COAL-GAS RESIDUALS AND THEIR APPLICATION.*

BY

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THE destructive distillation of coal, as practised to-day, may be divided into two classes, the first being that practised in gas works, the second being the one practised by the coke oven operator. The latter method of distillation, or carbonization, may also be subdivided into two classes, or distillation with by-product recovery, and bee-hive oven distillation; as the latter yields no other product than coke, it will not be given any further consideration.

These two classes of distillation, or carbonization, lead to two very different methods of operation; the object of the gas works operator is to produce a maximum yield of gas possessing certain required qualities, such as candle-power and thermal value, with the recovery of certain by-products, while the object of the coke oven operator is to produce a maximum of low-volatile coke, the recovery of by-products, in some instances, being entirely neglected.

The quantity of gas produced, as well as the production of coke and other by-products, is entirely dependent upon the character of the coal distilled, as well as on the character of the carbonizing plant. Gas intended for cooking or illuminating purposes must possess certain characteristics, and must consequently be purified, as the crude gas contains substances which are of a harmful character, and, if retained in the gas, these substances would be liberated during combustion; but these substances all possess a commercial value, and, with the exception of coke and retort graphite, the by-products secured from a gas works are therefore due to the necessity of cleaning the gas before it can be used for domestic purposes.

The principal by-products consist of coke, retort graphite, tar,

* Presented at a meeting of the Section of Physics and Chemistry held Thursday, January 6, 1916.

naphthalene, ammonia, cyanogen, and sulphur. Owing to the necessity, in many cases, of selling domestic gas on a candle-power basis, it is not advisable to remove such valuable products as benzol and toluol from the gas works product, and, as a rule, these constituents must therefore be sought in the products from the coke oven.

The appended diagram, adapted from one prepared by W. J. Butterfield, approximates the average yield of primary products, the return of secondary products secured from the primary, as well as the ultimate yield of some of the more important subsequent products, the amounts secured being based on the distillation of 100 tons of coal in gas works practice.

While this diagram gives the total amount of coke produced as 70 tons per 100 tons of coal carbonized, the amount of coke of salable size will hardly average more than 50 tons, and often less, due to the amount used as fuel in the producers which supply the heat required for distillation, and to the amount of breeze produced by handling. In Germany this coke breeze is worked up into briquettes, but little has been done in this particular in this country, probably due to our still illimitable supply of coal, and to our negligence in the conservation of our resources.

The salable coke produced in coke ovens amounts to from 60 to 65 per cent. of the weight of coal carbonized, this latter coke being distinguishable from gas works coke in that it is better adapted for metallurgical purposes.

The amount of graphite produced in the retort is dependent upon the type of retort used, as well as on the heat of carbonization employed, also on the character of the coal distilled; this graphite has quite some commercial value.

The moment the gas is released from the coal, and when it is subjected to cooling, it begins to condense and to drop various compounds of a hydrocarbon nature, these compounds being deposited in conjunction with an aqueous solution of ammonia salts combined with dust and soot; these hydrocarbon substances, together with the dust and soot, form tar.

After the gas has been subjected to this process of cooling, or after the tar and a portion of the ammonia compounds have been removed, the gas is usually subjected to a washing process for the removal of the remaining ammonia, or the ammonia may be directly absorbed by passing the gas through a sulphuric acid bath.

NON-VOLATILE RESIDUE
70 TONS

COKE
70 TONS (GROSS)

RETORT CARBON
0.10 TON.

OVEN COKE
60 TONS
(NET SALEABLE)

GAS
(OXIDE PURIFIED)
1,200,360 Cu Ft.

GAS COKE
47½ TONS
(NET SALEABLE)

USED ON WORKS
AND FREEZE
22½ TONS.

GAS
(CATALYTICALLY PURIFIED)
550 B.T.H.U. PER CU.FT.
1,200,000 Cu.Ft.

GAS
(PARTLY DE-BENZOLIZED)
550 B.T.H.U.
1,198,000 Cu.Ft.

BENZOL
75 GALLS.

GAS
(DE-BENZOLIZED)
500 B.T.H.U.
1,188,000 Cu.Ft.

BENZOL
150 GALLS.

BENZOL
(DE-TOLUOLIZE)
195 GALLS.

BENZENE
100 GALLS.

PRODUCTS FROM THE DISTILLATION OF 100 TONS

COAL
100 TONS

GAS
16.85 TONS
(1,213,200 Cu. Ft.)

CARBON
DISULPHIDE
72 LBS.
(360 Cu. Ft.)

CYANOGEN
120 LBS.
(840 Cu. Ft.)

PRUSSIAN BLUE
224 LBS.

YELLOW PRUSSIAN
336 LBS.

SODIUM CYANIDE
224 LBS.

SULPHURET'D HYDRO.
1065 LBS.
(12,000 Cu. Ft.)

SULPH. ACID (100%)
1.4 TONS

SULPH. ACID (SP GR. 1.71)
1.8 TONS

SURPLUS ACID
0.075 TONS

1.125 TONS

SULPHUR
26

BENZOL
225 GALLS.

TOLUENE
30 GALLS.

RESIDUES AND
LOSS
95 GALLS

OF 100 TONS OF BITUMINOUS COAL.

COAL
100 TONS

VOLATILE PRODUCT
30 TONS.

AMMONIACAL LIQUOR
7.8 TONS
(1750 GALLS.)

+ SCRBR. WTR.
3500 GALLS.

AMMONIA
672 LBS.

LIGHT OIL
298 LBS.
(34 GALLS.)

BENZOL
112 LBS.
(12½ GALLS.)

NAPHTHA
AND LOSS
186 LBS.

BENZENE
5 GALLS.

TOLUENE
1½ GALLS.

RESIDUES
AND LOSS
6 GALLS.

NAPHTHA

CRUDE PHENOL
108 LBS.
(17 GALLS.)

CARBOLIC
ACID
37 LBS.

CRESYLIC
ACID
58 LBS.

SULPHATE OF AMMONIA
2688 LBS.

HYDRO.
S.
Fr.)
10 (100%)
NS
DIO (SP GR. 1.71)
ONS

1.125 TONS

PRODUCTS

5.

The cyanogen in the gas may be removed either before or after the removal of the ammonia, the gas, in the first case, being washed with an iron solution with the consequent formation of ammonium ferrous-ferrocyanide, this being an insoluble product, while in the second case the gas is washed with a solution of hydrated lime and iron, this latter product being a soluble one; these products are generally converted into potassium ferrocyanide, commonly known as yellow prussiate of potash, or into sodium ferrocyanide. At present the removal of cyanogen from coal gas is a very profitable investment, but, besides this, its removal is of distinct advantage in operation, as the presence of cyanogen has a very deleterious effect on all steel work, and especially on gas-holder sheets.

The sulphur compounds are usually removed in the purifiers, but a portion is absorbed during the process of washing and condensing; this constituent, principally in the form of hydrogen sulphide, is usually absorbed by oxide of iron, but little lime being used for this purpose to-day. The sulphur thus absorbed is removed from the oxide of iron and converted into sulphuric acid. Unless special requirements call for the removal of carbon bisulphide it is retained in the gas, as its removal entails quite some difficulties and its economy is open to question.

The apparatus usually employed in gas works practice is so constructed as to remove not only the so-called impurities, but also valuable by-products by condensation and absorption, the removal by condensation being due to the fact that the coal is distilled at very high temperatures, thus causing the formation of various gaseous products which do not remain in the gaseous state at ordinary temperatures, and which are therefore readily removed during the process of cooling.

This short explanation of the method of operation and the statement of the nature of the by-products to be expected enables us to give a more detailed description of the products and their uses.

Coke is the first by-product obtained through the dry distillation of coal, and it is the residue left in the retort or oven chamber after the volatile products have been driven off. The composition of the coke is, of course, dependent upon the character of the coal carbonized; it is hard and brittle, and varies in color from very dark to silver gray, being composed of highly complex com-

pounds of carbon, hydrogen, oxygen, nitrogen, and sulphur. The porosity or density of coke is dependent upon the type of retort used for distilling and upon the method of quenching and handling the coke after it has been ejected from the retort; in gas works practice vertical retorts produce a coke of maximum density, due to the fact that the weight of the coke itself causes a sintering of the coke particles. Gas works coke is generally used for domestic purposes, the metallurgist depending in most cases on the product received from the coke oven.

The late Prof. Vivian B. Lewes, of England, said: "Among the factors that lead to the commercial supremacy of a country, by far the most important is the command of fuel or other source of power; and England's position in the past has been governed largely by her coal fields, which in little more than a century raised her to the forefront as a commercial power. The very abundance of our coal supplies was a source of weakness, as it led to outrageous waste, polluted our atmosphere to a criminal extent, and so encouraged uneconomical methods of using it as seriously to deplete our available stock, the result of which has been the increase in price during the last few years, and the certainty that the future will see further advances but no fall to the old rates. The day of cheap coal has gone, never to return."

If this statement is true for England, how much more so is it applicable to our own conditions, where so much remains to be done in conserving our fuel beds, and this conservation can be greatly aided by a concerted effort to educate the user in the benefits to be derived from the burning of coke; but, here again, we find that in the manufacture of metallurgical coke the warning has not been heeded, and this industry in many instances exhibits a prolific waste which is almost criminal. The change from the bee-hive to the by-product oven is very slow, but it is progressing; we find that in 1893 the bee-hive ovens produced 9,464,730 short tons of coke, the by-product ovens producing only 12,850 tons during this same period; in 1901 the product was: bee-hive ovens 20,615,983 tons, by-product ovens 1,179,900 tons; in 1910, bee-hive ovens 34,570,076 tons, by-product ovens 7,138,734 tons; and in 1913 the bee-hive oven product amounted to 33,584,830 tons, while that from the by-product ovens was 12,714,700 tons. It is true that the total consumption of coke has increased, but while that produced by the bee-hive ovens in 1893

amounted to 99.99 per cent. of the total, this was decreased to 94.59 per cent. in 1901, to 82.88 per cent. in 1910, and to 72.54 per cent. in 1913.

A series of tests made by the American Radiator Company to determine the efficiency of domestic fuels showed that gas coke of nut size led the list with an efficiency of 78.7 per cent., followed by gas coke of egg size with 75.43 per cent.; Pittsburgh coke with 71.40 per cent.; anthracite coal with 66.30 per cent., and Pocahontas coal with 66.10 per cent. It was also shown that in ease of kindling Pocahontas coal stood first, but gas coke of nut size was a close second, followed by gas coke of egg size, Pittsburgh coke, and anthracite coal last. Gas coke burns with an even, smokeless fire, it is easily controlled and clean to handle; it is also probably the most economical fuel on the market, and there is no reason why it should not displace many forms of domestic fuel now in use, thus greatly assisting in conserving our coal supply and adding benzol and toluol, with their subsequent products, to our source of national wealth.

Retort graphite is produced by the decomposition of the hydrocarbons in the gas, these latter constituents having been deposited on the walls of the retort. Owing to its poor heat-conducting qualities, it must be removed periodically from the inside of the retorts, clay retorts requiring more frequent cleaning periods than do those made of silica.

This graphite has found its most important application in the production of carbon electrodes, the raw graphite being thoroughly cleaned, crushed into a powder, and then formed into a plastic mass by the admixture of coal-tar and lamp-black; this mass is formed into rods by passing it through a hydraulic press.

The rod thus formed is then baked in a kiln, where the coal-tar is decomposed by heat, producing graphitic carbon, which combines with the retort graphite and forms a hard but brittle mass.

Tar is chiefly removed from the gas by progressive condensation, and, when removed in this manner, is accompanied by so-called gas liquor, or ammonia liquor, these two liquids being later separated by virtue of their difference in specific gravity. The gas, after this treatment, still contains a certain amount of tar in the shape of a fog or mist, and this is usually removed by friction in some sort of mechanical extractor.

These accepted methods of tar removal are now being re-

placed by others of greater value, such as the electric de-tarring system in which the gas is sent through an electric field, the action of which is to cause the tar to coalesce and drop out of the gas, and the system which embraces progressive washing combined with progressive cooling, in which, due to the fact that the gas is not cooled below the point where any volatile hydrocarbons are condensed or absorbed by the effluent, the tar is fractionated into pitch, heavy oils, and middle or light oils, without the usual interposition of a tar still.

Tar is one of the most valuable of all coal-gas residuals, and while, in this country, owing to economic conditions, it has found quite some extended use in its original form, it finds its greatest value in its application in the arts; the distillation of tar at certain temperatures produces a water-like oil, which in turn forms the base of so many of the beautiful coal-tar colors so much in demand at present. Carbolic acid, naphthalene, anthracene, and benzol are also produced by this distilling process, and each of these constituents in turn produces a long series of other products.

Naphthalene is one of the gas constituents which accounts for a great deal of the trouble experienced in present-day methods of carbonization, but its removal can be accomplished by washing the gas with a suitable oil, such as anthracene or creosote oil, or water gas tar, the resultant emulsion being gradually cooled, thus causing a separation of the naphthalene crystals.

The formation of naphthalene is probably due to the high heats employed in present-day carbonization, it being a generally-accepted fact that this formation is brought about by a partial decomposition of the tar in the gas. Fortunately, the greater portion of the naphthalene produced goes over into the tar effluent and is thus removed with the latter, as its excessive presence in the apparatus and gas mains usually causes a stoppage. Naphthalene is also due to the character of the coal used, and upon the time of contact between the gas and the hot coke and hot retort walls. Besides other domestic uses, naphthalene is of great importance at present in the production of dyes.

Cyanogen is a carbon-nitrogen compound, and it is probably produced during the period of carbonization in the form of hydrocyanic acid by the decomposition of some of the ammonia due to the contact of the gas with the hot coke and the hot retort walls, this statement being substantiated by the fact that the

quantity of cyanogen produced by the carbonization of any particular coal bears a certain relation to the amount of nitrogen (ammonia-producing agent) in the coal.

In its gaseous form cyanogen is colorless and very poisonous; in combination with potassium it forms potassium cyanide, this latter compound having found its largest application in the cyanide process of gold extraction, which process depends upon the solubility of gold in a dilute solution of potassium cyanide in the presence of air or some other oxidizing agent; this process is best adapted for use with free-milling ores after the greater portion of the gold has been removed by amalgamation, thus recovering such portions as were not taken up by the amalgam, the gold being later usually separated from the cyanide solution by an electric or metallic precipitation process.

Potassium ferrocyanide is the base of a great many cyanogen products, one of the principal products being Prussian blue; this coloring matter is obtained by mixing the potassium ferrocyanide with a solution of ferrous sulphate, a grayish-white precipitate of ferropotassic ferrocyanide resulting, the mother liquor, which contains potassium sulphate, being removed from the precipitate by decantation. After this precipitate has been allowed to settle, it is washed with a large amount of water and then oxidized, this oxidation giving it the beautiful blue color required in the dyeing industry.

In one process covering the removal of cyanogen from gas, iron sulphate, commonly known as copperas, and ammonia are used as the two reagents necessary to combine with the cyanogen, and a certain portion of the ammonia thus removed from the gas remains in the cyanide cake, the final resulting compound being ammonium ferrous-ferrocyanide. This process, therefore, requires that the cyanogen be removed before the ammonia has been extracted, but in another process the ammonia is replaced by milk of lime, and consequently follows behind the ammonia extraction process, the final product being calcium ferrocyanide.

In another process used in England the cyanogen is removed from the gas by washing the latter with a solution of soda and ferrous carbonate, the resultant liquor being deprived of its ammonia by evaporation. This liquor is then pumped through a press where the insoluble matter is removed, the cleared solution being then crystallized, giving sodium ferrocyanide, or prussiate

of soda. This latter product is washed for purification and then recrystallized.

Ammonia is a nitrogen-hydrogen compound, and, besides being a source of great revenue to the coal-gas producer, its removal from the gas is necessary for both practical and hygienic reasons; its presence in the gas exercises a destructive influence on the brass and copper work of meters and gas fittings, and when burned in conjunction with gas it gives off noxious fumes of oxides of nitrogen.

The usual method employed for the removal of ammonia depends upon the solubility of ammonia in water, as at ordinary temperatures water can absorb about 708 times its volume of ammonia gas. Raw ammonia liquor from a gas works usually contains from one to two per cent. of ammonia, and, owing to the excessive cost of transporting this weak liquor, it is usually worked up into concentrated liquor, aqua ammonia, or ammonium sulphate.

Concentrated ammonia is a product obtained by distillation of the raw liquor with lime, and absorption, in water, of the ammonia evolved. It is used in the production of other ammonia compounds.

Aqua ammonia is a solution of ammonia in distilled water, a great deal of it, in a dilute solution, being used for cleansing purposes.

Ammonium sulphate is produced by distilling the liquor and absorbing the ammonia vapors in a sulphuric acid bath, thus forming the sulphate crystals; or it may be made by passing the gas, after the tar has been removed, directly through the acid bath, this being the so-called direct process. The only really direct process, however, is the one in which the ammonia in the gas is combined directly with the sulphur radical, the latter also existing in the gas, this compound being later oxidized. This process requires that the gas be washed with ammonium polythionate, the latter absorbing both ammonia and hydrogen sulphide, the resultant liquor being oxidized or regenerated by means of sulphur dioxide gas, and after the liquor contains about 35 to 40 per cent. of ammonium sulphate in solution it is boiled, resulting in the breaking down of the polythionates with the consequent precipitation of the sulphur; this sulphur is returned to the sulphur stoves for the further production of sulphur dioxide, while the cleared liquor is evaporated to crystallization, this

method of procedure therefore requiring no sulphuric acid for the production of the salts, but finding all of the necessary reagents in the gas itself. Sulphate finds its greatest use in the manufacture of fertilizer, it being the active nitrogen-carrying agent in this product; it is also used for the production of other ammonia compounds.

Ammonium chloride, commonly termed sal ammoniac, is produced by using hydrochloric acid as an absorbing agent, followed by evaporation and crystallization. Ammonium sulphate is the principal source of sal ammoniac production in this country, the sulphate being heated in conjunction with common salt for its formation. Sal ammoniac is used as an agent in the galvanizing process, for soldering, and as an agent in electric batteries.

Liquid anhydrous ammonia is produced by freeing the ammonia gas of all moisture and impurities, after which it is liquefied under pressure; this product is used in the production of low temperatures by the absorption of heat, as in refrigeration.

Ammonium carbonate is produced by heating ammonium sulphate in conjunction with calcium carbonate, and it finds its greatest application in the scouring of wool.

Ammonium nitrate is produced by neutralizing nitric acid with ammonia, and it is used in the manufacture of explosives.

There are many other ammonia compounds, but the ones here cited are the principal products, and they can all be prepared from ammonium sulphate, thus making this latter compound one of the principal by-products of coal distillation.

Benzol and its homologues are obtained during the process of tar distillation and from the products due to coke oven distillation, they being secured in the latter case by washing the gas with a suitable oil, the resultant product being purified by repeated distillation and washing, thus separating it into benzol, toluol, xylol, and solvent naphtha; the greatest usefulness of these products is in the production of dyes, explosives, artificial perfumes, and pharmaceutic compounds.

COAL-TAR AND BENZOL PRODUCTS.

A large number of our industries are dependent upon the use of coal-gas by-products for their successful operation, as is witnessed by the following statement, taken from the census of 1909. The

principal industries dependent upon coal-tar products, with the number of employees, capital invested, and annual value of product, are:

Industry	Employees	Capital	Product
Textile	916,000	\$1,841,000,000	\$1,685,000,000
Leather	62,000	323,000,000	328,000,000
Paper	81,000	400,000,000	260,000,000
Paints and colors	30,000	250,000,000	

Thus we find a total of 1,089,000 persons employed in these four industries, with a capital investment of \$2,814,000,000, and an annual product for the first three representing \$2,273,000,000 in value. Since the 1909 census these industries have all increased their production, and, when taken in conjunction with other manufacturers, such as the producers of shoe dressings, writing and printing inks, etc., it is perhaps safe to estimate that at present fully 2,000,000 persons find employment in industries which are dependent upon dyestuffs for their success.

Artificial dyestuffs, produced from the by-products of coal distillation, have practically displaced those formerly used, such as natural indigo, cochineal, fustic, madder, and many others, and this is properly so, because the artificial material is easier applied, has a greater brilliancy of color, and can be secured in a great variety of shades; but, unfortunately, our American industries have always depended on Europe to supply the necessary material. Statistics teach us that 80 per cent. of our coal-tar dye requirements are imported from Europe, principally from Germany, the other 20 per cent. being produced by American manufacturers; but here again we find that we must turn to Europe for our supply of the greater portion of the necessary intermediates, or raw product, before we can produce this 20 per cent. of coloring matter.

The present war soon brought about an acute situation among our manufacturers, as the stock on hand was soon depleted, and a replenishment became almost impossible. The seriousness of this situation can readily be recognized when I mention that "sulphur black" increased in price from 20 cents to as much as \$3 per pound; indigo from 15 cents to \$1 per pound; paranitraline from 15 cents to \$1.75; aniline oil from 10 cents to \$1.75; betanaphthol from 12 cents to \$1.50; and so on through the list. As regards the raw or primary material, I might mention that the

price of benzol has increased from 20 cents to as much as \$1.20 per gallon, with about 70 cents as a contract price, while toluol has increased from 25 cents to about \$6 per gallon, with a contract price of about \$4.25.

These conditions certainly compel us to turn seriously towards our own supply of tar and benzol and cause us to question ourselves as to our ability to do that which we have permitted others to do for us. Several American manufacturers have gone ahead vigorously in an attempt to supply our domestic needs, and credit for stepping into this breach must be accorded such firms as the Shoellkopf Aniline and Chemical Works, Inc., Buffalo, N. Y.; The Hudson River Aniline Color Works, Albany, N. Y.; W. Beckers Aniline and Chemical Works, Brooklyn, N. Y.; Central Dyestuff and Chemical Company, Newark, N. J.; and Heller and Merz Company, Newark, N. J.

Other concerns have taken up the manufacture of intermediate products from our raw material, and, while all of these manufacturers are being supported by the allied industries to-day, the question as to their future is still an open one, and reference to this will be made later.

We have the necessary raw material, tar and benzol, on hand, and a lack of these products will soon bring about their further recovery if the situation should demand it, as the greater amount of coal carbonized for the production of coke in America, as previously stated, is still produced in the wasteful bee-hive oven. Economic and commercial conditions have prevented the development of the dye and other allied industries in this country, and consequently our manufacturers have in the past diverted their raw material in great measure into the production of tar oils and pitches.

Tar is a very complex substance, and it has been estimated that it consists of a mixture in excess of two hundred chemical compounds. The constituents of tar are usually divided into three classes, the first being the hydrocarbons, the second the phenols, and the third the nitrogenous compounds, these classifications being made in accordance with the chemical reactions of the compound in question. The hydrocarbons, as can be seen from the name, are composed of hydrogen and carbon, and they are termed chemically indifferent substances because they exhibit neither alkaline nor acid properties. The hydrocarbon

compounds, of which benzene, toluene, xylene, naphthalene, and anthracene are the most valuable, form the principal portion of coal-tar. The phenols, or the second class of constituents, consist of oxygenated bodies of carbon, hydrogen, and oxygen, being known as the "tar acids." Owing to their weakly acid condition, they can be dissolved in caustic alkali solutions, but not in dilute acids. The most important members of the phenol group are carbolic acid and cresol. In the third class we find compounds composed of carbon, hydrogen, and nitrogen, these compounds being of a basic nature and soluble in acids.

The distillation of coal-tar thus serves to produce a number of fractions, and these fractions in turn form the base for manufacturing various other important products. Distillation of the average coal-tar usually gives us four fractions, the first being "light oil," which comes over at a temperature of between 70° and 160° C. (158° and 320° F.); the second is a "middle" or "dead oil," coming over between 160° and 230° C. (320° and 446° F.); the third is a "heavy oil," including anthracene oil, and it comes over at between 230° and 360° C. (446° and 680° F.), while the fourth is pitch, or the residue above 360° C.

The first fraction, or "light oil," produces such intermediate products as benzene, toluene, xylene, and phenol (carbolic acid), while the crude commercial products are benzol and solvent naphtha; the intermediate chemical products are nitrobenzene, aniline salts and oils, and carbolic acid, while the refined chemical products are the nitrotoluenes, diphenylamine, dyes, hydroquinone, and various medicines and drugs.

The "middle oil" gives us phenol, cresols, naphthalene, and heavy hydrocarbons as an intermediate product, the crude commercial products being creosote oil, lamp-black, and various disinfectants. The intermediate chemical products are carbolic acid, picric acid, phthalic acid, naphthols, naphthylamine, and salicylic acid, while the refined chemical products consist of picric acid, the picrates, and several other nitro-compounds used in the manufacture of explosives; naphthol dyes, colors, indigo, and refined carbolic acid.

The "heavy oils" produce cresols, naphthalene, anthracene, heavy hydrocarbons, and quinoline bases; the crude commercial products consist of oils used in road making, lamp-black, creosote oil, roofing and paving tars. The intermediate chemical prod-

ucts consist of anthraquinone and alizarin, while the alizarin dyes are known as the refined chemical products.

The fourth fraction consists of soft and hard pitch, a large portion of which is used in the manufacture of protective paints.

The manufacture of aniline dyes necessitates quite a number of very complicated chemical combinations, and the chief sources of this product are to be found in benzene, toluene, and phenol, or in the nitro-substitution products of these compounds; this material is used in conjunction with nitric, sulphuric, and acetic acids, alcohol, sodium nitrite, caustic alkalies, zinc dust, bromine, and chlorine.

The naphthol dyes are produced from phthalic acid, the naphthols and naphthylamines, etc., these being intermediate products derived from naphthalene. The eosin dyes are due to benzene and naphthalene through the medium of resorcin and phthalic acid; indigo is also a naphthalene product.

Anthracene is converted into anthraquinone by oxidation, and this in turn gives us the hydroxyanthraquinones and such derivatives as the alizarins, purpurin, etc., all of which are used in the production of alizarin dyes.

Carbolic acid, or pure phenol, is, as stated before, obtained from both the light and middle oils, and it can also be made synthetically from benzene; it is used as a drug as well as an antiseptic, and it occupies a very important rôle in the manufacture of picric acid and some of the dyes.

The manufacture of synthetic phenol, using benzol as a base, was not encouraged or practised in this country before the present war, and consequently little attention has been paid to this branch of conservation, and it may therefore be interesting to give a short explanation of its manufacture.

The benzol stripped from the gas, or secured as a distillation product from tar, is first sulphonated by mixing about 2.7 parts of 98 per cent. sulphuric acid with one part of benzol in a cast-iron vessel having a capacity of approximately 400 gallons, this vessel being supplied with means for both heating and cooling the liquid, the escaping matter passing through a reflux cooler, about 150 pounds of benzol being treated at a time. This mixing vessel is provided with an agitating device, and the agitator is set in motion as soon as the benzol is admitted, the sulphuric acid being in the mixer before the benzol is added.

As soon as these two liquids mix, the temperature rises to between 62° and 68° C. (144° and 154° F.), and when the chemical reaction produces no further increase, external heat is applied to a point corresponding to the boiling-point of benzol, about 88° C., or 190° F. This sulphonating process is usually completed in from seven to eight hours.

The sulphonic acid produced as per the above is run into a neutralizing vessel, the latter having a lead lining, where it is first neutralized with milk of lime, and then treated with waste calcium carbonate; this treatment is liable to thicken the liquor, and, if so, some water is added to thin it out, after which the mixture is subjected to a boiling temperature for about one-half hour, steam being used for this purpose. After the steam has been turned off, a volume of water amounting to 150 per cent. of the volume of the original sulphonation mixture is added, this being necessary in order to prepare the calcium sulphate for washing and filtration.

This mixture is now forced through a filter press, where it is also washed with water, the latter amounting to about 50 per cent. of the volume of the mixture. The resultant product is a calcium benzene-sulphonate mixture, and this is now treated with solid sodium carbonate in order that it may be converted into a sodium salt, while the precipitated calcium carbonate is used in neutralizing the sulphonation mixture. The sodium benzene-sulphonate solution is now evaporated, the resultant salt being dried and pulverized, this dried product being placed in a fusion vessel where about 500 pounds of caustic soda are melted with about 50 pounds of water for every 600 pounds of the dry sodium benzene sulphonate, the caustic soda and water being heated to about 270° C. (518° F.) before the sodium benzene-sulphonate is added; heating is continued up to about 315° C. (600° F.), a still further, but slight, rise in temperature taking place after the heat is turned off, the operation being considered complete when all of the sodium salt has been dissolved and the mixture is thin.

The resultant product is now removed from the fusion vessel by means of ladles and placed on shallow trays, where it is allowed to cool, after which it is crushed and dissolved in water, being then treated with sulphuric acid until sulphurous acid begins to go off, this sulphurous acid being finally blown out of the vessel with an air blast, thus separating the crude phenol from the mix-

ture, the latter being then distilled, and the phenol crystals recovered by crystallization. The phenol crystals obtained in this manner usually contain some sulphur compounds which produce disagreeable odors, but this can be removed by distilling the crude product in conjunction with animal charcoal.

The light oil fraction is also responsible for the production of photographic developers as well as of such drugs as phenacetin, acetanilide, antipyrine, aspirin, saccharine, and phenolphthalein.

The synthetic production of many perfumes also owes its existence to coal-gas tar, and it is almost impossible for the layman to differentiate between the natural products and the synthetic substitutes.

Modern coal-tar dye classification divides this product into eight classes, or

1. Acid dyes;
2. Tannin dyes;
3. Dye salts;
4. Sulphur dyes;
5. Vat dyes;
6. Mordant dyes;
7. Developing dyes;
8. Albumin dyes;

and they may be described as follows:

1. The greater portion of the acid dyes consist of sodium salts of sulphonic acids or organic acids or nitro acids, and they are represented by the azo dyes, the eosines, and picric acid. They are used principally for dyeing wool and silk, this material being dyed directly with the aid of an acid or an acid salt in the bath. Cotton is not dyed by these compounds.

2. The tannin dyes are also classed as basic dyes, consisting in large part of hydrochloric acid salts of color bases; if cotton is first treated with tannin we find that it is easily dyed, but we find that wool and silk can be dyed directly without the aid of this intermediate treatment.

3. The dye salts receive their names from the neutral or alkaline salts which are dissolved in the dye solution; they are also termed direct-cotton dyes and substantive cotton dyes, consisting usually of sodium salts of sulphonic or organic acids, the cotton fibre taking them up in this state. The dye-bath also receives some common salt or Glauber's salt.

4. The sulphur dyes consist of a class of colors which are very popular owing to their cheapness and fast qualities. The bath is made alkaline with the soluble sulphides, the color being later developed by oxidation after the cotton material has been removed from the bath.

5. The vat dyes show but little attraction for the common fibres, and they are fixed on the material by reducing them to their leuco compounds in the vat. The material to be dyed is immersed in this reduced dye and thus becomes saturated with it, after which it is exposed to the air, where the color is developed by oxidation.

6. The mordant dyes are of a weak acid character. In order to cause their retention by the fibre, they must be converted into color lakes by means of a mordant, with which the fabric is impregnated prior to treatment in the dye bath. The color known as Turkey red is an example of this class of dye, being made from alizarin, which is yellow and is almost insoluble; the cotton fabric to be dyed is first treated with aluminum salts and Turkey red oil, then is boiled in the alizarin, after which it is treated with calcium salt, the Turkey red color resulting.

7. The developing dyes, owing to their insolubility, cannot be applied directly to the fabric to be dyed, but they are produced upon the fabric itself by first saturating the latter with one soluble component and then immersing it in a second bath of another soluble component, these two components uniting and forming an insoluble dyestuff.

8. The albumin dyes will not adhere of themselves, and they require that the fabric be first treated with some strongly adhesive substance, the principal substance used for this purpose being albumin.

This classification of dyes is only mentioned in order to make somewhat clearer the complex nature of the dyer's art.

The coal-tar dyestuffs found their origin in England, where, in 1856, W. H. Perkin discovered mauve, a sort of violet; this was an accidental discovery, as Perkin was seeking something entirely different, but his chemical ability, combined with a keen business sense, caused him to persevere in this line of chemical research, and he lived long enough to find his crude beginning develop into an immense business which utilized a material, coal-tar, that had previously been considered worthless. The discovery of mauve was soon followed by magenta and fuchsin, while the

soluble blues were discovered in 1862, Hofmann's violet and Bismarck brown in 1863, naphthol or Martius yellow in 1864, and the nigrosines in 1867.

These beginnings soon drew the attention of the Germans to this new industry, and, recognizing the immense possibilities in its development, they very quickly applied their usual patient perseverance and intelligent research to the advancement of this new art; this resulted in the production of orange, red, malachite green, chrysodine, scarlet, metanil yellow, methylene blue, and the eosines between 1875 and 1878; auramine was first produced in 1883; tartarazine and benzopurpurine in 1884; Congo red, benzoazurine, and naphthol black in 1885; diamine red in 1886, and rhodamine in 1887. The early nineties saw the discovery of direct black for dyeing cotton, and acid and chrome black for dyeing wool. It was von Bayer who first succeeded in producing indigo, but many years of patient labor were required before a practical synthetic process permitted of placing this important dyestuff on the market in a commercial sense.

From the latest reports, I learn that the Dow Chemical Company, of Midland, Mich., is erecting, or has erected, a plant for the production of 5000 pounds of 20 per cent. indigo paste per day.

Realizing that industrial progress in this line meant commercial supremacy, the Germans quickly learned that success meant patient scientific research, combined with an adequate supply of raw material, with the result that by-product coke ovens were soon established in the immediate vicinity of their blast furnaces, where the distillation of the coal for the production of the necessary metallurgical coke soon supplied them with all of the by-products required in the development of this new art, an example which we might have followed in the past with great profit, and with relief of mind at present.

The cost of producing dyes in this country is said to be 44 per cent. greater than in Germany, as it is estimated that the cost of a plant capable of producing 3,000,000 pounds of dyestuffs per year would be \$104,000 in the United States and \$70,000 in Germany, while the labor required would amount to \$116,236 in the United States and \$61,493 in Germany. The cost of material would be \$443,000 in the United States and \$317,000 in Germany. These comparative figures show a vast difference in favor of Germany, and the successful establishment of this industry in our

country would require that protection in some form be given the American manufacturer in order to make up this discrepancy.

The discrepancy is even greater than these figures would seem to indicate, because the German manufacturer has been in the habit of selling us his surplus production, and that at a figure lower than the one paid by the domestic consumer. The establishment of this industry in the United States means opposition to the preëminent position of the Germans, whose success is based on a solid foundation of 30 years' standing, and which, therefore, becomes a standing challenge to our chemists and capitalists. We have the necessary raw material, and we possess constructive engineering ability of a character which can supply all of the needful apparatus, but, with all this, an almost unlimited capital and patience will be required.

But this is not all that is required, as chemists, trained in this particular work, are not numerous in this country, and their necessity is shown when it is mentioned that in one German works, producing about 500 colors, we find 300 chemists employed; of these about 100 are engaged in analytical work, and the other 200 are in charge of the actual manufacture of the dyes, thus placing the production of only two or three colors under any one chemist.

After the capital has been supplied, and this new industry has been properly started, it will be necessary to secure proper legislation prohibiting "dumping" on our shores, a performance heretofore practised by the Germans, as well as a prohibition against an unfair restraint of our trade due to the arbitrary action of the German monopoly which is now allowed by foreign law, but not permitted by our own. Any scheme entered into must therefore necessarily depend upon an effective law which will prevent the control of our markets by foreign monopolies in the same manner as a domestic monopoly is now prohibited.

Advices received from Germany indicate that the German monopoly will re-enter the American market as soon as the war is over, and that it will make tremendous efforts to regain this lost business, being prepared to make extraordinary concessions in order to take the business from its infant competitors. It therefore is required of us that we place this new industry on a firm foundation as soon as possible, and that we seek such Federal legislation as will permit the continuance of the project without financial loss.

The dyestuffs subject could be treated at greater length, but the explosives, due to coal-gas residuals, also claim some little attention. The picric acid produced from carbolic acid, or phenol, is the base of "lyddite," used by Great Britain; of "melinite," used by France, and of "shimose" powder, used by Japan; but toluene, a tar or benzol product, is responsible for the production of the new explosive, "trinitrotoluene," commonly known as "T. N. T.," so much used in the present war.

Both picric acid and "T. N. T." are manufactured by a sulphonating and nitrating process, the method of operation in both cases being somewhat similar in detail. Phenol is produced by permitting that fraction of tar distillation coming over at a temperature between 150° and 230° C. (302° and 446° F.) to stand and cool until the naphthalene crystallizes out, after which the mother liquor is agitated in the presence of a solution of caustic soda, the latter combining with the phenol and forming sodium phenolate. This sodium phenolate, due to its weight, sinks to the bottom of the mixing chamber, whence it is drawn off and treated with sulphuric acid, this latter treatment setting free the phenol. This compound is now run into a still and fractionated, the phenol coming over at a temperature between 180° and 190° C. (356° and 374° F.) and crystallizing in sharp, needle-like crystals from the distillate. An equivalent weight of concentrated sulphuric acid is now mixed with the phenol, and the mixture is heated in an iron vessel by means of a steam coil to a temperature of slightly above 100° C. (212° F.). The mixture is next allowed to cool slowly, after which it is dissolved in twice its weight of water, and then slowly added to three times its weight of nitric acid, the nitration being completed by heating with steam after all fuming has ceased. This final mixture is now allowed to slowly cool down, thus permitting the picric acid to crystallize out, after which it is purified by washing with warm water, and then recrystallized.

This explosive, due to its acid nature, combines with metals, and thereby forms picrates, the latter in some instances being much more sensitive to percussion and friction than picric acid itself; this is a serious drawback, as it renders the shell containing this compound subject to explosion while in storage or during transportation, by heavy jolting. This, as well as many other disadvantages, caused the explosives manufacturers to turn their attention to another source, and they finally evolved the present-

day trinitrotoluene. This compound is made by first converting the toluene into a mononitro compound, after which it is treated with nitric acid at a slight increase in temperature, thus converting the mononitro compound into dinitrotoluene, after which the latter is nitrated in a sulphuric acid solution with concentrated nitric acid, the final product thus formed being trinitrotoluene. This compound is also produced from orthonitrotoluene by means of a sulphonating process similar to that used in the production of picric acid, after which it is nitrated and the resultant crystals are then purified in alcohol, being recrystallized and the alcohol removed in a centrifugal hydro-extractor.

In these statements I have tried to explain to you the wonderful properties possessed by a by-product which some years ago was considered a waste, and I trust my words will assist in calling your lasting attention to the possibilities of creating and maintaining an industry which can only redound to our credit and which will certainly add to our national wealth by not only conserving a vast amount of fuel, but which will also retain in our country a large sum of money which is annually expended in the purchase of materials which should be manufactured in the United States.

The True Nature of Speech with Application to a Voice-operated Phonographic Alphabet Writing Machine. J. B. FLOWERS. (*Proceedings of the American Institute of Electrical Engineers*, February 9, 1916.)—That speech is a rapid variation in intensity of the voice and mouth-tone according to definite sound patterns, called letters of the alphabet, is proved by showing that speech is the result of action of the mouth-parts in varying the intensity of the voice and mouth-tones and through photographs taken with the string-galvanometer of each letter sound of the alphabet, showing definitely the characteristic variation in intensity of each tone for each letter of the alphabet. From the curves the phonographic alphabet is obtained by measuring the variations in intensity of the main tone of the record.

A design for a voice-operated phonographic alphabet writing machine is described. The object of this device is to record speech automatically in ink on paper in the form of an easily-read, compact system of natural characters called the phonographic alphabet. Its design comprises a high-power telephone transmitter controlling electric resonator circuits, the intensity of currents in which is measured by the vibration of mirrors reflecting light upon a selenium cell connected to a special recording pen.