distribution, as is often the case, the other by-products are substantially those of the coal gas industry.

I say "substantially" with intent for they would be identical

only by the most remote chance since it is recognized that, using the same coal, the products obtained differ in quantity and character when thermolyzed in the same retort with variations in the rate, degree and method of heating them, and with the pressures put upon, and that when the device employed, such as vertical or inclined retorts, or ovens of the many dimensions and forms known, is substituted for the horizontal retort of standard type, the conditions under which the thermolyses and metatheses take place are so varied that the products are materially varied both in composition and quantity, and this difference is emphasized

FIG. 5.

Refined storage tanks.

when the material treated differs, as does coal from different localities or even from the same locality but from different parts of the vein.

My presentation of the difficulties which beset the gas manufacturer in his endeavor to produce a gas of uniform character that will conform to the regulations or restrictions placed on him by the state or municipal legislation or ordinance with which he is environed may perhaps have quickened your interest or stimulated your incredulity. If so this part of my thesis is completed.

But I call attention to the fact that complex and variable as the gaseous products of soft coal distillation are, the tar and ammoniacal liquor which are by-products are subject to as marked variations in yields or in composition or both with differences in the coal used and the processes or devices employed and in their operation as the gas is and that these, but more particularly the tar, are the by-products which have lent special interest to the gas industry and which in the more recent years have proved to be important factors in its commercial success and in enabling this industry to maintain its place commercially in the presence of competing illuminants.

Of these by-products the ammoniacal liquor is chemically the simplest and yet it is complex and variable. It is produced from some of the nitrogen in the coal, and perhaps to a degree, when alkalis or alkaline earths are present from atmospheric nitrogen entering, or included in the chamber in which the destructive distillation of the coal is effected. Varying with the process employed and its operation the ammonia content appears in the condensates as carbonate, sulphide or polysulphide, chloride, cyanide, sulphocyanide, and probably in other combinations, from which it is released, to a greater or less extent, by the action of stronger hydroxides, such as calcium hydroxide, in the process of recovery when it is converted into the marketable forms of ammonia water or ammonium sulphate.

In this latter state of combination the nitrogen of the coal or the atmospheric nitrogen which has entered into this state of combination, has become available for food for vegetation, whereas before it was not so. This forcibly illustrates the correlation of country and city, of agriculture and manufacture, for while the coal remained unmined its nitrogen content was unavailable as plant food, but when that coal had been mined and employed in the manufacture of gas for city or town lighting its nitrogen content was not only released from its inert condition of combination but brought into such association, through subsequent treatment, as to be available for plant food. To-day a larger part of the available nitrogen necessary for use in compounded fertilizers or for direct use in agriculture comes from the gas industry, or from its closely correlated industry, the by-product coke industry.

The utilization of ammonium sulphate from the gas indus-

try in agriculture practically dates from the time of the governmental encouragement of the beet-root sugar industry in Germany. It is in this way correlated with the potash industry which has been so recently a serious topic for diplomatic negotiations and which to-day remains a grave problem for governmental solution. Personally I find the available nitrogen question to be a wider one than that of agriculture. I find it to be closely concerned with the ability of a nation to protect and defend itself in a prolonged warfare. I find that in the immediate past and to-day the supposed dominant nations have been and are, through the necessity for available nitrogen in warfare, dependent nations since they have sought for this available nitrogen the few sources of supply where it has been stored by nature's agencies working in a comparatively simple manner. I have elsewhere suggested⁵ that chemistry has in recent years released these nations from their state of dependency. It seems at first thought a far cry from the manufacture of gas, by which to extend the efficiency and efforts of the people of a nation, to its defense in time of attack, but chemistry has made this last relation relatively close and the gas industry, if properly directed, may reasonably be expected to become a factor in the defense of the nation and its managers may rightly feel that in wisely and justly directing the affairs of a gas company they are not only rendering a public service but a patriotic service also.

In the development of the ammonia recovery from coal gas a rather amusing and curious condition has developed. Originating as the gas industry did in England that country has maintained its supremacy in the production of by-products and when ammonia and ammoniacal compounds from this source began to assume economic importance there was devised in England a means for ascertaining the quantity of the valued component in a liquor by liberating it from its state of combination, through the aid of calcium hydroxide, and then measuring its neutralization with a standard solution of sulphuric acid which had been made up on the scale of Winchester gallons. This method of determining the ammonia content of liquors, known as "ounce-strength," was on its face obviously fair and equitable and was

⁵ "The Nitrogen Question from the Military Standpoint," U. S. Naval Inst., Proc. 35, 715, 1908. Smithsonian Report for 1909, 225-236.

shortly afterwards introduced into this country, but the difference in measures was overlooked and the standard sulphuric acid was made up with the U. S. gallon as the measure and ever since "ounce-strength" has had in the United States a different significance from that which it has had in England. Fortunately the content in real NH_3 or $(\text{NH}_4)_2\text{SO}_4$ is coming more commonly into use and the discrepancy of statistics which has existed between different countries is being reconciled.

The vagaries of nitrogen in forming its various associations

FIG. 6.

Loading tanks.

by which the many compounds of nitrogen found in the distillates from coal, from ammonia, and its multitude of substituted amines, to cyanogen with its numerous derivatives, result, is but one example of the multitude of complex changes and rearrangements of atoms and radical groups which occur during the process of gas making where the apparently simple method of heating the coal is employed. For numerous as the nitrogen compounds formed may be the known carbon compounds are many fold greater since they include, not only the many representatives of various known homologous groups of acyclic and

of cyclic hydrocarbons, but also many of the oxy, sulpho and nitrogen derivatives of these hydrocarbons.

Attention has been called to the necessary variations in the composition and character of the gas which must result from the variations occurring in the composition and constitution of the coal used; the differences in the forms, proportions and character of the devices used in the carbonization of this coal; and particularly in the methods employed in the carrying out of the process, but the effects of these many differences are, if possible, more obvious in the tar, which is one result, than in the gas, which is another result of the destructive distillation, and this fact is of prime importance for consideration by the gas works manager since tar stoppages are not infrequent sources of trouble in operation which may to an extent be remedied by so conducting the distillation process, in any system, as to obtain more liquid or less highly carbonized tars.

For it is well known and has long been known that in this distillation process heavy hydrocarbons or hydrocarbon derivatives of high boiling points, which have been evolved from the coal by heat, may condense before reaching the hydraulic main and fall back upon the incandescent coal mass in the retort or upon the incandescent walls of the retort or other container, where they are cracked, depositing carbon, which appears on the walls as gas carbon, and yielding lighter and more volatile gaseous products which again pass on to mix with the other gaseous products, but bearing with them some portion of the carbon, which has not been deposited, to foul the tar.

At the time that these splitting up processes are going on, or nearly simultaneously with them, building up processes may be taking place, for it is well known that under conditions such as obtain in gas retorts or in the gas making system in practical use, acetylene and acetylene homologues, such as methyl-acetylene, polymerize to benzene, and benzene homologues, such as mesitylene, which may again be decomposed into simpler products at more elevated temperatures and which pass partly to the gas and partly, and more largely perhaps, to the tar.

It is this complex, vile looking, evil smelling, adhesive, by-product, tar, which was for long a stumbling block in the development of gas lighting. Early in the progress of the industry efforts were made to utilize it, but they proved of so little avail

that when possible much of it was run off as a waste product into neighboring water courses destroying the fish, fouling the craft floating on the water and the structures bordering it, and giving rise to nuisances of a great variety of kinds. Among the unexpected results of this procedure I may recall that when in 1882, under orders from the Secretary of the Navy, I visited the Navy Yard at Brooklyn, N. Y., to investigate the cause of the corrosion of the copper sheathing of the newly fitted U. S. S. *Juniata*⁶ and of other vessels which had been fitted with suits of copper at the Brooklyn yard, I found in the Wallabout considerable deposits of coal tar which had been rejected by the adjacent gas works in earlier days, and my experiments tended to show that this tar had played an important part in the corrosion which entailed considerable loss.

FIG. 8.

Naphthalene mixer.

But this coal tar which was despised and rejected by man; which was a burden to the manufacturer and a nuisance to his neighbor, has, through the researches of the chemist, become a much valued and highly considered substance, and an aid to the gas industry, which it has helped to maintain and extend, and through which the demands for cheaper gas has partly been met. Its history is filled with romance. The first English patent ever issued relative to the destructive distillation of coal was that dated August 19, 1681, and granted to J. J. Becher and Henry Serle "for a new way of making pitch and tar out of pit coal." At the outset tar was therefore to be classed as the principal product with gas and coke as by-products of the coal tar industry, but the industrial development took other courses and the order of importance was reversed until the production of

⁶ Proc. U. S. Naval Institute 12, 391, 1886.

pitch and tar proceeded on such a scale that, as stated, the gas makers were compelled to dispose of it at almost any hazard and in every possible way, and yet to-day through another change in industrial development this tar has become, perhaps, the most highly prized, or at least the most intellectually honored, of all the products resulting from the destructive distillation of coal.

It is here that the real romance begins when studied by methods, such as those spoken of earlier in this paper as promising man information relative to the constitution of coal, and when by additional methods this blackish, viscous, forbidding appearing tar was examined it was found to be a storehouse of most interesting materials; and it has been found to be a storehouse of most fascinating possibilities and realizations.

It has been asserted that all foul smelling substances are composition of matter, and it is a fact that carbon disulphide which, notoriously, has long been condemned for its disgusting odor appears as a sweet, ethereal smelling compound when separated from its associates by the methods of purification devised by the chemists. Likewise it has been suggested that offensive looking bodies are composites. Whatever may be true of this theory in its general application it is certain that coal tar, which, in common with wood, water gas, petroleum, cotton-seed oil and other tars, of organic origin, is offensive in appearance and odor, is a product of the distillation of organic substances, and that all of these distillates are composites, and that when each of the chemically individual components of these compositions is separated from the composite mixture it appears in an agreeable condition to mankind as regards odor, or color, or as tried by other physical characteristics through which substances are differentiated or distinguished. For from coal tar there has been obtained the water white or colorless benzene and its equally colorless homologues which possess such pleasant odors and which give rise to compounds of such markedly pleasant odors that the series of hydrocarbons of which benzene is the initial member has been long since styled the aromatic series.

This is but the beginning of the enumeration of the hydrocarbons present in coal tar, for besides the benzene series there has been found present many of the conjugated derivatives of benzene, such as naphthalene, fluorene, phenanthrene, anthracene, and many others. Moreover there has been found present

besides ammonia, nitrogen containing compounds, such as aniline, the pyridines, the picolines, the quinolines and isoquinolines and many other nitrogen containing compounds; sulphur compounds, such as thiophene and the derivative thiophenes; and hydroxy compounds, such as the phenols, and the cresols. This review embraces but a limited number of the numerous compounds which go to make up the material styled coal tar. The number and amount of each varies with the source from which the tar is obtained and the manner and means by which it is produced.

FIG. 7.

Tar separator.

FIG. 9.

Dephlegmating condenser.

No one of these separate chemical substances is to be regarded as a by-product of the gas industry, for they are usually isolated from the coal tar in other establishments than gas manufacturing establishments. They are spoken of here only that we may note the effect and influence of the gas industry on other industries, and in doing so it may be proper to recall that the substances enumerated as occurring in coal tar are not only used by themselves to produce certain useful and beneficial effects, but that they are more largely employed as the raw materials

for further manufacture, and that from them we obtain not only compositions of matter such as cleansing compounds, paints, paint removers, and the like, but also many chemical compounds having most valuable properties. It is from these isolated components of coal tar that we now produce the many coloring matters, a large part of which are used as dyestuffs, such as the aniline colors, the synthetic alizarine, which has driven the natural madder dyes from the market and which has opened the area formerly devoted to the growth of the madder root to the cultivation of food crop, and synthetic indigo which is rapidly displacing the indigo produced from natural sources. Antiseptics and germicides, such as carbolic acid and the naphthols. Explosives such as picric acid and the trinitrotoluene, known as trotyl. Flavoring materials such as the methyl salicylate and vanilline. Perfumes such as geranoil and artificial musk. Febrifuges such as antipyrine, acetanilid and many other synthetic remedies. Sweetening principles such as saccharine, and photographic developers such as hydroquinone.

Numerous as the bodies mentioned are, they form but a very small part of the many substances which have been or may be derived from coal tar in its further manufacture, nor do they begin to exhaust the beneficent results which have followed this chemical utilization of what was formally a wasted by-product, for the coal tar dye industry has conferred a benefit of incalculable value upon bacteriology and upon all mankind by furnishing dyes which, when applied to microscopic preparations, make it possible to distinguish and recognize the germs of typhoid, cholera, tuberculosis, and other diseases; it is alleged that the industry was the principal cause of the establishment in Germany in 1877 of the imperial patent office; it is certain that the study of the constituents of coal tar and of their derivatives has created an almost new chemistry which development was largely facilitated by the ingenious speculations of August Kekulé regarding the constitution of the benzene ring advanced by him in a masterly treatise in 1865. Largely because of the insight which this theory of Kekulé gave man regarding the constitution of benzene and the possibility of obtaining from it, and its homologues, many of the chemical compounds already known and desired and many others indicated but not previously known, an enormous industry was created which within forty years from the promulgation of the theory employed more than 15,000 workmen in

Germany alone, producing products of a commercial value reaching to tens of millions of dollars and advancing the industry of mankind in a multitude of ways.

While coal gas tar has for more than a half century played a most important part in the chemical development of many countries, water gas tar which has been produced, particularly in this country, in very large quantities, has until recently been an unutilized by-product except in so far as it has been used for fuel, when mixed with breeze, under the retorts of boilers or as a source of power, in internal combustion engines, such as the Diesel engine, but through the investigations directed by Mr. W. H. Gartley, this material of which we have a most abundant supply has recently been made to yield its valuable components for use in further manufacture.

Water gas tar is a very complex mixture of a great many

FIG. 10.

Tar still.

hydrocarbons. The principal commercial hydrocarbons are probably as follows: Benzol, toluol, xylol, naphthalene, methylanthracene, phenanthrene, and probably in the pitch, chrysene and pycene. Water gas tar is formed in the carburetter and apparatus by the contact of the oily vapors, used in carburetting, with the highly heated checker brick. Its formation differs from that of coal tar, in that the temperature which obtains is moderate and is very exactly regulated and the time of contact is short and uniform, and furthermore, there is a high percentage of hydrogen present at the start due to the water gas which is to be carburetted. The free carbon, therefore, in water gas tar is very low compared with that in coal gas, and its composition is generally more uniform. The oil used for enriching carburetted water gas varies in character from the paraffine base oils of Pennsylvania and Ohio to the asphaltic base oils of Texas

and California. The presence of the hydrogen in water gas as affecting the formation of the tar is shown by the increased amount of olefines and the smaller amount of tar formed, which is more complex in its nature in the case of water gas tar than the tar formed by the simple decomposition of the oil.

The general differences between water gas tar and coal tar are that water gas tar has a very low free carbon content; corresponding fractions have a slightly lower gravity; a larger fixed carbon content; absence of oxygenated compounds and a general increase in methylated derivatives, especially in the higher hydrocarbons, this confirming, in general, Schulze's theory of

FIG. 11.

Fire column still.

pyrocondensations at lower temperatures. Water gas tar varies in character somewhat according to the original character of the oil and to the method of operation of the set, particularly as regards the temperatures carried in the fixing vessels.

The water gas tar as it leaves the apparatus exists generally in the form of vapor. This is dropped out when the temperature of the gas is reduced in the wash-box, scrubbers and condensers, and the last traces are removed in the P. & A. tar extractor. A considerable quantity of water is also condensed at the same time, and the mixture of oil and tar is separated by utilizing the differences in specific gravity. The crude tar thus

separated still contains considerable amounts of water held in suspension. This is further separated by storage of the crude tar in large tanks, where in time the water separates out to such an extent that the tar will contain not over 1 or 2 per cent. of water.

FIG. 12.

Steam stills.

The crude tar is distilled in a fire still; that is, one provided with direct fire, and is cut into a number of fractions such as light oil, creosoting oil and naphthalene oil. The residue in the still is worked up then, according to the temperature of the distillation, into road compounds and pitches. The naphthalene oil fraction is chilled, and the naphthalene separated out in centrifugal machines. The light oil is washed with sulphuric acid and soda, and redistilled in stills provided with dephlegmating columns into crude benzols, toluols, etc. These are further redistilled to obtain the pure products.

The relations between tars from various sources as tested in this research are set forth in the following tables.

COMPARATIVE ULTIMATE COMPOSITION OF COAL AND OIL AND
COAL-TAR AND WATER GAS TAR.

	Coal.	Coal-tar.	Oil.	Water gas tar.
Carbon	82.47	89.21	84.28	92.70
Hydrogen	6.01	4.95	13.46	6.13
Oxygen	6.81	4.23	1.41	.69
Nitrogen	1.88	1.05	.24	.11
Sulphur	2.83	.56	trace	.37
Heating value, B.t.u's..	15353	15708	19200	17193

COMPARATIVE DISTILLATIONS OF DIFFERENT TYPES OF TARs.

	Horizontal.	Coke oven.	Vertical.	Water gas.
Start to 105°	0.4	1.0	0.1	1.1
Specific gravity at 25° C. ...	1.2039	1.1696	1.1302	1.0679
Free carbon, cold C.S. ₂	21.16%	9.36%	5.83%	.30%
Distillation, per cent. by weight—				
105-170°	1.4	0.3	1.1	2.8
170-225°	10.8	10.0	13.9	9.0
225-270°	10.1	12.4	12.5	12.6
270-300°	4.4	4.3	4.9	10.6
300-360°	4.6	3.0	1.5	7.9
Above 360°	20.4	28.0	27.3	30.4
Coke	46.5	40.6	35.5	25.4

COMPARATIVE DISTILLATIONS OF THREE TYPES OF MATERIALS.

	Asphaltic oil.	Water gas tar.	Coal tar.
Specific gravity	.9177	1.1165	1.2090
Free carbon	.22	.90	19.80

Distillation—

	% by wt.	Gravity.	% by wt.	Gravity.	% by wt.	Gravity.
Start-110° ...	.32	.9105	.29	.9550	.52	.9862
110-170°	.75	.8215	1.44	.9637	3.06	1.0095
170-235°	6.25	.8436	14.61	.9900	13.39	1.0146
235-270°	23.51	.9604	24.05	1.0188	12.78	1.0357
270-315°	48.00	.8782	15.73	1.0422	10.57	1.0785
Residue	20.27	1.1471	43.31	1.2310	58.92	1.2850

The next table shows diagrammatically the products now commercially obtained from water gas tar.

WATER GAS TAR PRODUCTS.

Crude Water Gas Tar	Light Oil	Crude Benzol	{ Refined 90% Benzol.	{ C. P. Benzol.
			Residue	Refined Special Fraction.
		Crude Toluol	{ Refined Com. Toluol.	{ C. P. Toluol.
			Residue	Refined Special Fraction.
	Naphthalene Oil	Crude Solvent	{ Refined Solvent Naphtha	{ Refined Solvent Naphtha.
		Naphtha	Residue	C. P. Toluol.
		Crude Heavy	{ Refined Heavy Naphtha	
		Naphtha	Residue	
	Dead Oil	{ Naphthalene Salts....		
		Dead Oil		
	Creosoting Oil			
	Road Compound			
	Pitch			

FIG. 13.

Copperas mixing tanks.

FIG. 14.

Cyanogen washer.

It seems a far cry from the distillation of gas from coal to the extraction of gold from its ores and yet industries as different as these two are correlated. To explain, it may be recalled that nitrogen has been found in the coal and that it appears combined in the by-products in many different ways. Among them it is found in the gas, the tar, the ammoniacal liquor, and, after the gas is purified, in the purifying material, combined with carbon to form cyanogen and cyanogen compounds, such as the ammonium salts, the thiocyanates, and others. And a large part of the metallic gold now extracted from low grade gold ores and tailings is, following the process devised by MacArthur and Forrest and modified by many others, dissolved out by aqueous solutions of the alkali cyanides which can be operated so economically that in certain localities ores containing so small a gold content as one dollar per ton can be worked to profit.

There have been many methods of cyanide recovery devised. These are described by Robine and Lenglen.⁷ Among them is the Bueb process used to some extent in this country which consists briefly in scrubbing the gas, before its ammonia and sulphide is removed, with a solution of copperas whereby ammonium sulphate which remains in solution, and ferrous sulphide, which remains in suspension, are produced. The hydrogen cyanide and free ammonia in the gas now react with the ferrous sulphide giving ammonium ferrous ferrocyanide of the formula $(\text{NH}_4)_2\text{FeFe}(\text{CN})_6$. Some of this double ferrocyanide may be converted into soluble ammonium ferrocyanide by the reagents present and to prevent this the "mud" is either boiled or made slightly acid with sulphuric acid.

In either case the insoluble double ferrocyanide is formed and the mud changes color from almost black to light yellow. The final products are an insoluble double ferrocyanide, and a solution of ammonium sulphate, which are separated from each other by filtration. The process has been found to work best at temperatures not exceeding 100° F. Under these conditions 90 to 100 per cent. of the total cyanogen is extracted. On a yield of $1\frac{3}{4}$ pounds of cyanogen per ton of coal carbonized, equivalent to about 110 grains of cyanogen per 100 cubic feet of gas the amount of copper as required theoretically is 6.3

⁷ "Cyanide Industry." Trans. by J. A. LeClerc, with appendix by C. E. Munroe. John Wiley & Sons, New York, 1906.

. FIG. 15.

Neutralizing tanks.

FIG. 16.

Top of neutralizing tanks.

pounds and varies very little from this in practice. The ammonia absorbed in the process is equivalent to from 4 to 4.5 pounds of ammonium sulphate per ton of coal. About two-thirds of this appears as ammonium sulphate and one-third as insoluble ammonium compound in the press cake. The absorption of cyanogen by the Bueb method generally takes place in a standard washer. The gas should reach the washer freed from tar and at a temperature not over 100° F. The solution of copperas (ferrous sulphate) is run into the outlet end of the washer, where it is first converted into ferrous sulphide and ammonium sulphate. There is a tendency for the ferrous sulphide to adhere to and build up on the exposed surface. This would soon clog up the bundles in a standard washer, and for this reason the bundles in the last tray are replaced by large discs attached to the shaft and spaced about 3 inches apart. But even these gradually clog up and must be cleaned at times.

A device which kept the liquid in this chamber violently agitated would probably be preferable. In the original method of operating these washers the material was pumped forward from tray to tray whenever the first tray was saturated. This involved a great deal of pumping and it has been found that operating the washers on the same principle as an ammonia washer simplified the operation. The material in the inlet tray is tested from time to time by drawing off a small sample and acidifying with sulphuric acid. After stirring well a drop of this mud is put on a piece of white filter paper. Near it is put a drop of dilute ferric chloride solution so that the liquid from the two drops as they spread out on the paper will come together. A blue color occurring at the point where the drops meet is a sign that the mud contains an excess of ferrocyanide over iron and is therefore ready to be drawn off. If the material is saturated a slow stream of copperas solution is run into the outlet end of the washer. This forces the material in the different trays forward and the saturated acid overflows from the first tray. The copperas solution is kept running until the material in the first tray shows that it is no longer saturated.

In Germany the mud as it comes from the washers is generally sold to chemical works. At the Astoria plant of the Consolidated Gas Co. of New York mud is pumped into lead lined tanks heated to about 200° F. and acidified with sulphuric acid.

The addition of acid changes the color of the mud to light

FIG. 17.

High-pressure pumps.

FIG. 18.

Filter press ready for filling.

yellow. During this operation large quantities of hydrogen sulphide are set free and in order that this does not escape into the room the tanks are fitted with vent pipes connected to a fan which discharge the gases out of the building. Enough acid is used so that the material is slightly acid to litmus. The mud is again tested for soluble ferrocyanide with ferric chloride solution on a piece of white filter paper and if the blue color appears ferrous sulphate solution is added, a little at a time, until upon testing the blue color no longer appears. This converts all the cyanogen into an insoluble form.

The mud now consists of insoluble double ferrocyanide of ammonium and iron and a solution of ammonium sulphate with a little ferrous sulphate and very little free acid. This is pumped into filter presses (Fig. 18). After the press is full hot water is pumped through in order to wash as much as possible of the ammonium sulphate.

The wash water, which is a very dilute solution of ammonium sulphate, is used for making up the copperas solution. It is very difficult to wash out the ammonium sulphate. The best results are obtained by finishing the pressing with mud made by stirring up some of the finished press-cake with water until it disintegrates. The presses are about two-thirds filled with the neutralized mud from the washers and then finished with the mud made from the finished cake. In this way the gravity of the liquid coming from the presses is brought down from 8-10° Baumé to 1-2° before washing with water.

The solution of ammonium sulphate which runs from the filter presses is neutralized with ammonia. For this purpose some of the mud as it comes from the washers is boiled and the gases, principally ammonia and hydrogen sulphide, pass into the ammonium sulphate liquor from the presses. This not only neutralizes the free acid but also precipitates the small amount of iron present. This is necessary to avoid discoloration of the sulphate. The neutralized liquor is allowed to settle and the clear solution evaporated in lead lined pans. This solution contains approximately one pound of ammonium sulphate per gallon. The sulphate separates out on evaporation and is dried in a rotary drier (Fig. 24) by means of a current of air from a small blower heated by passing over steam radiators before passing through the drier. About 2.5 to 3 pounds of sulphate are produced per ton of coal carbonized.

FIG. 19.

Filter press partly opened and dumped.

FIG. 20.

Pile of press-cakes.

The cyanogen cake from the filter presses has approximately the following composition:

	Per cent.
Water	50 to 40
Cyanogen	22 to 28
Ammonia	5.3 to 7

About 6 pounds of press-cake are produced per ton of coal carbonized. When it first comes from the presses it is yellow in color, but on contact with air it rapidly turns deep blue to oxidation. It is sold to chemical works to be converted into sodium or potassium ferrocyanide. This is done by first distilling with lime which drives off the ammonia and forms calcium ferrocyanide. The solution of calcium ferrocyanide is filtered from the residue of iron hydroxide and is then treated with sodium or potassium carbonate, forming the corresponding ferrocyanide and calcium carbonate which settles out. The clear solution is then concentrated and the ferrocyanide crystallized.

Through the courtesy of Mr. Walter R. Addicks I am able to exhibit the following pictures of the cyanide recovery apparatus used in a gas works in this country.

No. 13—Shows tops of underground copperas mixing tanks with motor driven stirrers; copperas bins at the rear. Copperas solution is forced over to the cyanogen washers by steam pump on the left.

No. 14—Shows cyanogen washer which received the copperas solution from tanks shown in No. 13. After the copperas solution has extracted the CN from the gas it is returned to the factory in the form of cyanogen mud and stored in underground tanks under the filter press platform until ready to be worked up.

Nos. 15 and 16—Top of neutralizing tanks where the cyanogen mud is neutralized with sulphuric acid.

No. 17—Shows two of the five high pressure pumps which pump the mud from the neutralizing tanks through the filter presses.

No. 18—Shows filter press closed ready for filling.

No. 19—Shows filter press open and partly dumped; the press-cake is visible in the foreground.

No. 20—Shows pile of press-cake.

No. 21—Shows cyanogen press-cake bagged, ready for shipment.

No. 22—View of lead lined evaporating pan for sulphate

FIG. 21.

Cyanogen press-cake ready for shipment.

FIG. 22.

Evaporating pan.

liquor. Note steam header to the left, which is connected to lead pipe coils in bottom of pan.

No. 23—Shows ends of sulphate evaporating pans with piles of sulphate crystals on drain-boards.

No. 24—Shows rotary sulphate dryer with pile of sulphate under discharge end to left, and bags of sulphate in the foreground.

Unfortunately the demand for cyanides is not yet sufficiently large to warrant the cyanide recovery process being pushed very far.

Another by-product which warrants further consideration is the spent oxide. Material rich in sulphur has been burnt in acid chambers and it has been proposed for use in copperas making. Two sulphur recovery processes which have been demonstrated as feasible and operative in the laboratory are now being tested on a commercial scale in the factories, Burkheiser's recovery process being operated in connection with the Flemalle Grande coke ovens near Liege, Belgium, while Walther Feld's rival process is being employed at the gas works in Konigsberg, Germany. Both aim to produce ammonium sulphate from the ammonium compounds in the gas liquor and the sulphur compounds obtained from the coal. Feld's process is of special interest to the theoretical chemist in that the formation of the commercial product sought and the saving of the useful matter accomplished is effected through the aid of the tetrathionates and the controlling under manufacturing conditions of the reactions through which they are formed and those into which they will enter.

It may perhaps be admissible for me in closing to refer to a scheme for gas making at the coal mine which has interested me much for a long time. I perhaps cannot better present the matter than by quoting from an address made to the American Institute of Chemical Engineers in 1909.⁸

"I have long looked upon our present custom of transporting coal long distances to be converted into gas as uneconomic, for a not inconsiderable quantity of coal is burned to provide the energy with which to haul this coal. Not only that but, since the gas constitutes but a very small percentage by weight of the coal, there is a considerable waste in hauling the coke, with its

⁸ Trans. Am. Inst. Chem. Eng., 2, 100, 1909.

FIG. 23.

Sulphate evaporating pans.

FIG. 24.

Rotary sulphate dryer.

ash, and the by-products. Further, to provide for emergencies, large stocks of coal must be accumulated in advance at the gas works, and as coal, particularly gas coal, begins to deteriorate as soon as it is removed from the mine, there is a very considerable loss going on all the time from this cause. Further, as the by-products or residuals are now purchased in the crude states in relatively small quantities at the different gas works, a large part of their value is consumed in collecting and transporting them to central refineries.

"By producing the gas at the mine and shipping it by pipe line the cost of haulage of the coke, with its ash, and crude by-products is saved. The wastage of coal by weathering is saved. The cost of collection and transportation of the crude residuals is saved. Such coke as is not needed for industrial purposes can be converted in producers into gas which, by means of internal-combustion engines, can be used in generating electricity for distribution, and the ash from this coal can be put into the mine for use as a filler in place of coal.

"It is evident that gas can, under these circumstances, be made and delivered at a much less cost than is the case at present, though it may be necessary after long travel to enrich it near the point of consumption. Furthermore, the valuable areas now occupied by gas plants in our cities can be given up to more concentrated industries and cheap country lands be substituted for them."

The pertinency of this proposed scheme to the topic given me for consideration lies in the improved opportunity which this plan would afford for the utilization of the by-products, and I foresee that should this plan of gas generation at the mine ever be realized there would grow up about the gas generating plant a large number of industries based upon the utilization and further manufacture of the by-products, and that they would be greatly fostered, as would many other industries, by the very cheap gas, which could, under these circumstances, be produced for use as a source of heat, power or light, and which could be so cheaply produced as to enter, on the spot, into competition with water power as a source of electric energy. It is of interest to note that Sir William Ramsey has recently given this suggestion of carrying on the manufacture of gas at the coal mine his endorsement.