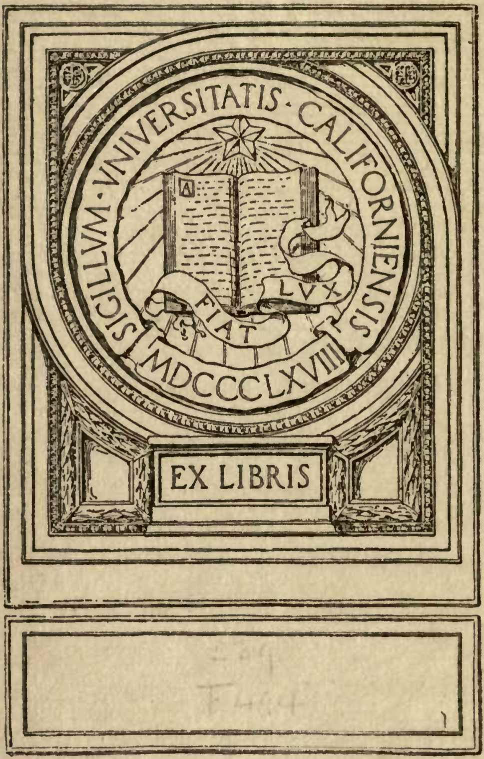
THE TREASURES OF COAL TAR

ALEXANDER FINDLAY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THE TREASURES
OF COAL TAR

COAL TAR TREE CHART

Illustrating the various chemical products derived from Coal and Coal Tar, designed in the form of a Genealogical Tree. 34″ × 36″.
Revised Edition.

BY WALLACE C. NICKELS, F.C.S.

THE TREASURES OF COAL TAR

BY

ALEXANDER FINDLAY

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'CHEMISTRY IN THE SERVICE OF MAN'
ETC.

WITH THREE FIGURES IN THE TEXT

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TO

MY MOTHER

PREFACE

In order that the effort now being made to promote the more widespread application of science, and more especially to render this country independent of others for the supply of the dyes necessary for the maintenance of our textile industry, shall not be relaxed, it is essential that the people as a whole should interest themselves in the work, and should gain some knowledge of what has been achieved in the past, and some understanding of the nature and complexity of the problems to be solved. As the matter is urgent, and of vital importance for the welfare of this country, the writer felt that, even in a time of much preoccupation, he could not refuse the invitation of the publishers to discuss in a readily intelligible manner the production and utilisation of coal tar, and to indicate, sufficiently fully for the general reader, the almost infinite variety of materials—dyes, drugs, perfumes, explosives—for the manufacture of which coal tar is the raw material.

Based on this invaluable by-product of the manufacture of coke and of illuminating gas, an industry, or rather a series of industries, has been developed ;

but although Great Britain played a predominant part in the early stages of this industrial development, she failed to retain the great advantages she had gained, and the manufacture of synthetic dyes and drugs became increasingly a German monopoly. To such an extent was this the case that, before the outbreak of war, Germany was producing more than three times the quantity of coal-tar products produced by all the rest of the world combined. It is true that dyes were manufactured in considerable amount in this country, but our manufacturers rested content, in too great a measure, with their dependence on German "intermediates," which, instead of making, they imported and worked up into dyes. In spite of the warnings uttered by our foremost chemists during the past thirty years, in spite of the object-lessons furnished by the destruction of the European madder and the decay of the Indian indigo plantations, this country failed to develop its coal-tar chemical industries on a national scale; and as a result of this failure she found herself, on the outbreak of war, placed in a position of great gravity. Perilously handicapped in our production of the munitions of war, threatened with the destruction of our textile industry through the cutting off of the supply of the German-made intermediates and dyes, and with the health of our people and army endangered through shortage of those synthetic drugs with which the German chemical industry had supplied us, we were brought face to face with our past neglect of chemical science and with our failure to encourage the application of that science in our industries. The chemists of the country were hurriedly mobilised, and the production of the essential munitions of war and of a sufficiency of drugs was ensured; the Government came to the help of the dye-making industry, and in the past two years, in spite of many handicaps, great progress has been made.

But what of the future? Can we feel sure that the lessons of the war have been learned and that the loss and bitter experience of the past three years will be turned to permanent gain? Have our people acquired that new outlook, that new mentality, which is the only safeguard of our future? As I have written elsewhere, we are all prone to blame our manufacturers and directors of industry, and to place on them the responsibility for our backwardness in the recognition of the value of science, but we have to remember that they are themselves but a part of the national system, and their organisation and outlook an expression of the national character and habit. Until we realise that our present unfortunate position is the result of a national defect, which shows itself most glaringly in our lack of interest in education and of a desire for knowledge, and until we realise the necessity for each and all of us gaining a new standpoint and outlook, gaining a new ideal, we cannot hope for a permanent improvement in the attitude of the country and manufacturers towards science and its applications. Lord Moulton has quoted the words of a German industrial chemist: "England talks now not only of holding her own in war, but beating us in our chemical industries. She cannot do it, and that is because the nation is incapable of the moral effort to take up an industry like that—which implies study, which implies concentration, which implies patience, which implies fixing one's eye on the distant consequences and not considering merely the momentary profit." That is a challenge which this country cannot refuse to take up, but, in taking it up, let us realise that success can be achieved only by a more general appreciation of science, by the cultivation and encouragement of chemical research in an enormously higher degree than in the past, and by the continual co-operation between science and technology. And it is important, also, to realise that it is not merely science in its immediate applications to industry that we must cultivate and encourage, but also, and more especially, pure science or "experimental research motivated solely by the desire to increase knowledge." The acquisition of knowledge must precede its application; chemical invention must follow chemical discovery. All the great discoveries, all the great advances have been made, not as a result of effort to achieve results of immediate industrial importance, but as the result of a patient and persevering pursuit of knowledge. In developing the coal-tar industries we can succeed if we will; let us will.

One point more must be borne in mind. Coal tar is produced not as a primary but as a by-product in the manufacture of illuminating gas and of metallurgical coke. Its production is therefore dependent on the demand for coal gas and for coke, and the outlet for the latter depends on the development of our metallurgical industries. A proper balance between output of, and the profitable outlet for, the different products and by-products of the distillation of coal must be established; and the whole series of interdependent and interlocking chemical industries must be carefully organised and developed so as to ensure the greatest efficiency and best utilisation of all the products. The question of the production and utilisation of coal tar and coal-tar products is one of great complexity as it is also one of great economic importance; and it must be treated as part and parcel of the much larger question of the most effective utilisation of our national reserves of coal.

My thanks are due to Messrs Longmans, Green & Co. for the use of the block of Figure 3, taken from my "Chemistry in the Service of Man"; to the Comptroller-General of the Department of Commercial Intelligence of the Board of Trade for particulars regarding the production of coal tar; and to Mr C. M. Whittaker, of British Dyes, Ltd., for information regarding dyes. I am also indebted to my wife for her assistance in passing the book through the press.

A. F.

Y GLYN, LLANFARIAN,
NR. ABERYSTWYTH, CARDIGANSHIRE,
September 1917.

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THE TREASURES OF COAL TAR

CHAPTER I

THE PRODUCTION OF COAL TAR

Coal, the fossilised and more or less completely carbonised remains of the luxuriant vegetations of a long bygone age, forms at once the source of much of our material wealth and the basis on which our industrial and commercial prosperity has been reared during the past hundred years. The coal mines of this country, worked at least as early as the thirteenth century, have since that time provided us, in ever-increasing amounts, with a valuable fuel both for domestic and industrial purposes. The introduction of coal, especially as a domestic fuel, was for a long time regarded with disfavour, and, even in the seventeenth century, met with an active boycott on the part of "the nice dames of London," who "would not come into any house or rooms where sea-coales were burned, nor willingly eat of meat that was either sod or roasted with sea-coale fire"—doubtless by reason of the pollution of the atmosphere by smoke and of the stench produced by the burning coal. At the present time, however, the normal annual consumption of coal in this country amounts to about 190,000,000 tons, of which about 40,000,000 tons are consumed for domestic heating.

But although it is on its use as a fuel, as a reservoir of energy derived from the sunlight of a long-distant past, that the material comfort and well-being of the people so largely depend, coal yet conceals within itself another wealth—long squandered through ignorance and even now but partially utilised—which the wizardry of Science has discovered and made available only within comparatively recent years. And it is of this wealth, or part of this wealth, derived from the chemical transformation of coal and from the black and viscid fluid, the coal tar, produced by the "destructive distillation" of coal, that it is the purpose of this book to treat.

Although coal had been used as a fuel as early as the beginning of the fourteenth century, it was not till near the end of the seventeenth century that the distillation of coal in closed vessels was carried out, the first English patent being granted in 1681 to J. J. Becher and Henry Serle for "a new way of making pitch and tarre out of pit-coale, never before found out or used by any other." At first an industry of very small proportions, it was not till the early years of the nineteenth century that the distillation of coal began to be carried out extensively, and then not for the purpose of producing tar and pitch, but, primarily, for the production of coal gas or illuminating gas. Although the production of an inflammable gas from coal had long been known, it was not till near the end of the eighteenth century that the Scotsman, William Murdoch, developed the process for the production of an illuminating gas for general use. Murdoch was for long associated with the engineering firm of Messrs Boulton & Watt, Birmingham, and it was in their works at Soho that coal gas was first used (in 1798) on a large scale as an illuminant. It was, however, only at a considerably later date that coal gas came into general use for the lighting of streets and public buildings.

When ordinary or bituminous coal is subjected to "destructive distillation" by heating in retorts out of contact with air, there are produced: (1) the combustible gas which we use for illuminating and heating purposes; (2) a watery liquor containing ammonia, derived from nitrogen compounds contained in the coal; (3) a thick, dark-coloured liquid, coal tar; (4) coke, which remains as a solid residue in the retorts. In the manufacture of illuminating gas the coal is heated in large fire-clay retorts at a temperature of about 1000° C. (about 1830° F.), and the products of decomposition are led away by a pipe the mouth of which dips under the surface of water contained in what is known as the hydraulic main (Fig. 1). Here part of the water and of the coal tar condenses, while the gaseous products pass away to a series of cooling pipes, exposed to the air, in which a further condensation of water vapour and of tar takes place. The ammonia present in the gas dissolves for the most part in the water produced, and the remainder is removed by passing the gas through "scrubbers." In this process the ammoniacal liquor, coal tar, and coke are merely by-products, spoken of as "residuals"; and although the coke has always been a by-product of considerable value which materially affected the price of the illuminating gas, the ammoniacal liquor and coal tar were for a number of years regarded as waste products of a disagreeable kind, the disposal of which involved not a little expense, and thereby retarded to some extent the development of the gas-producing industry. This condition of affairs, however, has been entirely changed, largely owing to the development of the great chemical industries which find their raw material in coal tar, as well as to the increased and increasing employment of ammonia compounds as fertilisers in agriculture, in the production of explosives, dyes, and soda (by the Solvay process), and in many other industries. In 1913, out of a total production from all sources of 432,000 tons, the gas-works

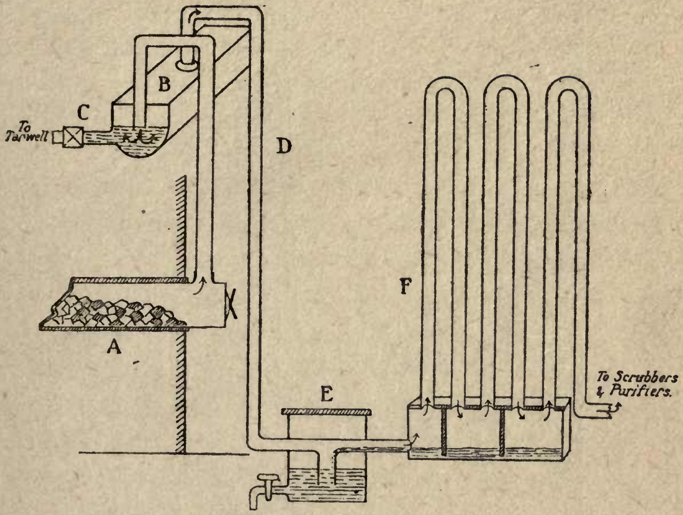

FIG. 1.—DIAGRAM OF GAS-MANUFACTURING PLANT.

A, retort in which coal is heated.
B, the hydraulic main.
C, outlet for the tar.
D, gas pipe.
E, tank in which the ammoniacal liquor collects.
F, cooling pipes.

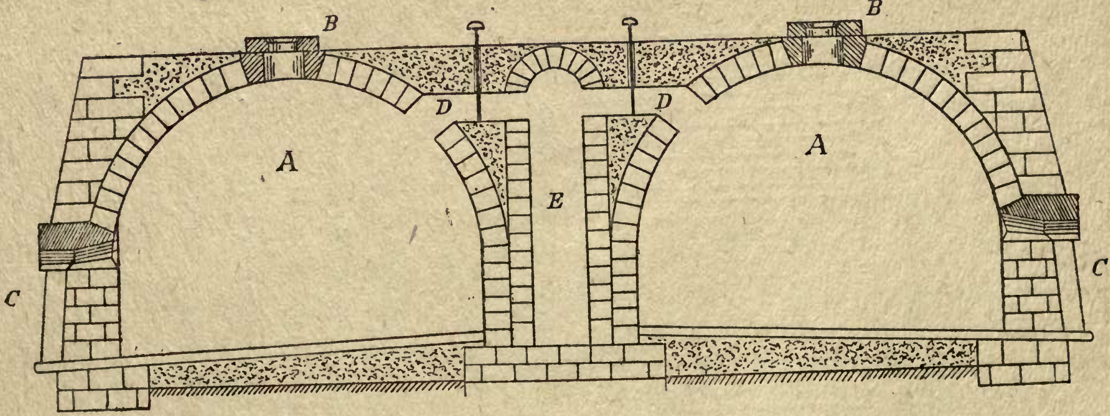

FIG. 2.—BEEHIVE COKING OVENS.

A, chamber in which the coal is coked.
B, opening through which the coal is introduced into the oven.
C, door of the oven.
D, flue from oven.
E, central flue.

of this country produced 182,180 tons of sulphate of ammonia, the value of which, in some cases, amounted almost to the cost of the coal distilled; while the production of coal tar in gas-works amounted, in 1910, to 830,000 tons. In all, about 20,000,000 tons of coal are now distilled annually in this country, primarily for the production of coal gas.

But it is not only for the production of gas that coal is now distilled. Even by the middle of the eighteenth century coke had to a large extent displaced wood charcoal and was very generally employed in the smelting of iron; and as our iron industry advanced and extended, so also the distillation of coal, primarily for the production of the hard and dense coke required for metallurgical purposes, became an industry of ever-increasing importance. For many years the coking of coal was carried out in "beehive" ovens, which are, as the name implies, chambers of beehive shape lined with firebrick. From seven to eight feet high and about twelve feet in diameter, these ovens are now generally arranged side by side in two rows so as to economise heat and allow of the hot products of distillation being carried off through a central flue for the raising of steam (Fig. 2). Through a hole in the top, the oven, still hot from previous use, is charged with coal to a depth of about three feet, the door of the oven being temporarily bricked up. Air in regulated amount is admitted to the space above the coal, where combustion of the evolved vapours takes place, and coking or carbonisation proceeds steadily from above downwards, owing to the heat reflected from the roof and walls of the oven. In this process the heat required for the coking of the coal is derived from the combustion of the gases distilled from the coal as well as from the combustion of part of the charge.

Although, in these beehive ovens, a hard, dense coke, admirably suited for metallurgical purposes, is produced, the process is a most wasteful one, because not only is a certain amount of coal lost through combustion, but all the volatile products of distillation, amounting to about one-third of the weight of the coal, are lost. In the early days of the industry, when there was little or no outlet for these products, when, at least, their commercial value was small compared with that of the coke, the consciousness of waste was scarcely awakened, and the coke producers made no attempt to recover and utilise the by-products of the coking process. Moreover, the introduction of coking ovens which allow of the recovery of the volatile by-products of distillation was resisted by the iron-makers, as it was thought—not, at first, without reason—that the coke produced in them was inferior to that produced in the old beehive ovens. But the prejudice which for long existed, more especially in Great Britain, has now been proved to be ground-less, and the increasing importance of ammonia and coal tar, and the necessity for greater industrial economy, are leading more or less rapidly to the abolition of the old beehive oven. Whereas in Great Britain in 1900 only ten per cent. of all the metallurgical coke was produced in by-product recovery ovens, in 1913 about sixty per cent. was so produced. In other words, of the 20,000,000 tons of coal converted into coke, about 13,500,000 tons were coked in by-product recovery ovens and 6,500,000 tons in beehive ovens. In the United States, similarly, about one-third of the metallurgical coke was produced, in 1914, in beehive ovens, without recovery of the by-products, whereas in Germany, in 1909, only about one-fifth of the coke was produced by this wasteful process. Although, in this respect, this country has lagged considerably in the rear of Germany, fairly rapid progress towards a more economical utilisation of our national resources in coal is being made; and this will doubtless be accelerated by the experiences of the past three years and the necessities of the future. Although the initial cost of the by-product recovery ovens is greater than in the case of the beehive ovens, it would appear, from evidence given before a Royal Commission on Coal Supplies in England, that the value of the by-products would not only provide a profit on the working of the plant, but would also, within ten years, pay off the capital outlay. At the same time it has to be borne in mind that in the future the successful development of the coking industry, with recovery of the by-products, must very largely depend on the development of all those closely interdependent industries—more especially chemical industries—which afford a remunerative outlet for the by-products of distillation, and it is of the highest importance that this country shall make a determined and well-directed effort towards this end.

The recognition of the importance of recovering the volatile matter produced in the coking of coal has, during the past thirty or forty years, led to great activity in the work of designing and construction of ovens adapted for the purpose, and several different types are at present in use. In one type, a modification of the Coppée oven, for example, the oven is formed by a chamber about thirty feet in length, two feet wide, and five feet high, heated by means of gas. A number of these ovens are generally arranged side by side and are charged from hoppers which run on rails over the series of chambers. As the coking proceeds, the volatile by-products pass away through pipes to a hydraulic main and condensers, where the ammoniacal liquor and the tar are collected; and the gas is then passed to gas-holders whence it is drawn off as required and used for heating the ovens. Since, with improved construction, considerably more gas is produced than is required for this purpose, the coke ovens are now a valuable source of gas supply, the excess gas being employed for heating, for the production of power, and even for illuminating purposes. Thus the city of Leeds, for example, takes a million cubic feet per day of coke-oven gas from the Middleton Estate and Colliery Company, this gas being then "enriched" with carburetted water-gas.

By the introduction of these ovens great economies have been effected owing to an increase in the yield of coke—upwards of seventy per cent. of the weight of coal being obtained as coke—and to the recovery of the very valuable by-products, ammonia and coal tar.

Coal, it must be borne in mind, is not a definite chemical substance, but a complex mixture of substances, the nature of which is not yet definitely known, and doubtless varies considerably in the case of the different kinds of coal. It will therefore readily be understood that the nature of the products as well as their relative amounts depend on the kind of coal distilled; and they depend, moreover, in a very marked degree on the general conditions under which the distillation of the coal is carried out—for example, on the temperature, size and shape of the retort, and on the time during which the volatile products remain in contact with the red-hot walls of the retort. As regards the composition, the most important points of difference are found in the nature of the so-called hydrocarbons (compounds of carbon and hydrogen) present in the tar. When the distillation is carried out at a low temperature (say about 450° C. or 840° F.), the tar contains mainly hydrocarbons belonging to the so-called aliphatic series (p. 38), suitable for use as motor spirit, and as illuminants and lubricants (vaseline). Tars of this description are produced, for example, in the distillation of coal for the production of coalite, in the manufacture of Mond gas, and in blast furnaces (mainly in Scotland) where raw coal is used in place of coke. When, however, the distillation is carried out at a high temperature (say about 1000° C. or 1830° F.), as is the case when coal is distilled for the production of illuminating gas or of the hard coke used for smelting and other metallurgical purposes, the prevailing hydrocarbons are those belonging to the "aromatic" class (p. 40), *e.g.* benzene and its derivatives. It is this kind of coal tar which is of such importance as furnishing the raw materials for the production of the innumerable dyes, drugs, perfumes, explosives, etc., the production of which now constitutes such an imposing and valuable industry.

Although the nature of the tar constituents, as well as their relative amounts, depends on the conditions under which the distillation is carried out, we may say that under the general conditions met with in gas and coking works, one ton of dry coal will yield, in addition to 11,000-12,000 cubic feet of gas, 20-35 lbs. of sulphate of ammonia, 56-120 lbs. of coal tar, and 1400-1800 lbs. of coke.

Owing, more especially, to the demand for metallurgical coke, the annual production of coal tar has now assumed very large dimensions. This country has always occupied a foremost place in the gas-producing industry, and she was also, for long, the premier producer of coal tar. But it is probable that by 1913 she had already lost to Germany her position of pre-eminence in the tar-producing industry owing to the great development in that country of the iron and steel industry, and the consequent demand for coke. Moreover, owing to the magnitude of the German chemical industries, most of the coal tar formed in the production of this coke was recovered, and Germany thereby made herself largely independent of this country for the supply of coal tar, of which, even in 1908, she imported from Great Britain 40,000 tons. Although, up to the outbreak of war, Germany imported from this country considerable amounts of anthracene and of phenol (carbolic acid), the development of the synthetic production of the latter compound from benzene will doubtless render its continued importation unnecessary.

In 1901 the approximate annual production of coal tar throughout the world has been estimated as follows:

United Kingdom . .	908,000 tons.
Germany . . .	590,000 ,,
United States . . .	272,400 ,,
France	190,680 ,,
Belgium, Holland, Sweden, and other European countries . . .	199,760 ,,
All other countries . .	227,000 ,,
	2,660,440 ,,

In the following years of the decade the amounts largely increased, as shown by the following approximate figures:

United Kingdom (1910)	1,380,000 tons.
Germany (1912) . .	1,082,197 ,,
United States (1912) .	564,000 ,,
France (1909) . .	214,800 ,,

CHAPTER II

THE DISTILLATION OF COAL TAR

CRUDE coal tar, as it is obtained from gas and coking works, although it may vary not a little according to its origin, is a thick, oily, dark-coloured liquid rather heavier than water (specific gravity about 1·2). In the early days of the coal-distilling industry this tar was, as has been said, a disagreeable waste product, the disposal of which was the source of much worry and annoyance to the producer no less than to the general public in the neighbourhood. As it was impossible, by reason of the nature of the material, to get rid of the accumulations of tar by running it into streams and rivers, the difficulty of its disposal was solved, to some extent, by burning the tar as a fuel. A certain amelioration was brought about by the use of coal tar as a paint for wood and metal work, and for this purpose the more volatile portions were removed by distillation, the "spirit" so obtained being used either as a substitute for turpentine in making varnishes or as a solvent for rubber in the manufacture of a waterproof material which is still known by the name of the original Glasgow manufacturer, Mackintosh. Much of the residue from the distillation was burned for the production of lampblack, which is used in the manufacture of pigments, blacking, and printer's ink.

Hitherto, the distillation of coal tar had been carried out only on a comparatively small scale, and the demand for tar lagged far behind the supply, until, in 1838, an entirely new situation was created through the introduction of a process for preserving or "pickling" timber (p. 27); and an industry which has now attained to enormous proportions was thereby inaugurated. Moreover, in the year 1845 another great stimulus was given to the coal-tar industry owing to the scientific investigations which were carried out by Professor Hofmann and his students at the newly-founded Royal College of Chemistry in London, investigations which not only led to the isolation from coal tar of some of its main constituents, but were the roots from which the vast modern industry of coal-tar dyes, drugs, and explosives has really grown. Owing to these developments, which we shall discuss more fully in the sequel, a demand was created for the more volatile portions of coal tar which had been rejected by the timber-pickling industry; and a more complete utilisation of the constituents of the tar was thereby made possible.

Although, in the past, crude coal tar was largely employed not only as a liquid fuel but also for the manufacture of roofing felt, the tarring of roads, and other purposes, the water and ammoniacal liquor present in the tar were found to be detrimental, so that now only a small amount of tar is used in the crude state, except in those cases where it is employed as a fuel. By far the greater proportion of the coal tar is now subjected to a process of distillation, a process first carried out systematically by Charles Blachford Mansfield [1] in 1848.

Coal tar, even after being freed from the water and ammonia with which, when it is received from the gas and coke works, it is intimately mixed, is not a single substance, but an exceedingly complex mixture of over two hundred different compounds, some of which are present, however, only in very minute amount. Although the complete separation and isolation of all these different substances is a matter of the greatest difficulty, and is not attempted in practice, it is possible, by subjecting the tar to a process of distillation, to separate it into a number of portions or "fractions" which distil over at different temperatures. The general principle on which the apparatus employed is con-

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[1] Mansfield was a pupil of Hofmann, and, under his direction, was the first to separate coal-tar naphtha into its constituents by fractional distillation. Unfortunately, in 1856, while carrying out this work, the contents of the still boiled over and caught fire. While endeavouring to extinguish the flames Mansfield was so severely burned that death supervened in a few days.

structed is illustrated by Fig. 3. Here, A is a vessel or " still " in which the liquid is boiled and so converted into vapour which passes through the long neck, B, to a spiral " worm " or condenser, C, kept cool by means of flowing water. The condensed vapour issues at D and can be collected in a " receiver." E is a tube by which water enters and F is the outlet for the warm condenser water.

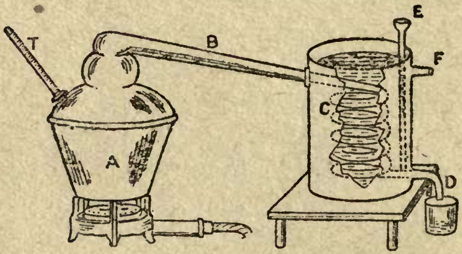

Fig. 3.—Apparatus used for Distilling Liquids.
(Illustration from " Chemistry in the Service of Man.")

T is a thermometer to indicate the temperature of the liquid in the still. In actual practice the still consists of a large iron boiler—capable of holding twenty tons or more of tar—set in brickwork and heated by a fire. Since the first fractions which distil over are rather volatile liquids at the ordinary temperature, the condensing coil is cooled by means of cold water; but as the distillation proceeds the substances which pass over solidify on cooling, and so the condenser is kept warm by means of hot water in order to prevent the choking of the coil.

By this process of distillation the tar is separated into a number of portions. First of all, while the temperature of the still gradually rises to 170° C. (338° F.), there distils over a light inflammable liquid known as "light oil." This is followed, between the temperatures of 170° C. and 230° C. (338° F. and 446° F.), by the "carbolic oils," so called because they contain the main portion of the carbolic acid present in the tar. At still higher temperatures, between 230° C. and 270° C. (446° F. and 518° F.), one obtains a complex mixture of substances constituting the "creosote oils"; and lastly there pass over, between 270° C. and 400° C. (518° F. and 752° F.), the "anthracene oils," the most important constituent of which is the hydrocarbon anthracene. After the different fractions have passed over there remains in the still a residue of pitch. By this process of distillation there are obtained, from one ton of tar, approximately:

12 gallons of light oils.
20 ,, carbolic oils.
17 ,, creosote oils.
38 ,, anthracene oils.
11 hundredweight of pitch.

The crude coal tar having in this way been separated into a number of different portions, each of these is then subjected to suitable chemical treatment and to repeated distillation in order to effect a more complete purification and separation into the different constituents. Thus the light oils are separated into "crude benzol,"—consisting of a mixture of the hydrocarbons, benzene, toluene, and xylene,—"solvent naphtha" and "burning naphtha," consisting of xylene and similar but more complex hydrocarbons. To obtain pure benzene and toluene, such as are required in the manufacture of dyes, drugs, and explosives, the crude benzol is "rectified" by distillation in a special still.[1]

In order to avoid confusion it may be stated that the hydrocarbons now known to British chemists as benzene (not to be confounded with benzine or benzoline) and toluene, were formerly called benzol (or benzole) and toluol, and these names are still employed commercially. The term benzol, however, is also applied in commerce to various mixtures of hydrocarbons, different grades

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[1] It may be mentioned that although benzene and toluene were formerly obtained solely from coal tar, considerable quantities of these compounds are now obtained from coke-oven gas by "scrubbing" it with creosote oil. Indeed, this is now a more important source of crude benzol than coal tar. Since the removal of these hydrocarbons diminishes both the illuminating power and the calorific value of the gas, the above process is not applied in large measure to ordinary coal gas, although, at the present day, owing to the exigencies of war, considerable quantities of these valuable compounds are obtained from this source.

of "benzol" being produced for use in the arts. Thus we have the various grades known as 90 per cent., 50 per cent., and 30 per cent. benzol, these terms being applied to liquids of which 90, 50, or 30 per cent. distils over at temperatures up to the boiling-point of water (100° C. or 212° F.). The composition of these three grades of commercial benzol is shown in the following table:

	90 per cent. benzol.	50 per cent. benzol.	30 per cent. benzol.
Benzene .	80·9	45·4	13·5
Toluene .	14·9	40·3	73·4
Xylene .	2·2	12·4	11·7
Impurities .	2·0	1·9	1·4

The portion of the tar distillate known as "carbolic oils" or "middle oils" is likewise separated by chemical and physical treatment into its chief constituents. On allowing it to cool down there separates out from it a considerable quantity of a hydrocarbon known as naphthalene, and the residual oil is then sold as "crude carbolic acid," for the manufacture of disinfectants. On gently heating the crude naphthalene it sublimes or passes into vapour which, on cooling, solidifies in the form of large crystalline flakes. In this way it is purified. Much of the crude carbolic acid also is refined by treatment with alkali and acid and subsequent distillation. By this means pure carbolic acid or phenol, as it is called by chemists, is obtained, together with a mixture of three similar compounds known as cresylic acids or cresols.

The "creosote oils" or "heavy oils" consist of a number of different compounds which, however, are not separated from each other. These oils are merely "fractionated" in accordance with the specifications of the wood-pickling industry.

From the "anthracene oils" there is obtained, by suitable treatment, the important hydrocarbon anthracene, which is used as the starting substance in the manufacture of alizarin, and of other important dyes.

Although the amounts of the different compounds obtained vary with the nature of the tar and the treatment to which it is subjected, the following numbers will give a sufficiently exact idea of the relative quantities of the most important constituents yielded by one ton of tar :

Benzene and toluene	25 lbs.
Phenol	11 ,,
Cresols	50 ,,
Naphthalene	180 ,,
Creosote	200 ,,
Anthracene	6 ,,

Benzene, first discovered by Faraday in 1825, is a colourless, mobile liquid which boils at 80·5° C.

(176·9° F.), and yields a readily inflammable vapour. **Toluene** is a similar compound which boils at 111° C. (231·8° F.). **Phenol** or carbolic acid is, in the pure state, a white crystalline solid which melts at 41° C. (105·8° F.). Owing to the very large amounts of this compound used in the manufacture of dyes, drugs, and explosives, the supply obtained from coal tar is quite insufficient, under present conditions, to meet the demand, so that phenol is now manufactured in large amount from benzene. For this purpose benzene is first treated with concentrated sulphuric acid, and the resulting product then fused with caustic soda. **Naphthalene** is a white crystalline solid which melts at 80° C. (176° F.), and **anthracene** is also a white crystalline solid which melts at 213° C. (415° F.).

CHAPTER III

THE CONSTITUENTS OF COAL TAR AND THEIR APPLICATIONS IN THE RAW STATE

In the later chapters of this book we shall discuss some of the marvellous transformations which chemists have effected in the constituents of coal tar, transformations which are the basis of those great chemical industries of synthetic dyes and drugs whose development during the past half century has so impressed the public mind. But it must not be forgotten that there are other industries dependent on the distillation products of coal tar; industries which if not, like the chemical ones, suffused with romance, contribute in no small measure to the welfare of man and together make up a large part of the wealth derived from coal tar. Indeed, it is probably to these industries which depend on the use of the coal-tar products in the raw state that the tar distiller mainly looks for the maintenance of his profits, and a brief account of them must not be omitted here.

Benzol and Naphtha

Although it is as a raw material in chemical industry, in the manufacture of dyes, drugs, and explosives, that pure benzene and toluene find their chief use, large quantities of the various grades of commercial benzol are now employed as solvents in the preparation of paints and varnishes, and for other purposes. The use of benzol as a solvent goes back, indeed, to the earliest days of coal-tar distillation, although at that time it was the higher boiling fractions which mainly found employment. At the present day, however, the industrial applications of the lower boiling fractions, the higher grades of commercial benzol, have attained a great and increasing importance. By reason of its solvent power, benzol is largely employed as a detergent for the removal of grease, wax, and paint spots (for which purpose it is frequently mixed with alcohol and ammonia), and as a solvent for gums and resins in the manufacture of varnishes and lacs, as well as of enamel, bronze, and aluminium paints, of which a natural gum or resin, such as Damar gum, forms the base. Similarly, by reason of its solvent power for resins, benzol is used in the preparation of paints used in painting resinous woods, the partial solution of the resin by the benzol affording a better penetration or "tooth" to the paint. Of great importance, also, is the use of benzol in the preparation of rubber solutions for use as cements and insulating varnishes, and as a solvent for sulphur monochloride in the cold vulcanisation of rubber. In recent times benzol has been used in large amount, more especially in France and Germany, as a motor fuel, and in the future it will doubtless find, in this direction, a vastly more widespread application. This cannot but exercise a powerful influence on the whole coal-tar industry.

The higher boiling fractions of the "light oil," the naphthas, find their chief applications as solvents in the preparation of rubber waterproof material, and as illuminants for use in large open spaces; and the flaring light of the naphtha lamp has cast its beams for many years now over the wares on the costermonger's barrow and the stalls and booths of the open market-place.

In 1911 nearly 2,000,000 gallons of coal-tar solvents were produced in the United States, and were distributed among the different industries approximately as follows (Weiss):

Paint and varnish . .	47	per cent.
Rubber and rubber cements	18	,,
Imitation leathers . .	10	,,
Chemical manufactures .	11	,,
Miscellaneous . . .	14	,,

Similar details are, unfortunately, not available with regard to the United Kingdom.

Carbolic Acid and Naphthalene

"Crude carbolic acid," which is separated, as we have already seen, from the "middle oils" obtained in the distillation of coal tar, consists for the most part of various "tar acids," more especially carbolic acid and cresylic acid, the latter being a mixture of three isomeric compounds (see p. 44), known as cresols. Although the pure compounds, more especially pure carbolic acid or phenol (to give it its systematic name), are used to a large extent in chemical industry, they also find a very extensive application in the raw state as antiseptics and disinfectants. As such the cresols are more powerful, and at the same time less poisonous, than the more familiar carbolic acid or phenol.

Owing to a more widespread knowledge of the causes of disease and to greater efforts made in the promotion of hygiene, the demand for antiseptics and disinfectants has greatly increased during the past two or three decades, and as a consequence we now find on the market very many disinfectant preparations of which carbolic and cresylic acids form the basis. Since these acids are not very soluble, the preparation of concentrated disinfectants which would mix completely with water presented some difficulty; but this difficulty was overcome by the addition of a certain amount of soft soap (whereby the tar oils present are emulsified), and a large number of disinfecting fluids are now prepared on this general principle. For this purpose use is made not only of the carbolic and cresylic acids obtained from the carbolic oils, but also of the lower fractions separated from the creosote oils which are specially rich in cresols and other similar compounds. Thus the well-known liquid **lysol** consists essentially of a mixture of cresols (about 50 per cent.) with a potash soap (about 20 per cent.) prepared from linseed oil, and a certain amount of glycerin. The cresols also form the essential constituent of Jeyes' Fluid, Cresolin, and other disinfectants.

Phenol and cresol may also be incorporated in ordinary hard soaps or mixed with various other solid materials; and many disinfectants of this nature, more or less efficient, are now sold under different names.

Naphthalene, apart from its important uses in chemical industry, is now employed mainly as a disinfectant and as a preservative against the attack of moths and other insects.

Creosote

That tar and pitch are valuable preservatives for wood has long been known, tar having been used for this purpose even in the days of ancient Greek civilisation. But it is only in comparatively recent times that the antiseptic and preservative properties of tar have been applied on an extensive scale. Various antiseptics, such as corrosive sublimate and copper sulphate, were already in use for the preservation of timber and its protection against the attack of dry-rot and other fungoid growths, but the use of coal tar on a large scale dates only from the introduction of the timber-pickling process by John Bethell in 1838. This industry soon experienced a very rapid development owing to the growth more especially of railway and telegraph systems throughout this country and the world. As a preservative for wood which is buried in the ground or submerged in water, as a protective even against the formidable *Teredo navalis* and other marine organisms, coal-tar creosote has been found superior to all other materials.

In carrying out the "pickling" or "creosoting" of wood, the latter is placed in a large cylindrical boiler and the air is then very thoroughly exhausted by means of a pump. In this way the air is withdrawn from the pores of the wood. Creosote, heated to a temperature of about 100° C. (212° F.), is then allowed to flow into the boiler, the process of exhaustion being still maintained for some time in order that, at the higher temperature, the moisture in the wood may also be withdrawn. On now admitting air into the boiler, the creosote is injected into the cells of the timber, and the process of injection is completed by means of a force pump, the pressure within the boiler being raised to eight or ten atmospheres. In other processes the timber is impregnated with creosote under increased pressure, and then maintained for some time under greatly reduced pressure. Under this treatment a cubic foot of wood absorbs about one gallon of creosote oil.

When one thinks of the countless rows of wooden sleepers which mark out the railway tracks in the different countries of the world, of the never-ending lines of telegraph poles which carry their network of wires across whole continents, or of the wooden piles and wharves exposed to the waters of every ocean, one will understand, in some measure, how important this creosote industry has become. Since by its treatment with tar oil the life of the wood is trebled or quadrupled, it will readily be realised not only that there is an enormous saving effected in the cost of upkeep of railway sleepers, telegraph poles, wooden wharves, etc., but that there is also a consequent great reduction in the consumption of timber—a matter of increasing importance in these days when the reserves of timber throughout the world are being rapidly depleted. In this country upwards of 50,000,000 gallons of creosote are produced annually, and most of this is used for the treatment of timber. In 1913, over 36,000,000 gallons of creosote, having a value of £592,000, were exported, mainly to the United States, where, owing to the enormous extent of the railway system, the demand for creosote oil is much greater than the supply.[1] It was this wood-pickling industry

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[1] " In 1913 the United States consumed, for timber preservation, over 90,000,000 gallons of creosote oil, and of this, 62 per

which "saved the situation" in the early days of coal-tar production, and it forms at the present day by far the most important outlet for the coal-tar oils.

The antiseptic and disinfecting properties of creosote oil, which are not entirely due to the presence of carbolic, cresylic, and other tar acids, have also led to the extensive use of creosote in the preparation of cattle washes, sheep dips, and general disinfectants. In this case the oil is generally mixed with a quantity of soft soap, whereby, owing to the emulsifying action of the soap, a very fine emulsion can be obtained with water.

Creosote oil, suitably fractionated by distillation, also finds application as a liquid fuel for internal combustion (Diesel) engines, as an illuminant (in the "Lucigen" lamp), in the production of lamp-black, for softening hard pitch, and for "scrubbing" coal and coke-oven gas for the recovery of benzene and toluene.

Refined Tars and Pitch

In recent years owing largely to improved methods of road construction and to the desirability, in view of the great increase of motor traffic, of obtaining dust-free roads, an increased demand for refined tars and pitch has sprung up. For some time, it

cent. was imported from Europe. Between 60 and 70 per cent. of the total quantity of oil consumed was used for the treatment of railway ties, some 25,000,000 being thus treated" (E. Stansfield and F. E. Carter: Report to Department of Mines, Canada).

is true, there existed considerable prejudice against the practice of sprinkling the roads with tar owing to the supposed harmful effects of the tar on surrounding vegetation and the irritating action of the dust from such roads on the eyes. But the fear of harmful effects has been shown to be without real foundation, and the tar-sprinkling of many of our main thoroughfares has proved a great boon. The tar used for this purpose must be fractionated so as to satisfy the requirements of the Road Board, the specification of which lays it down that: "The tar shall be free from water, and on distillation shall yield no distillate below 140° C. (284° F.), nor more than 5 per cent. of distillate up to 220° C. (428° F.), which distillate shall remain clear and free from solid matter (crystals of naphthalene, etc.), when maintained at a temperature of 30° C. (86° F.), for half an hour. Between 140° and 300° C. (284° and 572° F.) it shall yield not less than 15 per cent. nor more than 21 per cent. of the weight of the tar."

The various grades, also, of hard and soft pitch, obtained as residues from the distillation of coal tar, have found valuable applications as road-binding material, in the preparation of tar-mac, for filling the joints between paving stones, for the manufacture of roofing felt, for making coal briquettes, for electrical insulation and for other important purposes.

CHAPTER IV

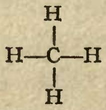
MOLECULAR ARCHITECTURE

In the preceding chapters we have seen how from the black, unsavoury liquid, coal tar, various substances have been isolated and have found important applications in the general structure of our modern civilisation. But the benzene, the toluene, and the other materials to which reference has already been made exist as such in the tar, and their separation from this liquid and their applications, important as they are, are not such as to make any powerful appeal to the intellect or arouse a feeling of wonder in the mind. Far otherwise is it, however, with those marvellous transformations which have been brought about in these substances by chemists; transformations which have produced from some eight or nine colourless liquids or solids, dyes in infinite variety which rival Nature's products in range of colour and delicacy of tone; drugs and anæsthetics which purge the blood of its evil humours and give relief from pain; the sweet-smelling essences of flowers; and explosives which give power and strength to the arm of man in peace as well as in war. These are triumphs of the human intellect and as such command the admiration and wonder of thinking men. Not only has the chemist prepared numberless compounds hitherto unknown, but he has entered into competition with Nature herself and has successfully broken the monopoly which heretofore she had enjoyed in the production of many important compounds. So successful, indeed, has the chemist been, that these artificial products have, in some cases at least, driven the natural products entirely out of the market. But this rivalry with Nature, the task of building up or synthesising numerous highly complex compounds from the simple materials contained in coal tar, would have been hopeless without the aid of some guiding principle. It is necessary, therefore, before passing to the discussion of the substances which have been evolved by chemists from the constituents of coal tar, to give a short account of the theory of molecular structure by which chemists have directed their labours. The understanding of the processes by which these compounds are produced will thereby be facilitated.

For convenience in representing chemical elements and compounds, the Swedish chemist Berzelius introduced, a century ago, a system of *symbols*, each of which consists of one or two letters and represents one atom of the particular element. Thus, C, H, O, N, for example, represent one *atom* or smallest particle of the elements carbon, hydrogen, oxygen, and nitrogen respectively. But a compound can be regarded as being formed by the combination or uniting of the atoms of the constituent elements in certain definite proportions, and so we can conveniently represent the *molecule*, or smallest particle of a compound, by writing the symbols of the constituent elements side by side. Thus, CO represents a compound of carbon and oxygen, the molecule of which contains one atom of carbon and one atom of oxygen; and NO, similarly, represents a compound of nitrogen and oxygen. Frequently, however, the molecule of a compound is formed by the combination of elements in more than one atomic proportion, and so we write, for example, H_2O, which is the *formula*, as it is called, for water. This formula indicates that the molecule of water contains two atoms of hydrogen and one atom of oxygen. The formula NH_3, similarly, which is the formula for ammonia, indicates that the molecule of this compound contains three atoms of hydrogen united with one atom of nitrogen.

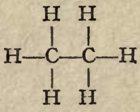
It might, perhaps, be thought that an infinite number of compounds could be formed by the combination of the atoms of two elements in different proportions, *e.g.* HO, H_2O, H_3O, etc. But although no *a priori* reason can be given against the possibility, it has been found that, as a matter of fact, elementary atoms do not possess this unlimited power of combination; and the recognition of this important fact is embodied in the *doctrine of valency*, a doctrine which we owe to the late Sir Edward Frankland. As no element is known which has a lower combining power than hydrogen, this element is taken as the standard of reference and is said to have unit combining power or unit valency, or to be univalent. Oxygen, one atom of which can combine with two atoms of hydrogen (as in water, H_2O), is said to be bivalent, and carbon, one atom of which can combine with four atoms of hydrogen, is said to be quadrivalent. Since an atom of carbon is never found to combine with more than four atoms of hydrogen, the carbon is, in this case, said to be saturated; and the compound CH_4, which represents methane or marsh gas, is spoken of as a **saturated hydrocarbon.**

Although there is, of course, no material link or bond between the atoms, we can, nevertheless, represent union between atoms as if it were material, by means of a line or lines, according to the valency of the atom. Thus we can represent the molecule of methane by the diagrammatic or graphic formula,



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

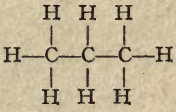
But the element carbon is remarkable among all the elements in its property of combining also with other atoms of carbon and so forming " chains " of carbon atoms ; and we therefore obtain a series of compounds which may be represented by the diagrams :



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

C_2H_6 (Ethane)

;



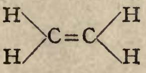
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

; etc.

C_3H_8 (Propane)

This series of hydrocarbons is generally known as the methane series, and to it belong gasoline, petrol, vaseline, and paraffin wax.

There are also other hydrocarbons which contain a lower proportion of hydrogen and are therefore said to be **unsaturated.** Thus, if we take away two hydrogen atoms from each of the compounds of the methane series, we obtain hydrocarbons which can be represented by the formulæ :



C_2H_4 (Ethylene)

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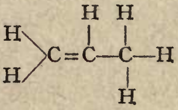


; etc.

C_3H_6 (Propylene)

These constitute another series of hydrocarbons known by the name of the first member, ethylene.

These diagrammatic formulæ, it should be emphasised, are not intended to represent the spatial arrangement of the atoms ; there is, indeed, reason to believe that these " chains " of carbon atoms would form a spiral in space. These formulæ, rather, are intended merely to indicate that in the molecule of a compound the constituent atoms are not present in disordered array but are associated in some definite manner, certain atoms being attached, as it were, to certain other atoms, although by no material bond or connection, just as a satellite may be said to be attached to a planet. We can, therefore, also write the above formulæ in a somewhat more compact form, and represent propane, for example, by the formula $CH_3{\cdot}CH_2{\cdot}CH_3$ (the "bond" between the carbon atoms being now represented by a dot), and propylene by

$$CH_2 : CH{\cdot}CH_3.$$

This theory of chemical structure, which depends, as we see, on the recognition of the quadrivalency of the carbon atom, is due to August von Kekulé, and was put forward by him in 1858. The origin of the theory has been recounted by Kekulé himself. During a period of residence in London he was returning from a visit paid at Islington to where he stayed at Clapham. "One fine summer evening," he relates, "I was returning by the last omnibus, 'outside' as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie, and lo! the atoms were gambolling before my eyes! Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain," . . . And then he adds: "I spent part of the night in putting on paper at least sketches of these dream-forms." From these sketches were developed the structural formulæ of which examples have just been given.

The saturated hydrocarbons, methane, ethane, etc., may be regarded as the parents of a countless brood of other compounds derived from them by the substitution or replacement, direct or indirect, of one or more hydrogen atoms by the atoms of other elements or by groups of elements ("radicles") which pass from compound to compound like single atoms. Thus, by substituting one atom of hydrogen in the saturated hydrocarbons by an atom of iodine, we get a series of **iodides,** $CH_3{\cdot}I$, $C_2H_5{\cdot}I$, $C_3H_7{\cdot}I$, etc.; or by substituting one atom of hydrogen by the group OH (hydroxyl), we obtain a series of compounds known as **alcohols** ("alcohol" in chemistry is a generic name), thus, $CH_3{\cdot}OH$, methyl alcohol or "wood-spirit"; $C_2H_5{\cdot}OH$, ethyl alcohol or "spirits of wine"; and so on, the groups of atoms CH_3, C_2H_5, being known as methyl and ethyl.

It will readily be understood from this that the possible number of compounds is exceedingly large, and, for this reason, the study of the compounds of carbon—the number of which at the present day exceeds 150,000—has developed into a special branch of chemistry known as organic chemistry.

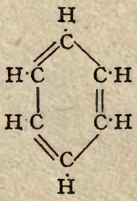
Since the hydrocarbons of the methane series are formed of "chains" of carbon atoms, so also are the compounds derived from them; and since the natural animal and vegetable fats and oils are amongst these compounds, the term "fatty" or "aliphatic" (ἄλειφαρ = fat) has been applied to the whole group or class of compounds.

In studying the carbon compounds we meet with a phenomenon which, although not unknown in the compounds of the other elements, is found with extraordinary frequency amongst the former. This is the phenomenon to which the name of *isomerism* has been given.

One of the fundamental laws of chemistry states that the composition of a compound—that is, the nature and number of the atoms present in the molecule—is constant and definite (*Law of Constant Proportions*), and for long it was believed that the converse statement also was true, namely, that only a single compound could exist corresponding with a particular composition. As the number of compounds became multiplied, it began to be observed more and more frequently that the same elements might be united in the same proportions and yet yield compounds with entirely different properties. It is to this phenomenon that the term isomerism is applied. Just as the same set of bricks can, by varying their arrangement, be formed into structures of totally different kinds, so also the same atoms can, by varying their arrangement within the molecule, give rise to different atomic structures, or different compounds. We are led, therefore, to the recognition of the fact that the properties of a compound depend not merely on its composition, but also on its internal structure, or the arrangement of the atoms within the molecule. A knowledge of this atomic arrangement or *constitution* of the molecule is of the highest importance, and is, indeed, essential for the successful building up or synthesis of a compound from simpler materials, such as we shall discuss in the following chapters. It is because the theory of Kekulé enables one to represent molecular constitution and to foresee the possible existence of isomeric compounds that it has exercised such an important influence on the development of organic chemistry. Thus, if we have the compound $CH_3{\cdot}CH_2{\cdot}CH_3$, it is clear that we can replace one atom of hydrogen in this compound by an atom, say, of iodine, in two ways, so that we should obtain either the compound $CH_3{\cdot}CH_2{\cdot}CH_2I$, or the compound $CH_3{\cdot}CHI{\cdot}CH_3$, the iodine being attached, in the former case, to a terminal carbon atom, and in the latter case to the intermediate carbon atom. Accordingly, there should exist two and only two different compounds having the composition C_3H_7I; and as a matter of fact two compounds and only two are known.

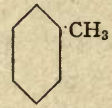
Although a number of hydrocarbons belonging to the methane series are found in the tar which is produced by distilling coal at a low temperature, they are not met with in the ordinary gas or coke-oven tar, and they are of only secondary importance in the manufacture of coal-tar dyes and other products. The most important compounds occurring in gas and coke-oven tar are, as we have seen, benzene, toluene, xylene, phenol, cresol, naphthalene, and anthracene, these being the compounds from which, for the most part, the endless array of dyes and other coal-tar products has been derived. These compounds, however, belong to quite a different class from those already described; they possess a totally different *constitution*, and belong, as it were, to a different type of molecular architecture. From the fact that many of the compounds which occur naturally and belong to this group possess a distinct odour or "aroma," the term "aromatic" has been given to the compounds belonging to this division of organic chemistry.

Just as we have seen that methane may be regarded as the first parent of the compounds belonging to the aliphatic group, so benzene (C_6H_6) may be called the parent of the aromatic compounds ; and it is to Kekulé also that we owe the elucidation of the structure of this important hydrocarbon. Again Kekulé had a dream. He was now (1865) in Ghent and dozed before the fire. Again he saw the atoms gambolling before his eyes, the chains twining and twisting in snake-like motion. "But look ! What was that ? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke" ; . . . but the picture Kekulé had seen of the snake which had seized hold of its own tail gave him the clue to one of the most puzzling molecular structures, the structure of the benzene molecule, a ring of six carbon atoms to each of which a hydrogen atom is attached. Thus we obtain the structural formula of the benzene molecule :

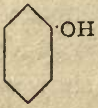


the "ring" of carbon atoms being written in the form of a hexagon instead of in the form of a circle. Since this structure occurs very frequently in the formulæ of coal-tar products, it is generally simplified to the skeleton form by omitting the symbols for carbon and hydrogen. We thus obtain as the diagrammatic representation of the benzene molecule the simple hexagon:

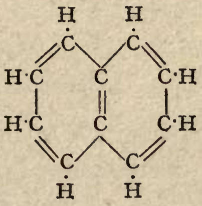
From methane, as we saw, many other compounds could be derived by replacing one or more atoms of hydrogen by the atoms of other elements and by radicles or groups of elements. So also from benzene whole series of compounds can be similarly derived. Thus, if we replace one atom of hydrogen by the group or radicle CH_3 (methyl), we obtain the hydrocarbon **toluene**, the formula of which, $C_6H_5{\cdot}CH_3$, will be represented by the diagram:



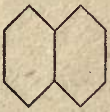
Similarly phenol or carbolic acid is derived from benzene by the replacement of one atom of hydrogen by the group OH (hydroxyl), and so we obtain the formula $C_6H_5{\cdot}OH$ or



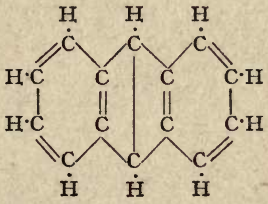
In the case of naphthalene, which is a hydrocarbon having the formula $C_{10}H_8$, we have two benzene "rings" joined together thus:



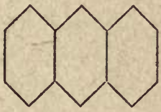
or, more simply,



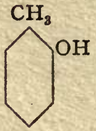
whereas, in the case of anthracene, $C_{14}H_{10}$, we have three "rings":

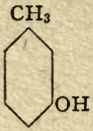


or



In the case of the aliphatic compounds we saw how, according to the theory of Kekulé, the existence of isomeric compounds could be foreseen and explained. In the case of the compounds derived from benzene, similarly, isomerism can occur, but this isomerism is found only when more than one atom of hydrogen is substituted or replaced. Thus, for example, when one atom of hydrogen is substituted by the methyl group, CH_3, and another by the hydroxyl group, OH, we can obtain three different arrangements, represented by the formulæ:





and these three different arrangements correspond with three distinct isomeric compounds known respectively as ortho-cresol, meta-cresol, and para-cresol, the terms ortho-, meta-, and para- referring to the *relative* positions of the two substituting groups. These three isomeric cresols occur, as we have seen, in coal tar, and have powerful antiseptic properties. Ortho-cresol melts at 31° C. (87·8° F.), meta-cresol at 5° C. (41° F.), and para-cresol at 36° C. (96·8° F.).

It may seem, perhaps, to some that whatever psychological or speculative interest the dreams and theories of Kekulé might possess, they could have no importance for the practical life of the people. And yet it is just these theories which form the very basis and fundament of those great chemical industries which command the wonder and respect of all. For the advance and development of organic chemistry,—described by Wöhler as a "tropical forest primeval, full of the strangest growths, an endless and pathless thicket, in which a man may well dread to wander,"—the theories of molecular structure were as important as is a map to a traveller in an unknown land. Without them we could not have witnessed what is, perhaps, the crowning achievement of organic chemistry, the synthesis of many of Nature's own products as well as of the innumerable dyes, therapeutic agents, and other materials which are regarded as necessaries in our modern civilisation and in respect of which this country is now endeavouring to make herself independent of outside supplies. It was, indeed, largely if not mainly owing to her neglect of pure science and of scientific theory, and owing to the fact that "the English manufacturer has considered that a knowledge of the benzol market was of greater importance than a knowledge of the benzol theory," that this country lost the pre-eminence in the coal-tar industry which in the early days, when that industry was controlled by chemists (like Perkin and Nicholson), she so fully enjoyed.

If there are any among the readers of this book who feel some dismay at the aspect of the formulæ which have been introduced in this chapter and which will be employed more frequently in the sequel, I would ask them to believe that if they will but make the slightest effort they will find nothing of which to be afraid, especially if they will bear in mind that these formulæ *need not be memorised.* No reader of ordinary intelligence will refrain from reading a work on architecture because of the drawings of pillar capitals, or of arches, or of the plans of buildings which accompany the text. On the contrary, without these drawings, how could the reader form a true mental picture of even a simple structure or understand the mutual relationships of its parts? So is it with the formulæ which we shall employ here. These formulæ are the plans, so to say, of molecular structures by which the reading and understanding of the text may be made more easy. By looking at these diagrams, these formulæ, one sees at a glance how the different compounds are related; how, for example, from benzene, the parent hydrocarbon, there have been evolved numerous other compounds of much more complex structure. We may, indeed, regard the hexagon, the diagram which we have used to represent the structure of the benzene molecule, as representing, so to say, a simple house to which succeeding owners may add at their pleasure—one a bow window, another a turret, a third an additional room, and so on—so that the original building becomes completely transformed. By means of our formulæ we shall be able readily to follow the successive changes which take place. The contemplation of these formulæ, moreover, has a value for the layman in that he will thus gain some idea of the complexity of the compounds and may come to appreciate more fully the ability of the chemists who have not only succeeded in unravelling the intricate details of molecular constitution, but have also built up these complex structures from more simple materials. The ordinary person is impressed by the grandeur or magnitude of some engineering triumph and may be overwhelmed by statistics of the number of bolts or nuts, or the weight of metal employed; but although the intricate structure of the molecule cannot be seen by the eye, it must nevertheless impress the mind of every thoughtful person. Indeed, until the imagination of our people can be fired by the mental contemplation of these great chemical achievements we shall never be able to gain for chemistry and for chemical study that measure of interest, respect, recognition, and encouragement which alone will enable this country to hold her own in the industrial competition of the world.

CHAPTER V

THE PRODUCTION OF DYES FROM COAL TAR

From time immemorial, men, denied by nature the more varied and gorgeous colourings of the animals, have delighted in staining their bodies or dyeing their garments by means of the various colouring matters with which the animal and vegetable creation supplied them—the colouring matter of logwood; the animal dye carmine or cochineal which was used in this country to dye the scarlet tunics of our soldiers; the blue dye, indigo or woad, one of the oldest of dyes; the red dye, alizarin, obtained from the root of the madder plant and employed in the production of Turkey red; and the costliest and most famous dye of the ancient world, Tyrian purple, obtained from a shell-fish found on the eastern shores of the Mediterranean. Until the middle of the nineteenth century these and some other dyes, mainly of animal or vegetable origin, were practically the only dyes with which man was acquainted. But in 1856 a new chapter, and one of the highest importance in the history of dyes, commenced with the discovery of the once favourite synthetic dye, mauve, which found its last use for colouring the postage stamps of the late Victorian era. This dye was prepared from crude aniline, which was in turn produced from the benzole derived from coal tar, and it was the first of a long list of synthetic dyes prepared by chemists from the constituents of coal tar. Starting from benzene, toluene, phenol, naphthalene, anthracene, and a few other constituents of the thick black liquid, coal tar, which less than a hundred years ago was a useless waste material and a nuisance to the gas manufacturer, synthetic dyes, to the estimated value of nearly £20,000,000, are now manufactured annually, more than two-thirds of this amount being produced, in 1913, in Germany. These dyes have, by reason of their almost infinite variety and applicability, their range of colour and delicacy of tone, ousted the natural dyes to a very large extent from the dye-works.

It is, of course, now universally known that these numerous coal-tar dyes are not present as such in the coal tar, but that they are obtained from the constituents of coal tar by a more or less complex series of chemical reactions. Thus, from some eight or nine primary constituents of coal tar (benzene, toluene, xylene, phenol, cresol, naphthalene, anthracene, etc.), there are produced, by the action of various chemical reagents—nitric acid, sulphuric acid, chlorine, caustic soda, etc.—some two hundred and ninety "intermediate" compounds, and from these "intermediates," by their mutual combinations and interactions, the finished dyes are prepared, of which upwards of nine hundred actually find application at the present time. The production of a dye, therefore, is by no means a simple operation, except in a very few cases, and is, in most cases, a very complex process involving, it may be, fifteen or twenty distinct and separate chemical reactions. That the industry of dye-manufacture is a very intricate one will, therefore, be readily understood, and if success is to be attained, each step in the process of manufacture must be scientifically controlled and carried out with the highest degree of efficiency. But a further very serious complication is introduced owing to the fact that in the preparation of many of the intermediates, "by-products" are produced in varying amounts, and for these by-products a remunerative outlet must be obtained. Even when all the products formed in the manufacture of a given intermediate can be used up in the manufacture of dye-stuffs, the demand for the dye-stuffs thus obtained may differ very greatly, and by no means always in the same direction or in the same measure as the intermediates. The problem of working up, completely and remuneratively, without waste and without over-production, all the by-products formed in the manufacture of the intermediates, is one of the utmost importance for the success of the industry. Owing to the enormous development of her organic chemical industry, embracing the manufacture of dyes, drugs, perfumes, and "fine" (organic) chemicals generally, the solution of this problem has become more easy for Germany than for any other country.

Although Great Britain is one of the largest producers of coal tar, she has, hitherto, manufactured only a small number of the intermediates required for the production of the finished dyes, and has contented herself with importing many of the most important intermediates from Germany. If, therefore, this country is to gain her independence in respect of the manufacture and supply of dyes, she must undertake, in the future, the production of the necessary intermediates on a greatly more extensive scale than in the past. In this direction very marked advance has been made since the outbreak of the war.

The value, in round figures, of the estimated production of coal-tar dyes in 1912 is given in the following table:

Germany	£13,500,000
Switzerland	1,290,000
Great Britain	1,190,000
France	1,000,000
United States	750,000
Other countries	2,000,000
	£19,730,000

In 1913 Great Britain imported dyes to the value of £1,946,224, the value of the dyes obtained from Germany amounting to about £1,800,000. Of all the dyes used in this country in the textile, fur, feather, paint, and other industries, only about 10 per cent. were of home manufacture.

In the year 1845, largely owing to the efforts of the Prince Consort and of the Queen's physician, Sir James Clark, there was founded the Royal College of Chemistry in London, and A. W. Hofmann, a young German chemist who had been trained under the renowned Justus von Liebig at Giessen, was appointed Professor of Chemistry. For some time chemists had been interesting themselves in the nature and composition of coal tar, and Hofmann and his students engaged energetically in the work of investigation. One of the earliest results to be obtained was the isolation from coal tar of the hydrocarbon benzene, a compound which was first discovered by Michael Faraday in 1825[1]; and after the work of Mansfield (p. 15), coal tar became the chief source of the compound. As early as 1834 Mitscherlich had shown that when benzene is treated

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[1] In 1815 oil-gas was introduced as an illuminant, and was supplied to the consumers in cylinders into which the gas had been pumped under a pressure of thirty atmospheres. Under this pressure a portion of the gas condensed to a liquid, and from this liquid Faraday isolated benzene, or bi-carburet of hydrogen as he called it.

with concentrated nitric acid, it is converted into an oily liquid, nitro-benzene, $C_6H_5{\cdot}NO_2$, which, even before the introduction of the coal-tar dyes, was manufactured in small quantity and used, under the name of **Essence of Mirbane,** for scenting soap. Nitrobenzene, in its turn, as was found by Béchamp in 1854, could be converted into aniline,[1] $C_6H_5{\cdot}NH_2$, by acting on it with a mixture of acetic acid and finely divided iron. We see, then, that coal tar became not only a convenient source of supply of benzene, but also, through the chemical transformation of this substance, of the compound aniline. Entering into this heritage of knowledge, W. H. Perkin, who had, as one of Hofmann's students, been trained in an atmosphere of purely scientific investigation, made his important discovery of the first coal-tar dye. It was in 1856, while engaged in an attempt to produce the naturally-occurring alkaloid quinine from simpler substances, that Perkin treated a solution of aniline in dilute sulphuric acid with potassium dichromate. As a result, there separated out from the liquid a dark-coloured, resinous mass, and from this unpromising material Perkin separated the first-known aniline dye, which he somewhat later manufactured and sold under the name of "aniline purple," or "Tyrian Purple," or "mauve," the name given to it by the

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[1] Derived from anil, the Portuguese name for indigo, from which aniline was first obtained in 1826.

French dyers to whom, as we learn, the industrial application of this dye was largely due. "I distinctly remember," said Sir William Perkin at a later date, "the first time I induced a calico-printer to make trials of this colour that the only report I obtained was that it was too dear, and it was not until nearly two years afterwards, when French printers put aniline purple into their patterns, that it began to interest British printers."

The successful industrial production of mauve depends on the successful production of nitrobenzene from benzene, and of aniline from nitrobenzene; and although these two "intermediates" had already been prepared in small quantities, their production on a large scale presented a number of difficulties to the pioneers in this industry. Instead of the glass flasks in which, hitherto, nitrobenzene had been prepared by the action of fuming nitric acid on benzene, Perkin employed a large cast-iron cylinder, capable of holding between thirty and forty gallons of liquid, and furnished with a stirrer which could be worked by a handle. Since a sufficiently large supply of fuming nitric acid could not at that time be obtained, Perkin used a mixture of sodium nitrate and concentrated sulphuric acid, and, later, a mixture of concentrated nitric and sulphuric acids. The conversion of nitro-benzene into aniline was effected in large iron stills by means of iron filings and acetic acid, this acid, however, being replaced at a later date by the cheaper hydrochloric acid or muriatic acid. By the action of the acid on the iron, hydrogen is produced, and this "reduces" the nitrobenzene, or replaces its oxygen by hydrogen, and so yields aniline. The methods used at the present day for the manufacture of these two very important compounds are essentially those which were introduced by Perkin; and in thus working out the details of the process of manufacture of aniline, now perhaps the most important of all the coal-tar "intermediates," Perkin performed a service of the highest value to the coal-tar colour industry.

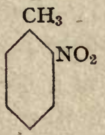
The success which attended the introduction of mauve, the vogue of which among the women of 1859 became so "epidemic" that *Punch* referred to it as "The Mauve Measles," naturally led chemists to try the action on aniline of other oxidising agents (substances capable of giving up oxygen to other substances) than the potassium dichromate used by Perkin; and although they did not succeed in displacing the latter for the preparation of mauve, their efforts led to the discovery of a new dye, **aniline red, magenta,** or **fuchsine.** The formation of this red dye had been observed by several chemists, even as early as 1856, and although it was manufactured in small quantity in France in 1858-9, by a process due to Verguin, the greatest success in its manufacture was achieved, in 1860, by two English chemists, Medlock and Nicholson, former pupils of Hofmann, who prepared it by the action of arsenic acid on commercial aniline. The manufacture of this important dye was carried out by Messrs Simpson, Maule and Nicholson, and the "crown" of magenta crystals prepared by this firm was one of the most notable exhibits of the International Exhibition of 1862. Stirred by this and by the other exhibits of English dye manufacturers, Hofmann was prompted to make the prediction: "England will, beyond question, at no distant day become herself the greatest colour-producing country in the world, nay, by the strangest of revolutions, she may, ere long, send her coal-derived blues to indigo-growing India, her tar-distilled crimsons to cochineal-producing Mexico, and her fossil substitutes for quercitron and safflower to China, Japan, and the other countries whence these articles are now derived." At that time England was pre-eminent in the industrial production of the coal-tar dyes as she was pre-eminent in the production of the raw materials of their manufacture, but in the subsequent years, largely through her failure to recognise the vital importance of persistent chemical research, she had to yield pride of place to Germany. Let us, however, still hope that the faith in science which has been awakened in the people of this country during the years of war will yet enable us in the years of peace to regain our lost position and so realise the prophecy made by Hofmann in 1862.

The brilliancy of the new aniline dyes and the great success they achieved owing, partly, to the simplification which their use brought about in the process of dyeing, made a very powerful appeal to the imagination of the scientific chemist no less than to the business instincts of the manufacturer. "A new world was disclosed full of magic promise, and all joined eagerly in the search, the manufacturer and the professor, the business man and the adventurer; for the one a new gold-mine, for the other new opportunities of fruitful investigation." To such an extent, indeed, were the energies of chemists directed along this one channel that it was feared by some that the general progress of chemical science would be gravely prejudiced. But the check, if any, was but temporary, for the co-operation which then existed between the scientific investigator and the chemical technologist, a co-operation which this country must endeavour once more to re-establish, proved most beneficial; and the new materials which the manufacturer soon placed at the disposal of the investigator led to a far greater extension of chemical science than would otherwise have been possible.

Just as aniline formed the basis of manufacture of mauve and of magenta, so magenta became, in its turn, the starting-point for the preparation of a series of new dyes, the number of which now began rapidly to increase. In 1861 Girard and de Laire prepared **aniline blue** or **Lyons blue** by heating magenta with aniline in presence of benzoic acid; and by treating this dye with concentrated sulphuric acid, E. C. Nicholson, in 1862, produced the more valuable **Nicholson's blue** or **water blue**, which possessed the great advantage of being soluble in water and in solutions of alkalies, and was better adapted for dyeing wool than the dyes previously prepared. Hofmann, also, prepared brilliant but not very stable violet dyes, **Hofmann violets,** by acting on magenta with methyl iodide and ethyl iodide.

But although the preparation of new dyes and the perfecting of their industrial production were carried on with much vigour along the lines opened up by W. H. Perkin, chemists were not unmindful of the need of more theoretical investigations for the purpose of determining the composition and unravelling the constitution of these important new substances. Without such knowledge the dye industry could not be placed on a secure scientific basis and its further development ensured. In this work of investigation Hofmann took a leading part, and in 1862 he showed that the dye magenta was the salt of a base[1] which he called **rosaniline.** Moreover, in 1864 he confirmed what had already been discovered by Nicholson, that magenta cannot be obtained by the oxidation of pure aniline but only of commercial aniline which contained the two isomeric substances, ortho- and para-toluidine, as impurities.

We have already seen that coal-tar contains not only benzene but also several other similar hydrocarbons, more especially toluene; and in the early days of the industry the separation of these was not carried out very effectively. In other words, the benzol obtained by the distillation of the coal-tar always contained larger or smaller amounts of toluene. When this commercial benzol was treated with a mixture of nitric and sulphuric acids there were produced not only nitrobenzene but also two isomeric nitro-toluenes, namely, ortho- and para-nitrotoluene (see p. 44):



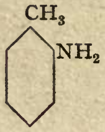
Ortho-nitrotoluene

Para-nitrotoluene

and when these nitrotoluenes are "reduced" by

[1] Chemists are accustomed to classify substances into acids, bases, and salts. An acid is a substance with a sharp, sour, or acid taste (*e.g.* vinegar or acetic acid), which can combine with or neutralise a base (*e.g.* ammonia or soda), with production of a "neutral" substance, a salt.

means of iron and hydrochloric acid, the two corresponding **toluidines** are produced :

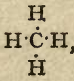


Ortho-toluidine

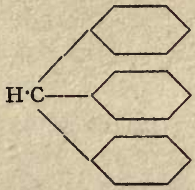
Para-toluidine

It was to the presence of these compounds in the aniline employed that the discovery of magenta, as, indeed, also of mauve, was due.

But although Hofmann succeeded in determining the composition of magenta and of some of the other dyes then known, the true relationships which existed between these dyes could not be understood without a knowledge of the structure or constitution of the molecule. This knowledge, made possible by the theories of structure put forward by Kekulé (p. 36), was finally obtained in 1878 by the two German chemists Emil and Otto Fischer, who showed that the parent of rosaniline, magenta, and a number of other dyes derived from aniline, is a hydrocarbon called triphenylmethane. This compound can be regarded as arising from methane, $\overset{\text{H}}{\underset{\text{H}}{\text{H}\cdot\dot{\text{C}}\cdot\text{H}}}$, by the replacement of three of the hydrogen atoms by the group **phenyl** or C_6H_5, that is, a molecule of benzene from which one hydrogen atom has been removed. We



therefore obtain as the formula of this parent hydrocarbon:



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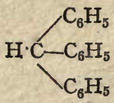
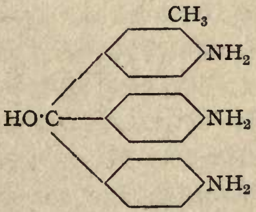


$$\mathrm{H{\cdot}C}\begin{matrix}\diagup \mathrm{C_6H_5}\\ -\mathrm{C_6H_5}\\ \diagdown \mathrm{C_6H_5}\end{matrix}$$

When a mixture of aniline, ortho-toluidine, and para-toluidine is oxidised, rosaniline is produced:



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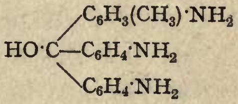
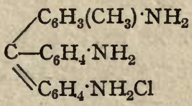


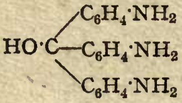
$$\mathrm{HO{\cdot}C}\begin{matrix}\diagup \mathrm{C_6H_3(CH_3){\cdot}NH_2}\\ -\mathrm{C_6H_4{\cdot}NH_2}\\ \diagdown \mathrm{C_6H_4{\cdot}NH_2}\end{matrix}$$

(the relation of which to the parent hydrocarbon, triphenyl-methane, is readily seen), and this base unites with hydrochloric acid, with elimination of water, to yield rosaniline hydrochloride or magenta:

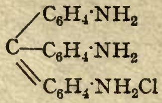


$$\mathrm{C}\begin{matrix}\diagup \mathrm{C_6H_3(CH_3){\cdot}NH_2}\\ -\mathrm{C_6H_4{\cdot}NH_2}\\ = \mathrm{C_6H_4{\cdot}NH_2Cl}\end{matrix}$$

When a mixture of aniline and para-toluidine is oxidised, another base, **para-rosaniline,** is obtained, and this also gives rise to dyes similar to those given by rosaniline, to which they are, structurally, closely related, as the formulæ show:



Para-rosaniline



Para-rosaniline hydrochloride (red dye)

The theory of the structure of the benzene molecule put forward by Kekulé, and the elucidation of the constitution of rosaniline and para-rosaniline which it rendered possible, not only enabled one to understand the exact relations between the different dyes, the Hofmann violets, aniline blue, etc., which had already been prepared, but new and better processes for the synthesis of these and other dyes could be introduced. Thus the old process for the manufacture of para-rosaniline and rosaniline (magenta) has given place to the "New Fuchsine" process in which para-rosaniline is prepared from formaldehyde and aniline, while rosaniline is prepared from formaldehyde, aniline, and ortho-toluidine.

The hydrogen atoms of the three NH_2-groups present in rosaniline and para-rosaniline can be replaced by various groups, such as methyl (CH_3), ethyl (C_2H_5), phenyl (C_6H_5), benzyl ($C_6H_5{\cdot}CH_2$), etc., by acting on the compounds with methyl chloride, ethyl chloride, aniline, benzyl chloride, etc. In this way whole series of dyes can be obtained, like the Hofmann violets, which were prepared by replacing three hydrogen atoms in rosaniline by methyl or ethyl groups; and aniline blue, which is derived from magenta by the replacement of three hydrogen atoms by phenyl groups. Since, therefore, a varying number of hydrogen atoms can be replaced by different groups, it will readily be understood that from the parent dye, magenta, quite a considerable number of derived dyes can be prepared.

The production of the Hofmann violets, we have seen, involves the introduction of new reagents, methyl and ethyl iodide or chloride, and for the preparation of these, methyl alcohol or "wood spirit" and ethyl alcohol or "spirits of wine" are required. The development of the dye industry, therefore, depended on and was accompanied by the development of other chemical industries; and the industrial production of the large number of different compounds used in the manufacture of dyes becomes a matter of supreme importance for the success of dye-manufacture. By the introduction of new reagents, moreover, other new compounds, other intermediates, can be prepared, and these, in turn, may become the starting-point for other series of dyes, the dye industry thereby growing rapidly in diversity as a tree grows by the ramification of its branches. Thus, by heating aniline with methyl chloride, the compound dimethyl-aniline is produced, and by acting on this with an oxidising agent a beautiful violet dye, known as **methyl violet,** is obtained, and is largely used as a staining liquid in microscopy and in the manufacture of indelible pencils. It consists of a mixture of dyes which may be regarded as derived from para-rosaniline by the replacement of four, five, and six atoms of hydrogen by methyl groups. The pure hexamethyl derivative of para-rosaniline (with six atoms of hydrogen replaced by methyl groups) is obtained from dimethyl-aniline and phosgene (from carbon monoxide and chlorine), and is known as **crystal violet.** By the action of methyl chloride on methyl violet, a brilliant green dye, **methyl green,** is obtained.

The production of new dyes by the replacement of hydrogen by different groups of atoms leads us to the consideration of a subject of the highest importance, the relation between colour and constitution.

Put in general terms, a substance possesses colour only when it has the power of absorbing light of a certain wave-length while allowing light of other wave-length to pass through. When a substance absorbs the green rays, for example, the light which passes through will show the complementary colour, namely, purple red. In other words, the substance will appear of this colour.

From the study of a large number of substances the conclusion has been reached that colour is associated with the presence of certain groups or arrangements of atoms in the molecule—such groups being known as "chromophors" or colour-bearing groups.[1] In the dyes which we have already mentioned the colour is believed to be due to a modification of one of the benzene rings. But although the character of a dye-stuff is derived from its chromophor, the actual colour and shade may be very distinctly altered by the introduction of different groups into the molecule. Thus, if we write down the different primary colours, namely,

Greenish-yellow,
Yellow,
Orange,
Red,
Purple,
Violet,
Indigo,
Cyanide-blue,
Bluish-green,

it is found that the introduction of methyl and ethyl groups, and still more the introduction of

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[1] When a chromophor is present in a compound the latter is said to be a "chromogen," and may or may not be coloured. To convert the latter into a coloured substance, it is necessary to introduce certain groups (especially OH and NH_2), called "auxochromes."

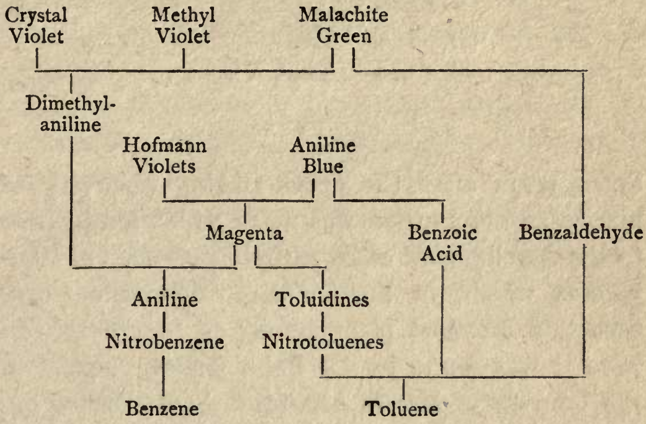
phenyl, benzyl, and other groups derived from benzene, produces a change of colour in the direction shown by the arrow. This fact is well illustrated by the dyes which have already been mentioned, for by introducing three methyl or ethyl groups into the molecule of magenta (red), Hofmann obtained violet dyes. Moreover, by increasing the number of such groups the violet shade becomes bluer, as is shown in the case of methyl violet and crystal violet, which contain five or six methyl groups. But, as we have said, the phenyl group has a more powerful effect than the methyl or ethyl group, and so we find that when it is introduced into a molecule in place of hydrogen, the alteration of shade or colour is much greater. This is illustrated by aniline blue, which is obtained by replacing three hydrogen atoms in magenta by three phenyl groups. Since, by the introduction of certain other groups, the shade or colour can be altered in the opposite direction to that indicated by the arrow, it will readily be understood how it becomes possible not only to prepare a considerable number of parent dyes, but also, from these dyes, to produce, at will, a great variety of shades and colours simply by the introduction of different groups into the molecule of the parent dye.

To attempt a full discussion of all the dye derivatives of triphenyl-methane would be impossible within the limits of space available here, and would, moreover, be a very tedious matter for the general reader. But reference may be made to one other dye of importance, discovered in 1878. It has already been noted that as a result of the introduction into the dye industry of methyl chloride and iodide, the preparation of dimethyl-aniline [$C_6H_5{\cdot}N(CH_3)_2$] became possible. Similarly, in place of the two methyl (CH_3) groups, other groups can be introduced into aniline, as has already been indicated, and from these derivatives of aniline other series of dyes can be obtained by the action of benzaldehyde or bitter almond oil. Thus, dimethyl-aniline gives rise to the well-known dye, **malachite green** or **Victoria green**, and diethyl-aniline [$C_6H_5{\cdot}N(C_2H_5)_2$] to the dye **brilliant green.**

The synthetic production of these two and other dyes necessitating the use of benzaldehyde depended for industrial success on the discovery of a cheaper and better source of this compound than that already existing. Hitherto, benzaldehyde had been obtained by the fermentation of bitter almonds. In this process the compound, amygdalin, present in the almonds, undergoes a decomposition with production of benzaldehyde and certain other substances. At the present day, however, this compound, formerly obtainable only from vegetable sources, is manufactured in large quantities from the coal-tar hydrocarbon, toluene; and from this same source is also obtained the compound benzoic acid, which, as we have seen, is used in the manufacture of aniline blue (p. 58). Thus the dye industry goes on increasing in diversity, drawing into its service one compound after another, and depending, therefore, not only on the persistent and untiring work of the research chemist but also on the success with which the technologist can carry out on an industrial scale the discoveries of the investigator. And any country which aims at developing a dye-making industry which will render it independent of other countries must learn to produce, with the utmost economy, the large number of " intermediates " of which that industry makes use.

The dyes which have so far been mentioned will dye silk and wool directly, but will dye cotton only with the aid of a mordant. Although not characterised by great fastness to light, the dyes of the triphenyl-methane series possess, for the most part, great brilliance, and are, in consequence, much esteemed for the dyeing of those materials—ribbons, for example—for which brilliancy is more valued than fastness. Owing to the introduction of other series of dyes, however, the further development of the triphenyl-methane dyes has practically ceased.

The relations between the different dyes mentioned in this chapter are shown in the following diagram[1]:



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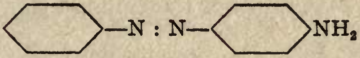
[1] For a more complete representation of the relationships between the coal-tar crudes, intermediates, and finished dyes, the reader is referred to the Chart drawn up by Thomas H. Norton and published by Messrs George Allen & Unwin, Ltd., 40 Museum Street, London, W.C.

CHAPTER VI

AZO-DYES

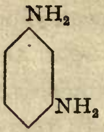
SOME years after the epoch-making discovery of mauve an observation was made which led in time to the development of an entirely new class of compounds which, in number and importance, now occupy a foremost place among coal-tar dyes. In 1860 it was found by Dr Peter Griess, chemist in the brewery of Messrs Allsopp & Sons, Burton-on-Trent, that when nitrous acid acts on aniline, or on any other derivative of benzene containing the amino-group (NH_2), an unstable compound—a so-called diazo-compound—is produced. The diazo-compounds which were thus obtained possessed the very important property of combining or "coupling" with aromatic amines (compounds containing the NH_2-group), or with phenols (compounds containing the OH-group). In this way were produced the so-called **azo-dyes**, which have found their special application as wool-dyes, and which owe their colour to the presence of the chromophoric azo-group or pair of linked nitrogen atoms, $—N:N—$. Even in 1863, although its constitution was not then known, an azo-dye, **aniline yellow**, had been prepared and put on the market, with only a limited success; but it was not till 1876, and after the constitution of the compounds had been elucidated, that the production of azo-dyes began to undergo a rapid development. Many hundreds, even thousands, of azo-dyes have now been prepared, and a very considerable number have been found suitable for use as dyes.

When aniline is "diazotised" by the action of nitrous acid, and the resulting compound then "coupled" with a molecule of aniline, a compound is obtained which can be represented by the graphic formula

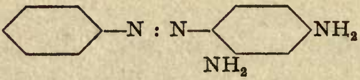


This is a basic substance and can form a salt with hydrochloric acid, yielding thereby the dye **aniline yellow**, a dye which, on account of its fugitive nature, is now no longer used except in the manufacture of other dyes. If, however, aniline yellow is treated with a highly concentrated sulphuric acid, two sulphonic acid groups (SO_2OH) enter the molecule, and a more stable dye, **acid yellow**, is obtained. This process of sulphonation, as was pointed out by the late Sir W. H. Perkin, is one of the highest importance in the production of stable dyes.

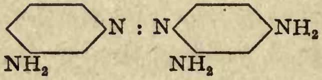
If, after diazotising aniline one couples the product, not with aniline but with a benzene derivative containing two amino-groups, namely, meta-phenylene diamine,



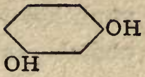
one obtains the compound



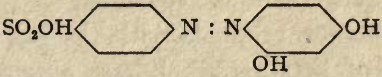
the salt of which with hydrochloric acid constitutes the orange-red dye **chrysoidine.** Or, again, if one diazotises meta-phenylene diamine and couples the product with another molecule of this compound, there is formed



the salt of which with hydrochloric acid constitutes **Bismarck brown.**

But we can couple the diazo-compounds not only with compounds containing the amino-group, but also with compounds containing the hydroxyl-group (OH), *e.g.* phenol, cresol, salicylic acid, etc., and in this way another series of azo-dyes is obtained known as the tropæolines. Thus, for example, if one diazotises not aniline itself but the sulphonic acid derivative of aniline, known as sulphanilic acid, SO_2OH  NH_2, and if one then couples the product with the compound resorcinol, 

(a substance derived from benzene), there is obtained the compound



a dye known as **tropæoline O.**

Not only can one produce azo-dyes from aniline, toluidine, phenol, etc., and from their derivatives, but one may also use similar compounds derived from other hydrocarbons. In this connection the coal-tar hydrocarbon naphthalene has been found of especial value, and very many dyes have now been produced from the amino- and hydroxyl-derivatives of this compound. By thus drawing naphthalene within the sphere of the dye industry, an important outlet was secured for this coal-tar product—otherwise but little used—and at the same time a large number of valuable new dyes were obtained.

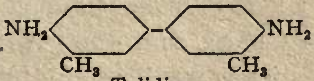
Just as we have seen that phenol and aniline are derived from benzene by the replacement of a hydrogen atom by a hydroxyl- or amino-group, so from naphthalene one can obtain similar compounds—**naphthol** and **naphthylamine.** Owing to the peculiar constitution of naphthalene, however, two isomeric naphthols and naphthylamines can be obtained, known as alpha-naphthol and beta-naphthol, alpha-naphthylamine and betanaphthylamine. These very important compounds, as well as their sulphonic acid derivatives, are now manufactured in large quantities and used in the production, more especially, of azo-dyes. By diazotising aniline, toluidine, xylidine, etc., and coupling the products with the sulphonic acid derivative of beta-naphthol, one obtains a series of red dyes known as **Ponceaux,** the shade varying according to the amino-compound (aniline, toluidine, etc.) employed. And, similarly, other dyes can be obtained by diazotising the naphthylamines or their derivatives, and coupling the products with various amino-compounds, phenols, naphthols, etc. Moreover, in those cases where a diazo-compound is coupled with an amino-compound, the process of diazotisation can be repeated, and dyes containing two azo-groups, *e.g.* **Biebrich scarlet,** can thus be obtained. Many of these are of great importance.

From what has now been said, some idea will be gained not only of the large number of azo-dyes which can be obtained, but also of the increasing number of "intermediates" made use of by the dye industry. Moreover, for the production of all these azo-dyes, nitrous acid is necessary for carrying out the first step in the process, that is to say, the diazotising of the initial amino-compound. This nitrous acid is produced from sodium nitrite, and this, in turn, is obtained by heating sodium nitrate with lead. Until recently, one was dependent for sodium nitrate on the large deposits of this salt in Chile, but in the past decade the production of nitric acid directly from the air has opened up a new source of supply of this important salt. In this matter of the utilisation of atmospheric nitrogen for the production of nitric acid and other compounds of nitrogen, this country has lagged behind not only Germany but nearly every other civilised country in the world. There seems, however, to be now some hope that this past neglect will be repaired.

Although most of the dyes to which reference has already been made, dye silk and wool directly, vegetable fibres, *e.g.* linen and cotton, must first be mordanted before they will take up the dye from the bath. It was therefore an event of the first importance when, in 1884, the German chemist Böttinger discovered a new group of azo-dyes which were able to dye cotton and linen directly without requiring a mordant. In this discovery is to be found undoubtedly one of the reasons for the outstanding importance of the azo-dyes.

These direct cotton dyes contain two azo-groups or two pairs of nitrogen atoms, and are derived from compounds similar to benzidine and tolidine, in which there are two benzene rings joined together, thus :

Benzidine

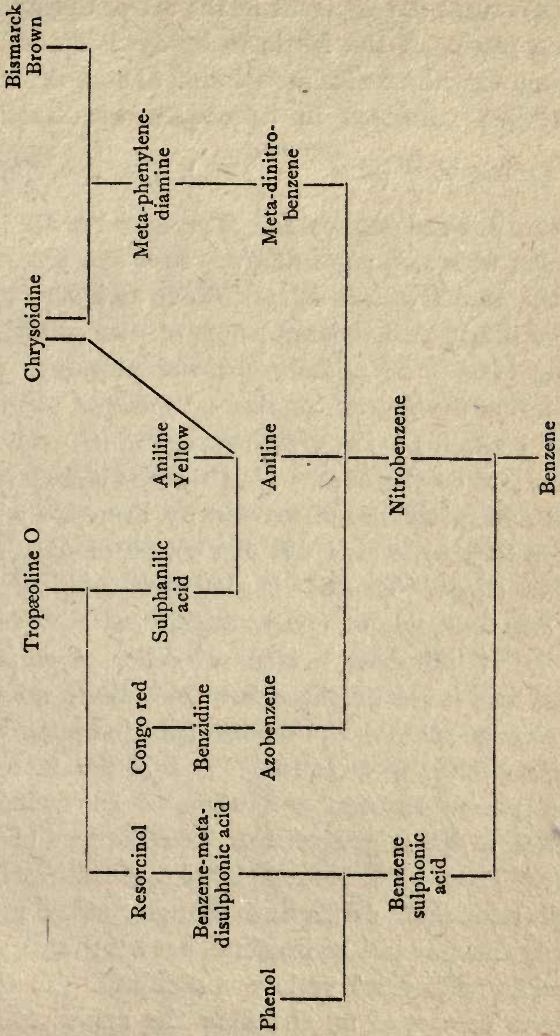


Tolidine

When these compounds, which are prepared from benzene and toluene respectively, are acted on by nitrous acid, both NH_2-groups are diazotised, and the product can then couple with two molecules of amine or phenol. When benzidine, for example, is diazotised and the product coupled with two molecules of sulphonated naphthylamine, the red dye, **Congo red,** is obtained. This was the first direct cotton dye to be synthesised, and led to the preparation of a large number of similarly constituted dyes, covering the whole range of colour, all of which possess the valuable property of dyeing cotton without the aid of a mordant. The chart on the following page indicates the relationship of some of the azo-dyes to the hydrocarbon benzene.

The simplest azo-dyes are yellow, but, as has already been pointed out, the shade and colour can be altered very greatly by the introduction of different groups. In this way dyes of deeper and deeper tone, from the vivid scarlets known as xylidine scarlet and Biebrich scarlet—successful rivals of the natural dye cochineal—to blue, violet, brown, and black, have been produced; and this change of colour is effected, more especially, by the introduction of groups derived from naphthalene. By the introduction of nitro-groups (NO_2), green dyes, *e.g.* **diamine green,** are obtained.

As a result of the introduction of the azo-dyes


Bismarck Brown
Meta-phenylene-diamine
Meta-dinitro-benzene
Chrysoidine
Aniline Yellow
Aniline
Nitrobenzene
Benzene
Tropæoline O
Sulphanilic acid
Congo red
Benzidine
Azobenzene
Resorcinol
Benzene-meta-disulphonic acid
Benzene sulphonic acid
Phenol

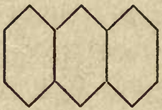
an important development in the art of dyeing has taken place. If the fabric to be dyed is first impregnated with an alkaline solution of beta-naphthol and then immersed in a solution of diazotised para-nitraniline (NO_2NH_2), the dye, **para-nitraniline red** or **para-red,** is produced *on the fibre.* Dyeing with this pigment dye—as a dye produced on the fibre is called—is carried out on a very large scale, nearly two thousand tons of para-nitraniline being produced annually for the purpose. This process of dyeing can, similarly, be carried out with *dyes* containing an amino-group which can be diazotised on the fibre. Thus there is a very complex dye primuline, discovered by Professor A. G. Green in 1887, which will dye cotton directly of a yellow shade. This dye is somewhat fugitive, and is, consequently, of comparatively little value in itself. If, however, a piece of calico, dyed with primuline, is passed through a cold, dilute solution of nitrous acid, the primuline (which contains an amino-group), is diazotised; and if the fabric is then passed through a solution of an amine or phenol, a dye is produced or "developed" on the fibre. Thus, with beta-naphthol, **primuline red;** with resorcinol, **primuline orange**; with meta-phenylene-diamine, **primuline brown**; and with salicylic acid, **oriol yellow** is obtained. To these colours developed on the fibre the name of "ingrain dyes" is given; or, since the solution of the diazo-compound has, on account of its instability, to be kept cool by means of ice, the name "ice colours" is also sometimes applied to this group of dyes.

Another pigment dye to which we may here refer, a dye which carries us back again to the substance, aniline, from which the first artificial colouring matter was prepared, is the very important black dye, **aniline black**. This dye, which has a very complex structure, and is not an azo-dye, is obtained by a modification of the process first used by Perkin in the production of mauve, the dye being formed, however, directly on the fibre. Thus, if a piece of cotton is first steeped in a solution of aniline in hydrochloric acid and afterwards immersed in a cold solution of sodium bichromate, a fast black colour is developed on the fibre. Various improvements have more recently been introduced for the purpose both of cheapening the dye and of obtaining more readily a black which will not turn green; and it has been found by Professor A. G. Green that in the presence of certain substances the oxidation of the aniline may even be effected by atmospheric oxygen.

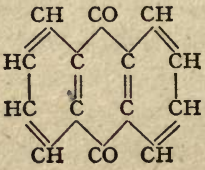
CHAPTER VII

ANTHRACENE DYES AND VAT DYES

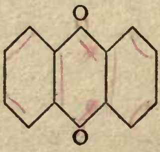
We have already seen how, owing to the introduction of the azo-dyes, the coal-tar hydrocarbon naphthalene, through its derivatives the naphthylamines, the naphthols, and their sulphonic acids, became one of the important raw materials in the coal-tar dye industry. In a like manner, as a result of the all-transforming genius of the chemist, another coal-tar hydrocarbon, anthracene, has also been made to play a rôle of the highest importance in the production of colouring matters. This hydrocarbon, as we have already seen (p. 43), has the formula $C_{14}H_{10}$, and can be represented graphically by three rings joined together, thus:



By oxidation this compound is readily converted into an orange-coloured substance, **anthraquinone,**

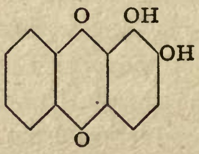


or



This structure forms the nucleus of a considerable number of important dyes, and more especially of **alizarin**, the colouring matter of the madder. This dye, which is capable of dyeing cotton of a bright red colour—the so-called Turkey red—is one of the oldest and best-known dye-stuffs employed by man (to which, indeed, its use in the dyeing of Egyptian mummy-cloths bears witness); and, although now partly displaced by the azo-dyes, it is still very extensively used for the dyeing of cotton goods. Fifty years or so ago, in the South of France and extending eastwards to Asia Minor, great tracts of land, about 400,000 acres in extent, were devoted to the cultivation of the madder plant (*Rubia tinctoria*), and produced about 80,000 tons annually of madder roots. When these roots are crushed and allowed to ferment certain compounds which they contain, known as glucosides, undergo decomposition with production of the sugar glucose and various colouring matters, of which the most important are alizarin—so called from the name, alizari, given by the Arabs to the madder root—and purpurin, dyes which were first isolated in 1826 by the French chemists Robiquet and Colin. But in 1868 far-reaching economic changes were initiated by the discovery, due to Graebe and Liebermann, of the chemical nature of alizarin and by its artificial production from what was then a waste by-product of the distillation of coal, the hydrocarbon anthracene; and in 1869 the commercial production of alizarin from anthracene was commenced by Perkin in England. Since that time the natural dye-stuff has been completely superseded by the synthetic, and the widespreading lands over which the madder once bloomed are covered now with other crops; and an industry which was valued at about £4,000,000 annually has passed from the field to the factory. By this revolution, also, anthracene, which once tar distillers did not trouble to separate from the "last runnings" of the stills, and which was either burnt or used as a lubricant, became greatly in demand and its value was enhanced from pence to pounds.

The preparation of alizarin is simple. Anthracene is first converted into anthraquinone by heating with potassium bichromate and sulphuric acid, and the anthraquinone then converted into its sulphonic acid derivative by heating with concentrated sulphuric acid. When this compound is fused with caustic soda, in presence of a quantity of potassium or sodium chlorate, alizarin or dihydroxy-anthraquinone (anthraquinone with two hydroxyl groups)

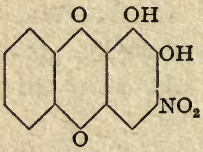


s formed. In this process we see the first triumphant success of the chemist in the artificial production of a natural colouring matter, and in this way the madder dye can be manufactured much more cheaply than Nature can produce it.

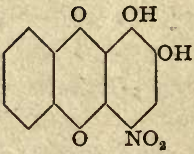
Alizarin is a compound which is insoluble in cold water, and is generally put on the market in the form of a paste containing 10 or 20 per cent. of alizarin. Over 2000 tons of this dye-stuff are now manufactured annually, and of this and other anthracene dyes the United Kingdom imported, in 1913, over 3000 tons, of the value of about £270,000.

The main importance of alizarin lies in its widespread use in cotton dyeing and printing. Unlike some of the azo-dyes to which reference has been made, alizarin will not dye either vegetable or animal fibres directly, but only with the aid of mordants. As mordants, substances are mainly used which give rise to oxides of metals with which the dye forms an insoluble compound or *lake*, and the colour produced on the fibre depends on the metallic oxide used. With alumina as mordant, alizarin gives a bright red colour (as in Turkey red); with oxide of chromium maroon is obtained; whereas with oxide of iron alizarin produces a violet shade. Orange shades can also be produced by using tin salts as mordants.

Besides alizarin, a large number of other derivatives of anthraquinone are used as dyes. By introducing three, four, five, and six OH-groups into the molecule of anthraquinone, one obtains **purpurin** (which is also found along with alizarin in the madder root), **alizarin bordeaux, alizarin cyanine R,** and **anthracene blue,** which give red, violet, and blue shades. By the introduction of the nitro-group (NO_2) into alizarin, one obtains **alizarin orange** and **alizarin brown,**



Alizarin Orange

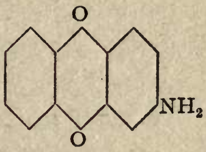


Alizarin Brown

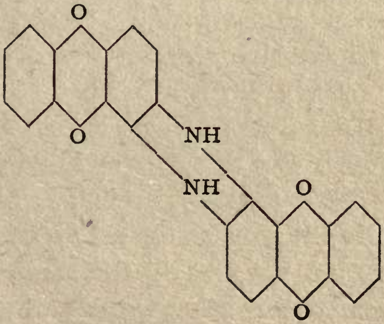
and by the introduction of the sulphonic acid group (SO_2OH), **alizarin red S.** The introduction of still other groups into the molecule of anthraquinone gives rise to dyes of widely varying shades—browns, greens, blues, and violets—the shade obtained depending both on the nature of the group introduced and on its position in the molecule (*cf.* p. 65).

Closely related to the anthracene dyes are the acridine dyes, some of which are used mainly for dyeing leather of a yellow colour. One of these dyes, trypa-flavine or acri-flavine, has recently found important application as an antiseptic (p. 110).

One of the most important developments in recent years has been the production of a series of dyes known as the indanthrenes, a series of dye-stuffs derived from anthraquinone and possessing exceptional fastness to light and to cleansing agents. Although first discovered only in 1901, by R. Bohn of the Badische Anilin- und Soda-Fabrik, these dyes are now manufactured in twelve or thirteen different shades covering the whole range of colours from red to blue. On account of their fastness they are largely employed in the dyeing of Sundour and other guaranteed "fadeless" fabrics. The first and one of the most important of these dyes, **indanthrene blue,** was obtained by fusing an amino-derivative of anthraquinone,



with caustic alkali, whereby two molecules of this compound were caused to join up and yield indanthrene blue, thus:



Other indanthrene dyes, derivatives of anthraquinone, have also been obtained, such as, **indanthrene yellow** or **flavanthrene, indanthrene red, indanthrene green,** etc., as well as the dyes known as **algol yellow, algol red, helindon yellow,** etc. Until recently, none of these dyes had been manufactured in England, but in the present year (1917) indanthrene blue was manufactured by British Dyes, Ltd., and placed on the market under the name of **chloranthrene blue,** and a second blue anthracene dye-stuff for wool and silk has also been placed on the market under the name of **alizarine delphinol.**

Some years after the introduction of indanthrene blue there was discovered, by a strange mishap, a new method of making this compound and others of a similar kind. It befell in this way. For the production of another dye derived from anthraquinone, a dye called sky-blue alizarine, the necessary ingredients were heated for some time in a vessel made of iron. In the course of time new apparatus had to be installed; and with this apparatus no sky-blue alizarine was obtained, but something entirely different. What could be the reason of the failure? The process was carried out in the same way as before and under the same direction. The apparatus, certainly, was new, but it was exactly the same as the old apparatus. And yet, no; it was not exactly the same. The new apparatus, instead of being entirely of iron, had a

After this book had passed through the press, the production of a number of anthracene dyes was announced by Solway Dyes Co., Carlisle (an offshoot of Morton Sundour Fabrics, Ltd.), the production of such dyes having been begun, on a commercial scale, as early as February 1915. So far, the manufacture of the following dyes has been taken up by the above firm, the Company's trade name for the dye being given in brackets: Indanthrene yellow G. (Caledon yellow); indanthrene blue (Caledon blue); indanthrene dark blue B.O. (Caledon purple); indanthrene green B. (Caledon green); indanthrene brown B.B. (Caledon brown); indanthrene red B.N. (Caledon red); indanthrene pink B. (Caledon pink); indanthrene violet R. Extra (Caledon violet); alizarine sapphirole (Solway blue); alizarine cyanine green (Kymric green).

copper lid. But surely that could not be the cause of the different behaviour. Yet so it was, for the small trace of copper derived from the lid exerted a powerful catalytic influence, as it is called, on the reaction. Merely by its presence the copper greatly accelerated the reaction in one particular direction, and so led to the production not of sky-blue alizarine but of an indanthrene dye. By utilising this property of copper indanthrene blue and other valuable dyes, belonging to this and similar series, could be obtained. To some the discovery of this process may appear merely as a "lucky chance," but it must be remembered that it is only he who has the discerning eye and the understanding mind who can turn the "lucky chance" to profit. It is, however, part of the romance of scientific investigation that the "lucky chance" is also one of the rewards that come to those who actively and persistently till the virgin soil of science.

Besides those already mentioned, several other series of dyes are known derived from the constituents of coal-tar, but although a number of these dyes are of much importance (*e.g.* the rhodamines, the saffranines, etc.), a discussion of them would lead beyond the limits allowable. To one important series of dyes, however, known as the sulphur or sulphide dyes, a brief reference must be made. These dyes, which have only recently been extensively introduced, are obtained by heating various organic materials with sulphur and sodium sulphide, and are now manufactured in large quantity and in various shades of red, yellow, brown, green, violet, blue, and black. These dyes are, at the present time, in much favour with dyers, for most of them are substantive or direct-dyeing colours, and possess a fastness to light and to washing at least equal to that of such a fast dye as indigo. For the production of these sulphide dyes aromatic amino-compounds and nitro-derivatives of the phenols are most suitable for use, but a number have also been obtained from anthraquinone. Three of these sulphur dyes, Khaki yellow C, Khaki Brown C, and Cross Dye Black F.N.G., are largely used at the present time for the production of khaki colour on cotton.

The series of dyes to which reference has just been made, the sulphur dyes as also the indanthrene dyes derived from anthraquinone, belong to what are called by dyers, *vat-dyes*. Owing to the insolubility of these dyes in water, it is not possible to prepare dye-baths in the ordinary manner; and for the purpose of dyeing a less direct method must be employed. In using these dyes advantage is taken of the fact that they are comparatively readily reduced to compounds (so-called leuco-compounds), which are soluble in alkalies. The material to be dyed is therefore dipped in the alkaline solution of the leuco-compound—now generally produced from the dye by reduction with sodium hydrosulphite—which is readily taken up both by animal and vegetable fibres. On exposing the material to the air, the original dye-stuff is produced in the fibre in an exceedingly fast form, owing to the oxidation of the leuco-compound by the atmospheric oxygen. Sometimes the leuco-compound of the dye is colourless or very faintly coloured, but in other cases, *e.g.* in the case of the indanthrene dyes, the leuco-compound may have a very marked colour which is generally different from that of the original dye-stuff. Thus, indanthrene yellow or flavanthrene yields a blue leuco-compound which, on exposure to the air, changes into a fast yellow dye. Similarly, indanthrene red and indanthrene green yield purple and blue reduction compounds respectively, which are taken up by the fabric from the bath and which then, on exposure to the air, change to red and green. Although, formerly, vat-dyeing was a somewhat difficult and uncertain process, it has now been rendered as easy and as simple as dyeing from the ordinary dye-bath. That this is so is due largely to the careful investigation of the process consequent on the successful artificial production of by far the most important of the vat-dyes, indigo, a discussion of which is reserved for the following chapter.

CHAPTER VIII

INDIGO AND ITS DERIVATIVES

Of all the dyes now in use none equals in commercial importance or has aroused such general interest as indigo, not only owing to the fact that its production from coal-tar hydrocarbons constitutes one of the greatest achievements of pure and applied chemistry, but also by reason of the enormous economic consequences of that success. Known from a very remote period, indigo was, until about twenty years ago, obtained solely from certain species of plants, the *Indigoferæ*, cultivated more especially in India, China, and Egypt. Even in Europe, as late as the seventeenth or eighteenth century, an indigo-bearing plant, the woad (*Isatis tinctoria*), was cultivated to no small extent, and its cultivation still lingers on in the eastern counties of England. In the sixteenth century, with the opening up of trade with the East, the superior Indian indigo began to make its appearance in Europe, but for many years, owing to the influence of those interested in the growing of woad, its introduction met with a powerful opposition, and the use of the "devilish drug," as it was called, was prohibited by law. In the eighteenth century, however, this ban was removed and the use of Indian indigo gradually extended over the whole of Europe. As a consequence, the Indian indigo plantations came to control the markets of the world.

Indigo does not occur as such in the plant, but as a glucoside, called **indican**, which is found almost exclusively in the leaves. To obtain the indigo, the cut plant is placed in steeping vats and covered with water. Owing to the presence of an enzyme (or ferment) in the leaves, fermentation takes place and the indican undergoes decomposition into glucose and the leuco-compound (p. 88) of indigo. On agitating the resulting solution with air, this leuco-compound is oxidised with production of indigo, which separates out as an insoluble powder. Although indigo-blue or indigotin is the main constituent, the natural indigo also contains varying amounts of other compounds, indirubin or indigo red, indigo brown, indigo yellow, and indigo gluten.

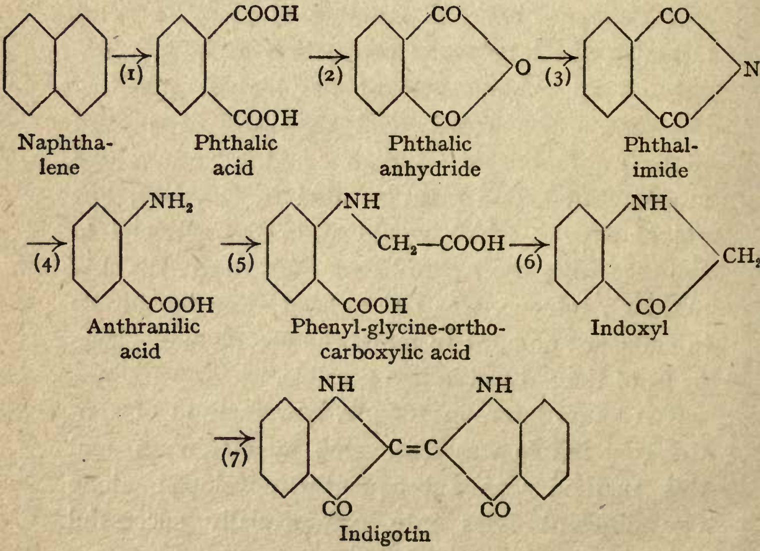
The industry was a large and lucrative one. In 1896-7 the area under cultivation amounted to 1,583,808 acres, and the weight of indigo produced was 8433 tons, the value of which amounted to about £4,000,000. It was a rich prize, therefore, which the large German chemical manufacturers saw before them when they set themselves earnestly to capture the indigo market by producing the dye artificially. The fight was a long one, for seventeen years the struggle went on, and close on £1,000,000 was spent on the campaign, but in the end the genius and resourcefulness of the chemist, the persistence and enterprise of the directors of German chemical industry—*themselves expert chemists*—won the day; and in October 1897 synthetic indigo was placed on the market in competition with the product from the Indian plantations. And what, to-day, is the result of the competition? Since 1896-7 the area under cultivation for indigo fell from 1,583,808 acres to 214,500 acres in 1912-13; and whereas, in 1896, India exported indigo to the value of over £3,500,000, in 1913 her export was only worth about £60,000. In 1913, on the other hand, Germany exported nearly 6700 tons of pure synthetic indigo (indigotin or indigo-blue), valued at about £2,750,000. In the above period, moreover, the price of pure indigo was about halved.

Whether the decline of the Indian indigo plantations will continue cannot be foreseen. Until recently, the processes employed in recovering the indigo were crude and unscientific, but in recent years many improvements have been effected, and new species of plants, producing a larger proportion of indigo, have been introduced. Further improvements in this direction may still be possible, and as many dyers still feel a preference for the natural product, for securing certain effects at least, it is possible that the Indian production of natural indigo may still be maintained. A considerable change has, however, already been produced in Indian agriculture, and many acres of land formerly under cultivation for indigo have been made available for the growth of cotton or of food-stuffs.

As far back as 1880 the artificial production of indigo was first achieved by the German chemist Adolf von Baeyer, who used as his raw material the coal-tar hydrocarbon toluene. The patent of this process was acquired jointly by the two largest dye-manufacturing firms in Germany, the Badische Anilin- und Soda-Fabrik of Ludwigshaven, and Meister, Lucius & Brüning of Hoechst. But although the laboratory production of indigo constituted an achievement of the highest scientific importance, its commercial development proved to be impracticable. Indigo could, of course, be manufactured, and manufactured in quantity, but not at a price which would allow the artificial to compete with the natural dye. Moreover, the raw material, toluene, was not at that time procurable in sufficient amount to make the complete displacement of the natural indigo possible.

Ten years later, in 1890, a new method of synthesising indigo was discovered by Heumann, and this method was subsequently developed along two different lines into commercially successful processes. Both methods involve a considerable number of distinct reactions and require the use of a number of different substances, of which sulphuric acid, ammonia, chlorine, acetic acid, and sodium are the chief; and the success of the synthesis as a whole depends on the success with which each step of the process can be carried out, and on the cost of the substances employed. We shall now see how the great difficulties involved were overcome.

In the process worked at Ludwigshaven the starting-point in the synthesis is naphthalene, one of the most abundant constituents of coal-tar; and the various steps of the process can be represented, graphically, thus:

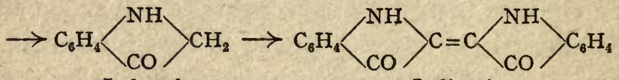


(1) Naphthalene is converted into phthalic acid by heating with fuming sulphuric acid; (2) phthalic acid, on being heated, passes into phthalic anhydride; (3) phthalic anhydride, on being heated with ammonia, yields phthalimide which (4) on being treated with bleaching powder or with sodium hypochlorite, forms anthranilic acid. By the action of monochloracetic acid on the latter, (5), phenylglycine-ortho-carboxylic acid is produced, and (6) this compound, on being fused with caustic soda, passes into indoxyl; (7) and on oxidising this substance with atmospheric oxygen, indigo-blue or indigotin is formed. On attempting to carry out this series of operations on a large scale, it was found that all the steps, except the first, could be carried out in a commercially successful manner. In the case of the first stage of the process, however, it was found that the conversion of naphthalene into phthalic acid did not proceed sufficiently readily, and the cost involved was so great that it rendered the industrial production of indigo unremunerative. A small obstacle, apparently, but a very effective one! While engaged in an endeavour to overcome this difficulty, a fortunate mischance came to the assistance of the manufacturer, for, through the accidental breaking of a thermometer immersed in the heated mixture of naphthalene and sulphuric acid, it was discovered that mercury acts as an efficient catalyst in the conversion of naphthalene

into phthalic acid, and facilitates the process to such a degree as to allow it to be carried out with commercial success. It was, in fact, this fortunate discovery that first ensured the success of the synthetic production of indigo.

Another process, likewise based on the work of Heumann, has also been successfully developed, and has been employed for many years by the firm of Meister, Lucius & Brüning. In this case benzene forms the starting-point. In the manner already described (p. 54), benzene is converted first into nitro-benzene and then into aniline. By the action of monochloracetic acid on aniline, phenyl-glycine is produced, and when this is fused with sodamide, indoxyl is formed and can then be converted into indigotin by oxidation, as in the previous process.[1] The steps of this process can be represented thus:

$$\underset{\text{Benzene}}{C_6H_6} \longrightarrow \underset{\text{Nitro-benzene}}{C_6H_5{\cdot}NO_2} \longrightarrow \underset{\text{Aniline}}{C_6H_5{\cdot}NH_2} \longrightarrow \underset{\text{Phenyl-glycine}}{C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}COOH}$$



Indoxyl Indigotin

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[1] In August 1916 the indigo factory at Ellesmere Port, formerly belonging to the German firm, Meister, Lucius & Brüning, was transferred to Messrs Levinstein, Ltd., of Blackley, Manchester, and by the end of that year British-made synthetic indigo was placed on the market. Although, owing to the exigencies of the war, chloracetic acid was commandeered by the British Government, a method of producing phenyl-glycine without the use of that compound was successfully worked out by the chemists of the British company, and an adequate supply of British-made indigo (known as Indigo LL) is now available.

The commercial success of the production of indigo depended, however, not only on the success with which the different steps in the process could be carried out, but also on the production of the necessary reagents at a sufficiently low cost. In the first process the conversion of naphthalene requires a fuming sulphuric acid of a much greater concentration than the acid produced by the old leaden-chamber process; and, moreover, large quantities of sulphur dioxide were formed during the reaction, the recovery of which in an advantageous manner was an essential condition of success. These requirements, therefore, led to the development of the so-called "contact process," in which a mixture of sulphur dioxide and air is passed over heated platinised asbestos. The sulphur dioxide combines with the oxygen of the air to form sulphur trioxide—which unites with water to form sulphuric acid—and the trioxide is passed into concentrated sulphuric acid. In this way fuming sulphuric acid, or "oleum" as it is technically called, is produced. From this description the process doubtless appears to be a very simple one, but on attempting to employ it for the industrial production of fuming sulphuric acid, a difficulty was met with which seemed at first to be insurmountable. On passing the mixture of sulphur dioxide and air over the platinised asbestos all went well for a time; but soon the reaction stopped and no more sulphur trioxide was formed. After a considerable amount of investigation the cause of this behaviour was traced to the presence of minute quantities of arsenic in the sulphur dioxide, but it still required some years' further work before a successful method of removing this arsenic was discovered. For the production of chlorine, also, of which enormous quantities were required for the manufacture of hypochlorite and of monochlor-acetic acid, the old method of obtaining the gas from hydrochloric acid was useless, and a new method had to be introduced, namely, by passing a current of electricity through a solution of common salt or of potassium chloride, the chlorine being then obtained in a pure state by liquefaction. In this process, also, caustic soda and hydrogen are produced; the former of these is required for the conversion of phenyl-glycine-ortho-carboxylic acid into indoxyl, and the latter is now available for the production of ammonia (also used in the indigo synthesis), by direct combination with the nitrogen of the air. The acetic acid, of which 3000 tons are used annually in the manufacture of indigo, is obtained by the distillation of 150,000 cubic yards of wood. The whole most impressive story of the development of the manufacture of synthetic indigo is one of unshakable faith in science, of chemical and engineering ability and resourcefulness, and of untiring perseverance.

Closely related, chemically, with indigo is that other ancient dye, **Tyrian purple.** Some years ago the nature of this dye was investigated by a German chemist, Friedländer, who extracted it from the glands of two species of marine snail, the *Murex brandaris* and the *Murex trunculus,* and ascertained that this most valuable of all the ancient dyes is a derivative of indigo in which two atoms of hydrogen are replaced by bromine ; and this dye, for which, however, there is now no demand, can be prepared, artificially, with comparative ease. Other chlorine and bromine derivatives of indigo are also known, and some are used as dyes under the name of Ciba dyes.

CHAPTER IX

DRUGS, PERFUMES, AND PHOTOGRAPHIC DEVELOPERS

In the sixteenth and seventeenth centuries, following on the long period of alchemistic activity and the somewhat sterile search for the "philosopher's stone," chemistry, under the influence of Paracelsus, found its main glory in acting as the handmaid of medicine, and its chief task in the preparation of drugs and in the study of their action on the human organism. But the efforts of those early medico-chemists, or iatro-chemists as they have been called, have been completely eclipsed by the brilliant discoveries of the modern organic chemist, who has made available for use a large array of new drugs and medicinal preparations. Since many of the most important of these substances are prepared from the constituents of coal tar, it will readily be understood that this branch of chemical industry—as indeed the whole domain of the so-called "fine" (organic) chemicals—has been developed mainly in Germany, and this largely as an offshoot or companion industry of the manufacture of artificial colouring matters. This is accounted for partly by the fact that in many cases the raw materials of manufacture are the same, and that many of the reagents and coal-tar "intermediates," required for the manufacture of dyes, serve also for the manufacture of drugs, perfumes, and other organic chemicals. But a further reason is to be found in the greater encouragement given to the study of chemistry and to chemical research, which has made possible the extraordinary achievements in the domain of synthetic dyes and drugs.

Although the production of synthetic drugs may be said to date from the discovery of chloroform and of chloral by Liebig in 1832—and who will be so bold as to assess the value of these discoveries to mankind?—it was not till 1881 that the first drug derived from the constituents of coal tar was prepared. In that year were discovered **kairine** and other antipyretic derivatives of quinoline, a compound which is produced by heating aniline with a mixture of sulphuric acid and glycerin, in presence of nitrobenzene. These antipyretics had, however, but small success. In 1883 Ludwig Knorr prepared the important febrifuge, **antipyrine** or **phenazone,** of which very large quantities were at one time consumed. The commercial success, indeed, of this drug was so great that, before the expiration of the patent, the profits in one year are stated to have amounted to no less than £60,000. In the preparation of this compound there is used a substance known as **phenyl-hydrazine** which is prepared from aniline, and this in turn from benzene. The investigation of the physiological action of antipyrine, undertaken on account of its supposed chemical relationship with the alkaloid quinine, led to the discovery of its valuable antipyretic properties. It was the first of a series of synthetic antipyretics which have, with a certain amount of success, entered into competition with and partially displaced the natural alkaloid quinine. It may, however, be said that valuable as these drugs have proved to be, they are drugs which combat the symptoms of disease and not the disease itself, and they do not possess the specific curative properties shown, for example, by quinine in relation to malaria.

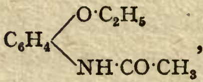
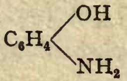
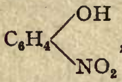
A derivative of antipyrine, known as **pyramidone,** has also been introduced as an antipyretic. It is more powerful than antipyrine, and has been found to possess certain advantages over the latter, more especially in not exercising an injurious influence on the heart.

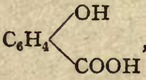
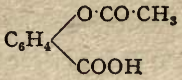
In 1887 antipyrine met with a powerful competitor, **antifebrine,** and it is to the discovery of this substance, more especially, that the great development which has taken place in recent times in the industrial production of synthetic drugs, is due. The discovery of the antipyretic properties of antifebrine was due to a mistake on the part of a laboratory boy who supplied this substance in place of naphthalene. During a pharmacological investigation of the substance its strongly antifebrile action was detected, and from a chemical analysis it was learned what the substance really was.

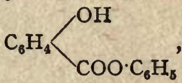
Antifebrine is the trade name for the compound known in chemistry as **acetanilide,** which, as is shown by the formula, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5$, is formed by the combination of acetic acid, $CH_3{\cdot}CO{\cdot}OH$, with aniline, $NH_2{\cdot}C_6H_5$, with the elimination of the OH-group from acetic acid and a hydrogen atom from aniline. Mixed with bicarbonate of soda, acetanilide has also been sold as a "headache powder."

The discovery of the physiological action of antifebrine, and the circumstances, more especially, under which that discovery was made, greatly stimulated the investigation of the physiological action of other substances. As a result of these investigations, interesting relationships between physiological action and chemical constitution became known. Thus, the physiological action is found, in many cases, to be due to the presence of certain groupings of atoms in the molecule, and can be modified or even entirely altered by the introduction of different groups into the molecule. Thus, aniline itself is a powerful febrifuge, but at the same time it is highly poisonous, owing to its destructive action on the red blood corpuscles.

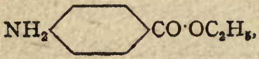
By introducing the group $CH_3{\cdot}CO$ (acetyl), the compound is rendered more stable and the toxicity is, in consequence, reduced.

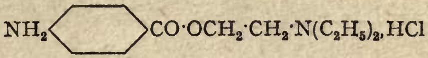
Similar considerations led also to the production, in 1887, of another antipyretic and antineuralgic drug, **phenacetine,**  $C_6H_4\begin{cases}O{\cdot}C_2H_5\\NH{\cdot}CO{\cdot}CH_3\end{cases}$, the derivation of which from  $C_6H_4\begin{cases}OH\\NH_2\end{cases}$ (para-amino-phenol) is obvious. This compound is prepared from phenol in the same way as aniline is prepared from benzene (p. 54), by converting phenol into a nitro-phenol,  $C_6H_4\begin{cases}OH\\NO_2\end{cases}$, and then converting the nitro-group into the amino-group by means of iron and hydrochloric acid. Phenacetine is the most important and most largely used of all the synthetic antipyretic and analgesic drugs, over eight tons of this compound being imported into Great Britain in 1909.

Valuable medicinal preparations have also been derived in recent years from **salicylic acid.** This compound,  $C_6H_4\begin{cases}OH\\COOH\end{cases}$, prepared from phenol with the help of carbon dioxide or carbonic acid gas, possesses anti-neuralgic and anti-rheumatic properties, but its use gives rise to disorders of the digestion. By the introduction of the acetyl-group ($CH_3{\cdot}CO$), however, one obtains the compound, acetyl-salicylic acid,  $C_6H_4\left\langle\begin{matrix}O\cdot CO\cdot CH_3\\ COOH\end{matrix}\right.$, which, under the name of **aspirin,** has come to be recognised as one of the most valuable of the anti-neuralgic and anti-rheumatic drugs. Discovered in 1899, and formerly manufactured only in Germany, it is now produced by several firms in England and is sold under the registered trade names of **empirin** (Burroughs Wellcome & Co.), **regepyrin** (Boots), etc.

Other derivatives of salicylic acid are employed as intestinal antiseptics. Thus, by the introduction of the phenyl group into salicylic acid, there is produced the compound **salol,**  $C_6H_4\left\langle\begin{matrix}OH\\ COO\cdot C_6H_5\end{matrix}\right.$, a valuable intestinal antiseptic. It is readily prepared from phenol and salicylic acid, or even by heating salicylic acid alone. Other derivatives of a similar nature can also be prepared and find a similar application. These compounds, although not acted on by the stomach juices, are broken up by the alkaline secretions in the intestine, with production of salicylic acid. This compound then produces partial asepsis by restricting the development of bacteria and undue fermentative action in the alimentary canal.

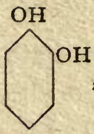
With regard to general antiseptics, we have already seen (p. 25) that phenol (carbolic acid) and, in a still greater degree, the cresols, have a powerful bactericidal action. The cresols, moreover, have the advantage over phenol in being less toxic to the organism. By the introduction of bromine into the molecule of phenol or cresol, the bactericidal action is greatly increased, so that pentabrom-phenol (phenol with five bromine atoms), for example, is about five hundred times as effective as phenol. Similarly, tetrabrom-ortho-cresol (ortho-cresol with four atoms of bromine) is a valuable antiseptic which is almost non-toxic, but which, even in a dilution of only 1 part in 200,000, will destroy diphtheria bacilli. It is, in this respect, 250 times as effective as phenol.

In 1832, as we have already seen, Liebig discovered the compound chloroform, the introduction of which as an anæsthetic by Sir James Simpson, in 1847, marked the beginning of a new era in operative surgery. But neither this nor any of the other general anæsthetics now employed are derived from coal tar. In recent years, however, a number of valuable local anæsthetics, derived from the constituents of coal tar, have been prepared and introduced as substitutes for the naturally occurring alkaloid cocaine. Thus, **anæsthesine,**  is an important local anæsthetic prepared from benzoic acid, which is, in turn, prepared indirectly from toluene, and **novocaine** is a similar compound of rather more complex constitution,



Stovaine, alypine, and **beta-eucaine** are also valuable local anæsthetics (the last-mentioned is also used in the treatment of sciatica and neuralgia) in the preparation of which coal-tar products play a part.

Some of these anæsthetics are frequently used along with another compound, adrenaline, which, although not an anæsthetic, has powerful physiological properties. When adrenaline, the active principle of the supra-renal glands, is injected subcutaneously or even applied externally to the skin, it produces a violent contraction of the arteries, with the result that the blood pressure rapidly rises, the blood is driven away from the injected tissues, and " bloodless " surgery becomes a possibility.

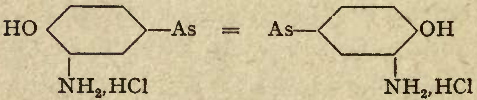
Adrenaline was isolated for the first time by a Japanese chemist, Takamine, in 1901, from the supra-renal glands of sheep and oxen, close on 1000 lbs. of tissue (representing the glands from 20,000 oxen) being required to yield 1 lb. of adrenaline. Within a few years, however, the chemical nature of adrenaline had been ascertained, and a process for preparing it on an industrial scale was worked out in the laboratories of the great dye-manufacturing firm of Meister, Lucius & Brüning, in Germany. It is now placed on the market under the name of **suprarenine.** It is a derivative of the compound catechol, 

, which, although usually prepared from guaiacol, a constituent of beech-wood tar, may also be prepared from phenol or carbolic acid.

It has already been pointed out how the industry of synthetic drugs is closely related to that of synthetic dyes; and this relationship has become a still closer one in recent years owing to the important discovery of "dye drugs" which we owe mainly to the brilliant investigations of Paul Ehrlich in Germany. The synthetic substitutes for quinine are, as we have seen, merely symptomatic drugs, but the work of Ehrlich opened up a new field and led to the discovery of drugs which exercise specific curative properties.

Guided by the principle that a drug acts only on organisms by which it is absorbed, Ehrlich studied the effect of various dyes on different tissues and cells, and showed that certain dyes will "stain" certain tissues but leave others unstained, just as certain colouring matters will dye wool but not cotton. Thus the dye, methylene blue, is absorbed by and stains only the living nerve, so that when the dye is injected into a living animal the nerve tissues, but not the surrounding structures, are stained. Similarly, different bacteria can be distinguished by their selective absorption of dyes. This property of selective absorption has been turned to use with especial success in the treatment of diseases due to protozoal parasites, because it becomes possible to introduce into an organism substances which are poisons for the parasites but are not absorbed by and are therefore not harmful to the cells of the organism itself. Thus, investigation showed that certain azo-dyes of the type of Congo red are poisons to trypanosomes, the trypanosome of the South American horse disease, "mal de caderas," being destroyed by the dye trypan red, and the trypanosome of the cattle disease, "piroplasmosis," by another azo-dye, **trypan blue,** derived from tolidine and naphthalene. These dyes are therefore specific curative agents for these diseases. Similarly, **atoxyl (arsamin** or **soamin**), the sodium salt of a compound obtained by heating arsenic acid with excess of aniline, has the property, when injected into the body, of killing the parasite *Trypanosoma gambiense,* which causes the disease of "sleeping sickness."

Still more important is the success with which the property of selective absorption has been utilised in finding a cure for the disease syphilis, which is due to a micro-organism, the *Spirochæte pallida.* It has been known from the time of Paracelsus that mercury is a specific against this disease, but mercury is harmful also to the human organism. The problem, therefore, which Ehrlich set himself was to prepare a compound which would contain a toxic material and which would be absorbed by the germ of the disease but not by the human organism. After many trials and many failures he prepared the now well-known remedy **salvarsan,** or as it is also called "606," which is the serial number of the compound in Ehrlich's record of preparations. This compound, now manufactured in England by Burroughs Wellcome & Co., under the name **kharsivan,** is a benzene derivative similar in structure to an azo-dye but containing two arsenic (As) atoms in place of the azo-group (—N : N—), thus :



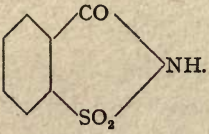
As one of the most recent examples of "chemotherapy" based on selective absorption, there may be mentioned the discovery by Dr Browning, of the Bland-Sutton Institute of Pathology in London, that the yellow coal-tar dye, **trypa-flavine** or **acri-flavine**—a derivative of a compound known as acridine—has the most valuable property that while it destroys the germs of blood-poisoning it does not interfere with the white "warrior cells" of the blood, which are the natural defence of the patient against the septic organisms. It is, therefore, an ideal antiseptic as compared with the ordinary antiseptics which destroy with equal impartiality the pathogenic organisms and their natural foes, the white "warrior cells."

Owing to the practical monopoly enjoyed by Germany in the manufacture of synthetic drugs, this country was placed, by the outbreak of war, in a position of great gravity as a result of the cutting off of German supplies; and the shortage of drugs which was thereby produced was clearly reflected in a great increase in price, as shown in the following table:

EFFECT OF THE WAR ON THE PRICE OF SYNTHETIC DRUGS

	Price per pound.			
	Immediately before war.	Jan. 1, 1915.	Jan. 1, 1916.	Jan. 1, 1917.
	s. d.	s. d.	s. d. s. d.	s. d.
Acetanilide . .	0 10	2 0	6 9–7 0	2 10
Acetylsalicylic acid .	2 0	6 6	48 0–50 0	18 6
Phenacetin . .	2 9	6 6	60 0	92 6
Phenazone . .	6 6	9 6	75 0	33 0
Salol . . .	1 10	4 9	47 0	10 6
Salicylic acid .	1 0	5 0	20 0	4 9
Sodium salicylate .	1 3	5 0	22 0	5 9

The situation, however, serious as it was, was prevented from becoming disastrous through the efforts of the academic chemists of the country. The chemical laboratories of our Universities and Technical Colleges were converted into miniature factories, and a supply of the most necessary drugs was ensured. In time the work of production could be taken up by the regular manufacturers, and supplies also began to be obtained from neutral countries, more especially Switzerland and the United States. That a vast improvement in the situation has now taken place is amply shown by the prices quoted in the last column of the above table.

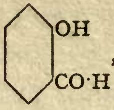
Not only has the chemist garnered from the boundless treasures of coal tar colouring matters which rival the manifold tints of flowers, but he has also evolved from that same uninviting source substances which surpass in sweetness the sweetest of Nature's products. During the course of a purely scientific investigation carried out in the laboratory of Professor Ira Remsen in the Johns Hopkins University in America, Dr C. Fahlberg, in 1879, accidentally discovered that one of the compounds which he had prepared possessed a remarkably sweet taste; and he afterwards (in 1887) manufactured the compound and placed it on the market under the name of **saccharine.** The substance is derived from toluene, which, by successive treatment with concentrated sulphuric acid, chlorine, ammonia, and oxidising agents such as permanganate of potash, is transformed and built up into the final product, benzoic sulphimide or saccharine,  It is a white crystalline powder and has a sweetness *five hundred times* greater than that of cane sugar. How great was the disaster which threatened to overtake the cane and beetroot sugar industry as a result of this discovery can readily be understood. It was as if the story of the madder plantations (p. 81) was going to be retold for the sugar plantations of the West Indies and other parts of the world. The whole machinery of Government intervention and supervision was therefore set working, and the general use of saccharine as a sweetening agent in articles of human consumption was prohibited, the manufacture of the compound being put under licence and its sale placed in the hands of the druggist. This step, however, was taken not merely, perhaps not even mainly, for the sake of upholding a threatened industry, but from a recognition of the fact that saccharine, unlike sugar, has no nutritive value at all, and that, although it is of importance as an edulcorant for use, more especially, by those to whom sugar is forbidden (*e.g.* those suffering from diabetes), its uncontrolled and unlimited consumption is harmful and even poisonous to the human organism. Saccharine is a medicament, and should be treated as such.

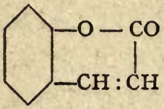
Saccharine is a substance which dissolves in water only with difficulty. By treating it with carbonate of soda, however, it is converted into a sodium salt of saccharine which, although somewhat less sweet than saccharine itself, readily dissolves in water. Similarly, one can obtain the readily soluble ammonium salt, which has the remarkable property that it is even sweeter than saccharine itself, its sweetness being *six hundred times* greater than that of cane sugar.

Formerly manufactured almost exclusively in Germany and Switzerland, preparations of saccharine are now made in England and sold in tabloid form under the name of **saxin** (Burroughs Wellcome & Co.).

While we may regard the synthetic production of colouring matters and drugs as being one of the greatest achievements of organic chemistry, and one which must take an important place in the history of human endeavour and of human civilisation, notable success has also been obtained in the artificial production of those sweet-smelling essences and spices which in all ages and by all peoples have been held in high esteem. In some cases the chemist has succeeded in preparing substances which are identical with those to which the odours of the flowers are due; in other cases the synthetic products merely imitate the naturally occurring perfumes and spices. In some cases the sweet-smelling substance is built up, step by step, from the simple compounds, benzene, toluene, etc., occurring in coal tar; in other cases these perfumes are obtained by the transformation of naturally occurring, complex compounds, as in the transformation of the compound eugenol (occurring in oil of cloves) into **vanillin,** the active principle occurring in the vanilla bean, or of the compound citral (a constituent of oil of lemon-grass) into **ionone** or imitation violet. Not even in the case of the purely synthetic perfumes, however, are all the compounds derived from coal tar.

The first of the naturally occurring perfumes to be prepared by the chemist—and first of all by W. H. Perkin in 1868—from the products of coal tar was **coumarin,** the fragrant principle of the Tonka bean, of the sweet woodruff (*Asperula odorata*), and of certain clovers, and used in the preparation of the perfumes known as Jockey Club and New-Mown Hay.

This compound can be prepared from phenol or carbolic acid. Phenol is first converted into salicylic aldehyde, 

, a substance which is obviously closely related to salicylic acid (p. 104), and the salicylic aldehyde can then, as W. H. Perkin showed, readily be transformed, through the agency of acetate of soda, into coumarin, 

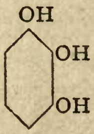
. Vanillin, also, although generally obtained from oil of cloves, can also be prepared from toluene.

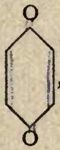
To these earliest synthetic sweet-smelling substances numerous others have since been added, so that from the constituents of coal tar the main odoriferous principles of a considerable number of naturally occurring essential oils and perfumes have now been prepared. Among these one may mention oil of winter-green (**methyl salicylate,** from wood spirit and salicylic acid), oil of bitter almonds (**benzaldehyde,** from toluene), hawthorn blossom (**anisic aldehyde,** from phenol), oil of cinnamon (**cinnamic aldehyde,** from benzaldehyde or from toluene), *Spiræa ulmaria* or meadowsweet (**salicylic aldehyde,** from phenol). Imitation musk perfumes can be prepared from toluene; and nitrobenzene, as we have already seen (p. 53), was prepared at an early date and used, under the name of "essence of mirbane," as a substitute for oil of bitter almonds.

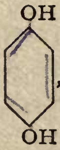
Owing to the synthetic production of these and many other odoriferous compounds at a cost very much less than that of the natural perfumes, a very great extension of the use of such substances for the scenting of soaps, creams, and other toilet preparations, has taken place.

But if the chemist by his transformation of the constituents of coal tar has revolutionised the art of dyeing and the science of therapeutics, and has produced compounds which rival the perfumes of the violet and the rose, he has exercised also an important influence on that most practised of all the arts, photography. The photographic dry plate or film is coated with a layer of gelatin containing a fine emulsion of the light-sensitive salt, silver bromide. This salt is, however, not equally sensitive to all the rays of light, but is mainly affected by blue and violet rays, while red and yellow light has practically no action. A photograph taken with such a plate will, therefore, not reproduce a multi-coloured object with the proper colour-values—the yellows, for example, will appear darker than the blues. By dyeing the film with different coal-tar dyes, however, the plate can be made sensitive to light of different colours, and, in this way, "orthochromatic" and "panchromatic" plates have been prepared, the former specially sensitised for green and yellow, the latter sensitised for light of all colours.

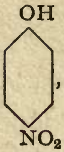
But coal tar provides for the needs of the photographer not only by furnishing him with colour-sensitive plates, but also by placing at his service a considerable number of different "developers," or substances by which the latent photographic image can be made to appear. Since the character of the image depends to some extent on the developer employed, the intelligent worker is enabled readily to obtain the special effect desired.

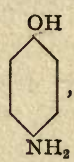
Substances suitable for use as developers belong to the class known as "reducing" substances, and must contain two or more hydroxyl (OH) groups, or at least one hydroxyl group and one amino (NH_2) group. Of such substances quite a number have been prepared from the constituents of coal tar, and find a more or less extensive use. One of the most familiar and most widely used of these is "pyro," or **pyrogallic acid,** or **pyrogallol**, as it is known in chemistry. This is a derivative of benzene containing three hydroxyl groups, thus:  ;

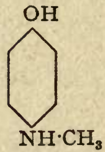
but although it can be prepared synthetically from phenol (and therefore also from benzene, p. 20), it is usually prepared from gallic acid, and is therefore not strictly to be included among the coal-tar products. The first true coal-tar product to be used as a photographic developer was **hydroquinone,** a substance which has found much favour with amateurs (especially when combined with other developers), because of the fact that it does not, as pyro does, stain the fingers. Although this compound had long been known it was not till 1880 that its use as a photographic developer was suggested by Sir William Abney. First obtained from quinic acid, which is found in the medicinal extract of Peruvian bark, it was later discovered that it could very readily be prepared from aniline, and the production of the compound was thus established on a commercially successful basis. By treating aniline with a cold solution of sulphuric acid and bichromate of soda, it is converted into a compound, 

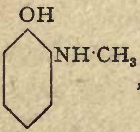
, known as quinone ($C_6H_4O_2$), and this substance can then be readily converted into hydroquinone, 

, by treatment with sulphurous acid or a solution of sulphur dioxide in water.

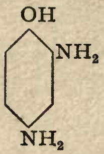
Since hydroquinone yields strong and sometimes rather harsh negatives it is very frequently combined, for general use, with some other developer, which gives softer effects. One of the commonest of these is "metol." When phenol is treated with a mixture of nitric and sulphuric acids, it yields para-nitrophenol, 

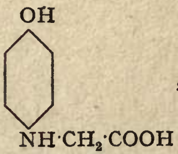
, and when this is "reduced" with tin and hydrochloric acid, it is converted into para-aminophenol, 

, just as nitrobenzene is converted by similar treatment into aniline. The salt of this para-aminophenol with hydrochloric acid is the effective constituent of the developer **rodinal.** If one replaces one of the hydrogen atoms of the amino-group by the methyl-group (CH_3), one obtains the compound, 

, which is used as a developer under the name of **scalol.** The salt of scalol with sulphuric acid is the effective constituent of the developer **metol.** The compound 

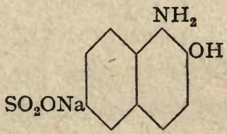
, which is isomeric with "scalol," forms the basis of the developer **ortol.**

Amidol is another developer also derived from phenol, but containing two amino-groups, thus: 

; and **glycin,** a somewhat more complex compound, having the formula, 

, is obtained by heating para-aminophenol (see above) with monochloracetic acid, $Cl{\cdot}CH_2{\cdot}COOH$.

The above compounds are all derived from the coal-tar hydrocarbon benzene, but similar developers have also been derived from naphthalene. Of these the best known is **eikonogen,** a compound discovered by the late Professor Meldola. Its relation to naphthalene (p. 43) is clearly seen from the formula,



In view of the enormous development of the practice of photography, it will readily be realised how great is the wealth derived, in this particular direction alone, from the invaluable coal tar.

CHAPTER X

EXPLOSIVES

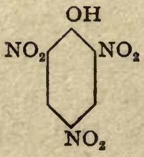
THE history of civilisation is, in large measure, the history of man's ability to utilise, control and direct energy, and in this respect the civilisation of the nineteenth and twentieth centuries shows an enormous advance on that of all previous times. And it excels not only by the amount of energy which it turns to useful account, but also by the degree to which it can concentrate energy; for material progress may depend just as much, and even more, on the concentration of energy as on the actual amount of energy expended. Herein lies the value of explosives, which represent highly concentrated forms of potential energy, capable of being set in motion at will, and of producing stupendous results. In the peaceful progress of civilisation, no less than in the devastation and ruin of war, explosives have played an all-important part, and have made possible the great engineering works of the world, like the Suez and Panama Canals, or the removal, in 1885, of the reefs, known as Hell Gate, in the channel of the East River at New York. On this occasion over one hundred tons of explosives, rackarock and dynamite, were employed, and millions of tons of rock were dislodged. But this "blast" was small compared with the earth-shattering explosion of four hundred and fifty tons of high explosive which preceded the capture of the Messines Ridge by the British Army on the morning of June 7th, 1917.

An explosive may be defined as a substance or mixture, solid or liquid, capable of undergoing extremely rapid combustion or decomposition, with production of gaseous substances which occupy a volume it may be ten or twelve thousand times as great as that of the explosive itself. In the case of gunpowder, cordite, and other propellants (low explosives), there is a rapid combustion of the explosive, but in the case of high explosives—to which class all the coal-tar explosives belong—the molecules of the compound are in a somewhat unstable condition, and, when subjected to a suitable shock, undergo decomposition into more stable substances. This decomposition is generally initiated by means of a "detonator," or substance which is, comparatively, very sensitive to shock, and the "explosive wave" which is set up is transmitted with a very great velocity—amounting in some cases to more than four miles per second—and so causes an almost instantaneous decomposition of the explosive.

Although the first real explosive, black gunpowder, was discovered (by Roger Bacon) in the thirteenth century, no further advance in the chemistry of explosives was made until the nineteenth century. In that century a number of new and very powerful explosives were introduced, and although two of the most important of these—guncotton and nitroglycerin (dynamite)—are not derived from coal tar, derivatives of this have, in recent times, begun to play a most important part, especially in connection with naval and military operations.

The first coal-tar explosive to be obtained was **picric acid.** Although discovered in 1771, it was not till 1843 that it was prepared from phenol, by the action of a mixture of sulphuric and nitric acids. The substance is now also prepared from benzene, from which compound, also, phenol itself is now largely produced owing to the greatly increased demand for this substance.

Picric acid, or tri-nitro-phenol (to give it its chemical name), is derived from phenol by the replacement of three hydrogen atoms by three nitro-groups (NO_2), as is represented by the formula $C_6H_2(NO_2)_3 \cdot OH$, or



It is a lemon-yellow coloured crystalline substance which found its first use, and still finds use to a slight extent, as a dye for silk and wool; and it readily stains the skin also of a yellow colour. The explosive decomposition of picric acid can be effected by means of a suitable powerful detonator, but, under ordinary conditions, it is a quite stable substance which melts at a temperature of 122° C. (252·6° F.), and, when strongly heated, burns with production of a large amount of black smoke. This stability and insensitiveness to ordinary shocks and blows are clearly a great advantage from the point of view of safety in handling; and the substance picric acid was adopted in 1885 by the French Government as a high explosive for filling shells, under the name of mélinite (from the honey-like appearance of the molten compound), and some years later by the British Government, under the name of lyddite (from Lydd, in Kent, where its explosive properties were tested). Other countries, also, have adopted picric acid as a high explosive for military purposes, and it forms the sole or main constituent of the explosives **pertite** (Italy), **shimosite** (Japan), and **Dunnite** (United States). Some idea of the power of this explosive will be gained from the statement that when one pound of picric acid is exploded it liberates an amount of energy equal to that required to raise a weight of over a ton to a height of more than a hundred yards.

From meta-cresol (p. 44), tri-nitro-cresol (known in France as **crésylite**), similar to tri-nitro-phenol (picric acid), has also been prepared. It is less powerful than picric acid, but has sometimes been used for mixing with the latter in order to lower its melting-point, and so render it less inconvenient to manipulate. Its ammonium salt was formerly used as a high explosive by Austria under the name of **ecrasite.**

Although picric acid itself is comparatively insensitive to shock, it has the disadvantage that it forms compounds (picrates) with metals, such as lead, copper, iron, etc., which are much more sensitive to shock and which may cause premature explosion of the shell. Hence the necessity for coating the interior of the shell with a varnish. The priming composition known as **Brugère powder** is a mixture of ammonium picrate and saltpetre (potassium nitrate).

From phenol and methyl chloride there is prepared the compound anisole, $C_6H_5{\cdot}OCH_3$; and by nitrating this one obtains **tri-nitro-anisole,** an explosive which has recently been used by the Germans for filling bombs.

From the hydrocarbons of coal-tar, also, powerful explosives can be prepared. Of these the most important is undoubtedly **tri-nitro-toluene,** obtained by nitrating toluene with a mixture of concentrated sulphuric and nitric acids. It forms a white crystalline substance which melts at a much lower temperature (81° C. or 177·8° F.) than picric acid, is even less sensitive to mechanical shock and rough usage than this explosive, and does not form dangerously explosive salts with metals. Although it acts as a powerful explosive when exploded by means of a suitable detonator, it is a comparatively stable substance, so stable, indeed, and safe to handle, that it does not come under the provisions of the Explosives Act with respect to its manufacture, transport, and storage. The advantages which tri-nitro-toluene thus possesses over picric acid led to its adoption by Germany in 1902, and by other Governments at a later date, as a high explosive for filling shells; and for this purpose it has, although a less powerful explosive than picric acid, largely displaced that compound. It has also to a large extent taken the place of gun-cotton as the explosive filling for torpedoes and submarine mines. In the British Services it is known as **trotyl,** or as T.N.T. When ignited, trotyl, like picric acid, burns without explosion as a rule, but disastrous explosions have also occurred through the combustion of large quantities of the compound, especially in presence of ammonium nitrate.

The combustion of T.N.T., as well as its decomposition by detonation, are accompanied by the production of dense black clouds of carbonaceous or sooty matter, owing to there being insufficient oxygen in the compound to combine with all the carbon present; and this has led to the nicknames of "Coal boxes" and "Jack Johnsons" being applied to the shells filled with this explosive. In order to secure more perfect combustion and, at the same time, to reduce the amount of trotyl required, ammonium nitrate (NH_4NO_3), a substance containing an excess of oxygen, is frequently added. In this way the British service high explosive **amatol**, a mixture of trotyl and ammonium nitrate, is obtained.

Not only is trotyl used as an explosive by itself, but it also forms a constituent of a number of composite explosives. Thus, the Austrian explosive **ammonal** is a mixture of trotyl (30 per cent.), ammonium nitrate (47 per cent.), aluminium powder (22 per cent.), and charcoal (1 per cent.). By the combustion of the aluminium powder the temperature of the explosion is considerably raised and the explosive force consequently increased. Trotyl also forms a constituent of the Belgian high explosive **macarite** (trotyl and lead nitrate), and of the blasting explosives **rexite** and **Withnell powder.**

Di-nitro-toluene, in which only two NO_2-groups are present, is also used to some extent in the preparation of composite explosives for blasting purposes. Of these the most important are the various **cheddites** (so called from Chedde, in France, where they are manufactured), consisting, for example, of ammonium perchlorate and di-nitro-toluene, mixed with a small amount of castor oil, to diminish the sensitiveness of the mixture to friction. Other similar mixtures are also prepared under the name cheddite.

Although of less importance than tri-nitro-toluene, the nitro-derivatives of benzene are also used to a considerable extent, more especially in the production of composite blasting explosives. Even nitrobenzene ($C_6H_5 \cdot NO_2$), itself, although not an explosive, is used as a combustible material in such explosives as **rackarock** (potassium chlorate and nitrobenzene) and **petrofracteur** (potassium chlorate, nitrobenzene, potassium nitrate, and antimony sulphide). These explosives belong to the class known as Sprengel explosives, in which the oxygen producer (potassium chlorate, etc.) and the combustible substance (nitrobenzene, etc.) are kept separate and mixed just when and where the explosive is to be used. The employment of such explosives is prohibited in Great Britain.

Di-nitro-benzene, also, although it can be detonated only with difficulty and is not used as an explosive by itself, forms a constituent of certain composite explosives, such as **securite** (di-nitrobenzene and ammonium nitrate); and chlordi-nitro-benzene (or di-nitro-benzene in which a hydrogen atom has been replaced by chlorine), when mixed with ammonium nitrate, yields the powerful blasting explosive **roburite.** Tri-nitro-benzene, on the other hand, is an explosive which is more powerful than either picric acid or tri-nitro-toluene, but owing to the greater difficulty and expense of its manufacture has not so far come into general use.[1]

Other nitro-derivatives of coal-tar hydrocarbons, although of less importance than those already mentioned, have also been proposed for use as explosives, and have even been adopted to some extent. Of these one may mention di-nitro-naph-

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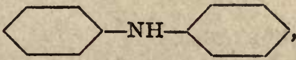
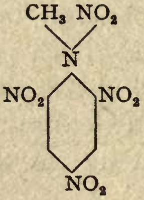
[1] The nitro-derivatives of benzene, and to a somewhat less extent tri-nitro-toluene, exercise a very marked toxic action, to which some individuals are more susceptible than others. Absorption of these compounds into the system, which takes place more especially through the skin, may give rise to dermatitis, toxic gastritis, toxic jaundice, and finally death. It is, therefore, of the highest importance not only that all factories in which T.N.T. (the most important of the nitro-compounds used at the present time) is made shall be efficiently ventilated, but the greatest cleanliness also must be observed on the part of the workers so as, more especially, to prevent continued contact of T.N.T. with the skin. The handling with the uncovered hands of T.N.T. or of articles which have been in contact with T.N.T. should be as far as possible avoided. As a measure of precaution it has been laid down as a rule by the Minister of Munitions, in respect of workers in T.N.T. factories, that "no person shall be employed for more than a fortnight without an equal period of work at a process not involving contact with T.N.T., or an equal period of absence from work unless such employment has been approved by the Medical Officer."

thalene, which is employed as a constituent of the blasting explosive known as **favierite** (ammonium nitrate and di-nitro-naphthalene) and of **schneiderite** (ammonium nitrate, 88 parts; di-nitro-naphthalene, 11 parts; resin, 1 part), used by the French for filling high-explosive shells.

It may be mentioned that these ammonium nitrate explosives, *e.g.* securite, roburite, favierite, are of importance on account of the fact that they are "safety explosives"; that is to say, they do not, on explosion, ignite mixtures of fire-damp and air, and can therefore be used for blasting purposes in coal-mines.

From aniline and other amino-compounds valuable explosives have also been prepared. Thus, in recent years, there has been obtained, by the nitration of aniline, the compound which goes by the common name of **tetranyl** (tetra-nitro-aniline), which promises to find more extensive application, especially as a primer; and by the nitration of diphenylamine, , there has been obtained the compound hexa-nitro-diphenylamine—a substance first introduced as the dye aurantia—which has recently been used to some extent by Germany for the filling of bombs. Diphenylamine is itself used as a stabiliser in military smokeless powders.

The discharge of the various coal-tar explosives, now known in considerable numbers, is brought about, as has already been mentioned, not by ignition (as in the case of gunpowder and cordite), but by the detonation of a more sensitive explosive. Until recently, fulminate of mercury (from mercury, nitric acid, and alcohol), alone or mixed with potassium chlorate, was practically the only detonator employed; but this detonator is both dangerous to handle and expensive to manufacture. The discovery, therefore, that the amount of fulminate required could be very greatly diminished if mixed with tri-nitro-toluene, or with picric acid, was one which has had results of great importance. Still better are the results obtained by means of a mixture of "tetryl" (tri-nitro-phenyl-methyl-nitramine, ), fulminate of mercury, and potassium chlorate.

Such are the main achievements of the chemist in producing those powerful engines of civilisation, explosives, from the constituents of coal tar. But year by year new compounds are being added to the armouries of the nations and the magazine of the engineer; and the successes of the past are but an earnest of still greater triumphs in the future.

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