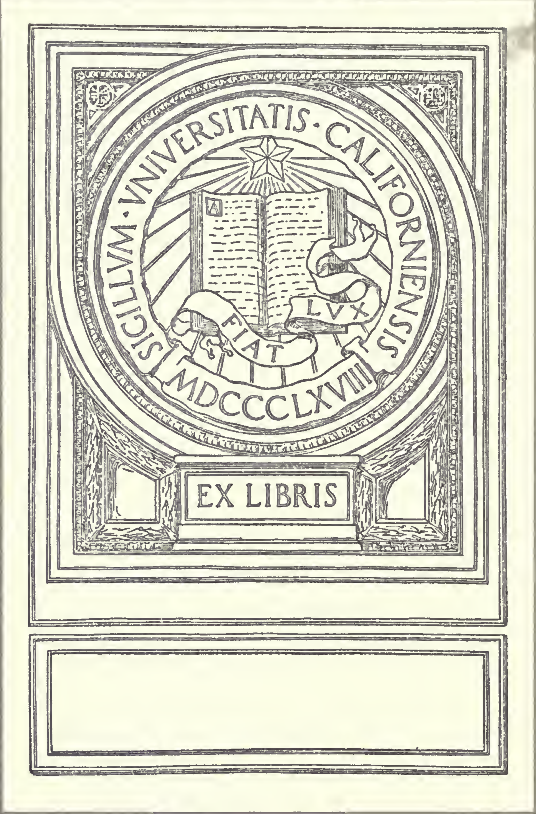

INDUSTRIAL CHEMISTRY

BEING A SERIES OF VOLUMES GIVING A
COMPREHENSIVE SURVEY OF

THE CHEMICAL INDUSTRIES

EDITED BY SAMUEL RIDEAL, D.Sc. LOND, F.I.C.
FELLOW OF UNIVERSITY COLLEGE, LONDON

ASSISTED BY

JAMES A. AUDLEY, B.Sc.
EDWARD DE BARRY BARNETT, B.Sc., A.I.C.
M. BARROWCLIFF, F.I.C.
H. GARNER BENNETT, M.Sc.
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D. A. SUTHERLAND, F.I.C.
C. M. WHITTAKER, B.Sc.
&c., &c.

COAL TAR DYES AND INTERMEDIATES

BY

E. DE BARRY BARNETT, B.Sc. Lond., A.I.C.
CONSULTING CHEMIST TO BAGLEY, MILLS AND CO., LTD., FORMERLY RESEARCH
CHEMIST TO LEVINSTEIN, LTD., AND WORKS MANAGER TO THE
STOCKTON-ON-TEES CHEMICAL WORKS, LTD.

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GENERAL PREFACE

The rapid development of Applied Chemistry in recent years has brought about a revolution in all branches of technology. This growth has been accelerated during the war, and the British Empire has now an opportunity of increasing its industrial output by the application of this knowledge to the raw materials available in the different parts of the world. The subject in this series of handbooks will be treated from the chemical rather than the engineering standpoint. The industrial aspect will also be more prominent than that of the laboratory. Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture. The influence of new inventions on the development of the industry will be shown, as also the effect of industrial requirements in stimulating invention. Historical notes will be a feature in dealing with the different branches of the subject, but they will be kept within moderate limits. Present tendencies and possible future developments will have attention, and some space will be devoted to a comparison of industrial methods and progress in the chief producing countries. There will be a general bibliography, and also a select bibliography to follow each section. Statistical information will only be introduced in so far as it serves to illustrate the line of argument.

Each book will be divided into sections instead of chapters, and the sections will deal with separate branches of the subject in the manner of a special article or monograph. An attempt will, in fact, be made to get away from the orthodox textbook manner, not only to make the treatment original, but also to appeal to the very large class of readers already possessing good textbooks, of which there are quite sufficient. The books should also be found useful by men of affairs having no special technical knowledge, but who may require from time to time to refer to technical matters in a book of moderate compass, with references to the large standard works for fuller details on special points if required.

To the advanced student the books should be especially valuable. His mind is often crammed with the hard facts and details of his subject which crowd out the power of realizing the industry as a whole. These books are intended to remedy such a state of affairs. While recapitulating the essential basic facts, they will aim at presenting the reality of the living industry. It has long been a drawback of our technical education that the college graduate, on commencing his industrial career, is positively handicapped by his academic knowledge because of his lack of information on current industrial conditions. A book giving a comprehensive survey of the industry can be of very material assistance to the student as an adjunct to his ordinary textbooks, and this is one of the chief objects of the present series. Those actually engaged in the industry who have specialized in rather narrow limits will probably find these books more readable than the larger textbooks when they wish to refresh their memories in regard to branches of the subject with which they are not immediately concerned.

The volume will also serve as a guide to the standard literature of the subject, and prove of value to the consultant, so that, having obtained a comprehensive view of the whole industry, he can go at once to the proper authorities for more elaborate information on special points, and thus save a couple of days spent in hunting through the libraries of scientific societies.

As far as this country is concerned, it is believed that the general scheme of this series of handbooks is unique, and it is confidently hoped that it will supply mental munitions for the coming industrial war. I have been fortunate in securing writers for the different volumes who are specially connected with the several departments of Industrial Chemistry, and trust that the whole series will contribute to the further development of applied chemistry throughout the Empire.

SAMUEL RIDEAL.

AUTHOR'S PREFACE

In the following pages the Author has endeavoured to give a clear account of the most important synthetic dyes and the intermediate compounds from which they are derived. No attempt has been made to enumerate all the intermediate compounds and dyestuffs actually manufactured, nor to give all the processes that have been proposed for the manufacture of those mentioned, but as far as possible the Author has confined himself to those processes most likely to prove of technical value. Also, the book being essentially one on Industrial Chemistry, information of purely academic interest has been largely omitted except in a few cases where it was thought advisable to give it.

The number of patents taken out by the German firms for the manufacture of intermediate products and dyestuffs is very large, and in spite of the optimistic claims made in the specifications, only a few of them are workable as commercial propositions. It has long been the custom of these firms, when taking up a subject, to put down a barrage of patents in order to block access and at the same time to act as a kind of camouflage and disguise the processes actually in use. For the same reason the specifications are usually carefully drawn up so as to give as little information as is compatible with validity, and much skill is exhibited in this direction. Consequently the reader who finds a patent describing a process in detail must not conclude that he has all the information necessary in order to manufacture. No doubt the description given will enable him to make the compound in question, but whether it will enable him to do so at a profit is quite another question.

In the same way the detailed descriptions of processes which appear from time to time in the technical Press must not be taken too seriously. The majority of them seem to be written either by men who have no technical experience or are written with intent to deceive.

There is no short cut to success in chemical industry, and the only satisfactory method is to gather all information available and then try out the various processes in the laboratory. Having selected the most promising, it must then be thoroughly examined with a view to determining the most economical conditions, which are not necessarily those giving the best yield. Manufacturing cost is made up of many items, such as cost of material, cost of power, labour, deterioration of plant, interest on capital, etc., and in determining the most economical process, each of these must be taken into consideration. For example, a process giving a good yield but requiring much time may well be less economical on the score of capital charges than another process giving a less good yield but requiring less time and hence less plant per unit output. In the same way deterioration is a serious item in a chemical works, and yield must frequently give way to lessened corrosion.

Finally, after the most economical conditions have been determined as far as possible in the laboratory, the process must be tried out on a semi-large scale in plant constructed on the same lines and of the same material as the proposed manufacturing installation but of about one-tenth the size. Unfortunately many British works omit this most important step and go on the theory that, if a process gives good results in glass apparatus on the laboratory scale, it will give equally good results in iron plant in the works. A greater mistake could not be made, and to transfer a process direct from the laboratory to the works is to court failure. Even if the laboratory process does prove well suited to large-scale operations, the practical hints gained by a semi-large scale trial will more than repay the cost of such experimental work.

For the benefit of those readers who are not accustomed to looking up patent literature, attention is drawn to the fact that two German works have been published dealing exclusively with organic chemical patents. These are Friedländer's "Fortschritte der Teerfarbenfabrikation," vols. i.–ix., 1877–1914, and Winter's "Patente der organischen Chemie," in three volumes, 1877–1905. In both publications the specifications are classified with regard to the chemical nature of the substances dealt with, each group being preceded by a carefully written survey. They form by far the most convenient source of patent information, and for this reason most of the references in the following pages have been given to the German patent rather than to the British. The third volume of Winter's "Patente" contains a table of German patent numbers, together with the numbers of the corresponding British, French, and American patents, the use of which frequently saves a weary search in the Patent Office.

E. DE BARRY BARNETT.

LONDON,
January, 1919.

CONTENTS

INTRODUCTION.

PART I.

THE INTERMEDIATE COMPOUNDS.

SECTION I.—NITRATION.

SECTION II.—AMIDATION.

SECTION III.—SULPHONATION.

SECTION IV.—HYDROXYLATION.

SECTION V.—MISCELLANEOUS INTERMEDIATES.

PART II.

THE DYESTUFFS.

ABBREVIATIONS

A. *Annalen der Chemie.*
A.Ch. *Annales de Chimie et de Physique.*
Am. *American Chemical Journal.*
Am. Soc. *Journal of the American Chemical Society.*
B. *Berichte der Deutschen Chemischen Gesellschaft.*
Bl. *Bulletin de la Société Chimique de Paris.*
C. *Chemisches Zentralblatt.*
C.r. *Comptes rendus de l'Académie des Sciences.*
Ch. Z. *Chemiker-Zeitung* (*Göthen*).
Dingl. *Dingler's Polytechnisches Journal.*
D.R.P. Patentschrift der Deutschen Reiches.
E.P. English Patent.
F.P. French Patent.
G. *Gazetta chimica itialiana.*
J. *Jahresbericht der Chemie.*
J. pr. *Journal für praktische Chemie.*
J.S.C.I. *Journal of the Society of Chemical Industry.*
J.S.D.C. *Journal of the Society of Dyers and Colourists.*
M. *Monatshefte für Chemie.*
Proc. *Proceedings of the Chemical Society.*
R. *Recueil des Travaux Chimiques des Pays-Bas.*
R.G.M.C. *Revue Générale des Matières Colorantes.*
Soc. *Journal of the Chemical Society.*
Z. *Zeitschrift für Chemie.*
Z. ang. *Zeitschrift für angewandte Chemie.*
Z. el. Ch. *Zeitschrift für Elektrochemie.*

COAL TAR DYES AND INTERMEDIATES

INTRODUCTION

Historical Sketch.—Although picric acid was obtained from phenol as far back as 1849, the expense of production was so great that it could not be manufactured for use as a dyestuff. The modern coal-tar colour industry dates from 1856, in which year W. H. Perkin, senior, obtained mauveine by the action of potassium bichromate on impure aniline, and set up a factory at Greenford Green for its manufacture. It must be borne in mind that at this period the constitution of benzene was quite unknown, and that the methods of obtaining it from coal tar were very crude, so that investigations of its derivatives could only be carried out with difficulty and more or less on the hit-or-miss principle.

Perkin's discovery naturally excited great interest, and immediately led to the investigation of the action of other oxidizing agents on crude aniline. This resulted in the discovery of magenta in 1859 by Verguin, who obtained it by heating aniline with stannic chloride and manufactured it on a commercial scale in conjunction with Renard frères et Frank at Lyons. Although Verguin was the first to manufacture magenta he was not the actual discoverer of the dyestuff, as it had been obtained from aniline and ethylene chloride by Natanson in 1856, and from aniline and carbon tetrachloride by Hofmann in 1857, although by neither of these processes was it made technically. Further study led to the introduction of the arsenic acid process in 1860 and the nitrobenzole process in 1861. Another important discovery, the full value of which was not recognized at the time, resulted from experiments made in the oxidation of aniline. In 1862 Lightfoot obtained aniline black, and in the next year patented methods of applying it to the fibre.

The study of benzene derivatives was still carried on by purely empirical methods, and in 1860 Girard and de Laire obtained the first synthetic blue dye (rosaniline blue) by heating magenta with aniline, without, however, understanding the nature of the chemical reaction. Rosaniline blue had the great disadvantage of being insoluble in water, but this was remedied by Nicholson in 1862, who obtained soluble sulphonic acids (Nicholson's blue) by treating it with sulphuric acid. This was an epoch-making discovery, as, a few years later, it rendered possible the use of azo bodies as acid dyes.

The next step was made by Hofmann, who recognized rosaniline blue as a phenylated rosaniline, and at once set to work to make the corresponding ethyl derivatives. This he achieved in 1863, when he introduced Hofmann's violet, obtained by treating rosaniline with ethyl iodide, and three years later the process was carried a step further by Keisser, who introduced a more highly ethylated compound, iodine green. These only had a short life as dyestuffs, as in 1866 Lauth and Bardy investigated the action of oxidizing agents on the recently discovered dimethyl aniline and obtained methyl violet. This was manufactured by the firm of Poirrier et Chappat and owing to its lower price, rapidly replaced Hofmann's violet. In the meantime the magenta process had not been neglected and several investigations had been carried out on the bye-products formed. These led to the isolation of chrysaniline by Nicholson in 1862, although its constitution as an acridine derivative was not recognized until 1884, and of saffranine by Perkin in 1863.

The next year, 1864, saw the introduction of the first azo colour (Bismarck brown), although it was not until twelve years later that the full importance of this discovery was recognized, by which time Griers and Kekulé had published their work on the constitution of the diazo and azo compounds.

Until 1865 aniline colours had only been obtained by purely empirical methods, but in this year Kekulé published his benzene theory, and at once placed the whole chemistry of the aromatic compounds on a scientific basis. One of the most important discoveries immediately following the enunciation of the benzene theory was the synthesis of alizarine in 1869 by Perkin in this country, and by Graebe and Liebermann in Germany. Apart from the commercial interest the discovery was notable, as it was the first time that a plant dyestuff had been made synthetically, and it was the first time that the process of alkali fusion was carried out on the large scale.

The year 1871 saw the introduction of fluoresceine and 1874 eosin.

Two important discoveries were made at this period. In 1873 Bretonierre obtained the first sulphide colour (cachou de Laval) by heating organic refuse such as straw, wood chips, and the like, with sulphur, and 1875 may be regarded as the birth year of the azo colours. It is true that the first azo colour (Bismarck brown) had been introduced twelve years previously, but it was not until the discovery of chrysoidine in 1875 by Caro that any great importance was attached to the azo compounds as dyestuffs. The next year saw the introduction of acid azo colours (Orange I., II., III. and IV.), and in 1878 Caro found that by using naphthionic acid in place of sulphanilic acid he obtained red azo dyes. The same year saw the introduction of naphthol sulphonic acids as components and led to the recognition of the influence of the position of the sulphonic acid groups, the Ponceaux being obtained by coupling diazotized xylidine with R or G acid. A year later the first disazo dye (Biebrich scarlet) was placed on the market, and four years after the first black azo dye was obtained by substituting naphthionic acid for sulphanilic acid.

In the meantime the other groups of dyes had not been neglected. In 1877 Caro had applied Nicholson's sulphonation process to magenta, and had obtained acid magenta, and in 1878 Döbner had introduced malachite green.

Lauth in 1876 obtained thionine (Lauth's violet), but the yields were so bad that it was never manufactured. The next year, however, saw the introduction of methylene blue by Caro, and the preparation of the first indamine by Nietzki.

The dyestuff industry was now firmly established on a scientific and commercial basis, and steady progress was made in all directions. The discovery in 1884 of Congo red naturally led to the preparation of many other direct cotton colours, and marked progress in this direction has been made.

The success which attended the synthesis of alizarine naturally raised hopes that a technically successful synthesis of indigo might be discovered, and the investigation was undertaken by Bayer. In 1880 he completed a synthesis, starting with nitrobenzaldehyde; but the cost of production was too high for the synthetic product to compete with that obtained from natural sources. Success was achieved by Heumann in 1897, who obtained the dyestuff by the alkali fusion of phenyl glycine or phenyl glycine ortho carboxylic acid, and so successful did this process prove that at the outbreak of the war the natural article had almost disappeared from the market. The introduction of the synthetic dyestuff at once led to closer investigation of the derivatives of indigo, and the introduction of the valuable chlor and brom indigos.

The next notable advance was achieved in 1903, when Bally introduced indanthrene. This was the first vat dyestuff other than indigo to be prepared, and naturally attracted great attention, and led to a very close study of the chemistry of anthraquinone. As a result of these studies a very large variety of anthraquinone vat dyes have been placed on the market, most of which are remarkable for their fastness to light.

Another very important class of vat colours is due to Friedländer's discovery on thioindigo in 1906, and in 1910 the introduction of hydrone blue showed that the sulphur melt in some cases could yield vat colours.

Technical Difficulties.—In the manufacture of dyestuffs on the technical scale cost of production is a very important problem. As a result it is impossible to use chemically pure intermediates, and it is not feasible to purify the product by elaborate methods. Consequently the intermediate products employed almost always contain a certain amount of impurity, especially in the case of the naphthol, naphthylamine and amino naphthol sulphonic acids, which usually contain isomers. The shade of the finished product is naturally affected by these impurities, so that it is very desirable to work always with intermediates of standard composition. If this is not done each batch of dyestuff will give a slightly different shade, and will require blending in order to bring it to standard.

The shade is often also affected by the conditions under which the dyestuff is made, and this is especially true of the sulphide colours. As it is almost impossible to reproduce exactly the same conditions for each batch, this can only be corrected by suitable blending of the finished product.

The dyer naturally insists that every consignment of a dye that he receives shall dye the same shade under the same conditions, and in order to fulfil this condition it is absolutely essential that every batch made in the dye factory shall be dyed out under standard conditions and the shade obtained compared with the standard. Any variation must then be corrected either by blending several batches or by mixing in some other suitable colour. As most commercial dyestuffs contain more or less salt, due to their being isolated by salting out, they must at the same time be brought up to standard strength.

From this it will be seen that the experimental dyehouse of a dye factory is one of the most important departments, quite apart from the research work carried on there with new colours.

In the actual manufacture of dyes the usual mechanical difficulties are experienced that are met with in most chemical factories. These are largely due to the corrosive nature of the substances handled, and to the mechanical weakness of materials that resist acid. Sulphuric acid can be handled in lead, although the hot, strong acid attacks it very vigorously, and if over 70 per cent. strength can be handled in iron. Strong, cold nitric acid can be handled in lead or iron, but attacks most metals very vigorously when dilute. Hydrochloric acid attacks all metals, and can only be handled in glass, stoneware, ebonite, or enamelled iron. Enamelled iron is satisfactory so long as the enamel remains intact, but it is easily chipped, and the first chip renders the vessel useless. For this reason autoclaves which require to be of enamelled iron are built of a steel outer case and thin enamelled iron liner.

Ferrosilicon alloys have come much to the front during the last five years, and resist acids excellently. Unfortunately they are expensive, very brittle, and too hard to be machined, so that at present their use is limited.

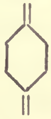
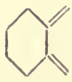
Future of the Industry.—Owing to the enormous strides that have been made in the colour industry since its foundation sixty-two years ago, it is difficult to indicate in what direction future developments will lie. A huge number of synthetic dyes have now been studied, of which about 1500 are actually on the market. Of these, some are extremely fast, whereas others leave much to be desired in this respect. As a rule the fast colours are a good deal more expensive than the fugitive ones, and it is probable that future research will largely be directed towards the production of fast colours at a moderate price. The main bulk of the trade is in cheap colours, the demand for the more expensive ones being comparatively small.

So far almost all the synthetic dyes have been derived from five hydrocarbons, viz. benzene, toluene, xylene, naphthalene and anthracene. During recent years a few colours have been obtained from phenanthrene and carbazole, and it would seem probable that the other constituents of coal tar will find application in the near future.

Up to 1914 about 80 per cent. of the world's production of dyes was centred in Germany owing to the recognition by that country of the value and necessity of research.

Owing to the abundant coalfields in this country and in the United States of America, cost of production should be lower than in Germany, and there would seem no reason why a dyestuff industry should not be established, provided those responsible will recognize that research by the best brains is *sine qua non.* Up till the present the chemist has been somewhat looked down on, and it is useless to hope to attract the best brains to a profession unless adequate remuneration is offered. To make the industry a success, duty-free alcohol must be available for manufacturing purposes, and the antiquated railway system of the country drastically revised. Dyestuff manufacture now covers almost the whole field of organic chemistry, and is intimately bound up with pharmaceutical and photographic chemicals and explosives. Since synthetic rubber will probably "arrive" in the near future it is obviously of very great national importance to establish the organic chemical industries on a firm basis.

Benzol, toluol, etc., are now available in large quantities, not only from gasworks but also from bye-product coke ovens, and it will be found that in future the manufacturers of these products will also be manufacturers of intermediates. This will effect considerable saving in cost of manufacture and transport, and will allow the dye makers, especially the smaller firms, to concentrate more fully on the finished product. Several schemes of this nature are under consideration and will no doubt be carried through on the conclusion of hostilities.

Colour and Constitution.—As soon as structural organic chemistry became firmly established investigators looked for some definite relationship between colour and constitution. Several theories were propounded, of which the quinonoid theory found most support. This stated that all compounds containing the structure  or  were coloured and, for a matter of fact, nearly all compounds that are coloured can be written so as to contain one of these structures. It was immediately argued that certain compounds, such as *m*-nitraniline and benzil, are coloured, although they cannot be written in a quinonoid form. To this the votaries of the quinonoid theory replied by asserting that the colour in these cases was due to a trace of impurity, and would disappear if the compound could be obtained absolutely pure. Such an argument was, of course, unanswerable.

The colour of a compound is due to selective absorption, and a substance which absorbs only those rays which are invisible to the human eye appears colourless. From this it is clear that the only satisfactory method of investigating the relation between colour and constitution lies in a close study of absorption spectra. During recent years a large number of investigations of this nature have been carried out, and the general conclusion arrived at that the property of selective absorption lies in the vibration of the molecule, and it is clear that a quinonoid structure is particularly susceptible to such vibration.

The qes tion cannot be more fully discussed in a book of this nature, but references will be found in the bibliography at the end of this introduction.

Nomenclature.—In the earlier days of the synthetic dyestuff industry the number of dyestuffs was very limited, and they were usually named either after their discoverer, *e.g.* Martius' yellow, Meldola's blue, or with some reference to their tinctorial properties. This latter system has given rise to names for dyestuffs which are quite misleading if taken as having any bearing on their chemical constitution. For example, azocarmine contains no azo group, alizarine yellow has no chemical relationship with alizarine, and anthracene brown is not derived from anthracene.

A much better system is now in fairly general use. Most of the big firms have a registered trade name for each class of dyes, individual dyes being named by adding a word representing a colour and initials, which usually denote shade, *e.g.* B=Blau (blue), R=Rot (red), G=Gelb (yellow), etc. Under this system the dyestuffs are, of course, classified according to their mode of application, viz. acid dyes, vat dyes, sulphide dyes, etc., without reference to their chemical constitution.

BIBLIOGRAPHY.

German patents dealing with organic chemistry, and with dyestuffs and intermediates in particular, are published in the following works :—

Friedländer, " Fortschritte der Teerfarbenfabrikation," vols. i.–xi., 1877–1914.

Winther, " Patente der organischen Chemie," 1877–1908, vols. i.–iii., vol. iii. being the index.

Heumann, " Anilinfarben u. ihre Fabrikation," vols. i.–vi., 1888–1908.

Of general accounts of dyes and intermediates, the following are the most important :—

Schultz, " Chemie der Steinkohlenteers," 1900–1901.

Nietzki, " Organische Farbstoffe," 1906.

Bucherer, " Lehrbuch der Farbenchemie," 1914.

Möhlau u. Bucherer, " Farbenchemisches Praktikum," 1908.

Georgievics-Grandmougin, " Lehrbuch der Farbenchemie," 1913.

Cain and Thorpe, " Synthetic Dyestuffs," 1913.

Several elementary text-books on coal-tar dyes have appeared during recent years, of which the following may be mentioned :—

Fay, " Chemistry of the Coal Tar Dyes," 1911.

Gardner, " British Coal Tar Industry," 1915.

Wahl and Atack, " Organic Dyestuffs," 1914.

Ramsay and Weston, " Artificial Dyestuffs," 1917.

Fort and Lloyd, " Chemistry of the Dyestuffs," 1917.

A complete list of dyestuffs actually on the market with their chemical composition, mode of application, and references, will be found in the following :—

Lehne, " Tabellarische Uebersicht ueber die kunstliche organische Farbstoffe," 1894–1906.

Schultz, " Farbstofftabellen," 1914.

The former of these gives experimental dyeings. An English translation of a former edition of the latter was published by Green in 1904, under the title " Systematic Survey of the Organic Colouring Matters." To this translation Green has added a short description of the chief intermediate compounds. These are treated in greater detail in :—

Cain, " Manufacture of Intermediate Products for Dyes," 1918.

Two books have been published devoted exclusively to naphthalene intermediate products, viz. :—

Reverdin u. Fulda, " Tabellarische Uebersicht der Naphthalinderivate," 1894.

Taüber u. Norman, " Derivate des Naphthalins," 1896.

The relation between the colour of a compound and its constitution is fully discussed in :—

Kauffmann, " Farbe u. Konstitution," 1904.

Kauffmann, " Auxochrome," 1907.
Kauffmann, " Fluoreszenz u. Chemische Konstitution," 1906.
Smiles, " Chemical Constitution and Physical Properties," 1910.
Watson, " Colour in Relation to Chemical Constitution," 1918.

The chief periodicals devoted to dyestuffs are :—
Journal of the Society of Dyers and Colourists.
Revue Generale des Matières Colorantes.
Färber Zeitung (Lehne).
Deutsche Färber Zeitung.
Leipziger Färber Zeitung.

And informative articles will often be found in—
Chemiker-Zeitung (Cöthen).

The application of the dyestuffs is treated in this series by Whittaker in " Dyeing with Coal-Tar Dyestuffs," and a bibliography will be found on page 11 of that book.

PART I.—THE INTERMEDIATE COMPOUNDS

SECTION I.—NITRATION

NITRO groups are invariably introduced into the nucleus by treatment with a mixture of nitric and sulphuric acids, although in some cases nitric acid alone is used. Technically the use of "straight" nitric acid, *i.e.* nitric acid unmixed with sulphuric acid, is to be avoided when possible, as it attacks metals and consequently must be handled in plant of stoneware or enamelled or acid-proof iron. It is true that strong nitric acid does not attack metals readily when cold, but water is formed during nitration, so that the acid becomes diluted. The function of the sulphuric acid is to combine with this water and so maintain the strength of the nitric acid.

When two nitro groups enter the same nucleus they take the meta position to one another, and sulphonic acid, carboxylic acid and aldehyde groups also direct to the meta position. Other groups, such as alkyl, halogen, hydroxyl and amino, direct to the ortho and para positions, a mixture of isomers usually being obtained when both ortho and para positions are available.

For convenience the nitro compounds can be divided roughly into two groups, viz. those derived from stable compounds, such as hydrocarbons, halogen hydrocarbons, sulphonic acids, etc., in which the nitration proceeds easily, and those derived from sensitive substances which can only be nitrated by special methods, *e.g.* phenols, amines, aldehydes, etc. The difficulty with these sensitive substances lies in the fact that they contain groups which are readily attacked by nitric acid, so that unless special precautions are taken decomposition takes place, usually accompanied by the formation of resinous substances.

Nitrations are almost invariably carried out in cast-iron vessels of about 1000 gals. or more capacity, as smaller vessels require an undue amount of labour. These nitrators are best cast in one piece, but are frequently built up from two or three sections, the joints being made with lead or asbestos washers. The depth should be about the same as the diameter, and the bottom slightly dished, a run-off cock being bolted to the lowest point. The cover carries an efficient agitator, manhole, charging orifices, one or more thermometers and a vent for carrying off nitrous vapours. This is usually carried through the roof of the building by means of a stoneware pipe, a slight pull (about $\frac{1}{4}''$ w.g.) being maintained by means of a steam jet. If benzole is being nitrated it is advisable to connect this vent with a condenser, as otherwise a good deal of benzole will be lost.

Temperature is a very important factor in nitrations and must be under absolute control, as excessive rise may cause the charge to fire, and unless adequate cooling is provided the charge takes an undue time to complete. Some factories rely on a water jacket only; but lead coils are much more satisfactory and give very little trouble if correctly designed. Ill-designed coils, however, are liable to burst. Whether coils or jacket or both are employed they are connected with both the water supply and with the steam main, in the latter case through a suitable reducing valve. If coils alone are used at least four should be provided, each being separately controlled, as by this means should one burst it can be isolated and the charge finished with the remaining ones.

The nitrators should be cast from a good close-grain iron, high in fixed carbon, but low in graphite, sulphur, and phosphorus. Acid-proof irons containing about 15 per cent. of silicon are sometimes used, but they are costly, fragile, and cannot be machined. Also the mechanical difficulties in casting large sizes are very great. They are very useful, however, when straight nitric acid has to be handled, *e.g.* in the nitration of phenol.

The composition of the mixed acid varies somewhat according to the nitro compound being made, but a good acid for making mono nitro compounds has the composition :

HNO_3	28
H_2SO_4	56
H_2O	16

If, however, much strong nitric acid is available, a mixture containing more nitric acid and correspondingly less water can be used. The optimum mixed acid is an economic problem which can only be settled by each factory after taking into consideration what other work is being carried on simultaneously.

Dinitro compounds usually demand a somewhat stronger acid, such as :

HNO_3	20
H_2SO_4	70
H_2O	10

the spent acid being fortified with nitric acid and used for mononitration.

The nitration is carried out either by slowly adding the substance to be nitrated to the mixed acid or *vice versâ.* In making mono nitro compounds it is usually best to adopt the latter procedure, as there is less danger of dinitro compounds being formed. The amount of mixed acid is calculated so as to allow a slight excess of nitric acid, usually about 5 per cent. more than that required by theory. The duration of the nitration is almost entirely dependent on the cooling, and, unless a refrigerator is used, may take a quite excessive time during the summer months.

In selecting hydrocarbons for nitration care should be taken only to use those free from unsaturated paraffins. Some of the benzole and toluol on the market, especially that obtained from cannel coal and rather low temperature carbonization, unless properly purified is apt to be rich in ethylenic compounds. These are attacked by the mixed acid, and frequently cause emulsification, and hinder the proper separation of the nitro compound.

As most nitro compounds are insoluble in sulphuric acid of moderate strength, the winning of them from the nitration mixture is very simple. The mixture is simply allowed to stand, when it separates into two layers which are drawn off separately. If the nitro compound is solid at the ordinary temperature, separation is allowed to take place at a sufficiently high temperature to maintain the nitro compound in a liquid condition. The freshly separated nitro compound always contains a certain amount of mineral acid. This is removed by washing with water, with or without the addition of alkali. The spent or waste acid should contain under ½ per cent. of nitric acid, and is reconcentrated for further use.

Continuous nitration processes have been described, but have never come into general use.[1]

In carrying out nitrations care should be taken to make certain that the reaction is taking place, which can be done by careful observation of the thermometer. Sometimes it happens in cold weather that no action takes place at first, and in this case it should be started by gentle warming. Otherwise no reaction may take place until the whole of the ingredients have been mixed, when nitration may set in with explosive violence.

Care should also be taken to ascertain that the substance to be nitrated is reasonably free from water, as to the author's knowledge at least one disastrous fire has been caused through water having settled out of toluol.

As nitro compounds are poisonous and are readily absorbed through the skin, the plant should be designed so that the workers are not exposed to vapours, and so that they do not have to handle the nitrated substances. In Great Britain the Factory Act compels the provision of special clothes and special accommodation for workers engaged in the manufacture or handling of nitro and amido compounds of benzole and toluole.

Mononitrobenzole.—Nitrate at 25° C. and finally heat slowly to 70°. The yields obtained are almost quantitative. B.p. 205° C., m.p. +3° C., sp.gr. 1210.

Formerly a nitrobenzole consisting of a mixture of nitrobenzole *o*- and *p*-nitrotoluol, and a little nitroxylol, was prepared by nitrating heavy benzole, and used for making "aniline oil for red." These heavy nitrobenzoles, however, are no longer manufactured, as magenta makers prefer to blend their own oil.

Dinitrobenzole.—The introduction of a second nitro group into the benzene nucleus leads almost exclusively to the meta derivative, although small quantities of the ortho and para isomers are formed simultaneously. *m*-Dinitrobenzole, however, is the only one of any technical importance, as the others cannot be obtained in sufficient quantity, and their derivatives are manufactured by indirect means. In manufacturing dinitrobenzole, benzole is first nitrated to the mononitro compound in the usual way. The spent acid is then removed but the nitrobenzole left in the nitrator, and the same amount of mixed acid as first used slowly added, the temperature at first being maintained at 70° C., but towards the end being raised to 100° C., so that the product remains liquid during nitration. The composition of the second dose of mixed acid may be the same as the first, but it may with advantage contain slightly less water. After nitration is complete the charge is allowed to settle while hot, and the spent acid and dinitrobenzole separated as usual. M.p. 91° C.; b.p. 297° C.; sp.gr. 1370 at 95° C.

In washing dinitrobenzole it must be borne in mind that it dissolves fairly easily in boiling water. Hence provision must be made for preserving the wash waters until they have cooled, and then collecting the crystals that separate out. If a continuous washing process is employed, which consists in agitating the molten dinitrobenzole in a slow stream of boiling water, this can conveniently be done by leading the washings through a series of water-cooled lead gutters and collecting the crystals from time to time with a rubber squeegee.

Mononitrotoluol.—Nitrate at 35° C. and then heat slowly (about 1° C. every two minutes) to 80° C. and maintain at this point for one hour. The heating must be slow, as heavy frothing is apt to take place. The yields are almost theoretical.

Toluol occurs to a considerable extent in Borneo petroleum, but can only be separated with the utmost difficulty. If, however, the fraction containing the toluol is carefully washed free of unsaturated compounds and then nitrated, only the toluol is attacked, and as mononitrotoluol boils at over 200° C. the fractional separation from the paraffins becomes a simple matter.

The mononitrotoluol obtained by the nitration of toluol is a mixture of all three isomers in the proportion of about 57 per cent. of ortho, 40 per cent. of para, and 3 per cent. of meta. It has a sp.gr. of 1160 and is sold as M.N.T. mixture. On cooling to −10° C. most of the para isomer separates out and can be freed from ortho by whizzing. The expressed oil must then be fractionated *in vacuo* and again cooled and whizzed in order to obtain the ortho nitrotoluol in a reasonable state of purity. *m*-Nitrotoluol is of no technical importance.

o-Nitrotoluol ..	m.p. −10·5° C., b.p. 223° C., sp.gr. 1168
m-Nitrotoluol ..	m.p. 16° C., b.p. 230° C., sp.gr. 1168
p-Nitrotoluol ..	m.p. 54° C., b.p. 238° C., sp.gr. 1123

Many authors have stated that the proportion of isomers formed depends on the temperature of nitration; but this is erroneous.[2]

Dinitrotoluol.—Of the three possible dinitrotoluols only 2·4-dinitrotoluol is of any technical importance. It is prepared by the further nitration of either *p*-nitrotoluol or of M.N.T. mixture. The former gives a somewhat purer product, but the more general procedure is to use M.N.T. mixture. The nitration is carried out at 60–65° C. by adding 2¼ parts of mixed acid to 1 part of M.N.T. and finally cooking the charge at 80° C. for half an hour. A stronger mixed acid is used than is necessary for the preparation of mononitro compounds, viz. :—

HNO_3	30
H_2SO_4	64
H_2O	6

but here again the composition is varied to suit what strength of nitric acid is available for mixing. The waste acid contains some 5 per cent. of nitric acid, and can be revivified for mononitration, or denitrated and concentrated.

Pure 2·4-dinitrotoluol melts at 70·5° C. and the commercial product prepared from *p*-nitrotoluol usually within a degree or so of this. That prepared from M.N.T. mixture, however, contains about 7 per cent. of oil (consisting of other dinitrotoluols), and, unless this is removed by whizzing or pressing, the melting-point is somewhat lower.

Trinitrotoluol.—Toluol on exhaustive nitration gives a trinitro compound (T.N.T.) much used as an explosive but of no use as an intermediate.

Nitroxylol.—Since commercial xylol consists of about 60 per cent. of *m*-xylol and 40 per cent. of a mixture of the ortho and para isomers, its nitration product is naturally a complicated mixture. The main constituent, however, is 1·3-dimethyl–4-nitrobenzole. The isomers are not usually separated, but the crude nitro compound reduced to the amino compounds and used as such.

Nitrochlorbenzole.—When chlorbenzole is nitrated under circumstances similar to those used when making nitrobenzole a mixture of the ortho and para nitro compounds is formed. As chlorbenzole is much less volatile than benzole there is no necessity to nitrate at such a low temperature, a temperature varying from 35° at the beginning to 50–60° C. towards the end being suitable, as under these conditions the charge remains liquid. After separating the product from the spent acid it is washed up and then cooled, whereby a large proportion of the para isomer separates out and is removed by filtration and subsequent whizzing. If the oil is submitted to a fractional distillation *in vacuo* it can be divided into two parts, one rich in ortho and one rich in para. This latter fraction deposits the para isomer on cooling. This is collected and the oil united with the fraction rich in ortho. This is then again fractionated, and this alternate fractional distillation and cooling continued systematically until fractionation is complete.[3] It is more economical, however, not to carry the separation too far, but to separate part of the ortho and para and then nitrate the residue for dinitrochlorbenzole.

o-Nitrochlorbenzole .. m.p. 32·5° C., b.p. 245° C. at 753 mm.
119° C. at 8 mm.
p-Nitrochlorbenzole .. m.p. 83° C., b.p. 238° C. at 753 mm.
113° C. at 8 mm.

Dinitrochlorbenzole.—The only technically important isomer is 1-chlor-2·4-dinitrobenzole. This can be obtained from chlorbenzole by the entrance of two nitro groups, the nitration being carried out in one step. More usually, however, the nitration is carried out in two steps, as in the manufacture of *m*-dinitrobenzole. In this case either the crude mixture of mononitro compounds is used direct, or the isomers are partly separated and the residue then nitrated.

Dinitrochlorbenzole being exceptionally toxic, special precaution must be taken to protect the workers handling it. M.p. 38° C.

Nitro groups invariably enter the *naphthalene* nucleus in the α-position.

α-Nitronaphthalene.—Commercial naphthalene is frequently rich in ethylenic hydrocarbons, and if attempts are made to nitrate a sample of this nature heavy frothing takes place and an oily mess is produced which is quite valueless. Good qualities of commercial naphthalene, however, nitrate easily, although there is generally some loss due to oxidation. The naphthalene should be finely powdered and added to the mixed acid through a sieve, as otherwise it has a tendency to ball together.

As naphthalene is volatile some factories connect the fume pipe of the nitrator with a vertical reflux condenser jacketed with hot water. Cold water must not be used as it condenses the naphthalene in the solid condition and causes endless trouble with choked pipes. The two following methods of working will be found to give good results :—

(1) One thousand pounds of finely ground naphthalene are shaken slowly through a sieve into a mixed acid composed of 800 lbs. of nitric acid (sp.gr. 1390), 800 lbs. of concentrated vitriol, and 3200 lbs. of waste acid from a previous charge, the temperature being maintained at 45° C. The spent acid is then separated and the crude nitro compound washed up.

(2) One thousand pounds of naphthalene are slowly added to 1800 lbs. of mixed acid of the composition :

HNO_3	32
H_2SO_4	53
H_2O	15

the temperature being maintained at 70° C. and the charge subsequently cooked for 6 hours at the same temperature.

An interesting process has been patented[4] which may become of interest in view of the forthcoming production of large quantities of weak nitric acid from atmospheric sources. It is based on the observation that whereas straight nitric acid of 25 per cent. strength does not attack naphthalene either hot or cold, nitration takes place when an electric current is passed through the acid. The process has not been used technically up to the present, but now that acid-proof iron can be obtained in satisfactory quality and the mechanical difficulties in manipulating it are to some extent overcome, no difficulty should be experienced in designing a suitable plant.

M.p. 61° C. when pure, but the commercial product melts at 56–58° C.

Dinitronaphthalene.—Further nitration of naphthalene leads to a mixture of 1·5- and 1·8-dinitro compounds, although when the nitration is carried out at a low temperature, and in the presence of a large excess of sulphuric acid, 1·3-dinitronaphthalene is said to be formed.[5] It, however, is of no technical importance.

The nitration is best carried out by adding mononitronaphthalene to mixed acid of the composition—

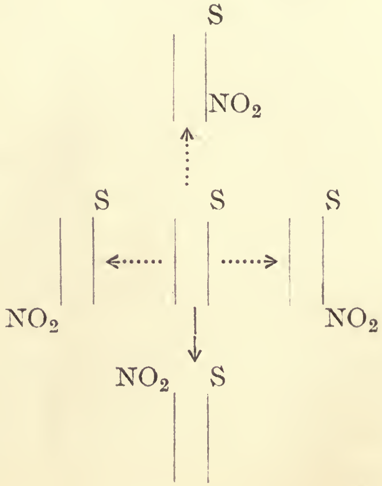
HNO_3	32
H_2SO_4	62
H_2O	6

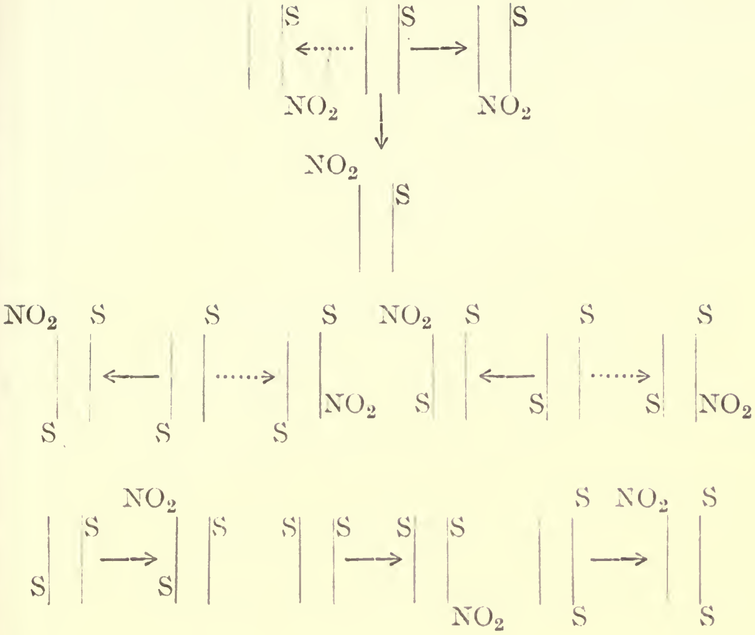
the temperature being maintained at 70° C.

The isomers are formed in the proportion of 1 part of 1·5- and 2 parts of 1·8-dinitronaphthalene. As the former is only soluble in 125 parts of cold pyridine whereas the latter is soluble in 10 parts, their separation does not present great difficulties. They can also be separated by taking advantage of their different behaviour with oleum.[6]

1·5-dinitronaphthalene	m.p. 217° C.
1·8 dinitronaphthalene	m.p. 170° C.

Nitronaphthalene Sulphonic Acid.—When the naphthalene sulphonic acids are nitrated a variety of nitro compounds are obtained. The following diagram, taken from Heumann's "Anilinfarben u. ihre Fabrikation," shows the orientation taken by the entering nitro group. The chief product is shown by a full arrow, side products by dotted arrows—





Of these the most important are those obtained by the nitration of naphthalene-β-sulphonic acid.

The nitration is carried out by dissolving 230 parts of the sodium salt in 1150 parts of vitriol, the temperature not being allowed to rise above 30° C. The solution is then cooled and nitrated between 0–10° C. with mixed acid containing 70 parts of nitric acid.[7] The isomers are separated by the fractional crystallization of their barium salts, or by taking advantage of the fact that in strong hydrochloric acid or dilute sulphuric acid (1 : 2), the 1·6-acid is fairly soluble, but the 1·7-acid almost insoluble.

Nitroanthraquinone.—Nitro groups only enter the anthraquinone nucleus in the α-positions.

The mononitro compound is formed when anthraquinone is dissolved in 20 times its weight of sulphuric acid at 50° C. and nitrated at this temperature by the addition of the calculated amount of nitric acid. As it is soluble in sulphuric acid it can only be isolated by running the charge on to crushed ice. The crude product is somewhat impure, but it is only used for making the amino compound, and the impurities are eliminated during reduction. By using double the quantity of nitric acid and cooking the charge for about 12 hours at 80° C. a mixture of 1·5- and 1·8-dinitroanthraquinone is obtained. These can be separated by extraction with acetone in which the 1·5 compound is insoluble.

NITRATION OF AMINES.

Amino compounds present difficulties in nitration as they are readily oxidized by nitric acid, and the nitrous acid so evolved attacks further quantities, so that unless special precautions are taken the product usually consists chiefly of resinous matter.

The best procedure is to protect the amino group by combining it with some group which is readily split off after nitration, such as an acetyl or benzylidene group. Nitration then takes place normally in the ortho and para positions, provided care is taken to select suitable conditions to avoid hydrolysis. When nitration is complete the protecting group is split off by heating with dilute acid.

o-**Nitraniline.**—This is the least important of the three nitranilines, and is obtained as a side product in the manufacture of *p*-nitraniline from acetanilide. It can be obtained as the sole product if the para position is first blocked by a sulphonic acid group, subsequently removed by heating with hydrochloric acid under pressure. In these circumstances, however, it is best to substitute oxanilide for acetanilide.[8] M.p. 71·5.

p-**Nitraniline.**—This most important base can be made by three methods.

(*a*) *From benzylidene aniline.*[9] The aniline is first converted into its benzylidene (azomethine) derivative by warming with the calculated amount of benzaldehyde :

$$\mathrm{PhN}\boxed{\mathrm{H_2O}}{=}\mathrm{CHPh} \rightarrow \mathrm{PhN{=}CHPh} + \mathrm{H_2O}$$

This benzylidene derivative melts at 42° C., and is readily separated from the water simultaneously formed, as on standing warm it settles out as a lower layer and can be drawn off. It is nitrated as follows: 181 kilos are added slowly to 70 kilos of concentrated sulphuric acid, the temperature not being allowed to rise above 50° C., and the cooled mixture then nitrated by slowly adding 21·6 kilos of mixed acid containing—

HNO_3	31
H_2SO_4	48
H_2O	21

The nitration must be carried out at a temperature not exceeding 10° C., and the nitrator should be made of enamelled or acid-proof iron. When the nitration is complete the mixture is diluted with its own volume of water and then steam distilled. This hydrolyzes the azomethine compound, the benzaldehyde passing over with the steam and being collected for further use. The residue is then neutralized with soda and deposits *p*-nitraniline on cooling. The yield is about 90 per cent. of theory, and the loss of benzaldehyde small with properly designed plant and efficient chemical control. Careless working, however, leads to excessive loss.

(*b*) *From acetanilide.*—This is the best known process, gives good results, and is easy to carry out as follows:—

400 lbs. of sharply dried and finely powdered acetanilide are slowly added to 800 lbs. of concentrated sulphuric acid, which is kept well agitated in a cast-iron nitrator. Considerable heat is evolved, but the temperature must on no account be allowed to rise above 40° C., as if it does the anilide will be hydrolyzed. The whole of the anilide must dissolve in the acid, which it does fairly easily provided it is finely ground. The solution is then nitrated at 35° C. with 760 lbs. of mixed acid of the composition—

HNO_3	26
H_2SO_4	50
H_2O	24

and after nitration allowed to stand overnight. It is then run into 200 gals. of warm water contained in a lead-lined vessel. A yellow precipitate of nitroacetanilide separates, which is hydrolyzed and dissolved on heating to 100° C. for 2–3 hours. No resinous products should be formed with good working, but if they are they are removed at this stage. After cooling to 50° the resulting clear solution is run on to 1 ton of crushed ice. The orthonitraniline, being much the weaker base, separates out and is filtered off and whizzed. The *p*-nitraniline remains in solution as its sulphate and is precipitated by neutralizing the mineral acid, ice being simultaneously added so that the temperature does not rise above 30° C. It is collected, whizzed, and recrystallized from boiling water, which is best done under pressure. The yields are about 25 per cent. of ortho and 60 per cent. of para, calculated on theory.

(*c*) *From Phthalanil.*—Although the acetanilide process works well, the acetic acid is lost, and consequently attempts have been made to use an acid that is recoverable. This has been achieved with phthalic acid,[10] the process being carried out as follows: 2·23 kilos of phthanil are dissolved by gentle warming in 14 kilos of concentrated vitriol and then nitrated below 3° C. with 2·55 kilos of a mixed acid containing 25 per cent. of nitric acid. After pouring on to crushed ice the nitrophthanil is heated with 1·1 kilos of aniline for 1 hour at 170–180°. Double decomposition takes place under these circumstances with production of nitraniline and phthanil, and on subsequent distillation with steam unchanged aniline and *o*-nitraniline pass over. From the residue *p*-nitraniline is extracted with boiling water and the insoluble phthanil dried and used for the next charge.

Although of no technical importance the preparation of *p*-nitraniline from *p*-chlornitrobenzole by heating under pressure with alcoholic ammonia and sodium iodide is worth mentioning.[11] The yields are 66 per cent. of theory, whereas without the addition of iodide they are only 2½ per cent.

m-**Nitraniline.**—This technically important base cannot be obtained by nitration. Its manufacture by the partial reduction of *m*-nitraniline is described in the section on amino compounds, page 30. M.p. 114° C.

NITRATION OF PHENOLS.

Like the amines the phenols are troublesome to nitrate unless the hydroxyl group is first protected. From a technical point of view there are very few nitrophenols of importance, and of these only two are made by direct nitration, viz. *o*- and *p*-nitrophenol. Of the others, 2·4-dinitrophenol is made by splitting out chlorine from dinitrochlorbenzene, the process being described on page 66, and picric acid either by nitrating phenol sulphonic acid, or better, by nitrating 2·4-dinitrophenol. The latter nitrates readily as, owing to the presence of the two nitro groups, it has lost most of its phenolic characteristics.

Nitrophenol.—The ortho and para isomers are obtained in about equal quantity when phenol is nitrated. The nitro groups enter the nucleus very readily and the nitration is carried out with very dilute nitric acid. Oxidation always takes place simultaneously with production of tar, but if carefully supervised the yields are fair, 100 lbs. of phenol yielding nearly 50 lbs. of each isomer, and the tar can be got rid of without any great trouble.

Owing to the weakness of the acid used, the nitrator must be made of enamelled or acid-proof iron or aluminium. The process is carried out as follows :—

Phenol (660 lbs.) is slowly added to 3800 lbs. of nitric acid of 20 per cent. strength, care being taken that the whole is kept well agitated and that the temperature does not exceed 30° C. The temperature is fairly easy to control, but in the summer months it may be advisable to add ice to the acid. In this case, of course, a somewhat stronger acid is used to compensate for the dilution due to the melting ice, and it is as well to start with one quarter of the required acid and after adding one quarter of the phenol to add another quarter of acid, and so on. Also as a matter of convenience, the phenol may be liquefied with a little water, allowance being made for the water thus used when making up the acid. After the whole of the phenol has been added the agitation is continued for an hour or two, and then the thick black oil separated, thoroughly washed and *mineral* acid carefully neutralized with soda (use congo paper). On distilling with steam, superheated if possible, the ortho-nitrophenol passes over mixed with a little unchanged phenol, and after a further distillation with steam is pure. The residue consists of *p*-nitrophenol and tar and is treated with a strong solution of 250 lbs. of caustic soda. The sodium salt crystallizes out and is washed with alkaline brine until all the tar is removed. It is then dissolved in water and decomposed with dilute sulphuric or hydrochloric acid. If the resulting *p*-nitrophenol is boiled with animal charcoal and recrystallized from water it is obtained as snow-white needles; but this is a troublesome process, as in the presence of water it melts at 48° C., and for most purposes recrystallization is quite unnecessary.

o-Nitrophenol can be obtained as the sole product if phenol-*p*-sulphonic acid is nitrated and the sulphonic acid group subsequently removed by heating under pressure,[12] or if the hydroxyl group is protected by combination with toluol-*p*-sulphonyl chloride, although this latter process is only economically possible when the sulphonyl chloride is available as a bye-product from saccharine manufacture.[13]

REFERENCES AND LITERATURE.

[1] D.R.P. 201,623; 228,544; 274,854.

[2] "Direkte Einfürung von Substituenten in den Benzolkern." Holleman. Leipzig, 1910. Pages 93–98.

[3] D.R.P. 97,013.

[4] D.R.P. 100,417.

[5] D.R.P. 96,227.

[6] *B.* **35,** 3403.

[7] D.R.P. 67,017.

[8] D.R.P. 66,060.

[9] D.R.P. 72,173.

[10] D.R.P. 141,893.

[11] *B.* **39,** 1953.

[12] D.R.P. 43,515

[13] D.R.P. 91,314; E.P. 24,193^{97}.

As nitro compounds enter largely into the manufacture of explosives an account of some of them will be found in modern works on this subject, particularly in R. Escales, "Nitrosprengstoffe," Leipzig, 1915. Other modern works on the subject are: Chalon, "Les Explosifs Modernes," Paris, 1911; Marshall, "Explosives," London, 1917; and Colver, "High Explosives," London, 1918.

SECTION II.—AMIDATION

PRIMARY, secondary, and tertiary amino compounds are all used in the manufacture of dyestuffs, although the primary compounds are by far the most important. As a rule the secondary and tertiary amines are prepared from the primary, but in some cases the secondary and tertiary groups can be introduced direct.

Technically, so far as dyestuff intermediates are concerned, only three methods of introducing the amino group into the nucleus are made use of, viz. the reduction of the nitro (and nitroso) compounds, reduction of the azo compounds, and displacement of the hydroxyl group. Of these the reduction of the azo group is not often resorted to as, although good results are obtained, the majority of compounds used as intermediates can be obtained more economically by other means.

The reduction of the nitro compounds is invariably achieved on the large scale by means of iron turnings and hydrochloric acid, except when benzidine and its derivatives are being prepared. The acid acts more or less as a catalyst, only a small quantity being necessary, and as a rule only about 2½ per cent. of the amount required to convert the iron into ferric chloride is used. The reaction then proceeds according to the equation—

$$9Fe+4H_2O+4ArNO_2=4ArNH_2+3Fe_3O_4$$

and little or no lime is required to liberate the base. If, on the other hand, sulphuric acid is employed, excess must be taken and the base subsequently liberated by lime. This of course would increase the cost, and in addition the corrosion of the plant would be much more severe, as lead-lined vessels would be unsuitable owing to the scouring action of the iron turnings.

In carrying out reductions, care must be taken to keep the reaction well in hand. Considerable heat is evolved, and if the reduction gets out of control the whole charge may boil over, and in any case there will be very serious loss through the amino group being split off as ammonia.

Reduction of nitro compounds is usually carried out in cast-iron vessels of 700–1000 gallons capacity. The older type, still in use in some works, is in the form of an horizontal cylinder with an agitator shaft pasing through the centre, to which are fixed paddles of such length that they just clear the sides of the vessel. When the shaft is in motion these paddles pick up the iron and throw it through the liquid. In modern factories, however, the vertical type is preferred, the agitator in this case being anchor shaped. In some cases it is made hollow for the introduction of steam; but this is a quite unnecessary complication, and it is better to introduce the steam through a special pipe.

Internal coils are never used for heating or cooling, and in most cases a jacket is dispensed with; but if one is provided the process is under better control and can be carried out in less time.

The cover of the vessel is provided with suitable charging holes, steam inlets, and an opening which can be connected with a reflux condenser while reduction is going on, and with an ordinary condenser when the amino compound is being steamed off.

It is usual to cast the vessels in two parts, as the bottom part always corrodes first, partly by the action of the acid and partly by the scouring effect of the metallic iron. Another plan is to insert a loose cast-iron liner at the bottom, or even to line the lower part with acid-proof brick.

In some factories it is usual to place the whole of the iron and acid into the reducer and then to add slowly the nitro compound; but the reaction is more easy to control if only a small proportion of the iron is first added, the rest being fed in gradually from time to time.

As amino compounds have strong toxic properties every precaution must be taken to protect the workers.

Aniline.—This is the most important intermediate, and is invariably manufactured by the reduction of nitrobenzole. The working of a charge is usually carried out as follows :—

The still is charged with 1 cwt. of iron turnings, 10 gallons of crude muriatic acid, and 6 gallons of water, the agitator started and live steam blown in to warm up. At the same time the nitrobenzole (1000 lbs.) is run in slowly. Much heat is evolved, and nitrobenzole and aniline distil off, but are returned by the reflux condenser. A brisk reaction must be maintained by adding more iron from time to time (about half a ton in all will be required), but the reaction must never be allowed to become violent, as if it does there will be heavy loss through ammonia being split off and benzene formed. The reduction takes about 10 hours, and requires steam-heating towards the end to render it complete. The condenser is then reversed and the aniline distilled over with steam.

The condensed water, after separation of the oil, contains about 3 per cent. of aniline, and is fed to the boilers for generating steam for the next charge. Clean steam, however, must be used towards the end so as to leave the iron residues free of aniline.

The aniline oil thus obtained is either used as such or is purified by fractionation *in vacuo*, when the first portions that come over contain water and benzene. The yield of aniline oil from 1000 lbs. of nitrobenzole is on the average 720 lbs., or 1000 lbs. of benzole give 1100 lbs. of aniline.

M.p 6° C.; b.p. 71° C. at 9 mm., 92° C. at 33 mm., 182° C. at 760 mm.; sp.gr. 1025 at 15° C. The commercial article should have the correct density and 98 per cent. should distil within two degrees.

The electrolytic reduction [1] of nitrobenzole has been described, as has also the reduction by sodium disulphide,[2] but they cannot compete with the iron method.

The catalytic reduction by passing a mixture of nitrobenzole and water gas over nickel at 300–400° C. has been tried, but is not yet a commercial success.[3]

Aniline Salt, $C_6H_5NH_2HCl$.—This is used to a large extent for making dyestuffs and intermediates, and is sold for aniline black dyeing. It is manufactured by slowly adding 130–135 parts of pure commercial hydrochloric acid to 100 parts of aniline, the whole being well agitated. Much heat and fume is evolved, and the pipe through which the acid is added must dip below the surface of the aniline. The manufacture is best carried out in stoneware or enamelled iron vessels with an agitator of the same material, as if timber is used the product has a yellow colour. After cooling, the salt is filtered off, whizzed in a vulcanite-lined hydro extractor and then dried at 50° C. on lead or enamelled trays. The liquors are used for making the next charge of aniline. M.p. 192° C.

Toluidine.—The ortho and para isomers are the only ones of any technical importance, and they are manufactured from the corresponding nitrotoluols by methods exactly similar to those used for aniline, but as the para isomer solidifies at 40° C. warm water must be used for the condensers. "Toluidine mixture" is made by the reduction of "M.N.T. mixture," and consists chiefly of *o*- and *p*-toluidine.

o-Toluidine ..	m.p. below —20° C., b.p. 197° C., sp.gr. 1003
p-Toluidine ..	m.p. 45° C., b.p. 198° C., sp.gr. 1046

Xylidine.—Xylidine is obtained by the reduction of crude nitroxylol and is a complex mixture of five or more isomers, of which 4-aminoxylol is the chief component. The isomers are troublesome to separate, although several methods have been described.[4]

m-**Nitraniline.**—By carrying out the process under suitable conditions *m*-dinitrobenzole can be reduced to *m*-nitraniline by means of iron and hydrochloric acid, only about 1 per cent. of diamine being formed at the same time.[5] The process, however, is a troublesome one, and much better results are obtained by the use of sodium polysulphide,[6] the reduction being carried out as follows :—

Four kilos of flowers of sulphur are dissolved in 15 kilos of crystallized sodium sulphide and 65 litres of water by boiling, and 10 kilos of powdered *m*-dinitrobenzole added slowly. Much heat is evolved and the addition should be regulated so as to keep the whole boiling. Boiling is then continued for half an hour, precipitated sulphur removed by filtration, and the liquor allowed to cool. The *m*-nitraniline crystallizes out in the pure state, and the yield is over 80 per cent. of theory. M.p. 112° C.; b.p. 285° C.

p-**Nitraniline.**—This is always obtained by the nitration of acetanilide (page 22), although its manufacture from *p*-nitrochlorbenzole and ammonia has been patented.[7]

m-**Phenylenediamine.**—This is obtained by reducing *m*-dinitrobenzole with iron and hydrochloric or acetic acid, the process being carried out as follows:—

Two hundred litres of water and 200 kilos of *m*-dinitrobenzole are heated to boiling by blowing in live steam. Sixteen kilos of hydrochloric acid are then added and iron borings fed in slowly. About 450 kilos of iron will be required, and it must be added at such a rate that a brisk but not too violent reaction is maintained. If the reaction becomes too vigorous ammonia will be lost, and if it stops it may start again with explosive violence. It is best followed by watching the reflux condenser. Reduction is complete when a sample dropped into filter paper leaves no yellow stain. The charge is then made alkaline and extracted several times with boiling water, the latter extracts from one charge being used for extracting the next charge. Factories preparing their own intermediates merely bring the solution thus obtained to standard strength and use it without isolating the base in the solid state. If, however, the base is for sale the solution is concentrated either in lead-lined pans or in a multiple-effect evaporator, and the base then thrown out as the hydrochloride by adding excess of hydrochloric acid, or evaporation is taken further until a paste is obtained, the base being sold in this form. This paste, which is the usual commercial form, is almost black. If the pure base is desired it is readily obtained by distilling the paste *in vacuo* or in a current of carbon dioxide. The water passes over first and then the almost pure base. M.p. 63° C.; b.p. 287° C.

***p*-Phenylenediamine.**—There are two processes in use for manufacturing this base, by one of which it is obtained by the reduction of *p*-nitraniline and by the other by the reduction of aminoazobenzene.

The reduction of *p*-nitraniline is carried out as follows :—

The pan is charged with 200 kilos of iron borings and 200 litres of water, and after heating to boiling, 9 litres of muriatic acid (28 per cent.) are run in. The *p*-nitraniline (200 kilos) is then fed in slowly, the vigorous reaction that sets in after each addition being allowed to subside before the next addition is made. When the whole has been added, another 14 litres of muriatic acid is run in and the reduction continued until a sample gives a colourless spot on paper. The charge is then made faintly alkaline, boiled up, and then decanted off through a filter. On concentration the free base is obtained.

The aminoazobenzole process is probably somewhat more economical, and is carried out as follows :—

Aniline salt (130 kilos) is dissolved in 500 kilos of aniline and at a temperature of 25–30° C. a concentrated aqueous solution of 65 kilos of sodium nitrite run in slowly. After heating for two hours at 40° C. the whole is allowed to stand overnight in order to complete the formation of aminoazobenzole. This can be isolated by adding excess of hydrochloric acid at a temperature not exceeding 70° C. and then cooling, when the hydrochloride crystallizes out.

For the purpose of manufacturing phenylenediamine this is not done, the whole charge being pumped into a reduction pot surrounded with a steam jacket and previously charged with 100 kilos of iron borings, a little water and 3 litres of 28 per cent. muriatic acid. Reduction is carried out at 30–40° C. and takes about 12 hours. When colourless, the charge is boiled up, the aniline blown off with steam, and the solution decanted through a filter and concentrated. M.p. 147° C.; b.p. 267° C.

Monomethyl Aniline.—This is prepared by heating methyl alcohol with aniline hydrochloride or with aniline and sulphuric acid in an autoclave at 200° C. As high pressures are attained (25–30 atmospheres) the size of the autoclaves is limited. They are best provided with an enamelled iron lining as lead-lined autoclaves cannot be considered as safe.

When sulphuric acid is used the proportions are 70 parts aniline, 42 parts methyl alcohol free from acetone, and 8 parts of R.O.V. The heating is carried out at 200° C. When the hydrochloride process is used the proportions are 55 parts aniline salt and 16 parts methyl alcohol. The temperature is raised to 180° C. for 3 hours during which time the pressure increases from 5 to 25 atmospheres. The pressure is released, and the heating continued for another 8 hours, after which the whole is made alkaline and the methyl aniline blown over with steam.

Methyl aniline can also be obtained by condensing aniline with formaldehyde and then reducing the azomethine compound with zinc dust and caustic soda, or the two steps can be carried on simultaneously.[8] A third process consists in heating aniline and methyl alcohol at 220° C. in the presence of iodine.[9] B.p. 192° C.; sp.gr. 976.

Dimethylaniline.[10]—This is obtained in much the same way as monomethyl aniline, *i.e.* by heating aniline hydrochloride or sulphate with methyl alcohol in autoclaves fitted with enamelled iron liners. If sulphuric acid is used the charges are 80 kilos of aniline, 78 kilos of methyl alcohol, and 8 kilos of R.O.V. The heating is carried out at 230° C., and requires about 10 hours. The pressure goes up to 30–35 atmospheres. In the hydrochloride process 100 kilos of aniline salt and 80 kilos of methyl alcohol is the usual charge, heating being carried out as before. After cooling, the pressure is released and the gases led through a condenser and water scrubber to recover the excess of methyl alcohol, the charge then blown over into a still, neutralized and distilled with steam. Methyl alcohol passes over first and then the dimethyl aniline. The yield is over 90 per cent. of theory.

To avoid the high pressure attained in the above process, the methylation is sometimes carried out with methyl chloride as follows : [11]—

Aniline (50 kilos) is well agitated in an autoclave with milk of lime made from 40 kilos of quicklime and 75 litres of water. The whole is heated to 100° C. and methyl chloride pumped in at 5–6 atmospheres pressure. About 62 kilos of methyl chloride are required, and the time taken is about 3 hours. The charge is then distilled with steam. A third process [12] consists in heating aniline with methyl alcohol and iodine at 230° C. for 7 hours. B.p. 192° C. ; sp.gr. 960.

Mono- and Di-Ethylaniline.—These are obtained by processes exactly similar to those employed for the corresponding methyl derivatives, except that only the hydrochloride process can be used.

Monoethylaniline ..	b.p. 206° C., sp.gr. 954.
Diethylaniline ..	m.p. 38° C., b.p. 216° C., sp.gr. 939.

m-**Toluylenediamine.**—This is made by the reduction of dinitrotoluol with iron and hydrochloric acid. M.p. 99° C. ; b.p. 280° C. The melting-point of the commercial article depends largely on the melting-point of the dinitrotoluol used in its manufacture.

o-**Aminophenol.**[13]—This is obtained from the corresponding nitro-compound by reduction. The reduction is best brought about by adding sodium hydrosulphite to the boiling aqueous alkaline solution until colourless, the aminophenol crystallizing out on cooling, but can also be brought about by sodium sulphide in alkaline solution. M.p. 170° C.

p-**Aminophenol.**[14]—This is obtained by the reduction of *p*-nitrophenol by sodium sulphide and caustic soda, by iron and hydrochloric acid or by sodium hydrosulphite in alkaline solution. Curiously enough it can also be obtained by the simultaneous oxidation and reduction of nitrobenzole, this being one of the few cases in which a hydroxyl group can be inserted directly into the benzene ring. The reaction is brought about electrically [15] or by treating nitrobenzole with zinc dust and concentrated sulphuric acid at 80° C.[16]

Aminosalicylic Acid.[17]—When salicylic acid is suspended in concentrated sulphuric acid (3 parts) and nitrated at 0–10° C. by the addition of a mixture of nitric and sulphuric acid, 2-oxy-5-nitrobenzoic acid is formed almost exclusively. This is filtered off from the waste acid and reduced with iron in the usual way. Aminosalicylic acid can also be obtained by the simultaneous oxidation and reduction of *m*-nitrobenzoic acid by treating it with concentrated sulphuric acid and zinc dust at 50–60° C.

Diaminostilbenedisulphonic Acid.[18]—When *p*-nitrotoluol is sulphonated by heating with 3–4 parts of 20 per cent. oleum the sulphonic acid group enters the ortho position to the methyl group. The sulphonic acid is very easily isolated by salting out, and if boiled with caustic soda and then reduced, yields diaminostilbenedisulphonic acid. A better process, however, is to oxidize with sodium hypochlorite and then reduce the dinitrostilbenedisulphonic acid thus formed. The oxidation is carried out by dissolving 24 kilos of *p*-nitrotoluolsulphonic acid in 8 parts of water at 80° C., and then at this temperature adding 70 litres of hypochlorite solution containing 150 grams of active chlorine and 30 grams of caustic soda per litre. After cooling the oxidation product is filtered off and reduced by ferrous sulphate and ammonia.

α-**Naphthylamine.**—This is manufactured from *α*-nitronaphthalene in the same way that aniline is made from nitrobenzole, but the reduction must be carried out at a lower temperature, as otherwise there will be heavy losses caused through over-reduction with loss of ammonia. The process is carried out as follows: The reducing vessel is charged with 2000 lbs. of iron borings, 10 gallons of muriatic acid of 25 per cent. strength and a little water. Steam is blown in to raise the temperature to 50° C., and then 1500 lbs. of crude, air-dried nitronaphthalene fed in little by little so that a temperature of 50° C. is maintained. After the whole has been added the charge is digested at the same temperature over night, and then neutralized with milk of lime and the naphthylamine distilled off with superheated steam.

As it is not very volatile with steam this is best done by running the charge on to shallow iron trays arranged in a stove and then blowing in strongly superheated steam. As naphthylamine sets readily, warm water must be used for the condensers. The almost black product thus obtained is purified by distillation *in vacuo*. M.p. 51° C.; b.p. 300° C.

β-Naphthylamine.[19]—This can only be obtained from β-naphthol by heating with ammonia. In the older process the manufacture was carried out by heating 10 parts of β-naphthol with 8 parts of 25 per cent. ammonia for 24 hours at 200° C., the product being then washed with caustic to remove unchanged naphthol and finally distilled under reduced pressure. Considerable quantities of dinaphthylamine are, however, always formed as a bye product, and although better results are obtained by employing zinc chloride ammonia or calcium chloride ammonia. the process has now been replaced by one in which ammonium sulphite and ammonia are used. This is carried out by heating 114 parts of β-naphthol with 116 parts of ammonium sulphite, 500 parts of water, and 120 parts of 20 per cent. ammonia in an autoclave at 120–150° C. After cooling, the naphthylamine is filtered off and washed with a little caustic soda. If the process has been carried out at a temperature not exceeding 150° C. the product is practically free from dinaphthylamine, but at higher temperatures this is formed. In this case the crude naphthylamine is dissolved in acid, the dinaphthylamine removed by filtration and the free base then precipitated with soda. M.p. 112° C.; b.p. 294° C.

The sulphite process [20] has the great advantage that less secondary amine is formed, and that the reaction takes place at a much lower temperature, and consequently the pressures attained are not so great. It is reversible and can be used for converting amino groups into hydroxyl groups or *vice versâ*, and also can be employed for making secondary or tertiary aliphatic amines or secondary aromatic amines from phenols or primary amino compounds. It is more applicable to the naphthalene series than to the benzene series, although some benzene derivatives such as resorcinol can be treated by it.

When an aromatic hydroxyl compound is heated with sodium sulphite, an ester of sulphurous acid is formed, but this is so readily hydrolyzed by caustic soda that equilibrium is reached almost at once :

$$\mathrm{ArOH+Na_2SO_3 \rightleftarrows ArOSO_2Na+NaOH}$$

If a bisulphite is used, however, no caustic is liberated, so that the ester is formed :

$$\mathrm{ArOH+NaHSO_3=ArOSO_2Na+H_2O}$$

and this on heating with excess of ammonia gives a primary amine—

$$\mathrm{ArOSO_2Na+NH_3=ArNH_2+NaHSO_3}$$

If instead of sodium bisulphite, ammonium sulphite and excess of ammonia are used, the two steps can be carried out in one operation—

$$\mathrm{ArOH+NH_3=ArNH_2+H_2O}$$

and the same reaction takes place if an organic amine is substituted for the ammonia.

As the formation of primary amine from sulphite ester and ammonia is a reversible one, excess of ammonia must be used. Sulphite esters are also formed when primary amines are heated with excess of bisulphite—

$$\mathrm{ArNH_2+NaHSO_3=ArOSO_2Na+NH_3}$$

If the ester is then boiled with caustic soda hydrolysis takes place and the phenol is obtained, while heating with a primary amine causes formation of a secondary amine—

$$\mathrm{ArOSO_2Na+Ar'NH_2=ArNHAr'+NaHSO_3}$$

This secondary amine is not affected by sulphite, so that the two steps can be carried out in one operation by heating a primary amine, or a mixture of two primary amines, or a primary amine and a phenol with sodium bisulphite.

These reactions are very generally applicable to the naphthols and naphthylamines, but there are certain well defined exceptions of which the following are the most important:—

No α-naphthol derivatives in which a sulphonic acid group is present in the ortho or meta position, *i.e.* at 2 or 3, will react.

No β-naphthol derivative in which a sulphonic acid group is present in the meta position, *i.e.* at 4, will react.

Aliphatic amines behave in the same way as ammonia, but aromatic amines present some exceptions, and α-naphthyl arylamines cannot be obtained by this process.

Thus although a sulphite ester can be very readily obtained from 1-naphthol-4-sulphonic acid or 1-naphthylamine-4-sulphonic acid and will react with ammonia or methylamine, it will not react with aniline or any other aromatic amine. On the other hand, the sulphite esters obtained from β-naphthol or β-naphthylamine derivatives react normally with ammonia or aliphatic or aromatic amines, except when there is a sulphonic group at 4.

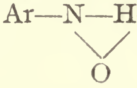
Brönner's Acid [21] (2-naphthylamine-6-sulphonic acid).—This can be obtained by heating the corresponding 2-naphthol-6-sulphonic acid with aqueous ammonia at 180° C. or in the presence of ammonium sulphite at 120° C.

F-Acid [22] (2-naphthylamine-7-sulphonic acid).—Obtained by heating 2-naphthol 7-sulphonic acid with two parts of 20 per cent. ammonia at 250° C. for 6 hours, or at a lower temperature by the sulphite process.

Amino G-Acid [23] (2-naphthylamine 6-8-disulphonic acid).—Obtained by passing ammonia gas over G-salt at 200–250° C. or by the sulphite process.

Amino R-Acid [24] (2-naphthylamine-3-6-disulphonic acid).—Obtained from R-salt by heating in a current of ammonia gas at atmospheric pressure at 200–250° C., or with aqueous ammonia in autoclaves at the same temperature. Better yields are obtained, however, by the sulphite process.

Aminonaphthol-R-Acid [25] (1-2-aminonaphthol-6-sulphonic acid).—This is obtained from β-naphthol-6-sulphonic acid by dissolving in ice-cold dilute hydrochloric acid and then slowly adding a solution of sodium nitrite. The nitrosonaphthol sulphonic acid thus formed is not isolated, the solution being at once reduced with iron. After precipitating the iron with alkali the amino acid is salted out.

When a nitro compound is reduced in alkaline solution the reduction takes a somewhat different course. Under these circumstances the first compound produced is an azoxy compound,  $\mathrm{Ar{-}\underbrace{N{-}H}_{O}{-}Ar}$, which on further reduction passes into an azo compound, $Ar—N=N—Ar$, and finally into a hydrazo compound, $ArNH—NHAr$. Of these the azoxy compounds are of little or no technical value, and the important azo-dyes are invariably prepared by a different method (Part II., Section III.). The hydrazo compounds, however, are of the greatest importance owing to the peculiar rearrangement they undergo under the influence of acids. These cause a molecular rearrangement with the production of a diamino diphenyl derivative.

If both para positions to the hydrazo group are free, a p_2-diaminodiphenyl is produced. If both are occupied an o_2-diaminodiphenyl is obtained; but it is only the para compounds (benzidines) that are of technical importance. Under some conditions the rearrangement does not go so far, an aminodiphenylamine being the product (semidine change); but these are of little value technically, and the manufacturer's object is always to produce the benzidine compound.

The reduction is almost invariably carried out in aqueous alcoholic solution with caustic soda and zinc dust, only a small quantity of caustic being used, as it acts more or less as a catalyst—

$$2ArNO_2+5Zn+H_2O=ArNH-NHAr+5ZnO$$

When the reduction is complete, *i.e.* when the solution has become colourless, the alcohol is blown off with steam and the mass of zinc oxide and hydrozo compound thrown on to a 60-mesh sieve and thoroughly washed with water.

The zinc oxide passes through the screen, but the crystalline hydrazo compound is retained. The rearrangement is carried out at 35° C. by slowly adding hydrochloric acid so that an acid reaction is maintained, and then boiling for a few minutes. The reduction can be brought about without alcohol if a large excess of caustic is used and the agitation is sufficiently vigorous to maintain an emulsion; but the yields are not so good, as aniline is produced simultaneously. Also the reaction is very violent and is easier to keep under control in aqueous alcoholic solution.

The use of iron and caustic soda[26] has been advocated and claims made that excellent yields are obtained, and that the caustic can be recovered as the ferrite produced is decomposed on dilution into ferric oxide and caustic soda, but other investigators assert that the presence of iron, even the walls of iron vessels, greatly enhance the production of aniline.[27] Reduction by electrical means has also been described and with zinc dust at its present high price would probably be economically sound.[28]

Benzidine [29] (*p*-diaminodiphenyl).—Reduction is best carried out in a stoneware or iron vessel (preferably enamelled) provided with an agitator, reflux condenser, and suitable charging holes, and which can be heated or cooled by means of a jacket. The charge is worked as follows:—

The pan is charged with 200 kilos of nitrobenzole, 100 litres of spirit, 200 litres of water, and 600 litres of caustic soda solution of 35 per cent. strength, and the whole brought to the boil. Zinc dust is now fed in slowly so as to keep the charge boiling, the amount required depending on the quality but usually being about 350 kilos. This takes about 3 hours, at the end of which time the charge should be colourless. If not, a little water, and if necessary some more zinc is added. When reduction is complete the alcohol is blown off with steam and recovered, and the charge then run on to a 60-mesh vibrating screen and thoroughly washed in a stream of water. When all the zinc oxide has been washed away the crystalline hydrazo benzene is suspended in twice its weight of water at 35° C. and a slow stream of hydrochloric acid run in so that an acid reaction is maintained. When the acid reaction becomes permanent the whole is heated to boiling, filtered, and the benzidine then precipitated as its insoluble sulphate by adding sulphuric acid. This is filtered off, washed and usually sold in the form of a paste. If desired the free base can be obtained from it by decomposition with caustic soda, and subsequently purified by recrystallization from boiling water, in which it is very sparingly soluble, or by distillation *in vacuo.*

M.p. 127° C.; b.p. 401° C. The free base dissolves in 106 parts of water at 100° C. and in 2447 at 12° C.

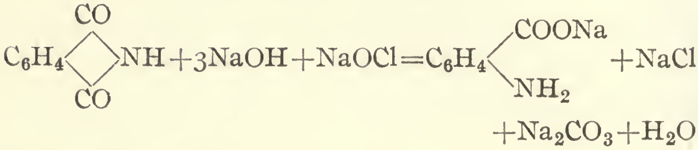
Tolidine (4.4′-diamino-3.3′-dimethyldiphenyl).—This is obtained from *o*-nitrotoluol in exactly the same way as benzidine is obtained from nitrobenzole. M.p. 129° C.

Dianisidine (4.4′-diamino-3.3′-dimethoxydiphenyl).—This is obtained by the alkaline reduction of *o*-nitroanisole and subsequent rearrangement of the hydrazo compound. This nitroanisole is best obtained from *o*-nitrophenol by treatment with dimethyl sulphate. Dianisidine melts at 168–170° C.

The *diarylamines* can be obtained by heating the primary base with its hydrochloride, or by heating a primary aromatic amine, or a mixture of two primary amines, or a mixture of a primary amine and a phenol with a trace of iodine.[30] The diarylamines of the naphthalene series can also be obtained by the sulphite process described on page 37.

Diphenylamine.[31]—This is the only diarylamine that has found extensive application in the manufacture of dyestuffs. It is made by heating 195 kilos of aniline salt with 93 kilos of aniline in an autoclave with enamelled iron liner for 36 hours at 230° C. The melt is then extracted with *dilute* hydrochloric acid to remove aniline, and the residue distilled under reduced pressure. M.p. 54° C.: b.p. 310° C.

Anthranilic Acid[32] (*o*-aminobenzoic acid).—Owing to the importance of this acid for the synthetic production of indigo many methods have been proposed for its manufacture, but the only satisfactory one is by the rearrangement of phthalimide or phthaliminic acid—



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH+3NaOH+NaOCl=C_6H_4\left\langle\begin{matrix}COONa\\NH_2\end{matrix}\right.+NaCl+Na_2CO_3+H_2O$$

In order to obtain good yields the amount of caustic soda used must not be less than that shown by the equation, and the amount of hypochlorite must be exact. The process is carried out as follows :—

Phthalic acid is neutralized with ammonia, the solution evaporated to dryness and the residual ammonium phthalate heated to 225° C. The salt melts and water and ammonia are given off. When no more ammonia is evolved the melt is run into flat trays, allowed to cool, and then broken up and recrystallized from water in order to get rid of unchanged ammonium phthalate. One part of the phthalimide thus obtained, after being finely ground, is added simultaneously with 2 parts of solid caustic soda to 7 parts of water in a jacketed agitator pan, water being run through the jacket to prevent any undue rise in temperature. After cooling 10 parts of sodium hypochlorite solution (electrobleach), containing exactly 5·06 per cent. of NaOCl, are added, when the temperature rises automatically to 50–60°. To complete the change the solution is heated to 80° C. for half an hour and then cooled and free alkali neutralized with hydrochloric or sulphuric acid. On adding excess of acetic acid the majority of the anthranilic acid is precipitated. It is filtered off and what remains in solution thrown down as the difficultly soluble copper salt. M.p. 145° C.

α-Aminoanthraquinone.[33]—This can be obtained by heating potassium anthraquinone-α-sulphonate with ammonia under pressure, but is more readily obtained by adding α-nitroanthraquinone to a boiling solution of two parts of sodium sulphide. The amino compound separates out as a dark red powder which after filtering from the red or purple-coloured liquor and washing is almost pure. M.p. 243° C.

The 1-5- and 1-8-diamino compounds are obtained in the same way from the corresponding compounds, but are better obtained from the corresponding disulphonic acids by heating with ammonia.

β-Aminoanthraquinone.[34]—This is obtained by heating sodium anthraquinone–β-sulphonate (silver salt) with ammonia, but poor yields are obtained unless some substance is added to destroy the sulphite formed. This can be done by the addition of barium chloride, but better results are obtained by adding a suitable oxidizing agent such as manganese dioxide (Weldon mud) or sodium dichromate. Almost theoretical yields are obtained by heating 125 parts of silver salt, 156 parts of manganese dioxide (80 per cent. MnO_2), 130 parts of water, and 580 parts of 25 per cent. ammonia at 200° C. for six hours. After cooling, the product is freed from manganese by treatment with sulphurous acid. M.p. 302° C.

2-6- and 2-7-diaminoanthraquinone are obtained in the same way from the corresponding disulphonic acids.

REFERENCES AND LITERATURE.

[1] D.R.P. 116,942; 117,007; 127,815; 130,742; 131,404.
[2] D.R.P. 114,809.
[3] D.R.P. 139,457.
[4] D.R.P. 39,947; 87,615; 71,976.
[5] D.R.P. 67,018.
[6] *Ch. Ztg.*, **37**, 229.
[7] D.R.P. 148,749.
[8] D.R.P. 75,854; E.P. 1028^{16}, 1034^{16}.
[9] D.R.P. 212,506.
[10] *Ch. Ztg.*, **34**, 641, 667, 681, 690.
[11] *Rev. prod. Chim.*, 1917, 20, 68.
[12] D.R.P. 250,236.
[13] D.R.P. 95,755.
[14] *Bl.* [3], **11**, 1043, *Z. ang.*, 1897, 172. *B.*, **15**, 3037; **39**, 3495. D.R.P. 82,426; 95,755.
[15] Elbs, "Electrolytic Preparations," p. 80.
[16] D.R.P. 96,853.
[17] *B.*, **22**, 3239.
[18] D.R.P. 106,961; E.P. 5351^{97}.
[19] D.R.P. 117,471.

[20] *J. pr.* [2], **69,** 49; **70,** 345; **71,** 433; **75,** 249; **77,** 403; **79,** 369; **80,** 201. D.R.P. 109,102; 114,974; 115,335; 117,471; 121,683; 122,570; 126,136.

[21] D.R.P. 22,547.

[22] D.R.P. 43,740.

[23] D.R.P. 27,370.

[24] D.R.P. 27,370.

[25] *Soc.*, **39,** 47.

[26] D.R.P. 138,496.

[27] *Z. ang.*, 1893, 163.

[28] *Z. ph. ch.*, **34,** 660. *B.*, **33,** 2329. D.R.P. 116,474; 122,046.

[29] *Z. ang.*, 1893, 67, 163. *B.*, **33,** 2329. D.R.P. 116,474; 122,046; 172,569. F.P. 458,033.

[30] D.R.P. 241,853.

[31] *Z.*, 1886, 235.

[32] D.R.P. 55,988.

[33] D.R.P. 175,024; 181,722.

[34] *B.*, **12,** 1567. D.R.P. 256,515; 267,212.

The electrolytic reduction of nitro compounds is discussed by Brand in "Elektrochemische Reduktion organischen Nitroköpfer," 1908.

SECTION III.—SULPHONATION

THE general method of introducing the sulphonic acid group into an aromatic nucleus is treatment with concentrated sulphuric acid or oleum. Isomers are frequently formed and are often only separated with difficulty.

In the benzene series the entering group takes the ortho and para position to alkyl or hydroxyl groups or halogen atoms, and the meta position to nitro groups. Amino groups direct strongly to the para position.

In the naphthalene series the matter is much more complicated and the position of the entering group depends very largely on the conditions under which sulphonation is carried out. At a low temperature the α-position is occupied, whereas at higher temperatures it is the β-position that is taken, and α-naphthalene sulphonic acids usually pass into the corresponding β-isomers on heating alone or with a neutral solvent. The sulphonation of naphthols and naphthylamines is even more complicated.

In some cases the orientation of the entering groups is influenced by catalysts, anthraquinone giving α-sulphonic acids when sulphonated in the presence of mercury salts, but β-acids when no catalyst is present.

Sulphonation is carried out in cast-iron kettles very similar to those used for nitration. When temperatures not above 150° C. are used, heat may be applied by lead or steel coils or by a steam jacket. Higher temperatures call for the use of direct fire or an oil bath, or the sulphonator may be cast with channels in the walls and superheated water or vitriol circulated in these. Vitriol is also employed as a heating and cooling medium when coils are used and has much to recommend it, as should a coil burst less damage is done, but its high viscosity and low specific heat are disadvantages.

In many cases when volatile compounds are to be sulphonated, the sulphonation is carried out in closed vessels (autoclaves) under pressure in order to maintain a sufficient temperature to allow sulphonation to be completed without use of excessive amounts of acid. These should never be heated by steam coils, as should one burst the steam blowing into the hot acid may cause such pressure that the autoclave explodes. Direct fire or vitriol are the best means of heating under these circumstances, but a water or brine bath can be used when temperatures of about 100° C. only are required.

When sulphonation is complete, the contents of the kettle are run out from a bottom cock where this is provided, or alternatively are blown out by compressed air when it is not, the charge drowned in water or crushed ice contained in large vats constructed of oak or pitchpine which may or may not be lead lined. If the sulphonic acid is insoluble in acid it is then merely necessary to filter it off. If soluble it is either salted out by the addition of common salt or the solution is neutralized with milk of lime, the precipitated gypsum filtered off and well washed, and the solution of the calcium salt then treated with an equivalent of sodium carbonate. This precipitates the calcium as carbonate, and after this has been removed by filtration the liquor is concentrated until the sodium salt of the sulphonic acid crystallizes.

It does not pay to substitute chalk for the rather more expensive lime, as the resulting frothing is very troublesome. As sulphonation always takes place with the formation of water the sulphonating acid becomes more and more dilute as the reaction proceeds, until finally such a point is reached that it no longer acts. To remedy this either a very large excess of acid must be employed or oleum is substituted for the ordinary acid. If too strong an acid is used, polysulphonic acids may result; but this can be prevented either by keeping the temperature down at first and only raising it when the acid has become diluted by the water formed, or what is better, by starting with an acid of moderate concentration and adding oleum slowly so as to maintain its strength.

In the case of benzole it has been proposed to carry on the sulphonation by forcing benzole vapour generated in a separate boiler through sulphuric acid maintained at such a temperature that the water formed is driven off as steam.[1] This, together with unchanged benzole, is condensed, separated, and the benzole returned to the boiler. Great economies in acid are said to be effected, but the process is a comparatively new one and no data are yet available as to its utility on a large scale. Chlorsulphonic acid is also in some cases used for sulphonating, and usually leads to sulphochlorides, $ArSO_2Cl$. It has also been proposed to carry out sulphonations at the ordinary temperature by the addition of infusorial earth, and most interesting results have been obtained by this method.[2] Lambert has carried out a great deal of work on sulphonation by polysulphates, and has found that a polysulphate of the formula $NaH_3(SO_4)_2$ is an excellent sulphonating agent.[3]

Sulphonation of quinonoid or nitro compounds can also be brought about by treatment with sulphites in aqueous solution. In quinonoid compounds the sulphonation takes place by addition, and in nitro compounds with the reduction or elimination of a nitro group. Nitrobenzole cannot be sulphonated by this method, as it gives a sulphaminic acid $ArNHSO_3H$, but *m*-dinitrobenzole readily gives *m*-nitraniline sulphonic acid, and nitrotoluols behave in much the same way, although the yields are not so good. α-Nitronaphthalene gives 1-naphthylamine-2.4-disulphonic acid, but α-nitroanthraquinone gives anthraquinone α-sulphonic acid, the nitro group being eliminated.

Sulphites occasionally replace halogen atoms, as in *o*-chlorbenzaldehyde, but the reaction is of no technical importance.

Benzene Series.

Benzene Sulphonic Acid.—The sulphonation can be carried out with R.O.V. in open vessels provided with a reflux condenser, but under these circumstances a very great excess of acid must be used. More satisfactory results are obtained by sulphonating in closed autoclaves, *e.g.* by heating benzole with 5 times its weight of R.O.V. to 100° C. for about two days. The usual modern process, however, involves the use of oleum, the benzole being slowly added to about 4 times its weight of fuming acid containing 8 per cent. of free anhydride. A great deal of heat is evolved, and at first the temperature should not be allowed to exceed 30° C. After the acid has become somewhat diluted the temperature is raised to 50° C. and maintained at this point until sulphonation is complete, *i.e.* until the whole of the benzole is dissolved. A stronger oleum can be used, but if this is done there is danger of formation of disulphonic acid and sulphone, $Ph-SO_2-Ph$. When sulphonation is complete the charge is usually run into water and limed out, but the acid can be salted out. The optimum conditions for salting out are to run 5 volumes of the charge into 9 volumes of brine.[4] The free acid is not prepared commercially, as it is troublesome to isolate, and the sodium salt is more suited for phenol manufacture.

Benzene Disulphonic Acid.—More vigorous sulphonation of benzole leads to a mixture of meta and para disulphonic acids, low temperature favouring the formation of the former, and high temperature and prolonged cooking favouring the latter. The presence of mercury salts also favours the formation of the para acid. Technically no attempt is made to separate the acids, as they both pass into resorcinol on fusion with caustic.

The sulphonation is carried out with 8–10 per cent. oleum exactly as in the case of the mono acid, but the solution of the benzole is completed by slowly raising the temperature to 100° C. After solution is complete the charge is cooked for two hours at 275° C., cooled, run into water, and limed out. A lower temperature, viz. 225° C., suffices if anhydrous sodium sulphate is added to the acid in the proportion of 1·1 parts of sulphate to 1 part of benzole.

As is the case with the mono acid, only the sodium salt is prepared.

Toluol Sulphonic Acids.—Toluol on sulphonation gives a mixture of all three sulphonic acids, of which the meta derivative is present only in very small quantities and is of no technical value.

Sulphonation with sulphuric acid or oleum leads to about 60 per cent. of para acid, the sulphonation being carried out by heating to 100° C. with 6 parts of R.O.V. A better procedure, however, is to add simultaneously 184 kilos of toluol and 240 kilos of 25 per cent. oleum to 400 kilos of R.O.V., the temperature being maintained at 14–16° C. If, on the other hand, the sulphonation is carried out with chlorsulphonic acid,[5] the ortho acid predominates, about 60 per cent. being formed. By employing sufficient chlorsulphonic acid the sulphochlorides are obtained direct and can be readily separated. This is the process usually employed in saccharine works, and is carried out by adding toluol slowly to 4 parts of chlorsulphonic acid, the temperature being kept below 5° C. After the whole of the toluol has been added the melt is stirred for 12 hours, run on to ice, and the sulphochlorides then collected.

Several methods have been proposed for separating the isomers, of which the following are the most important :—

(*a*) Separation by sulphuric acid. This separation is based on the fact that whereas the ortho acid is easily soluble in sulphuric acid of 65–70 per cent. strength, the para acid is difficultly soluble. On the other hand, the ortho acid is almost insoluble in sulphuric acid of 45–50 per cent. strength at low temperatures. The separation can be carried out by treating the mixed sodium salts with 4 parts of 66 per cent. sulphuric acid,[6] but is best combined with the sulphonation process. If this is carried out with oleum, as described above, and then 140 kilos of water or ice added slowly so that the temperature does not rise above 20° C., about 95 per cent. of the para acid separates in the pure state. By adding another 5 kilos of water and cooling to 10° C. a further small crop can be obtained consisting chiefly of the para acid, but contaminated with ortho. The filtrate is then diluted with 145 kilos of water and maintained at —5° C. for two days, when the whole of the ortho acid separates out pure. The mother liquor from this is sulphuric acid of 45 per cent. strength, and can be concentrated or used for sulphate of ammonia or other purpose. The crystals of sulphonic acid which separate contain sulphuric acid of crystallization, and have the formula $2C_7H_7SO_3H+H_2SO_4+H_2O$. They are dissolved in water and the solution limed out in the usual way.

(*b*) Separation of the sulphochlorides. These are either obtained by the direct method, *i.e.* by sulphonating with excess of chlorsulphonic acid, or by treating the mixed sodium salts with phosphorus trichloride or the magnesium salts with chlorsulphonic acid.[7] On cooling, the mixed chlorides to —20° the para isomer (m.p. 69° C.) separates out.

Other methods of separation, such as fractional crystallization of the salts and fractional precipitation of the sulphamides have been proposed, but are not in general use.

Sulphanilic Acid (*p*-aminobenzenesulphonic acid).—As the free acid is almost insoluble in cold water its isolation is very easy.

The sulphonation can be carried out by two methods, that employing excess of sulphuric acid being the least economical, but being still used in some of the smaller works whose output is not sufficient to justify expenditure on the special plant required by the baking process. In this case the aniline is added to twice its weight of vitriol and the charge then cooked at 180–190° until a sample is completely soluble in dilute caustic.

A more economical process consists in first converting the aniline into its acid sulphate. This can be done by adding the aniline slowly to the calculated amount of strong vitriol (100 parts of aniline require about 115 parts of R.O.V.), which must be done slowly as much heat is evolved, or the aniline can be dissolved in a more dilute acid and the solution then taken to dryness. The aniline sulphate thus obtained is then converted into sulphanilic acid by roasting for some hours at 210° C. The roasting can be carried out by spreading the sulphate on shallow iron trays in a suitable stove, but it is much better to use a revolving furnace. In either case sand is sometimes mixed with the sulphate to assist the penetration of the heat. The temperature should not be raised too quickly or the product will be of bad colour. If 4 hours is taken to reach 210° C., the sulphonation will usually be complete after a further 6 hours at this temperature; but the course of the reaction can be followed by periodically testing a sample with dilute alkali, or by observing the water which distils off. When sulphonation is complete the melt is cooled, broken up, and well washed with water. For most purposes the acid thus obtained is sufficiently pure but a better coloured product is obtained if it is dissolved in alkali and reprecipitated with acid, or is simply recrystallized. This treatment is, of course, necessary if sand has been added to the melt.

Metanilic Acid (*m*-aminobenzene sulphonic acid).—This acid cannot be obtained by sulphonating aniline. It is manufactured by sulphonating nitrobenzole, the *m*-nitrobenzole sulphonic acid thus formed being reduced without being isolated.

The sulphonation is carried out by adding 1 part of nitrobenzole to 4 parts of oleum containing 20 per cent. of anhydride. Very little heat is evolved and sulphonation is completed by heating to 80° C. until a sample is completely soluble in water. The melt is then cooled, poured into water (10 parts) and reduced by iron turnings ($1\frac{1}{2}$ parts). When reduction is complete, the iron and sulphuric acid are thrown down by lime and the solution of the lime salt converted into sodium salt in the usual way.

If desired the *m*-nitrobenzene sulphonic acid can be easily isolated by salting out, but it has no value except for making metanilic acid.

***p*-Nitrotoluol Sulphonic Acid** (1-2-4).—Sulphonation is carried out at 25–30° C. with 3 parts of 23 per cent. oleum, until a sample is completely soluble in water. On running the melt into 15 parts of brine the acid separates.

m-**Nitraniline-4-Sulphonic Acid.**—This is obtained by treating *m*-dinitrobenzole with sodium sulphite solution, when simultaneous reduction and sulphonation takes place.[8] The process is carried out by adding *m*-dinitrobenzole slowly to a warm 20 per cent. solution of sodium sulphite. As soon as the *m*-dinitrobenzole melts a brisk reaction sets in and a clear solution is obtained from which the sulphonic acid is precipitated on acidifying.

Phenylenediamine Sulphonic Acid.—*m*-Phenylene diamine-4-6-disulphonic acid is obtained by sulphonating *m*-phenylene diamine with oleum.[9]

p-Phenylene diamine sulphonic acid is obtained from *p*-phenylene diamine by oxidizing it to the quinone imide by bichromate and then treating this with bisulphite—

$$HN{=}C_6H_4{=}NH+NaHSO_3=NH_2C_6H_3\left\langle\begin{matrix}SO_3Na\\NH_2\end{matrix}\right.$$

It is not necessary to isolate the quinone imide, the process being best carried out by oxidizing the diamine in the presence of sodium bisulphite.

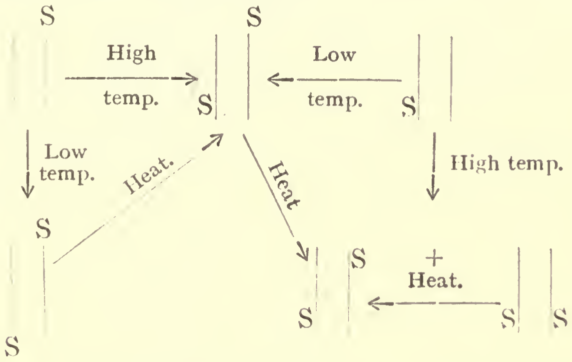
p-**Aminophenol Sulphonic Acid** is obtained in a very similar way by passing sulphur dioxide into a warm suspension of 6·3 kilos of nitrosophenol in 50 litres of water. After complete solution has taken place the whole is boiled, and on subsequent cooling the aminophenol sulphonic acid separates out. Some disulphonic acid can be obtained from the mother liquors.

NAPHTHALENE SULPHONIC ACIDS.

Owing to the enormous number of naphthalene, naphthol, naphthylamine, and aminonaphthol sulphonic acids that are of technical importance, no attempt can be made to treat them in detail. The manufacture of the more important ones will be described, but for the majority the reader must be referred to the literature (see pages 54, 55, 56).

When naphthalene itself is sulphonated the sulphonic group enters the α-position at low temperatures and the β-position at high temperatures, and if the α-acid is heated with sulphuric acid the sulphonic acid group wanders to the β-position.

These two acids on further sulphonation give a variety of disulphonic acids according to the conditions under which the sulphonation is carried out, the second group again entering the α-position at low temperatures and the β-position at high temperatures.



α-Naphthol on sulphonation gives a mixture of 1-2- and 1-4-naphthol sulphonic acid, both of which on further sulphonation pass into 1-naphthol-2-4-disulphonic acid. The α-naphthol sulphonic acids, however, are not usually made by the sulphonation of α-naphthol.

β-Naphthol when sulphonated at a low temperature yields 2-naphthol-1-sulphonic acid which is converted by excess of sulphuric acid into a mixture of 2-naphthol-6-sulphonic acid (Schäffer's acid) and 2-naphthol-8-sulphonic acid (Bayer's or Crocein acid). The relative amounts of these isomers depends on the conditions. Excess of sulphuric acid, prolonged heating, and a high temperature all favouring the formation of Schäffer's acid.

More exhaustive sulphonation leads to 2-naphthol-3-6-disulphonic acid (R-acid) and 2-naphthol-6-8-disulphonic acid (G acid).

The products obtained by sulphonating α-naphthylamine depend very much on the conditions. By roasting the sulphate, the 1-4 acid (naphthionic acid) is obtained, which prolonged heating with sulphuric acid converts into the 1-5 acid (Laurent's acid) and the 1-6 acid (Cleve's β- acid). Laurent's acid, however, is best obtained by sulphonating α-naphthylamine hydrochloride.

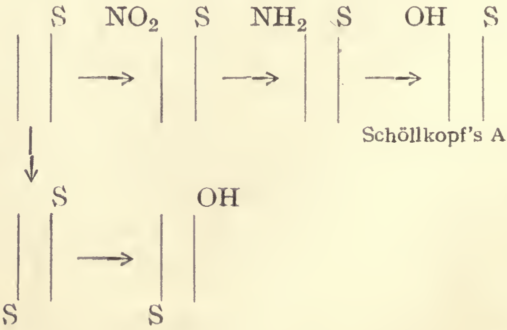
Another rearrangement takes place when sodium naphthionate is heated with naphthalene, the 1-2 acid being produced.

If α-naphthylamine is first converted into acet-α-naphthalide and then sulphonated, 1-naphthylamine-5-sulphonic acid is obtained.

β-Naphthylamine on sulphonation yields four monosulphonic acids, viz. 2-8, 2-5, 2-6, and 2-7-naphthylamine sulphonic acid. The relative proportion in which these acids are formed depends on the conditions as regards time, temperature, and concentration, but the most important of them, viz. the 2-6 acid (Brönner's acid) and the 2-7 acid (amino F acid), are best obtained from the corresponding naphthol acids by heating with ammonia.

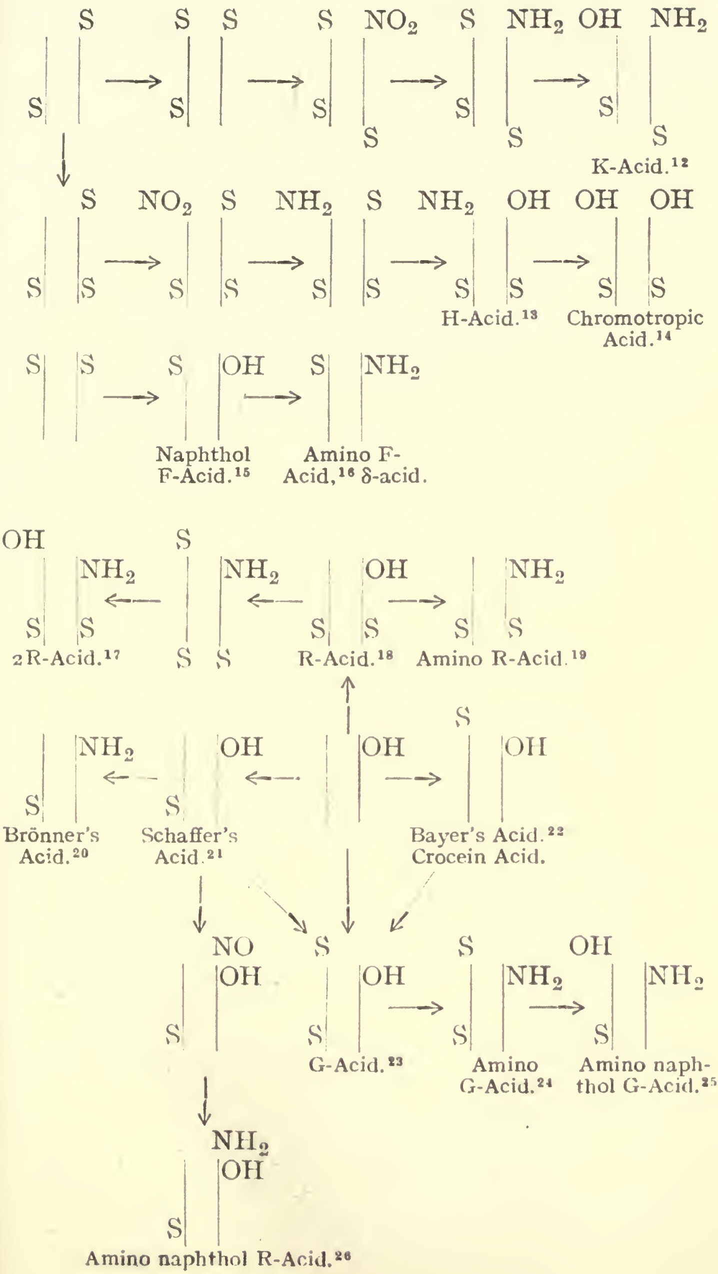
Finally, if acet-β-naphthalide is sulphonated the sulphonic acid group enters at 5 and 7, the most important product being the 5-7 disulphonic acid, which on fusion with caustic gives J-acid.

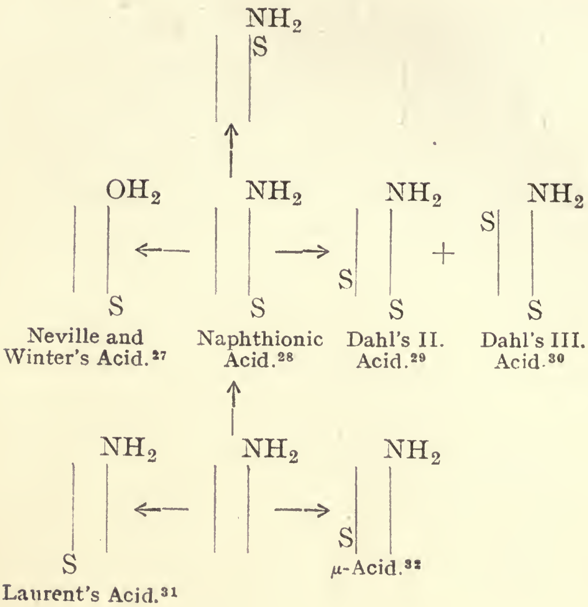
The following scheme indicates the method of formation of the chief technically important naphthol, naphthylamine and amino naphthol sulphonic acids together with their technical names :—

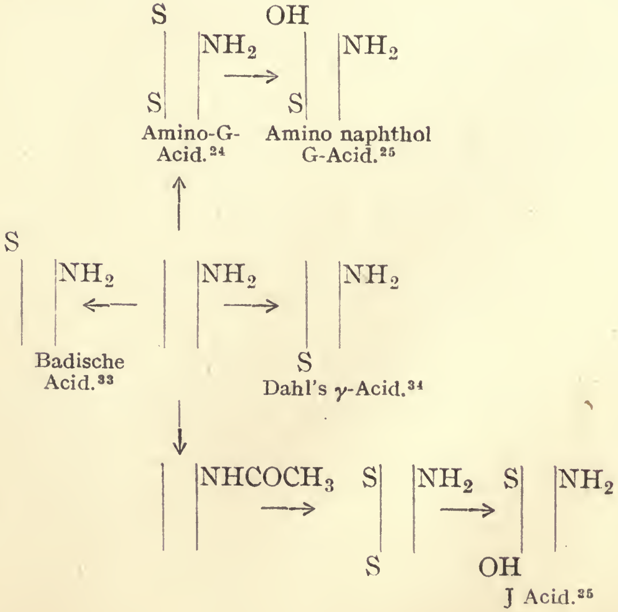


Schöllkopf's Acid.[10]

L-Acid.[11]


K-Acid.12
H-Acid.13
Chromotropic Acid.14
Naphthol F-Acid.15
Amino F-Acid,16 δ-acid.
2R-Acid.17
R-Acid.18
Amino R-Acid.19
Brönner's Acid.20
Schaffer's Acid.21
Bayer's Acid.22
Crocein Acid.
G-Acid.23
Amino G-Acid.24
Amino naphthol G-Acid.25
Amino naphthol R-Acid.26


NH$_2$
S
OH$_2$
NH$_2$
NH$_2$
NH$_2$
S
S
S
S
S
S
+
Neville and Winter's Acid.[27]
Naphthionic Acid.[28]
Dahl's II. Acid.[29]
Dahl's III. Acid.[30]
NH$_2$
NH$_2$
NH$_2$
S
S
Laurent's Acid.[31]
μ-Acid.[32]


S
OH
NH$_2$
NH$_2$
S
S
Amino-G-Acid.[24]
Amino naphthol G-Acid.[25]
S
NH$_2$
NH$_2$
NH$_2$
Badische Acid.[33]
S
Dahl's γ-Acid.[34]
NHCOCH$_3$
S
NH$_2$
S
NH$_2$
S
OH
J Acid.[25]

Naphthalene-α-Sulphonic Acid.—This acid can only be obtained when the sulphonation is carried out at a low temperature, as above 80° C. the β- acid is formed. The sulphonation can be carried out by heating 4 parts of naphthalene with 3 parts of R.O.V. for 8–10 hours at 80° C.; but not more than half the naphthalene is attacked by this method, and more satisfactory results are obtained by employing a lower temperature so that the naphthalene remains solid.[36] This process is worked as follows:—

One hundred kilos of naphthalene is shaken through a ½-mm. mesh sieve into 200 kilos of R.O.V., and the whole maintained at 40–60° C. for several hours until the whole of the naphthalene has disappeared. Naphthalene-α-sulphonic acid is formed, and as it is insoluble in acid of medium strength it separates out, and although its melting-point when pure is 80–85° C. the crude acid remains liquid even at 40° C. in absence of the solid phase.

It is very important to clean the sulphonator thoroughly between each charge, as if any solid sulphonic acid is left it will cause the next charge to crystallize. When sulphonation is complete, the lower layer of sulphuric acid is run off and the upper layer of liquid naphthalene sulphonic acid dissolved in water, filtered from unchanged naphthalene, and then limed out in the ordinary way. The process can be made a semi-continuous one as follows: Sulphonation is carried on for a few hours, and then the spent sulphuric acid (bottom layer) and crude sulphonic acid (middle layer) drawn off, the top layer of unchanged naphthalene floating in sulphonic acid being left in the sulphonator. To this is added more vitriol and more naphthalene, and the cycle again repeated.

Some β- acid is always formed simultaneously, but separation is easy by means of the lime salts, the salt of the α- acid being soluble in 16 parts of water and that of the β- acid only in 76 parts.

Naphthalene-β-Sulphonic.—Sulphonation is carried on with equal weights of naphthalene and R.O.V., the temperature scheme being as follows:—

Hour 1–3	..	Raised gradually to 160° C.
,, 3–6	..	Maintained at 160° C.
,, 7	..	Raised from 160–170° C.
,, 8	..	Maintained at 170° C.
,, 9	..	Raised from 170–180 C.
,, 10	..	Maintained at 180° C.

Total time 10 hrs.

During the last part of the cooking water and naphthalene distil off. When sulphonation is finished the melt is cooled, and then either run into salt solution or it is run into water and limed out in the ordinary way.

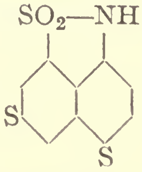
Naphthalene-1-5-disulphonic Acid.[37]—This is obtained when naphthalene is dissolved in 5 parts of 23 per cent. oleum, the temperature being kept at about 10° C., or by adding 1 part of sodium naphthalene-α-sulphonate to 2 parts of oleum at 20° C. and then heating for an hour at 70° C. After dilution the acid is salted out.

Naphthalene-1-6-disulphonic Acid.[38]—By the sulphonation of sodium naphthalene-β-sulphonate with 2 parts of oleum at 100° C., or with 5 parts of R.O.V. at 110° C.

Naphthalene-2-6- and 2-7-disulphonic Acids.[39]—These are both obtained when sodium naphthalene-β-sulphonate is treated with sulphuric acid at 170–180° C. and can be separated by means of their calcium salts. The 2–7 acid, however, is almost the sole product when the sulphonation is carried out in the presence of pyrosulphate.

Naphthalene-1-3-6-trisulphonic Acid.—By sulphonating with 8 parts of 24 per cent. oleum at 180° C., or with 6 parts of 40 per cent. oleum at 80° C. On nitration it gives 1-nitronaphthalene-3-6-8-trisulphonic acid. The nitration is carried out at 30° C. by adding a slight excess of nitric acid dissolved in concentrated sulphuric acid. The nitro acid is not isolated, the charge being run into water and then reduced to the *amino acid* with iron turnings. This latter is then isolated by liming out.

Naphthalene-1-3-5-trisulphonic Acid.—This is obtained from the 1-5-disulphonic acid by dissolving 2 parts of the sodium salt in 3 parts of monohydrate at 40° C. and then adding 2½ parts of 70 per cent. oleum. The melt is heated at 80–90° until a sample dissolved in water no longer gives a precipitate with brine. On nitration it gives 1-nitronaphthalene-4-6-8-trisulphonic acid. The nitration is brought about by cooling the melt to 20° C. and at this temperature slowly adding the calculated amount of nitric acid dissolved in twice its weight of R.O.V. The nitro acid is not usually isolated, the melt being run into water and then reduced by adding iron turnings. The *amino acid* readily passes into the sultam—



Naphthalene-1-3-7-trisulphonic Acid.—The sodium salt of the 3-7-disulphonic acid is dissolved in 3 parts of monohydrate and 1 part of 60 per cent. oleum added. The melt is cooked at 100° C. until a sample gives no precipitate with brine. The acid is not isolated but nitrated by cooling the melt to 15–20° C. and then adding slowly the calculated amount of nitric acid. The nitro acid obtained is nitronaphthalene-3-5-7-trisulphonic acid. On reduction with iron it gives the corresponding *amino acid*.

Bayer's or Crocein Acid (2-naphthol-8-sulphonic acid). —This is obtained by the sulphonation of β-naphthol, whereby 2-naphthol-1-sulphonic acid is first formed but passes very readily into the 2-8- acid (Bayer's or Crocein acid) and the 2-6- acid (Schäffer's acid). Working details depend on whether it is desired to make Schäffer's acid as well as Bayer's acid or only the latter. If Bayer's acid only is desired the process is carried out as follows [40] :—

Ten kilos of β-naphthol are slowly added to 20 kilos of R.O.V., great care being taken to prevent any rise of temperature taking place above 20° C. The naphthol dissolves, but after a short time heat is evolved and the whole sets to a pasty mass owing to separation of 2-naphthol-1-sulphonic acid. Any tendency to heat up must be most carefully checked, as otherwise Schäffer's acid will be formed. The whole is then allowed to stand for about a week with frequent agitation while the transformation is taking place. The course of the reaction is followed by boiling a sample for some time with its own volume of water. As long as any 2-naphthol-1-sulphonic acid is present β-naphthol will be precipitated. When this is no longer the case the melt, which has become thinner, is run into water and limed out. If it is desired to obtain the acid completely free from Schäffer's acid, this is best done through the lead salts.

Schäffer's Acid [41] (2-naphthol-6-sulphonic acid).—This is obtained together with Bayer's acid by the sulphonation of β-naphthol with 2 parts of R.O.V. at 50–60° C. The melt is limed out in the ordinary way and the sodium salts obtained. These are treated with sufficient caustic soda to allow of salt formation taking place with the hydroxyl group and the disodium salts carefully dried and extracted with 4 parts of boiling 90 per cent. spirit. Bayer's salt dissolves, but Schäffer's salt remains insoluble.

Separation can also be brought about by fractional crystallization of the sodium, potassium, or calcium salts.

G-Acid [23] (2-naphthol-6-8-disulphonic acid).—By the sulphonation of β-naphthol with 4–5 parts of R.O.V. at 60° C. for 36–48 hours, or at 20° C. for 8 days. It is always accompanied by some R-acid and Bayer's acid, and can be purified through its sodium, potassium, or barium salt, or the impurities can be thrown out by fractional precipitation with a diazo chloride.

R-Acid [18] (2-naphthol-3-6-disulphonic acid).—The sulphonation is best carried out by adding β-naphthol quickly to 4 parts of R.O.V. previously heated to 125° C. and then cooking the charge for 6 hours at this temperature. It is separated from the G-acid formed simultaneously by salting out with brine, when R-salt is thrown down and G-acid remains in solution, or by extracting the sodium salts with 3–4 parts of 80 per cent. spirit in which G-salt is soluble but R-salt insoluble.

Naphthionic Acid[28] (1-naphthylamine-4-sulphonic acid).—This is a most important intermediate, and is best made by roasting the acid sulphate of α-naphthylamine (*cf.* sulphanilic acid, p. 50). The best results are obtained when about 5 per cent. of oxalic acid is added. The process is carried out as follows :—

Fifty kilos of α-naphthylamine are melted at about 60° C. and run in a thin stream into 36½ kilos of R.O.V., the whole being very vigorously agitated. The temperature is then raised to 180° C. and the charge stirred until a thoroughly homogeneous mass is obtained. The oxalic acid (2–3 kilos) is then added and very thoroughly mixed in. Considerable frothing takes place, and allowance must be made for this when designing plant. The liquid mass is then run into trays and stoved at 180° C. for 10 hours. During the stoving it gradually goes solid, and after cooling is broken up and boiled with sufficient milk of lime to give a neutral solution. After filtering the acid is precipitated by addition of hydrochloric acid. It is almost insoluble in cold water (1 : 4000).

1-Naphthylamine-2-Sulphonic Acid.[42]—This is obtained through a curious rearrangement undergone by sodium naphthionate when heated with neutral solvents of high boiling-point, of which naphthalene is the best. The change is brought about by boiling sodium naphthionate with 3 parts of naphthalene under a reflux condenser for 3 hours. The naphthalene is then blown off by steam and the resulting aqueous solution, which is always slightly acid, neutralized with soda and filtered. The sodium salt of the sulphonic acid is then salted out with common salt. The free acid is soluble in 225 parts of cold water.

Laurent's Acid[31] (1-naphthylamine-5-sulphonic acid).—This is formed by sulphonating *a*-naphthylamine hydrochloride with oleum, and it is probably the chlorsulphonic acid formed which attacks the nucleus. The sulphonation is carried out by adding naphthylamine hydrochloride to twice its weight of 25 per cent. oleum at 5° C. The charge is then poured on to ice, and the acid collected and limed out. It is soluble in 1000 parts of cold water. It can also be obtained by sulphonating α-nitronaphthalene with chlorsulphonic acid and then reducing the nitro group.

μ-Acid or Cleve's β-Acid[32] (1-naphthylamine-6-sulphonic acid).—α-Naphthylamine is sulphonated with 5 parts of R.O.V. at 125° C. for 22 hours. After liming out the calcium salts are taken to dryness and 1-5-acid extracted with boiling alcohol and then disulphonic acids with methyl alcohol. The free acid is soluble in 1000 parts of cold water.

Dahl's No. III. Acid[30] **and Dahl's No. II. Acid**[29] (1-naphthylamine-4-7- and 4-6-disulphonic acids).—These are obtained simultaneously when naphthionic acid is sulphonated, the product consisting of about two parts of No. III. and one part of No. II. The sulphonation is carried out with 3½ parts of 25 per cent. oleum and requires about 3 days. Sulphonation is complete when 5 or 6 drops of the melt in 10 c.c. of water gives no precipitate on standing for a few minutes. The whole is then limed out and the calcium salts taken to dryness and extracted with 85 per cent. spirit, when No. II. salt dissolves and No. III. is left.

Badische Acid[33] (2-naphthylamine-8-sulphonic acid).—This is the chief product when β-naphthylamine is sulphonated. The sulphonation is best carried out by heating 200 lbs. of β-naphthylamine with 600 lbs. of R.O.V. for 6 hours at 100–110° C. After cooling the melt is run into 250 gallons of water and the crude acid filtered off and converted into the sodium salt. Impurities are then extracted by 6 parts of spirit.

2-Naphthylamine-5-7-disulphonic Acid.[43]—This is important as an intermediate product in the manufacture of J-acid, and is obtained by sulphonating acet-β-naphthylamine and then splitting off the acetyl group. The sulphonation is best carried out by adding 1 part of α-acetnaphthalide to 5 parts of 35 per cent. oleum, and at 5° C., and allowing the mixture to stand at 25–30° C. for 24 hours. A purer product is, however, obtained if 1-naphthylamine-

5-sulphonic acid is converted into its acetyl derivative and this then sulphonated. The process is then carried out as follows: Five kilos. of 1-naphthylamine-5-sulphonic acid is boiled with 3 kilos. of anhydrous sodium acetate, 5 kilos. of acetic anhydride and 30 kilos. of glacial acetic acid until fully acetylated, *i.e.* until a sample is no longer diazotizable. This takes about eight hours. The acetic acid, etc., is then distilled off and the product dissolved in water and salted out with Glauber salts. The sulphonation is brought about by adding to 40 kilos. of 30 per cent. oleum at 0–5° C. and then allowing to stand for 12–15 hours at 15–20° C. The melt is then run on to 80 kilos. of ice, and boiled for half an hour to split off the acetyl group. The acid separates out on cooling.

Amino G-Acid (2-naphthylamine-6-8-disulphonic acid).—This is usually obtained from the corresponding naphthol sulphonic acid (G-acid) by the action of ammonia, but can also be made by sulphonating β-naphthylamine with 4 parts of 25 per cent. oleum at 130° C.

ANTHRAQUINONE SERIES.

Anthraquinone is not easily attacked by sulphuric acid, and the production of its sulphonic acids usually requires the use of oleum and a high temperature. At the same time oxidation takes place with the production of oxy-anthraquinones as bye-products.

Normally the sulphonic acid groups enter the β-positions, but in the presence of mercury salts α-sulphonic acids are almost exclusively produced.

Anthraquinone-α-sulphonic Acid.[44]—One hundred pounds of anthraquinone are intimately mixed with a pound of mercury sulphate, and then added to 120 lbs. of 20 per cent. oleum and the charge cooked for 1 hour at 150° C. The melt is then run into 100 gals. of boiling water, unchanged anthraquinone removed by filtration and the acid then salted out as its potassium salt.

Anthraquinone-1-5- and 1-8-disulphonic Acids.[44]—

One hundred pounds of anthraquinone and 1 lb. of mercury sulphate are heated at 160° C. with 200 lbs. of 45 per cent. oleum until a sample is completely soluble in water. After cooling the melt is diluted with 200 lbs. of R.O.V. and the 1-5- acid, which is insoluble in sulphuric acid, filtered off and well washed with R.O.V. The united filtrates on dilution with half their weight of water deposit the 1-8-acid. Both acids are purified by dissolving in water and salting out with potassium chloride.

Anthraquinone-β-Sulphonic Acid.[45]—The sulphonation is carried out by heating anthraquinone with its own weight of 45 per cent. oleum, and slowly raising the temperature to 160° C. Without cooling the melt is then run into boiling water and unchanged anthraquinone (20–25 per cent.) removed by filtration. The object of running the melt while still hot into boiling water is to obtain this anthraquinone in a filterable condition. The liquors are then neutralized with caustic and on cooling deposit sodium anthraquinone-β-sulphonate, known technically as "silver salt" from its silvery appearance. A further quantity is obtained by concentrating the mother liquors. If these are then concentrated to a gravity of 1260 they deposit most of the Glauber salt, and after this has been removed the filtrate can be taken to dryness and some disulphonates mixed with sodium sulphate obtained.

Anthraquinone Disulphonic Acids.[46]—Further sulphonation of anthraquinone leads to a mixture of 2-6 and 2-7-disulphonic acids which can be separated by the fractional crystallization of their sodium salts. The sulphonation is carried out with 2–3 parts of oleum at 170° C. The same acids can be obtained from dichloranthracene.

REFERENCES AND LITERATURE.

[1] E.P. 101,973^{16}; 103,204^{16}.
[2] D.R.P. 71,556.
[3] D.R.P. 113,784.
[4] *Bl.* [4], **9**, 249; *Am. Soc.*, **20**, 549.
[5] D.R.P. 8764; 98,030; 118,393; 176,227. *B.*, **12**, 1048.
[6] D.R.P. 57,391.

[7] D.R.P. 35,211 ; 68,708 ; 79,234 ; 96,106 ; 142,116 ; 154,655. A.P. 692,598.

[8] *B.*, **29**, 2448. D.R.P. 86,097.

[9] D.R.P. 64,908 ; 78,834.

[10] D.R.P. 40,571 ; 74,644.

[11] D.R.P. 41,934 ; 77,446.

[12] D.R.P. 80,741.

[13] D.R.P. 62,368 ; 67,062 ; 69,722 ; 80,668.

[14] D.R.P. 67,563 ; 68,721 ; 69,190 ; 75,153.

[15] D.R.P. 42,112 ; 45,221.

[16] D.R.P. 39,925 ; 41,505 ; 42,272 ; 42,273 ; 43,740.

[17] D.R.P. 53,023.

[18] D.R.P. 33,916.

[19] D.R.P. 27,378. *B.*, **22**, 398.

[20] D.R.P. 22,547.

[21] *J. pr.*, **106**, 449 ; *A.*, **152**, 296.

[22] D.R.P. 33,857.

[23] D.R.P. 36,491.

[24] D.R.P. 27,378.

[25] D.R.P. 53,076.

[26] *Soc.*, **39**, 47.

[27] D.R.P. 26,012 ; 46,307 ; 77,446.

[28] *B.*, **13**, 1948.

[29] D.R.P. 41,957.

[30] D.R.P. 41,957.

[31] *B.*, **7**, 1367 ; **19**, 578 ; **20**, 2940, 3401. *A.*, **275**, 201. D.R.P. 42,874.

[32] *B.*, **20**, 74 ; **21**, 2370. *A.*, **275**, 200. D.R.P. 7,291.

[33] D.R.P. 20,760 ; 29,084.

[34] D.R.P. 29,084 ; 32,271 ; 32,276.

[35] D.R.P. 14,154.

[36] D.R.P. 50,411.

[37] D.R.P. 45,229.

[38] D.R.P. 45,229 ; 45,776. *B.*, **22**, 3328.

[39] D.R.P. 48,053 ; 61,730. *B.*, **9**, 592.

[40] D.R.P. 33,857.

[41] D.R.P. 30,077 ; 33,857. *J. pr.*, **106**, 449.

[42] D.R.P. 72,833.

[43] D.R.P. 69,555.

[44] *B.*, **36**, 4197 ; **37**, 67. D.R.P. 149,801.

[45] *A.*, **160**, 132 ; *B.*, **12**, 189, 589.

[46] *A.*, **158**, 323 ; **160**, 134. *B.*, **12**, 1288.

Sulphonation processes are treated by Wichelhaus in "Sulfurieren," 1911.

SECTION IV.—HYDROXYLATION

ALTHOUGH methods have been described by which an hydrogen atom in an aromatic nucleus can be oxidized to an hydroxyl group these methods are as yet of no technical value except in the case of one or two anthraquinone derivatives. As the most important of these are dyestuffs they are discussed in Part II., Section XI.

Halogen atoms attached to the nucleus are usually so firmly bound that they cannot be replaced without complete rupture of the molecule. Nitro groups, however, in the ortho and para position render the halogen atom somewhat less stable, but even *o*- and *p*-nitrophenols are only obtained from the corresponding nitrochlorbenzoles with the utmost difficulty, prolonged heating with aqueous caustic potash under pressure being necessary, and even then the yields are minute. Alcoholic potash has been tried, but it reduces the nitro group with production of azo- and azoxy- compounds.

When two nitro groups are present in the ortho and para positions the case is different, and under these circumstances the halogen atom is easily removed by boiling with sodium carbonate or lime in open vessels, or even by heating with water under pressure. The only compound of technical importance that is manufactured by this method is 2-4-dinitrophenol. This is obtained when 2-4-dinitro chlorbenzole is boiled with a 5 per cent. solution of sodium carbonate, the weight of carbonate used being the same as that of nitrochlorbenzole. The decomposition is complete in about 24 hours, the nitrophenol being then in solution as its sodium salt. On acidifying it separates out, and only requires to be washed and dried. It melts at 114° C.

As a rule hydroxyl groups are introduced by displacement of amino groups or sulphonic acid groups.

When an amino group is to be replaced, two methods are available, viz. the base is first diazotized and the diazo salt boiled with water, or the amino group is replaced directly by boiling with acids or alkalies, or with bisulphites, in this latter case a sulphite ester being formed as an intermediate product which on subsequent hydrolysis passes into the phenol :

$$ArNH_2 \rightarrow ArOSO_2 \rightarrow ArOH$$

The diazo reaction is of very general application, but in very many cases the yields are microscopic. In other cases, however, almost quantitative yields are obtained. As the diazo sulphates usually give better yields than the diazo-chlorides the base can conveniently be diazotized with sulphuric acid and sodium nitrite instead of hydrochloric acid, and this has the great advantage that lead-lined vessels can be used for the subsequent boiling. When diazotization is complete, the decomposition of the diazo sulphate is brought about either by simple boiling up, or, as is more customary, by allowing the solution of the diazo salt to run slowly into boiling dilute sulphuric acid. As nitrogen gas is evolved allowance must be made for frothing.

The replacement of the amino group by hydroxyl by heating with acids or alkalies depends very largely on the base. In the benzene series amino groups as a rule are only replaced when there are negative substituents in the ortho or para position. Thus aniline gives little or no trace of phenol, whereas *o*- and *p*-nitraniline give the corresponding nitrophenols in fair yield. Diamines and aminophenols react more readily than monamines, and *p*-nitroso dialkyl anilines react with exceptional ease, nitroso dimethyl aniline, for example, being readily split into dimethylamine and nitrosophenol when boiled with 3 per cent. caustic soda under a reflux condenser. The nitrosophenol is readily reduced, so that this method provides a process for manufacturing aminophenol, but it is usually found more economical to prepare nitrophenol and reduce this. It is used, however, in making aminophenol sulphonic acid (see p. 52).

In the naphthalene series amino groups are more readily replaced, especially when in the α-position, and the method is widely used in preparing the important naphthol sulphonic acids. α-Naphthol itself is manufactured by heating α-naphthylamine salts with water under pressure, and the replacement is facilitated by the presence of sulphonic acid groups in the molecule. For this reason the α-naphthol sulphonic acids are not manufactured by sulphonating α-naphthol, but by sulphonating α-naphthylamine and then replacing the amino group.

Although in some cases the replacement can be carried out in open vessels, better results are usually obtained by working under pressure, and although both acids and alkalies can be used to bring about the reaction the latter are usually to be preferred, owing to their less corroding effect on the plant. Hydrochloric acid can only be handled in autoclaves with an enamelled iron liner, but dilute sulphuric acid can be handled in lead-lined autoclaves provided the temperature is not too high. Acid hydrolysis allows of somewhat lower working pressures, as the ammonia evolved is absorbed; but this is usually more than counterbalanced by the corrosive properties of the liquors and by the danger of splitting off a sulphonic acid group, some of the sulphonic acids being easily hydrolysed.

The sulphite process frequently gives the best yields, but is not so generally applicable as acid or alkaline hydrolysis. It takes place at low temperatures, 90–110° C., so that open lead-lined vessels can be used, and as a rule it yields a product of exceptional purity. The sulphite ester is formed as an intermediate product, but not isolated, the hydrolysis being brought about by boiling the solution with caustic soda. The reaction is reversible and is much used for the production of amines. It is more fully discussed on page 36.

One of the most important methods of introducing a phenolic hydroxyl group consists in melting the sulphonic acid with caustic soda. Excess of caustic must be used, and more or less water is usually added. The temperatures employed vary with different sulphonic acids, but the reaction rarely proceeds at a reasonable speed below 180° C., and above 300–350° C. it is usually accompanied by heavy decomposition. The reaction is applicable to benzene, naphthalene, and anthraquinone sulphonic acids, and finds very wide application in the naphthalene series. Here sulphonic groups in the α- position are more readily replaced than those in the β- position, especially when another sulphonic acid group is present in the meta position. Of the α-naphthol and α-naphthylamine sulphonic acids, the group at 8 is more readily replaced than the group at 5; and of the β-naphthol and β-naphthylamine sulphonic acids, the group at 4 is most readily replaced, followed by that at 5 and finally by that at 8. Hence by carefully selecting the conditions of the melt the groups in polysulphonic acids can be replaced one by one. It must be borne in mind, however, that in the case of naphthylamine sulphonic acids there is always danger of simultaneously replacing the amino group.

Caustic melts are carried out in cast or wrought iron vessels, provided with a simple agitator, and heated either by direct fire or by an oil bath. In some cases a bottom discharge is provided, but many factories prefer a pipe passing through the cover and reaching almost to the bottom through which the finished charge can be blown by compressed air; but whatever form of discharge is used it must be of ample size and easily accessible, as owing to the high setting point of some melts stoppages are apt to occur. The melt is in some cases carried on at atmospheric pressure, in which case the pan should be provided with a reflux condenser, but in many cases better results are attained by using autoclaves. As caustic melts frequently froth badly ample allowance must be made for this. When the charge is finished it is either run slowly into water, or it is run off into shallow pans and allowed to set, being afterwards broken up and dissolved in water. The sodium salts of some phenols, *e.g.* α-naphthol, are almost insoluble in caustic, so that on standing they rise to the surface, and in this case a considerable amount of caustic can be recovered by running off the lower layer separately. In any case the sodium salt of the phenol is decomposed by hydrochloric acid, or in suitable cases by carbonic acid, and the phenol then isolated by any suitable means. If mineral acid is used sulphurous acid is liberated, and either collected in caustic soda as sulphite or used to neutralize part of the next charge.

Phenol.—In normal times the supply of phenol from coal tar is sufficient to meet the world's demand, and it is only made synthetically when the price rises sufficiently. During the war, however, the demand for picric acid has been so great that hundreds of thousands of tons of phenol have been made from benzene sulphonic acid, although the phenol process is rapidly being displaced by the chlorbenzole process. The melt is carried out at 300° C., with 3 parts of caustic to 4 parts of sodium benzene sulphonate, the temperature being finally raised to 330° C. and maintained at this point until the whole goes to a thin liquid. After dissolving and neutralizing the melt, the phenol is collected and purified by distillation, The yield is about 90 per cent. M.p. 42° C., b.p. 182° C.

Cresol.—The cresols are usually obtained from coal tar, but the ortho and para isomers can be obtained from the corresponding toluol sulphonic acids, or in about 75 per cent. yield from *o*- and *p*-toluidine by the diazo reaction.

o-Cresol	m.p. 31° C., b.p. 190° C.
m-Cresol	m.p. 4° C., b.p. 203° C.
p-Cresol	m.p. 35° C., b.p. 202° C.

Resorcinol (*m*-dioxybenzene).[2]—As all three benzene disulphonic acids pass into resorcinol on fusion with caustic there is no need to separate the isomers, and use is always made of the mixture of sodium benzene disulphonates obtained by sulphonating benzene.

The fusion is carried out with 2½ parts of caustic to 1 part of sodium benzene disulphonate at 270° C. and requires 8–9 hours. The melt is then dissolved in 8 parts of water, neutralized with sulphuric acid and filtered. On cooling most of the Glauber salt crystallizes out, and the resorcinol is then won from the liquor by continuous extraction with ether or amyl alcohol. The extraction plant is made of copper with brazed joints, and if chilled brine is used for the condenser the loss of ether is very small and should not exceed 1 per cent. The crude resorcinol thus obtained is either put on the market as such, or is first purified by distillation. M.p. 118° C., b.p. 276° C. It is very easily soluble in water, 100 parts of water dissolving 86·4 parts at 0° C., 147 parts at 12° C., and 229 parts at 30° C.

α-Naphthol.—This can be manufactured by the fusion of sodium naphthalene-α-sulphonate with two parts of caustic soda at 300° C., but when obtained by this process it is always contaminated with β-naphthol, as it is very troublesome to get the α-sulphonate free from the β-isomer. A much more satisfactory process[3] consists in heating α-naphthylamine sulphate with 5 parts of water to 200° C. in lead-lined boilers. The reaction is complete in 2–3 hours, and on cooling the α-naphthol crystallizes out. M.p. 94° C., b.p. 278° C.

β-Naphthol.—This is invariably manufactured from sodium naphthalene-β-sulphonate by fusion with caustic. The proportions in general use are 1 part of the sodium salt and two parts of caustic to which about 10 per cent. of water has been added. The fusion temperature is 300–320° C., and as sodium naphtholate is insoluble in caustic soda the melt on standing for a short time settles out and by withdrawing the lower layer most of the excess caustic can be recovered. The naphtholate, after breaking up, is dissolved in water and the naphthol precipitated by carbonic acid. It is usually purified by distillation *in vacuo*. M.p. 123° C., b.p. 285° C., with slight decomposition.

Neville and Winter's Acid[4] (1-naphthol-4-sulphonic acid).—This acid is usually spoken of as NW acid, and there are three processes in use for its manufacture, of which the sulphite process is the best.

(*a*) Sodium naphthionate (1 part) is diazotized in the usual way with sodium nitrite and hydrochloric acid, and the insoluble diazo salt filtered off and washed. It is then mixed with ten parts of water and run slowly into 18 parts of boiling 4½ per cent. sulphuric acid. On neutralizing and cooling the acid crystallizes out.

(*b*) Equal weights of sodium naphthionate and 50 per cent. caustic soda are heated in an autoclave for 10 hours at 200–220° C. The product is then run into water, the ammonia boiled off and the solution neutralized.

(*c*) Sodium naphthionate (32 kilos) is dissolved in 20 litres of water and 75 kilos of 40 per cent. sodium bisulphite solution, and the whole heated at 90° C. for 24 hours. After cooling hydrochloric acid is added until acid to congo paper and unchanged naphthionic acid (about 10 per cent.) filtered off. The filtrate is then made alkaline with caustic soda and boiled to hydrolyse the sulphite ester and remove ammonia. It is then acidified and boiled to remove sulphur dioxide and the NW acid finally salted out.

A modification of this process consists in dissolving naphthionate in 3 parts water and then passing sulphur dioxide at 100° C. for 30 hours.

L-Acid [5] (1-naphthol-5-sulphonic acid).—From naphthalene-1-5-disulphonic acid by fusing with 4 parts of caustic soda at 180° C. On acidifying the dissolved melt L-acid separates.

Schöllkopf's Acid [6] (1-naphthol-8-sulphonic acid).—This is best obtained from the corresponding amino acid by heating with 4 parts of water at 200° C. for 8 hours. It can also be obtained by the diazo process.

Chromotropic Acid [7] (1-8-dioxynaphthalene-3-6-disulphonic acid).—This is obtained by two methods.

(*a*) H-acid is heated with 10 parts of 5 per cent. caustic soda solution in an autoclave at 265° C. for 8 hours. The liberated ammonia is then boiled out and the solution neutralized when chromotropic acid separates or is salted out. H-acid is obtained from 1-naphthylamine-3-6-8-trisulphonic acid, and when chromotropic acid is being made the H-acid is not isolated. Instead the melt is dissolved in water, diluted until the alkalinity is 5 per cent. and this solution then heated as above.

(*b*) 1-Naphthylamine-3-6-8-trisulphonic acid is diazotized with sulphuric acid and sodium nitrite in the usual way and the diazo solution boiled until no more nitrogen is evolved. From this solution the sodium salt of 1-naphthol-3-6-8-trisulphonic acid[8] is obtained by liming out, and is then heated with 3 parts of 50 per cent. caustic soda at 170–220° C. until no more frothing takes place. The melt is dissolved in water and acidified. On cooling the chromotropic acid separates.

Aminonaphthol G-Acid[9] (2-8-aminonaphthol-6-sulphonic acid).—This is obtained from amino G acid (2-naphthylamine-6-8-disulphonic acid) by heating it in an autoclave at 185° C. for 7 hours with twice its weight of 40 per cent. caustic soda. The acid is deposited from the cold melt on acidifying.

J-Acid[10] (2-amino-5-naphthol-7-sulphonic acid).—From β-naphthylamine-5-7-disulphonic acid by heating in an autoclave with twice its weight of 50 per cent. caustic at 180° C. The melt is then run on to ice and acidified with hydrochloric acid. On cooling the J-acid crystallizes.

H-Acid[11] (1-8-aminonaphthol-3-6-disulphonic acid).—From the sodium salt of 1-naphthylamine-3-6-8-trisulphonic acid by fusing with twice its weight of caustic soda (containing 10 per cent. of water) at 180° C.

K-Acid[12] (1-8-aminonaphthol-3-5-disulphonic acid).—By heating sodium α-naphthylamine-3-5-8-trisulphonate with double its weight of 75 per cent. caustic soda in an autoclave at 170° C.

2R-Acid[13] (2-8 aminonaphthol-3-6-disulphonic acid).—By caustic fusion of 2-aminonaphthalene-3-6-8-trisulphonic acid at 200–260° C.

2S-Acid[14] (1-8-aminonaphthol-2-4-disulphonic acid).—

From 1-naphthylamine 2-4-8-trisulphonic acid by fusing with caustic at 180–190° C.

REFERENCES AND LITERATURE.

[1] *B.*, **7,** 77.
[2] *Dingl.*, **263,** 156.
[3] D.R.P. 74,879; 76,595.
[4] D.R.P. 46,307; 77,446; 109,102.
[5] D.R.P. 41,934.
[6] D.R.P. 74,644. *B.*, **20,** 3162; *A.*, **247,** 344.
[7] D.R.P. 67,563; 68,721; 69,190; 75,153.
[8] D.R.P. 56,058.
[9] D.R.P. 53,076.
[10] D.R.P. 75,469; E.P. 2614^{93}.
[11] D.R.P. 69,722.
[12] D.R.P. 80,741.
[13] D.R.P. 53,023.
[14] D.R.P. 80,668.

Some account of the caustic fusions will be found in Wichelhaus, "Sulfurienen, Alkalischmelze der Sulfosäuren, Esterifizieren." Leipzig, 1911.

SECTION V.—MISCELLANEOUS INTERMEDIATES

A FEW chlorine compounds have found application as intermediate compounds of which the most important are chlorbenzole, benzyl and benzal chloride and benzoyl chloride. The larger factories usually generate their own chlorine electrolytically, caustic soda being obtained simultaneously; but if this is not done it is far more satisfactory to purchase liquid chlorine in steel bottles than to generate it from pyrolousite and hydrochloric acid. Liquid chlorine comes into the market as a rule in cylinders containing 112 lbs., the present price (1918) being about 6*d*. per lb.

So long as the gas is kept dry, fittings of steel or even gunmetal can be used; but once it picks up moisture very heavy corrosion sets in, and only stoneware can be used with satisfaction. For this reason if iron vessels are being used for chlorination the vent should be connected with a drying tower down which a little sulphuric acid is kept trickling.

Chlorbenzole C_6H_5Cl.[1]—Benzole is not very readily chlorinated unless a chlorine carrier is used, and of the various chlorine carriers that have been proposed from time to time the best for manufacturing purposes is iron, or a mixture of iron and anhydrous ferric chloride. The plant used consists of a cast-iron steam-jacketed kettle provided with a thermometer, agitator, and charging holes. The reflux condenser must be of ample size, as in addition to condensing the benzole it has to carry off the hydrochloric acid gas liberated. Its upper end is connected to a stoneware wash tower down which water is allowed to percolate so as to collect the hydrochloric acid gas. This carries with it a good deal of benzole vapour, part of which is condensed in the tower and subsequently separated from the aqueous acid, and part of which is vaporized by the heat given off by the dissolving acid and condensed in a stoneware or enamelled iron condenser interposed between the tower and the flue. The kettle is charged with 600 lbs. of benzole, 2 lbs. of iron borings, and 2 lbs. of anhydrous ferric chloride, and chlorine then passed in through a perforated pipe. The rate at which the gas is run in is regulated by testing the exhaust from time to time. Should free chlorine be present it shows that the gas is being run in too quickly. At first a vigorous reaction sets in, and the benzole boils briskly, and it is generally necessary to run water through the jacket. About 600 lbs. of chlorine (measured by weighing the cylinders) are required, after which the product is distilled off under reduced pressure, and another charge of benzole run on to the catalyst which is left behind. The crude chlorbenzole is then fractionated, the first fraction containing a little unchanged benzole, and the last runnings consisting of a mixture of dichlorbenzoles. From these the greater part of the para isomer separates on cooling. If only monochlorbenzole is desired it is best to chlorinate at 40° C., and to break off when only half the theoretical weight has been taken up. The unchanged benzole is recovered in fractionating.

Monochlorbenzole	..	b.p. 132° C., sp.gr. 1106.
o-Dichlorbenzole	..	b.p. 179° C., sp.gr. 1328 at 0° C.
m-Dichlorbenzole	..	m.p. −18° C., b.p. 172° C., sp.gr. 1307 at 0° C.
p-Dichlorbenzole	..	m.p. 53° C., b.p. 172° C.

Benzyl Chloride $C_6H_5CH_2Cl$, Benzal Chloride $C_6H_5CHCl_2$, Benzotrichloride $C_6H_5CCl_3$.[2]—When toluol is chlorinated in the cold or in the presence of chlorine carriers the halogen atoms enter the nucleus with the production of the technically useless chlortoluols. On the other hand, when the chlorination is carried on at a high temperature in the absence of any carrier except phosphorus pentachloride the halogen enters the side chain, benzyl chloride, benzal chloride, and benzotrichloride being formed successively. Ultraviolet light also causes the halogen atom to enter the side chain, and practically none enters the nucleus when even cold toluol is chlorinated in direct sunlight.

The chlorination is carried out exactly as in the case of benzole, except that stoneware or enamelled iron vessels must be used as iron causes decomposition, and the toluol is heated to boiling before the chlorine is turned on. About 3 per cent. of phosphorus pentachloride is added as a catalyst, and before fractionating the product this must be washed out with water and dilute soda. In some works the chlorination is carried out in clear glass bottles set on a sand bath or a calcium chloride bath in the sun; but needless to say this is a most unsatisfactory method.

The best process consists in carrying out the chlorination in enamelled vessels in the interior of which is a quartz mercury lamp. When this is done no catalyst is added, and the chlorination can be carried out in the cold or at a moderate temperature, and the very disagreeable process of washing can be omitted.

The extent of the chlorination depends on whether benzyl chloride, benzal chloride, or benzotrichloride is desired as the main product, and it is controlled by weighing the cylinders of chlorine and by periodically testing the gravity of the charge.

In fractionating no attempt is made to separate benzal chloride from benzo trichloride, as they are used for making benzaldehyde and benzoic acid, and these are easily separated.

Benzyl chloride	..	b.p. 176° C., sp.gr. 1107.
Benzal chloride	..	b.p. 213° C., sp.gr. 1295.
Benzo trichloride	..	b.p. 213° C., sp.gr. 1380.

Benzoyl Chloride C_6H_5COCl.[3]—On the manufacturing scale this can be obtained by treating sodium benzoate with sulphuryl chloride, or by passing chlorine over the addition compound formed when sodium benzoate is treated with sulphur dioxide. The best process, however, consists in passing chlorine into benzaldehyde. Much heat is evolved and the aldehyde boils, but towards the end heat must be applied. When the reaction is complete the product is distilled. B.p. 198°, sp.gr. 1212.

Chloranthraquinone $C_6H_3Cl(CO)_2C_6H_4$.[4]—The monochloranthraquinones are best obtained from the corresponding sulphonic acids. The reaction is carried out by dissolving 40 parts of the sodium or potassium salt of the sulphonic acid in 1200 parts of water and 150 parts of concentrated hydrochloric acid. The solution is boiled under a reflux condenser and a solution of 40 parts of sodium chlorate in 200 parts of water run in slowly, when the chloranthraquinone separates out in the pure state.

α-Chloranthraquinone melts at 162° and β-chloranthraquinone at 210° C.

The dichloranthraquinones are obtained in exactly the same way from the disulphonic acids.

Benzaldehyde C_6H_5CHO.—Many methods have been proposed for manufacturing benzaldehyde by the direct oxidation[5] of toluol, but none have proved so satisfactory as the hydrolysis of benzal chloride :

$$PhCHCl_2+H_2O=PhCHO+2HCl$$

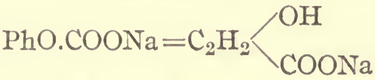
This decomposition can be brought about by boiling with caustic soda or milk of lime, best under pressure, but the catalytic method is the best.[6] This is based on the fact that hydrolysis is brought about by water at or below 100° C. if a little dry ferric benzoate or iron powder is added to the benzyl chloride. The addition of the ferric benzoate or iron powder must be made about half an hour before any water is added. The process is carried out as follows. Sixty kilos of benzal chloride is heated in a steam-jacketed enamelled iron kettle to 25–30° C. and 20 grams of iron powder added. After standing for half an hour 12 litres of water are run in and the whole heated slowly to 90–95° C. Hydrochloric acid gas is evolved, and the hydrolysis is complete in about 10 hours. The charge is then made alkaline with milk of lime and the benzaldehyde driven over with steam. If desired absolutely pure it is dissolved in bisulphite solution, separated from any insoluble matter and then liberated by adding sodium carbonate.

The hydrolysis of benzal chloride can be carried out more rapidly by adding 200 kilos of milk of lime (made from 34 kilos of lime) before the heating is started. Under these circumstances the mixture is heated with direct steam to 50° C., at which temperature the reaction sets in, the heat evolved being as a rule sufficient to complete it. The working costs are somewhat higher, as lime has to be used and the hydrochloric acid is lost; but considerable time is saved and the capital costs are smaller, as naked iron vessels can be used.

Benzaldehyde boils at 179° C.

Benzoic Acid C_6H_5COOH.—The alkaline residue left after the benzaldehyde has been blown off always contains benzoic acid derived from the benzotrichloride present in the benzal chloride, and on filtering and acidifying this is thrown down. If required in larger quantities it is merely necessary to use a crude benzal chloride of higher gravity, *i.e.* one containing more benzotrichloride. M.p. 121° C.

Salicylic Acid [7] (*o*-oxybenzoic acid).—This is obtained by the action of carbon dioxide on sodium phenolate, the carbonic ester at first formed undergoing a rearrangement :



$$PhO.COONa = C_2H_2\left\langle\begin{matrix}OH\\ COONa\end{matrix}\right.$$

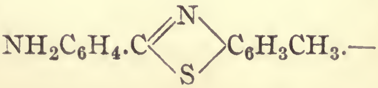
The phenol is dissolved in the calculated amount of caustic soda and the solution then rapidly evaporated in shallow iron pans heated by an oil bath. The solution must be taken to absolute dryness, and to prevent charring the pans should be heated by an oil bath and the contents kept in motion by revolving scrapers. The evaporation should be as rapid as possible, as otherwise the carbon dioxide in the air will decompose part of the phenolate. When thoroughly dry the salt is ground up, charged into autoclaves, and carbon dioxide pumped in. In some factories it is the custom to cool the charge until no more carbon dioxide is absorbed, *i.e.* until the formation of the carbonic ester is complete; but it is more usual to maintain the temperature at 120–140° C., so that the ester is rearranged as formed. In either case the phenolate must be absolutely dry, and in the form of a fine powder, and the autoclave should be provided with revolving arms so as to keep the phenolate turning over. When the change is complete the charge is dissolved in water, and saturated with carbon dioxide to liberate unchanged phenol, which is then removed by steam or by a suitable solvent. The salicylic acid is then precipitated with mineral acid, filtered off and washed and then usually purified by distillation *in vacuo* or by distillation with superheated steam. During the treatment of the sodium phenolate with carbon dioxide the temperature must not be allowed to rise much above 140° C., as if it does phenol is liberated and the product is also contaminated with *p*-oxybenzoic acid.

In some modern works the phenol and caustic are mixed in an iron pan fitted with a very efficient agitator and the solution taken to dryness *in vacuo,* heating being effected by superheated water circulating in channels cast in the walls of the kettle. The charge is then cooled below 100° C. by circulating cold water and carbon dioxide pumped in, the circulation of water being maintained so as to prevent undue rise in temperature. Very efficient agitation is required as otherwise the dry mass will adhere to the walls. This method of working is considerably quicker and in addition yields a purer product. The acid melts at 155° C.

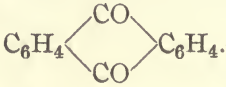
Phthalic Acid[8] (benzene-*o*-dicarboxylic acid).—On the manufacturing scale this is invariably obtained by the oxidation of naphthalene by sulphuric acid in the presence of mercuric sulphate. The process is carried out as follows: One thousand pounds of naphthalene are dissolved by gently warming with 15,000 lbs. of sulphuric acid monohydrate and about 500 lbs. of mercuric sulphate in a cast-iron sulphonation kettle. The solution is then pumped into another cast-iron kettle of considerably larger size, which is provided with a condenser, and is arranged for heating by direct fire. The solution is heated slowly, and oxidation sets in at 200° C. and is brisk at 250° C. Torrents of carbon dioxide and sulphur dioxide are evolved, and these are led back to the contact chambers of the oleum plant, where the sulphur dioxide is reconverted into sulphuric acid. The phthalic acid condenses together with the water and sulphuric acid which distil off. The temperature of the still is carried up to 300–350° C. and the distillation continued almost to dryness. On cooling the distillate practically the whole of the phthalic acid separates out, and after wringing in a centrifuge merely requires to be washed with a little water. If desired it can be purified by sublimation. It consists almost entirely of the anhydride. M.p. 213° C.

***p*-Nitrosodimethyl Aniline $ONC_6H_4NMe_2$.**—Dimethyl aniline (240 lbs.) is dissolved in 190 gallons of 17 per cent. hydrochloric acid contained in an oak or pitch pine vat provided with an agitator. Ice is then added until the temperature falls to 10° C., and then a solution of 208 lbs. of sodium nitrite in 80 gallons of water run in slowly through a lead pipe reaching well below the surface. During the addition crushed ice is added from time to time so that the temperature does not rise above 10° C. When the whole of the nitrite has been added the charge is allowed to stand for an hour or two and the nitrosodimethyl aniline hydrochloride then filtered off.

Michler's Ketone[9] (Tetramethyldiaminobenzophenone). —Phosgene is passed into dimethyl aniline contained in an enamelled iron autoclave until the increase in weight is 41 per cent. The autoclave is then closed, and the mixture of dimethylaminobenzoyl chloride and dimethyl aniline heated on the water-bath for 7 hours. Excess of dimethyl aniline is then blown off by steam, and the residue dissolved in hydrochloric acid and, after filtration, precipitated by soda. M.p. 179° C.

Dehydrothiotoluidine[10] 
$NH_2C_6H_4.C\langle{}^{N}_{S}\rangle C_6H_3CH_3$.—

If *p*-toluidine is heated with two molecules of sulphur for 24 hours at 180° C. a product is obtained which is a mixture of dehydrothiotoluidine, primuline base and unchanged *p*-toluidine. To avoid the production of primuline base the melt must be carried out in presence of excess of toluidine or with a suitable solvent such as naphthalene. Good yields of dehydrothiotoluidine are obtained by heating 4 parts of *p*-toluidine with 1 part of sulphur at 190–195° C. until no more sulphuretted hydrogen is evolved. After cooling the melt is broken up and excess of *p*-toluidine removed by distillation in steam. The dehydrothiotoluidine is extracted from the residue with dilute hydrochloric acid, and then precipitated by adding caustic soda. It can be got free from primuline base by extraction with solvents or by distillation. M.p. 191° C., b.p. 434° C.



Anthraquinone $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4$.—This is invariably obtained by oxidizing anthracene with sodium dichromate and sulphuric acid, and considerable care is required in selecting a suitable quality of anthracene although this point is not so important if it is first purified with pyridine. Some anthracene, especially that obtained from gasworks in which a mixture of ordinary coal and cannel coal is distilled, is rich in paraffin, and if such an anthracene is used for making anthraquinone endless trouble will be encountered through filters choking. Commercial anthracene usually runs about 45 per cent., and this can be oxidized to anthraquinone by using only the calculated amount of bichromate, as under these circumstances the impurities are left unaffected. It is much better, however, to bring the crude anthracene up to 95 per cent. by washing with pyridine. In any case the anthracene must be got into a suitable physical condition, as it is not very readily attacked by aqueous dichromate. This is best done by volatilizing it with steam superheated to 300° C. and then condensing by leading into a chamber with fine jets of water. The anthracene comes down as a sludge which is dewatered so as to give a paste, but must not be dried. The oxidation is then carried out as follows: The anthracene paste is suspended in boiling water and kept well agitated while a solution of sodium bichromate containing 100 grams of bichromate and 250–300 grams of sulphuric acid per litre is slowly run in. The addition must not be too rapid or excessive frothing will take place. When oxidation is complete the anthraquinone is filtered off and washed. If the anthracene has been purified by washing with pyridine the anthraquinone will be pure enough without further treatment; but if made from crude anthracene it is usually necessary to heat it with 2–3 parts of concentrated sulphuric acid at 130° C. The solution, without cooling, is then run into boiling water and the precipitated anthraquinone filtered off and washed. It is necessary to run the hot acid solution into boiling water in order to get the anthraquinone into a form that can be filtered. The spent chrome liquors from the oxidation of anthracene are concentrated and the chrome regenerated electrically.[11]

REFERENCES AND LITERATURE.

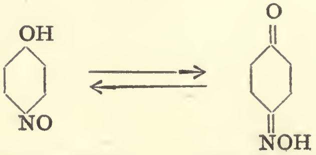
[1] D.R P. 219,242.
[2] *B.*, **18**, 608; *A.*, **272**, 149.
[3] *A.*, **3**, 262; **70**, 41; **106**, 302; **109**, 256. D.R.P. 210,805.
[4] *A.*, **381**, 2; *B.*, **46**, 2703. D.R.P. 205,195.
[5] D.R.P. 101,221; 127,388; 158,609; 175,295; 189,178.
[6] D.R.P. 82,927; 85,493.
[7] D.R.P. 29,939; 38,742; 73,279.
[8] D.R.P. 91,202.
[9] *B.*, **9**, 715, 1900.
[10] *B.*, **22**, 330, 422, 580, 968, 1063. D.R.P. 35,790; 53,938.
[10] *Mon. Sci.* [3], **8**, 421, 1159.
[11] D.R.P. 103,860; 109,012; 117,949.

PART II.—THE DYESTUFFS

SECTION I.—THE NITROSO-DYES

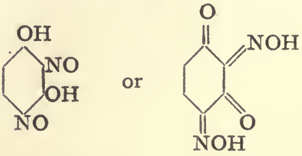
IN these the nitroso-group is the chromophore. They are of very minor importance and are, without exception, mordant colours. They are all nitroso-phenols and are obtained by the action of nitrous acid on the phenols. The nitroso-group enters the para-position if this is vacant, and the ortho-position if the para-position is occupied. The para-nitroso-phenols do not form lakes, and are useless as dyestuffs.

Since the nitroso-phenols are identical with the quinone monoximes (obtained by the action of hydroxylamine on the quinones) they are to be regarded as exhibiting tautomerism : [1]

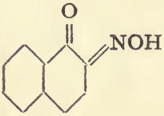


p-Nitroso-phenol. Quinone monoxime.

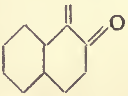
The dyes are usually applied on an iron mordant and give rise to fast shades of green. The most important member of the series is Fast Green O (dinitroso-resorcinol).[2]



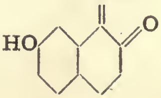
Other dyestuffs of this class are :—



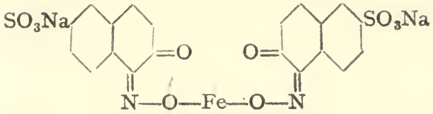
Gambin R.



Gambin Y.



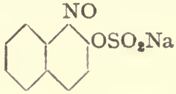
Dioxin.



Naphthol Green B.

This last is obtained by the action of iron chloride on the nitroso-compound obtained from Schäffer's acid. It is soluble in water and dyes from an acid bath.

Gambin γ (nitroso-β-naphthol) is also placed on the market in the form of its water soluble sulphite ester:



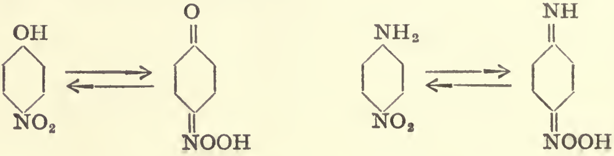
under the names of sulfamine and naphthine S. It gives very fast shades of green on an iron mordant, and finds considerable application in printing.

REFERENCES AND LITERATURE.

[1] *B.* **17**, 213, 801, 2060, 2581; **18**, 46 568, 2224; **19**, 340. *A.* **203**, 301.
[2] *B.* **8**, 631. D.R.P. 65,049.

SECTION II.—THE NITRO-DYES

THE dyestuffs of this group contain the nitro-group as chromophore. They are the polynitro-derivatives of phenols or amines in which at least one nitro-group is in the ortho- or para-position to the hydroxyl or amino-group. They are all acid dyes and as a rule occur in commerce as their sodium or ammonium salts. The acidity is probably due to the capacity of the *o*- and *p*-nitro-phenols of forming tautomeric nitrolic acids :—

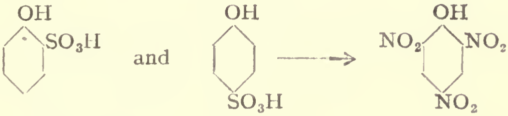


Direct evidence of this tautomerism has been obtained by the isolation of two esters of ortho-nitro-phenol.[1] One of these esters is coloured and labile, and is regarded as the ester of the *aci*-form of nitro-phenol. It passes into the colourless form which is stable and identical with *o*-nitro-anisole. As the salts of the nitro-phenols are always more highly coloured than the nitro-phenols themselves, it is probable that they are derived from the *aci*-form, and therefore have the quinonoid structure.

The ortho- and para-nitro amines also form highly coloured salts, and these are also probably derived from the nitrolic acid. Thus tetranitro-diphenylamine-*o*-sulphoxide is a yellow compound which dissolves in caustic soda to form a red sodium salt. On acidifying this solution the nitro-sulphoxide separates in a red form which rapidly passes into the yellow variety on heating.[2]

The nitro-dyes were formerly very largely used for colouring silk and wool yellow, but owing to their fugitive nature are now but little used.

Picric acid (*sym.*-trinitro-phenol) is of interest as being the first dyestuff prepared in the laboratory. It was obtained by Welter in 1799 by the action of nitric acid on silk. It is now manufactured by the action of nitric acid on phenol sulphonic acid :—



In carrying out the process the sulphonic acid is not actually isolated, nitric acid being added to the sulphonation mixture after it has been diluted to a suitable extent (cf. Naphthol Yellow S). A more modern process consists in first preparing dinitro-phenol from dinitrochlorbenzole and then nitrating this to picric acid.

Although prepared on a very large scale in the explosives industry, picric acid is no longer used as a dyestuff owing to the very fugitive nature of the shades obtained.

Martius yellow is the sodium or calcium salt of 2.4-dinitro-α-naphthol. It is prepared by the action of nitric acid on the corresponding naphthol disulphonic acid.

Naphthol Yellow S is the most important nitro-dye. It is much faster than any other member of the group and is made by the action of nitric acid on α-naphthol-2.4.7-trisulphonic acid. The naphthol trisulphonic acid is not actually isolated, the process being carried out as follows. α-Naphthol is added to four parts of 25 per cent. oleum and heated to 125° C. until trisulphonation is complete, a little more oleum being added if necessary. The melt is then cooled and run on to ice (2½ parts of ice to every part of oleum used) and the resulting solution filtered. The filtrate is then nitrated by heating to 50° C. with dilute nitric acid (sp.gr. 1420), allowing 2¼ parts of this acid to every part of α-naphthol. When nitration is complete the charge is allowed to stand over-night and the dyestuff then filtered off, washed with brine, and collected. It forms an orange-yellow powder, which dyes silk and wool from an acid bath.

Aurantia is *sym.*-hexanitro-diphenylamine.[4] It is prepared by condensing 2.4-dinitro-1-chloro-benzene with aniline and then nitrating the resulting dinitro-diphenylamine. The commercial article is the ammonium salt, but the dyestuff is no longer used.

REFERENCES AND LITERATURE.

[1] *B.* **39**, 1073.
[2] *Soc.* **95**, 1253.
[3] D.R.P. 10,785. *B.* **22**, 993.
[4] *B.* **7**, 1399; **9**, 1245; **11**, 845.

Picric acid and aurantia are both used as explosives, and descriptions of their manufacture will be found in modern works on explosives, especially in Escales' "Nitrosprengstoffe," Leipzig, 1915. Other works on the subject are Chalons, "Les Explosifs Modernes," Paris, 1911; Marshall, "Explosives," London, 1917; and Colver, "High Explosives," London, 1918.

SECTION III.—THE AZO-DYES

THIS is the largest and most important class of dyes and comprises all colouring matters containing the group ArN=NAr. It includes a few basic dyes, but the vast majority are acid dyes, a large number of which are substantative to cotton. The azohydrocarbons, *e.g.* azobenzene $C_6H_5N{=}NC_6H_5$, are coloured and give soluble coloured sulphonic acids but are of no value as dyestuffs, as they are devoid of tinctorial properties. Affinity for the fibre is only obtained by the introduction of hydroxyl or amino groups, carboxyl and sulphonic acid groups not having this effect. The property of dyeing cotton without a mordant also depends on the structure, and this point is further discussed on page 97. The azo dyes are invariably manufactured from two or more components, one of which must be a primary aromatic amine and the others phenols or primary, secondary or tertiary amines.

When a primary aromatic amine is treated with nitrous acid (sodium nitrite and hydrochloric acid), a diazo salt is formed :

$$C_6H_5NH_2+HNO_2+HCl \quad = \quad C_6H_5N{=}N{-}Cl+2H_2O$$

These diazo salts under suitable conditions "couple" with phenols and amines with the production of oxyazo or amino-azo compounds :

$$C_6H_5N{=}N.Cl+ArOH \quad = \quad C_6H_5N{=}N.ArOH+HCl$$

These are usually insoluble and hence unsuitable for use as dyestuffs, but their sulphonic acids dissolve easily and constitute the acid azo dyes. As almost all amines can be diazotized,* and as the diazo compounds thus obtained can

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* When both amino groups of a diamine are simultaneously diazotized the process is spoken of as "tetrazotizing."

be coupled with almost all amines, phenols and naphthols, the number of azo dyes that have been studied is very large. Dyes containing only one azo group are known as monazo dyes, and those with two, three, four, five or six, as disazo, trisazo, tetrakisazo, pentakisazo and hexakisazo- dyes. The diazo compounds as a rule are very unstable, and decompose at or just above the ordinary temperature. Hence diazotization is usually carried out in the presence of ice and the resulting solution or suspension of the diazo salt at once coupled with the second component. One or two diazo compounds can be separated and rendered stable by special treatment, and are sold as such for the production of "ice colours," *i.e.* colours in which the dyestuff is developed on the fibre by first padding the material with a phenol and then treating it with a diazo compound. The best known of these is Azophor Red, which is obtained by evaporating a strongly acid solution of diazotized *p*-nitraniline and then mixing with neutral salts.[1] Azophor Blue is tetrazotized dianisidine treated in a similar manner.[2] Nitrosamine Red is a paste obtained by treating diazotized *p*-nitraniline with alkali. It is a sodium salt which gives the diazo chloride on treatment with hydrochloric acid.[3]

Diazotization.—In most cases diazotization is an extremely simple process, and is carried out by dissolving or suspending the amine in dilute hydrochloric acid and then slowly adding the calculated amount of sodium nitrite solution. It is carried out in circular vats made of oak or pitch pine with a capacity of 1000–2000 gallons and provided with an efficient wooden agitator. The process is usually carried out at a temperature of 5–10° C., the cooling being effected simply by the direct addition of crushed ice. The nitrite should be added slowly, and after the whole has been added the product should show a *faint* reaction with starch iodide paper. When diazotization is complete the contents of the vat are run into another vat containing the second component. When the coupling is complete the dyestuff is salted out with common salt, collected in filter presses, dried (usually at about 50° C.) and ground up. In the manufacture of polyazo dyestuffs after the first coupling is complete it is frequently the case that the product has to be coupled with another component under different conditions, or the couple has to be diazotized and then again coupled. When this is the case it is not usual to isolate the intermediate compounds, but simply to run or pump the solution from vat to vat until all the steps are complete.

Most diazo salts have a tendency to unite with primary amines to form diazoamino compounds:

$$ArN{=}NCl + H_2NAr \quad = \quad ArN{=}N{-}NHAr + HCl$$

As this reaction does not take place readily in strongly acid solutions, excess of hydrochloric acid is always used in diazotizing, the usual proportion being 2½ molecules of hydrochloric acid for every molecule of sodium nitrite. If acetic acid is used about 40 molecules are required to render diazotization complete.

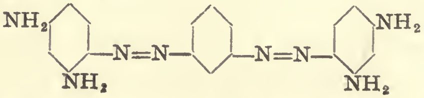
In cases where the tendency to form aminoazo compounds is very great, *e.g.* *p*-nitraniline, the nitrite solution must be added very quickly, so that the whole is diazotized before the diazochloride has time to unite with unchanged base.

Insoluble or slightly soluble bases can be diazotized in suspension, but with sparingly soluble sulphonic acids it is frequently advantageous to dissolve them in alkali and then precipitate with excess of hydrochloric acid, as by this means they are more readily attacked by the nitrous acid.

Aminonaphthols in which the amino- and hydroxyl groups are in the ortho- (1.2.) position to each other are oxidized by nitrous acid to the corresponding β-naphthoquinone. This oxidation, however, can be prevented by carrying out the diazotization in the presence of copper, mercury, zinc, iron, or nickel salts.[4] When this procedure is adopted only one equivalent of mineral acid is used, and in the case of an amino-naphthol sulphonic acid, no acid is used, the sulphonic acid liberating the nitrous acid. The amino naphthols can also be diazotized by replacing the mineral acid by acetic, oxalic, tartaric or phthalic acid.

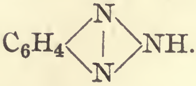
In the case of diamines it frequently happens that it is wished to diazotize only one amino group. In some cases this can be done by employing only one molecule of nitrite, but as a rule one of the amino groups must first be protected by acetylation, *e.g.* *p*-phenylenediamine and benzidine. In the case of benzidine, however, another method is available, as if an equimolecular mixture of benzidine and tetrazotized benzidine is allowed to stand for three days, double decomposition takes place with the formation of benzidine diazochloride. Disazo dyes, derived from *p*-phenylenediamine, with two different components, can also be obtained by coupling diazotized *p*-nitraniline with one component and then reducing the nitro group by means of sodium sulphide and subsequently diazotizing and coupling with the other component. It is difficult, however, to avoid reducing the azo group.

Some diamines, such as *m*-phenylenediamine, when diazotized couple so readily that diazo compounds can only be obtained by taking special precautions. Thus, if sodium nitrite is added to an acid solution of *m*-phenylene diamine, the tetrazo compound couples as soon as it is formed with two molecules of the unchanged diamine, the product in this case being the well-known dyestuff Bismarck Brown :



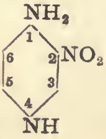
Tetrazotization can, however, be brought about by using a large excess of acid and adding the diamine to the nitrite.[5]

o-Phenylenediamine cannot be diazotized as it forms azoiminobenzene :[6]



$C_6H_4\langle N_2 \rangle NH.$

Negative groups, such as nitro and sulphonic acid groups, when in the ortho- or para- position to amino groups frequently prevent diazotization. Thus in the compound



only the amino group at 4 can be diazotized. After coupling, however, the remaining amino group is readily diazotized, and the same is the case if the amino group at 4 is acetylated.

In the benzene series, as a rule, both ortho- and para-amino azo compounds can be diazotized, but in the naphthalene series amino groups in the ortho position to an azo group are not attacked by nitrous acid.

Coupling.—The coupling of a diazo compound with a phenol is brought about in alkaline solution, the diazo solution being run slowly into an alkaline solution of the phenol, the whole being kept well agitated. The reaction takes place rapidly, and is usually complete in a few minutes; but the second component frequently unites very slowly with a tetrazotized base, and several days may elapse before coupling is complete.

It is important to have sufficient alkali present so that an alkaline reaction is maintained after the whole of the diazo solution has been added; but great excess of alkali is to be avoided, as this converts the diazo salt into the inactive anti-form.

The coupling with amines is brought about in neutral or faintly acid solution, and as it takes place readily in the presence of acetic acid the solution of the diazo compound and the amine can be mixed and sodium acetate then added until the whole is no longer acid to Congo paper. As a rule coupling takes place in the para- position to the hydroxyl or amino group, if this is free. If the para- position is occupied then coupling takes place in the ortho- position. If no para- or otho- position is free, as a rule no azo compound is formed, although in some cases the azo group replaces other substituents.

The above rules are fairly general, but there are some important exceptions, of which the following are the most important:—

Benzene Series.—*p*-Oxybenzoic acid and *p*-dimethyl amino benzoic acid couple in the para- position with elimination of carbon dioxide.

Dimethyl-*p*-toluidine, *p*-bromdimethylaniline and *p*-dimethylamino benzene sulphonic acid will not couple.

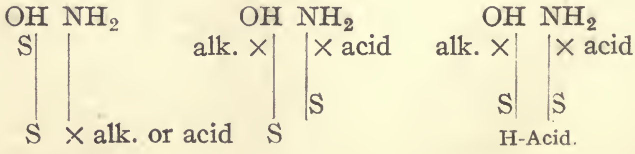
Naphthalene Series.—*a*-Naphthols containing nitro or sulphonic acid groups in the 3 or 5 positions couple in the ortho position. Otherwise they couple in the para position, if this is free. β-Naphthols couple only in the ortho-α-position. If this is occupied they do not couple. β-Naphthol-6-sulphonic acid (Schaeffer's acid) couples very readily, whereas β-naphthol-8-sulphonic acid (Crocein acid) couples with difficulty, so that negative substituents at 8 seem to have some hindering effect.

As a rule naphthylamines couple easily and have little or no tendency to form diazoamino compounds. α-Naphthylamine couples in the para- position when this is free, and in the ortho- position when it is occupied. β-Naphthylamine couples only in the ortho-α- position, and if this is occupied no azo compound is formed. β-Naphthylamine-6-8-disulphonic acid (amino acid G) does not couple or only couples with great difficulty, depending on the diazo compound.

The case of the amino naphthols is more complicated, and Bülow divides them into three classes,[7] viz. :—

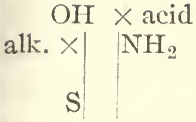
(1) Those which do not couple, viz. the sulphonic acids of 1.2 and 2.1.aminonaphthols.
(2) Those which couple in the same position whether in acid or alkaline solution.
(3) Those which give isomeric ortho azo compounds, depending on whether coupled in acid or alkaline solution.

The following formulæ give the chief aminonaphthol sulphonic acids, the cross indicating the position of the entering azo group, "alk." signifying that the coupling is carried out in alkaline solution, and "acid" in acid solution :

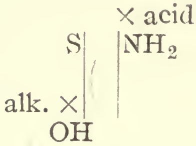


Aminonaphthol sulphonic acid S.

H-Acid.

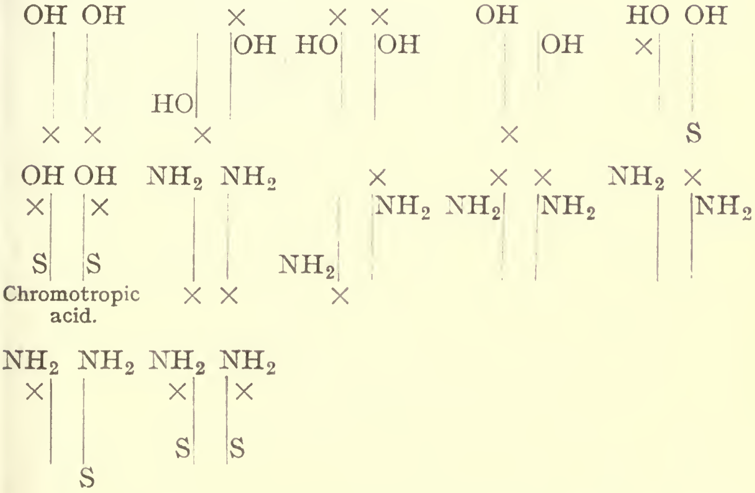


Aminonaphthol sulphonic acid G.



J-Acid.

The following formulæ give the coupling positions of the most important dioxy- and diamino-naphthalenes and their sulphonic acids :

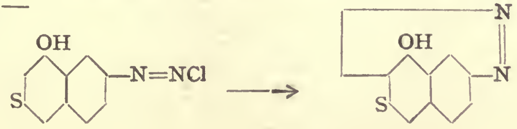


Chromotropic acid.

Phenol yields a mono-, dis- and tris- azo compound. Salicylic acid yields a monoazo compound with great ease, and a disazo compound with difficulty. Polyhydric phenols yield polyazo compounds, and different isomers are obtained under different conditions as regards alkalinity, etc.[8]

α-Naphthol gives a disazo compound, β-naphthol only a monazo. Monamines as a rule give only monazo compounds.

In some cases the azo group in one part of the molecule is capable of coupling with another part of the same molecule,[9] *e.g.*—



Colour and Constitution.—No definite laws are known governing the relation between the colour of an azo dye and its constitution, but certain generalities appear of which the following are the most important.

Simple azo compounds containing only benzene nuclei are yellow, brown or orange, and the colour deepens with increasing molecular weight, although carboxyl and sulphonic groups have but little effect.

Nitro groups have a considerable influence in deepening the colour, this effect being most marked when they are in the para position to the azo group, and least marked when they are in the ortho position.

Amino and hydroxyl groups deepen the colour, this effect being less marked when they are acylated, whereas alkylation frequently has the opposite effect, and in some cases the brightening of the colour on alkylation is remarkable. Alkoxy groups attached to the benzidine nucleus tend very strongly to produce blue and violet shades.

Tetrazotized benzidine coupled with two benzene rings gives yellow dyes, with two naphthylene rings red dyes. When coupled with one benzene and one naphthylene ring the colour is intermediate, viz. orange.

Azo dyes derived from H-acid tend towards blue shades, whereas green shades are apparently only obtained when there is a nitro group in the molecule.

There is a curious relationship between affinity for cotton and colour exhibited by benzidine dyes. All benzidine derivatives that give direct cotton colours, when tetrazotized and coupled with naphthylamine sulphonic acids give red dyes, and with naphthol sulphonic acids violet and blue dyes. On the other hand, benzidine derivatives not yielding direct cotton colours, give yellow or orange shades when coupled with naphthylamine sulphonic acids, and red shades when coupled with naphthol sulphonic acids.

Disazo dyes of the general structure

$$R'.N{=}N{-}R{-}N{=}N{-}R''$$

are red when R is a benzene ring, and black when a naphthalene ring derived from α-naphthylamine.

The orientation of the sulphonic acid groups in azo dyes is not without influence on the colour, although as a rule only slight differences in shade are produced. Thus, Orange IV. (sulphanilic acid→diphenylamine) is deeper coloured than the isomeric Metanil Yellow (metanilic acid → diphenylamine), and similarly in the naphthalene series dyes derived from R-acid are redder than isomeric dyes derived from G-acid.

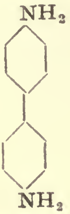
Dianisidine gives the purest blue shades when coupled with 1.8-dioxy- or 1.8-aminoxy-naphthylene sulphonic acids; but even benzidine gives blue shades with these acids, as do unsymmetrical dialkyl *p*-phenylenediamines when coupled with sulphonated 1.8-dioxy-naphthalenes.

Direct Cotton Colours.—The relation between chemical constitution and affinity for cotton is not understood, but a considerable number of bases are known which give azo dyes which are substantative to cotton. As a general rule, these are of the nature of para diamines, but there are important exceptions. Unsaturation also seems to increase the affinity.

The simplest base yielding direct cotton colours is *p*-phenylenediamine, and 1.4- and 1.5-diamino-naphthalene exhibit the same property as do also their sulphonic acids.

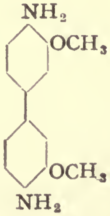
p_2-Diaminodiphenylamine also yields direct cotton colours.

The most important class of bases, however, includes benzidine and its derivatives, and here we find curious exceptions. The following all yield disazo compounds, which are substantative to cotton:



Benzidine.

Tolidine.



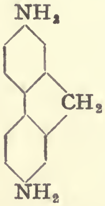
Dianisidine.

Dichlorbenzidine.

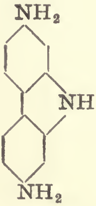
and in general all benzidine derivatives substituted in the ortho position to the amino groups.

If, however, there are any substituents in the ortho position to the diphenyl linkage, substantative dyes are not obtained. Thus, for example, when a sulphonic acid group is ortho to the amino group, substantative dyes are formed, whereas when meta to the amino group they are not; and the same holds true with halogen atoms and methyl, methoxy and carboxyl groups, etc.

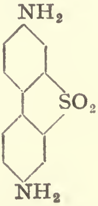
Substituents in the ortho position to the diphenyl bond, however, do not hinder the formation of direct cotton colours if they form part of a ring, all the following bases giving substantative cotton dyes :



Diaminofluorene.

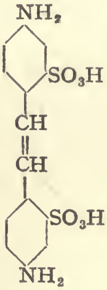


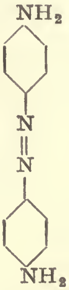
Diaminocarbazole.



Benzidine sulphone.

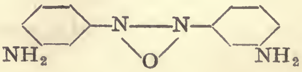
Diaminostilbene and its sulphonic acid both give direct cotton colours, as does also the analogous diaminoazobenzene





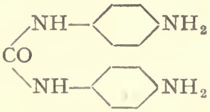
whereas the more saturated diaminodiphenyl methane and diaminodibenzyl do not.

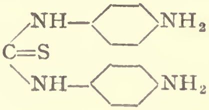
Diaminoazoxybenzole also gives direct cotton colours, although it is in no way a para diamine :



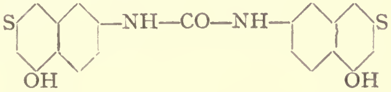
These colours, however, are dyed by a special method, viz. from a bath containing caustic, the goods then receiving an after-treatment with sulphuric acid.

A large number of amino-ureas and aminothio-ureas have been found to yield substantative azo dyes. The simplest of these are derived from *p*-phenylenediamine : [10]



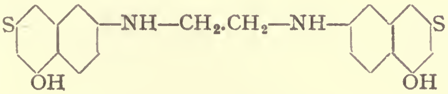


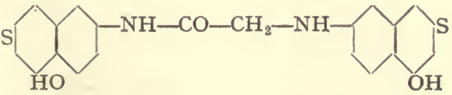
but more valuable dyes are obtained by using the corresponding derivatives of J-acid as a second component :



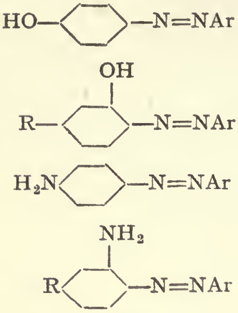
These dyes can be obtained either by coupling the urea with a diazo salt, or J-acid itself can be converted into an azo dye and the urea then formed by treatment with carbonyl or thiocarbonyl chloride. They are most valuable colours, most of the benzo fast scarlets belonging to this group.

J-acid itself gives substantative dyes, and this property is more strongly marked in phenyl J-acid, *m*-aminobenzoyl J-acid, and the compounds obtained by coupling two molecules of J-acid by means of ethylene chloride or chloracetyl chloride [11] :

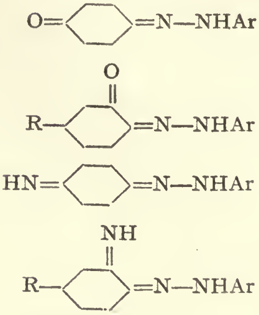




Constitution of the Azo-dyes.—The formulæ for the azo-dyes can be written either in the azo or the quinonoid form, *e.g.* :



Azo form.



Quinonoid form.

The quinoid structure receives support, at least in so far as ortho azo compounds are concerned, by the fact that *o*-oxy azo compounds do not form salts, and as a rule the amino group in *o*-amino azo compounds cannot be diazotized, and according to some authorities this quinonoid structure is supported by spectroscopic evidence.

On the other hand. the ease with which the azo group is split by reduction with the production of an amino compound rather points to the azo structure.

The question, which is chiefly of academic interest, cannot be said to be settled, and in all probability the truth will be found to lie in tautomerism.

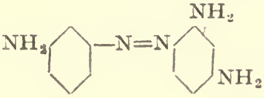
In the following pages the azo notation is always employed as it is the usual one, and renders the formation of the compounds under consideration more clear.

BASIC AZO DYES.

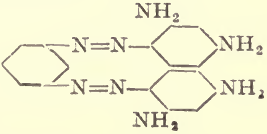
The number of these is limited and although still used to a certain extent their interest is historical rather than practical.

The simplest is aniline yellow (aminoazobenzene) which is interesting as the first azo dye discovered. It is manufactured by heating diazoaminobenzene with excess of aniline, or directly from aniline by treating the hydrochloride in the presence of excess of aniline with a concentrated solution of sodium nitrite at 40° C. It is not used as a dyestuff, but only as an intermediate compound.

Chrysoidine [12] is prepared by coupling one molecule of diazobenzene chloride with *m*-phenylenediamine. It gives bright yellow shades, but they are not fast. As crysoidine absorbs the chemically active rays it finds application in making "safe" lights for photographic dark rooms. Bismarck brown [13] is a mixture of a monazo and a disazo compound, and is obtained when sodium nitrite is added to acid solutions of *m*-phenylenediamine, the diazotized and tetrazotized base coupling as soon as formed. The constituents therefore have the composition :



and



Acid, Mordant and Afterchrome Azo Dyes.

All these contain one or more sulphonic acid groups.

Oxyazo dyes, of which one of the constituents is an ortho hydroxyl carboxylic acid, such as salicylic acid, form lakes with metallic salts, and hence are often dyed on mordanted fibre, as the colours are more fast than when no mordant is used.

Other oxyazo dyes have the property of forming lakes with chromium after they have been taken up by the fibre. These are dyed in the ordinary way without a mordant, the yarn being subsequently treated with potassium bichromate or chromium fluoride solution (after-chroming).[*] This after-treatment greatly enhances the fastness of the colour, but as a rule completely changes it, reds frequently being changed to blue or black. The property of after-chroming seems to be confined to ortho-oxyazo compounds, and is particularly marked when an orthoaminophenol, an orthoaminonaphthol or chromotropic acid is one of the constituents.

A third class of colours is known in which the chroming and dyeing take place simultaneously, ammonium bichromate being added to the dyebath. These are known as

[*] See Whittaker, "Dyeing with Coal Tar Dyestuffs," this series, p. 54.

autochrome or metachrome colours to distinguish them from afterchrome colours, and are mostly derived from picraminic acid or *o*-aminophenol.

The number of azo colours is very large, over a thousand being articles of commerce, and the following are merely a few typical examples. A full list will be found in Schultz, "Farbstofftabellen," together with notes on their preparation and chief tinctorial properties.

The notation employed is very simple, and is almost self-explanatory. The base mentioned first is the base which is diazotized and arrows point to the bases or phenols with which it is coupled, the words "alk." and "acid" denoting, when necessary, whether the coupling is carried out in acid or alkaline solution. If the product is further diazotized and coupled, this is notified in the same way by an arrow pointing in the same direction. On the other hand, if it is coupled with a diazo salt, this is shown by an arrow pointing in the opposite direction.

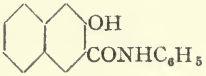
Orange I.	Sulphanilic Acid → α-Naphthol
Orange II.	Sulphanilic Acid → β-Naphthol
Methyl Orange	Sulphanilic Acid → Dimethyl Aniline
Fast Red A	Naphthionic Acid → Phenol
Naphthylamine Brown	Naphthionic Acid → α-Naphthol
Chromotrope 2R	Aniline → Chromotropic Acid
Chromotrope 2B	*p*-Nitraniline → Chromotropic Acid
Chromotrope 8B	Naphthionic Acid → Chromotropic Acid
Lanazyl Violet	H-Acid → Ethyl α-Naphthylamine
Lanazyl Blue	H-Acid → 1.5 Aminonaphthol
Chrome Yellow D	Brönner β-Acid → Salicylic Acid
Alizarine Yellow GGW	*m*-Nitraniline → Salicylic Acid
Biebrich Scarlet	Aminoazobenzene disulphonic Acid → β-naphthol
Crocein Scarlet	Aminobenzene sulphonic Acid → Crocein Acid
Resorcin Brown	Xylidine ↘ Sulphanilic Acid ↗ Resorcinol
Fast Brown G	Sulphanilic Acid ↘ Sulphanilic Acid ↗ α-Naphthol
Naphthol Blue Black	*p*-Nitraniline ↘ Aniline ↗ H-Acid
Naphthol Black	Amino G Acid → α-Naphthylamine → Amino R-Acid
Diamine Yellow N	Benzidene ↗ Phenol (subsequently ethylated) ↘ Salicylic Acid
Benzo Orange R	Benzidine ↗ Salicylic Acid ↘ Naphthionic Acid

Diamine Fast Red	Nitrobenzidine	↗ Salicylic Acid (coupled first) ↘ Neville and Winter's Acid
Congo Red	Benzidine	↗ Naphthionic Acid ↘ Naphthionic Acid
Benzopurpurine	Tolidine	↗ Naphthionic Acid ↘ Naphthionic Acid
Congo Corinth	Tolidine	↗ Naphthionic Acid ↘ Neville and Winters Acid
Azo Violet	Dianisidine	↗ Naphthionic Acid ↘ Neville and Winter's Acid
Benzo Indigo Blue	Benzidine	↗ α-Naphthylamine → 1.8-Dioxynaphthalene-4-sulphonic Acid ↘ 1.8-Dioxynaphthalene-4-sulphonic Acid
Columbia Black	Tolidine	alk. ↗ 2.8-Aminonaphthol-3.6-disulphonic Acid ↘ *m*-Toluylenediamine
Diamine Green G	Benzidine	alk. ↗ 1.8-Aminonaphthol-3-6-disulphonic Acid ↖ *p*-nitraniline ↘ Salicylic Acid
Congo Brown G	Benzidine	↗ Resorcinol ← Sulphanilic Acid ↘ Salicylic Acid
Sulphazurine	Benzidine sulphone disulphonic Acid	↗ Phenyl-β-naphthylamine ↘ Phenyl-β-naphthylamine
Brilliant Yellow	Diamino stilbene disulphonic Acid	↗ Phenol ↘ Phenol
Chrysophenine	Brilliant yellow with both hydroxyl groups ethylated	
St. Dennis Red	Diaminoazoxy benzene	↗ Neville and Winter's Acid ↘ Neville and Winter's Acid
Salmon Red	Diaminodiphenyl urea	↗ Naphthionic Acid ↘ Naphthionic Acid
Cotton Yellow G	Diaminodiphenyl urea	↗ Salicylic Acid ↘ Salicylic Acid
Brilliant Benzo Fast Violet	Diaminodiphenyl urea disulphonic Acid	↗ γ-Acid ↘ Phenyl-J-Acid
Cotton Yellow	p_2-Diaminodiphenyl urea	↗ Salicylic Acid ↘ Salicylic Acid

INGRAINE OR ICE COLOURS.

Azo dyes which do not contain sulphonic acid groups are insoluble in water, and hence cannot be used in the ordinary way. They can, however, be formed on the fibre by treating it with a phenol and then in a second bath with a diazotized amine. Owing to the necessity of carrying out the second operation in the presence of ice they are frequently known as "ice colours." The shades obtained are usually extremely fast, especially to washing.*

β-Naphthol is almost exclusively used as one component, although in recent years 2-oxy-β-phenylnaphthamide



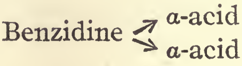
has been introduced with great success under the name Naphthol AS.

p-Nitraniline and dianisidine are the most usual amines, and can conveniently be used in the stabilized form of their diazo compounds.

Para Red is *p*-nitraniline → β-naphthol and Dianisidine Blue is $\text{dianisidine}\begin{array}{l}\nearrow \beta\text{-naphthol}\\ \searrow \beta\text{-naphthol}\end{array}$

DEVELOPED COLOURS.

These resemble the ice colours in so far that the final dyestuff is actually formed on the fibre by coupling. The first component to be applied, however, in this case is an azo dye. After it has been fixed it is either coupled with a diazo salt in a separate bath or the material is passed into a bath of nitrous acid whereby an amino group is diazotized, so that the dye on the fibre now contains a diazo group. It then couples with a suitable second component in a third bath. For example, the dyestuff



$$\text{Benzidine}\begin{array}{l}\nearrow \alpha\text{-acid}\\ \searrow \alpha\text{-acid}\end{array}$$

dyes cotton in reddish-blue shades. If the material is then treated with nitrous acid and subsequently passed through an alkaline solution of β-naphthol, deep navy blues are obtained which, unlike the original shade, are very fast.

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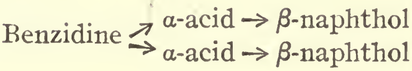
* See Whittaker, "Dyeing with Coal Tar Dyestuffs," this series, p. 59.

These navy blue shades are due to the formation of a tetrakisazo dye

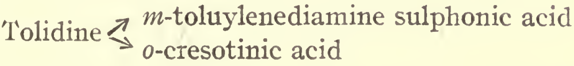


$$\text{Benzidine}\begin{array}{l}\nearrow \alpha\text{-acid} \rightarrow \beta\text{-naphthol}\\ \searrow \alpha\text{-acid} \rightarrow \beta\text{-naphthol}\end{array}$$

which is too insoluble to be used as such.

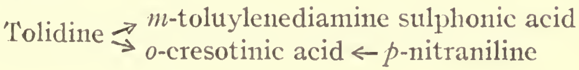
In the above case if *m*-toluylenediamine is substituted for β-naphthol, jet black shades are obtained.

Another example of a developed colour is Diamine Orange N. In this case the material is dyed with



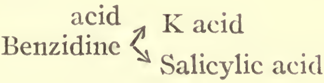
$$\text{Tolidine}\begin{array}{l}\nearrow m\text{-toluylenediamine sulphonic acid}\\ \searrow o\text{-cresotinic acid}\end{array}$$

and then developed with *p*-nitrodiazobenzene, the dyestuff formed being



$$\text{Tolidine}\begin{array}{l}\nearrow m\text{-toluylenediamine sulphonic acid}\\ \searrow o\text{-cresotinic acid} \leftarrow p\text{-nitraniline}\end{array}$$

Diamine green is applied in a similar way, the material first being dyed with



$$\begin{array}{c}\text{acid}\\ \text{Benzidine}\end{array}\begin{array}{l}\nearrow \text{K acid}\\ \searrow \text{Salicylic acid}\end{array}$$

and developed with *p*-nitrodiazobenzene.

Primulines are widely applied by this method (see p. 108).

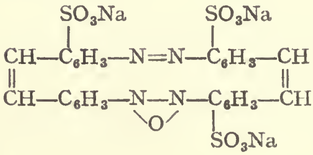
STILBENE DYES.

When *p*-nitrotoluol-*o*-sulphonic acid is heated with caustic soda solution fast yellow dyes are obtained, which, according to Green and his co-workers,[14] must be classed as azo dyes. The shade varies according to the temperature and duration of the treatment, and according to the concentration of the alkali, but the following gives some idea of the general conditions employed.

Sun yellow, Curcumin S.[15]—One part of sodium nitrotoluol sulphonate is dissolved in 3 parts of boiling water and 3 parts of caustic soda solution of 30 per cent. strength, slowly added. After neutralizing the dyestuff is collected in filter presses.

Direct Yellow G.[16]—One part of sodium nitrotoluol sulphonate is heated for 1½ hours with 12 parts of 10 per cent. caustic soda at 85° C., and then cooled and neutralized.

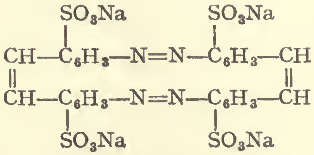
These dyes are no doubt complicated mixtures, but the chief constituent seems to be



$$\begin{array}{ccccccccccc} & & \mathrm{SO_3Na} & & & & & & \mathrm{SO_3Na} & & \\ & & | & & & & & & | & & \\ \mathrm{CH} & \text{—} & \mathrm{C_6H_3} & \text{—} & \mathrm{N} & = & \mathrm{N} & \text{—} & \mathrm{C_6H_3} & \text{—} & \mathrm{CH} \\ \| & & & & & & & & & & \| \\ \mathrm{CH} & \text{—} & \mathrm{C_6H_3} & \text{—} & \mathrm{N} & \text{—} & \mathrm{N} & \text{—} & \mathrm{C_6H_3} & \text{—} & \mathrm{CH} \\ & & & & \diagdown & \mathrm{O} & \diagup & & | & & \\ & & & & & & & & \mathrm{SO_3Na} & & \end{array}$$

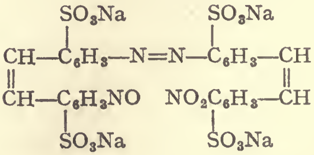
although they probably also contain azomethine derivatives, *i.e.* compounds containing the group —N=CH—

By careful reduction[17] orange dyes are obtained, *e.g.* direct orange, formed probably by the conversion of the azoxy group into an azo group :



$$\begin{array}{ccccccccccc} & & \mathrm{SO_3Na} & & & & & & \mathrm{SO_3Na} & & \\ & & | & & & & & & | & & \\ \mathrm{CH} & \text{—} & \mathrm{C_6H_3} & \text{—} & \mathrm{N} & = & \mathrm{N} & \text{—} & \mathrm{C_6H_3} & \text{—} & \mathrm{CH} \\ \| & & & & & & & & & & \| \\ \mathrm{CH} & \text{—} & \mathrm{C_6H_3} & \text{—} & \mathrm{N} & = & \mathrm{N} & \text{—} & \mathrm{C_6H_3} & \text{—} & \mathrm{CH} \\ & & | & & & & & & | & & \\ & & \mathrm{SO_3Na} & & & & & & \mathrm{SO_3Na} & & \end{array}$$

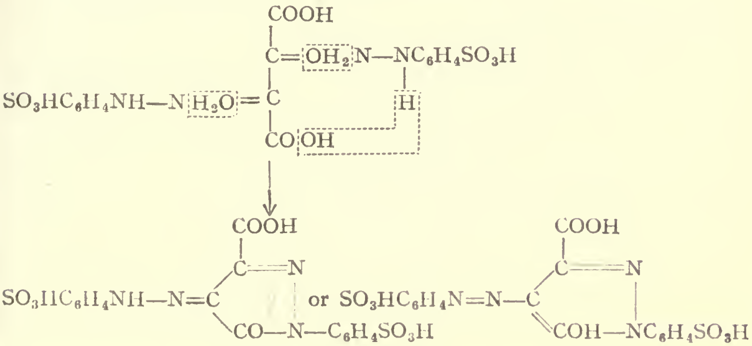
Oxidation, on the contrary, opens the azoxy linking giving the micado yellows :[18]



$$\begin{array}{ccccccccccc} & & \mathrm{SO_3Na} & & & & & & \mathrm{SO_3Na} & & \\ & & | & & & & & & | & & \\ \mathrm{CH} & \text{—} & \mathrm{C_6H_3} & \text{—} & \mathrm{N} & = & \mathrm{N} & \text{—} & \mathrm{C_6H_3} & \text{—} & \mathrm{CH} \\ \| & & & & & & & & & & \| \\ \mathrm{CH} & \text{—} & \mathrm{C_6H_3NO} & & & & & & \mathrm{NO_2C_6H_3} & \text{—} & \mathrm{CH} \\ & & | & & & & & & | & & \\ & & \mathrm{SO_3Na} & & & & & & \mathrm{SO_3Na} & & \end{array}$$

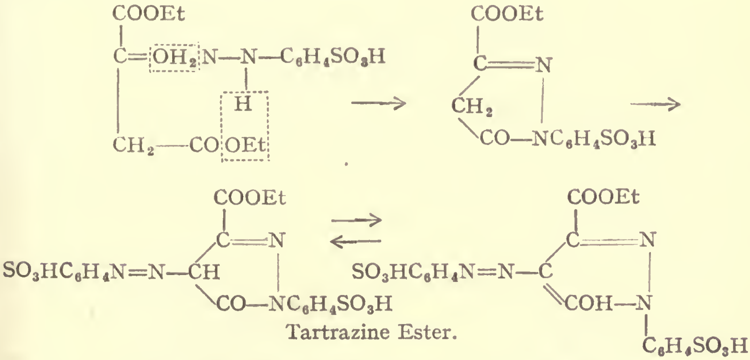
PYRAZOLONE DYES.

These are best classed as azo dyes, as they probably act tautomerically in the azo form. By far the most important is Tartrazine, which is manufactured by two methods. The older method consists in condensing dioxytartaric acid with phenylhydrazine sulphonic acid :[19]



Tartrazine.

A more modern method[20] consists in condensing one molecule of phenylhydrazine sulphonic acid with oxalacetic ester and then coupling the product with diazotized sulphanilic acid, the ester thus formed being subsequently hydrolysed :



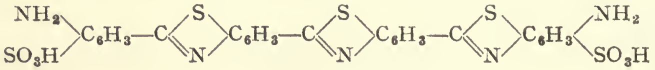
Tartrazine Ester.

Tartrazine has no affinity for cotton, but dyes wool in beautiful yellow shades, which are remarkably fast to light.

Other dyes containing the pyrazolone ring have been placed on the market, but they are of no great importance. They are all prepared by coupling diazo salts with pyrazolones.[21]

THIAZOLE AZO DYES.

As stated on page 81, when *p*-toluidine is fused with sulphur a compound, dehydrothiotoluidine, is formed which contains the thiazole ring. This substance has no tinctorial properties, but if more sulphur and a higher temperature is used a more complicated substance of very similar constitution is formed, which gives a soluble disulphonic acid having affinity for cotton. This has been named Primuline [22] and has the formula:



In its manufacture 10 parts of *p*-toluidine and 6½ parts of sulphur are heated together at 250° C. until no more sulphuretted hydrogen is formed. The melt is then cooled, ground up, and heated to 80° C., with 4–5 parts of 20 per cent. oleum until a sample is completely soluble in alkali. As the free acid is almost insoluble the melt is drowned in water, the precipitate filtered and washed, and then converted into its sodium salt by alkali.

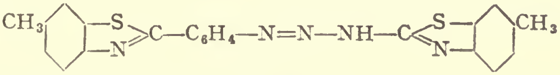
Primuline dyes cotton in bright yellow shades, but these are too fugitive too be of any value. Fairly fast shades, however, can be obtained by diazotizing on the fibre and then coupling, Primuline Red being obtained when β-naphthol is used as a developer and Primuline Bordeaux when ethyl-β-naphthylamine is used. These were the first developed or ingrain colours used, and so have historical interest.

Owing to the fact that the diazo salt of primuline is very easily decomposed by light, photographic effects can be obtained by drying the fabric in a dark room after diazotization and then exposing it under a positive transparency. On subsequent treatment with the alkaline β-naphthol the pattern comes out red on a white ground.

Primuline azo dyes are not confined to those which are developed on the fibre, the following being on the market as such :—

Cotton Yellow R	Primuline → Salicylic Acid.
Rosophenine SG	Primuline → Neville and Winter's Acid.
Alkali Brown	Primuline → *m*-Phenylene diamine.

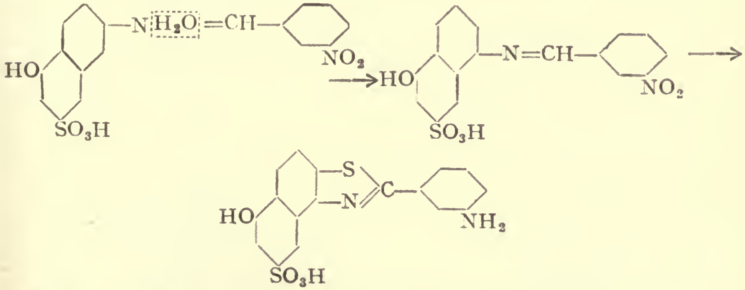
Clayton yellow[23] is derived from dehydrothiotoluidine sulphonic acid by diazotizing one molecule and coupling it with another. It is a diazo amino compound and is the polysulphonic acid of



The dyestuff makes a useful indicator, as although it is turned red by caustic alkali, it is almost unaffected by soda, ammonia, phenolates, and naphtholates.

In addition to this one or two true azo compounds are derived from dehydrothiotoluidine. Thus Diamine Pink is obtained when diazotized dehydrothiotoluidine is coupled with 1.8-chloronaphthol-3-6-disulphonic acid, and other similar dyes are obtained from dehydrothioxylidine.

An interesting series of thiazole dyes have been prepared by condensing *m*-nitrobenzaldehyde with 2-amino-5-oxynaphthalene-7-sulphonic acid and subsequent treatment of the resulting azomethine with sodium sulphide and sulphur.

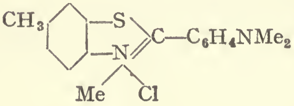


This gives red azo dyes when coupled with diazo compounds which when diazotized on the fibre and developed form very fast red shades, *e.g.* Diazo Brilliant Scarlet.[24]

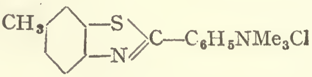
One or two thiazole dyes may conveniently be mentioned here, although they contain no azo group.

Mimosa.—This is a yellow dye obtained by treating diazotized primuline with ammonia.

Thioflavine T is a quaternary ammonium salt obtained by methylating dehydrothiotoluidine, and has the formula



or



and thioflavine S is its sulphonic acid.

Chloramine Yellow is an oxidation product of dehydrothio toluidine.

REFERENCES AND LITERATURE.

[1] D.R.P. 85, 387.
[2] Ibid.
[3] 94,495 ; 97,933.
[4] D.R.P. 155,083 ; 171,024 ; 172,446 ; 175,593 ; 176,618–19–20.
[5] *B*. **30**, 93, 2203, 2899. D.R.P. 103,660.
[6] *B*. **9**, 221.
[7] *Ch. Ztg*. **19**, 1011.
[8] *J. pr*. **78**, 384.
[9] D.R.P. 92,012.
[10] D.R.P. 46,737 ; 47,902.
[11] D.R.P. 122,904 ; 126,133 ; 126,801 ; 128,195 ; 132,511 ; 133,466.
[12] *B*. **10**, 213, 350, 388, 654.
[13] *Z*. 1867, 278.
[14] *Soc*. **85**, 1424, 1432; **91**, 2076; **93**, 1721.
[15] *B*. **19**, 3234; D.R.P. 38,735.
[16] D.R.P. 79,241.
[17] D.R.P. 46,252 ; 48,528.
[18] D.R.P. 42,466.
[19] *B*. **20**, 834; *A*. **294**, 219; D.R.P. 43,294.
[20] Friedländer V., 502. E.P. 765^{97}. *A*. **294**, 232; *Ch. Ztg*. **22**, 546.
[21] D.R.P. 193,141 ; 193,142.
[22] *B*. **22**, 422, 580, 968, 1063.
[23] D.R.P. 53,935.
[24] D.R.P. 163,040 ; 165,126–7.

Interesting sketches on the progress of azo dyes will be found in the various volumes of Friedländer's "Fortschritte."

The pyrazolone colours are well treated in "Die Pyrazolonfarbstoffe." C. Cohn (Stuttgart, 1910).

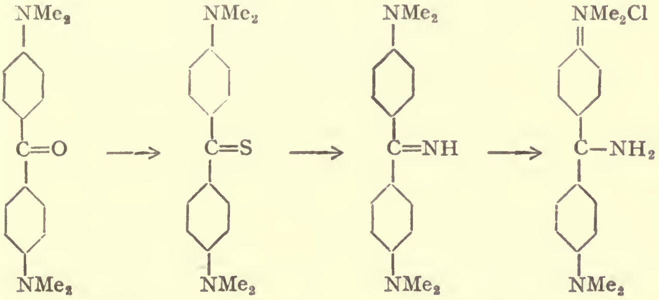
The history and structure of the diazo and diazonium salts are treated by Cain in "The Chemistry of the Diazo Compounds." London, 1908.

Special works dealing with azo dyes are :

Bülow, "Chemische Technologie der Azofarbstoffe." 1897.
Pauli, "Synthese der Azofarbstoffe." 1904.

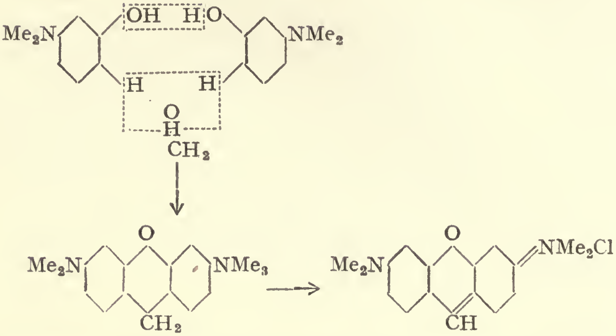
SECTION IV.—THE DIPHENYLMETHANE DYES

THIS is not an important class of colouring matter, but one or two numbers are worthy of notice. The simplest of these is auramine O, which was originally obtained by heating Michler's ketone with zinc and ammonium chlorides to 150° C.;[1] but a better process consists in heating the ketone with sulphur and sodium and ammonium chlorides in a stream of ammonia gas.[2] Probaoly the thioketone is first formed, the sulphur atom then being displaced by an imino group:



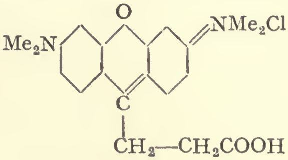
The corresponding *o*-toluidine derivative is auramine G.[3] Both dye yellow on a tannin mordant, but as they are readily decomposed by boiling water must be dyed at a low temperature.

One or two diphenyl methane derivatives containing the pyronine ring have also found application. The most important of these is pyronine G.[4] This is prepared by condensing dimethyl-*m*-aminophenol with formaldehyde and subsequent oxidation of the leuco base thus obtained:



The corresponding ethyl compound is pyronine B.

An interesting dyestuff, rhodoamine S,[5] is obtained by substituting succinic anhydride for formaldehyde :



Other dyestuffs containing the pyronine ring are mostly derivatives of triphenylmethane and are treated in the next section.

REFERENCES AND LITERATURE.

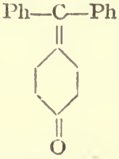
[1] D.R.P. 29,060.
[2] D.R.P. 53,614, 58,277.
[3] D.R.P. 67,478.
[4] D.R.P. 58,955, 59,033.
[5] D.R.P. 51,983.

SECTION V.—THE TRIPHENYL METHANE DYES

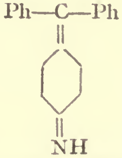
THESE are all amino- or oxy- derivatives of triphenyl methane and may be divided into four groups as follows:—

1. Malachite Green group, derived from p_2-diamino triphenyl methane.
2. Fuchsine or Rosaniline group, derived from p_3-triamino triphenyl methane.
3. The Rosolic acids, derived from p_3-trioxytriphenyl methane.
4. The Phthaleins, Rhodamines and Pyronines, derived from dioxy or diamino triphenyl methane carboxylic acid.

An alternative classification is to divide them into fuchsones and fuchsonimines according to whether they are derived from oxy or amino triphenyl methane.



Fuchsone.



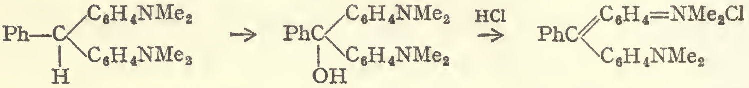
Fuchsonimine.

Technically the malachite greens and rosanilines are the most important.

The triphenylmethane dyes are remarkable for the brightness of their shades. The unsulphonated dyes are basic colours, the sulphonated members acid colours.

1. THE MALACHITE GREEN GROUP.

When p-amino triphenylmethane is oxidized the corresponding carbinole is formed. This is a colourless compound but is unstable, and in the presence of acids splits out water and passes into the highly coloured quinonoid compound, the dyestuff :

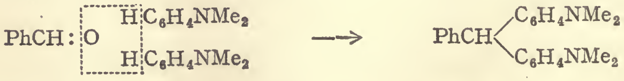


If this dyestuff is treated with alkali, the corresponding highly coloured and ionized ammonium base is formed. On standing, however, the colour fades and the electrical conductivity falls and the ammonium base passes into the colourless and non-ionized carbinol : [1]

On reduction the dyestuff passes into the triphenyl methane derivative, which must therefore be regarded as its leuco compound.

The malachite green dyes can be prepared by condensing benzotrichloride with an aromatic amine having a free para position : [2]

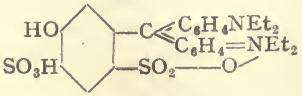
This process, however, is out of date, the dyes now being manufactured by condensing an aromatic aldehyde (benzaldehyde) with an aromatic amine, condensation taking place in the para position to the amino group.[3] The leuco compound thus formed is oxidized to the carbinol (usually with lead dioxide) and this converted into the dyestuff by treatment with hydrochloric acid :



Various agents have been proposed from time to time for bringing about the condensation, but anhydrous zinc chloride gives the best results. The aldehyde and the base in calculated quantities are stirred together in a steam-heated vessel, and the zinc chloride added slowly, the weight of chloride used being about the same as that of the aldehyde. The temperature of the melt is maintained at 90–110° C. for about two days, and then any unchanged aldehyde and/or base blown off by steam. The carbinol is then filtered off from the zinc chloride solution, washed, dissolved in dilute hydrochloric acid and oxidized with lead dioxide. After precipitating the dissolved lead with the calculated quantity of sodium sulphate the dyestuff is salted out, often as its zinc chloride double salt, by adding common salt and zinc chloride.

The simplest member of this group is Doebner's violet, prepared from benzaldehyde and aniline, but it is of no technical value. Far the most important member is malachite green itself, which is prepared from benzaldehyde and dimethyl aniline. Its dichloro- derivative, obtained from dichlor benzaldehyde, has been placed on the market as Victoria green. The corresponding ethyl compound, obtained from benzaldehyde and diethyl aniline, has found some application under the name of brilliant green.

Acid Malachite Green Dyes.—The sulphonated malachite green dyes have found application as acid wool colours. They can be obtained by condensing an aromatic aldehyde with a sulphonated base, or by sulphonating the leuco compound. One of the best-known of these sulphonated colours is Patent Blue V.[4] This is manufactured by condensing *m*-oxybenzaldehyde with diethyl aniline, and then treating the leuco compound thus formed with oleum at the ordinary temperature until a sample is completely soluble in water. The sulphonated leuco base thus obtained is oxidized to the dyestuff in the usual way. As the dyestuff contains both acid and basic groups, internal salt formation takes place:



Another process by which this dyestuff is manufactured consists in condensing *m*-nitrobenzaldehyde with diethyl aniline and then reducing the nitro group to an amino group. The amino group is then replaced by hydroxyl by the diazo reaction and the leuco base sulphonated as before.

A few dyes have been prepared which belong to the malachite green group and at the same time contain an azo group. They are not of great importance, but azo green is worth mentioning. This is prepared by condensing *m*-nitrobenzaldehyde with dimethyl aniline and then reducing the nitro group. The amino leuco base is then diazotized and coupled with salicylic acid in the usual way. The product dyes green on a chrome mordant, but the shades are very loose to soap.

2. THE FUCHSINE OR ROSANILINE GROUP.

The simplest and best known member of this group is fuchsine or rosaniline itself, the constitution of which was demonstrated by E. and O. Fischer in the following manner.[5]

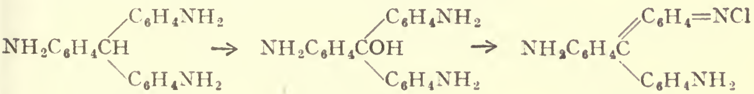
Rosaniline when reduced gives a colourless compound (paraleucaniline) which when diazotized and reduced by boiling with alcohol gives triphenylmethane.

On the other hand, triphenylmethane gives a trinitro compound which on oxidation gives a carbinol which passes on reducing the nitro groups into pararosaniline. Obviously paraleucaniline is a triamino triphenyl methane, but the position of the amino groups is uncertain.

Now when benzaldehyde is condensed with aniline a diamino triphenyl methane is obtained, which yields a dioxy derivative when the amino groups are replaced by hydroxyl by the diazo reaction. This dioxy derivative gives p_2-dioxybenzophenone when fused with alkali, and hence the amino groups in the diamino triphenyl methane must both have been in the para position to the methane carbon atom.

Again, *p*-nitrobenzaldehyde condenses with aniline to form a nitrodiamino triphenyl methane in which we are justified in taking for granted that the two amino groups are in the para position, and in which the nitro group must be in the para position. Since this on reduction gives leucaniline it follows that in this the three amino groups are all in the para position.

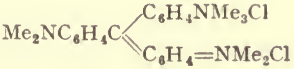
From this it is clear that the leuco bases of the rosaniline dyes are triamino triphenyl methanes and on oxidation pass into the corresponding carbinols and dyes in a manner exactly analogous to the malachite greens :



$$NH_2C_6H_4CH\begin{array}{l}\diagup C_6H_4NH_2\\ \diagdown C_6H_4NH_2\end{array} \rightarrow NH_2C_6H_4COH\begin{array}{l}\diagup C_6H_4NH_2\\ \diagdown C_6H_4NH_2\end{array} \rightarrow NH_2C_6H_4C\begin{array}{l}/\!\!/ C_6H_4{=}NCl\\ \diagdown C_6H_4NH_2\end{array}$$

Leuco-base. Carbinol. Dyestuff.

It is instructive to observe the change in colour that takes place on the entrance of alkyl or aryl groups into the amino groups. The unsubstituted rosanilines are red, but the alkylated members give various shades of violet or blue, depending on the number of alkyl groups. The hexamethyl derivative (crystal violet) when treated with methyl chloride forms an ammonium salt which is marketed as methyl green :



$$Me_2NC_6H_4C\begin{array}{l}\diagup C_6H_4NMe_3Cl\\ \diagdown\!\!\diagdown C_6H_4{=}NMe_2Cl\end{array}$$

Aryl groups have a similar but more pronounced effect in shifting the colour towards the blue end of the spectrum, the triphenyl rosanilines being blue dyes.

There are four processes for the manufacture of rosanilines.

(*a*) *Old Fuchsine Process.*—This is the original method, and is still largely used. It consists in oxidizing a mixture of bases, one of which must contain a free hydrogen atom in the para position to the amino group, and one of which must contain a methyl group in this position. If a mixture of equal molecules of aniline and *p*-toluidine is oxidized pararosaniline * is obtained. Pure rosaniline itself is not much

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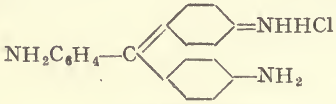
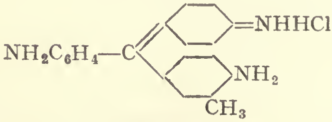
* The name pararosaniline was invented before the constitution was known, and was not given with reference to the position of the amino groups.

used except as an intermediate product in the manufacture of rosaniline blues (see p. 122), the commercial dyestuff, magenta, being obtained by oxidizing a mixture of aniline and *o*- and *p*-toluidine (aniline oil for red) and hence containing not only rosaniline but the isomeric substance, homorosaniline:



Pararosaniline.



Homorosaniline.

A very large number of oxidizing agents have been proposed, such as stannic chloride, mercuric chloride, arsenic acid and nitrobenzole. Of these the first two are far too costly for use on the large scale, and in any case the best results are obtained with arsenic acid and nitrobenzole, and both are used. Arsenic acid has the great disadvantage of being very poisonous, and it is impossible to obtain an arsenic-free product by its use, as it arsenates the bases to a certain extent. For this reason, and owing to the trouble of having to deal with strongly arsenical effluent, the process is almost obsolete. It is carried out by heating the mixed bases with syrupy arsenic acid to 180–190° C. for 10–24 hours.[6]

The oxidation with nitrobenzole [7] is much more satisfactory from a works point of view, and has now almost completely displaced the arsenic acid oxidation. Details naturally vary at different factories, but in all cases iron turnings, about 5 per cent. of the weight of the bases, are added to assist the oxidation, and it is usual to employ from one-half to one-third of the bases in the form of their hydrochlorides.

The proportion of bases used varies also in different works, but as a rule aniline and ortho and para toluidine are present in about equal quantities. It is not customary to use pure nitrobenzole for the oxidation, as it is more economical to employ the mixture of nitrobenzole and nitrotoluoles used in making aniline oil for red.

The process is carried out in a cast-iron kettle provided with a reflux condenser and an efficient agitator and heated by direct fire, gas firing being usually employed. The bases, or mixture of bases with the *dry* hydrochlorides, are well agitated with half their weight of nitrobenzole and heated to 190° C. The iron turnings are then slowly fed in and the agitation and temperature maintained until a sample on being withdrawn sets solid, which is usually the case after 10–12 hours. When the oxidation is complete the melt is run out into shallow iron trays and allowed to cool. It is then broken up, dissolved in water and unchanged nitrobenzole and bases blown off with steam, after which the grosser insoluble impurities are allowed to settle and the supernatant liquor drawn off and filtered. The filtrate on cooling first deposits a certain amount of a violet colouring matter, and this is removed by filtration before the main bulk of the magenta is allowed to separate. The separation of the magenta either takes place on simple cooling, or a certain amount of salt is added to the solution to render the dye less soluble. It is finally recrystallized from water containing some hydrochloric acid.

(*b*) *The New Fuchsine Process.*—When formaldehyde reacts with a primary aromatic base, such as aniline, condensation takes place with the elimination of water, anhydroformaldehyde aniline being produced :

$$H_2C{=}O + H_2NC_6H_5 \quad = \quad CH_2{=}NC_6H_5$$

If this is heated to 100° C. with aniline hydrochloride in aniline solution for some hours, condensation takes place, together with intramolecular rearrangement and p_2-diaminodiphenylmethane is formed :

$$CH_2{=}NC_6H_5 + C_6H_5NH_2 \quad = \quad (NH_2C_6H_4)_2CH_2$$

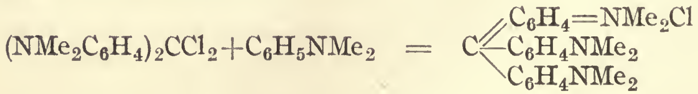
and this on heating to a higher temperature with aniline hydrochloride and an oxidizing agent readily yields magenta.[8] In factory practice it is usual to carry out the two latter steps in one operation by heating the formaldehyde condensation product with about twice its weight of nitrobenzole in presence of excess of aniline and aniline hydrochloride for some hours at about 170° C. As in the old process, it is usual to add some ferrous chloride or iron turnings to assist the oxidation.

The process is of wide application, as different bases can be used at the various steps and a wide variety of colouring matters thus obtained. It is largely employed for the manufacture of new fuchsine. This is made by condensing formaldehyde with *o*-toluidine and heating the resulting condensation product with *o*-toluidine in the presence of *o*-nitrotoluol as an oxidizing agent.[9]

(*c*) *Phosgene Process.*—This process is limited to the manufacture of alkylated rosanilines. It consists in allowing phosgene to react with a tertiary base, such as dimethylaniline, whereby a benzophenone derivative is formed:

$$2C_6H_5NMe_2+COCl_2 \rightarrow \underset{\text{Michler's Ketone.}}{NMe_2C_6H_4.CO.C_6H_4NMe_2}$$

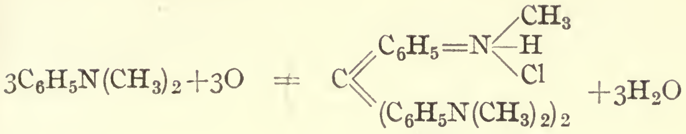
The ketonic oxygen atom is then replaced by two atoms of chlorine by treatment with phosphorus chloride and the resulting dichloride condensed with another molecule of a base :



$$(NMe_2C_6H_4)_2CCl_2+C_6H_5NMe_2 = C\left\langle\begin{array}{l} {=}C_6H_4{=}NMe_2Cl \\ {-}C_6H_4NMe_2 \\ {-}C_6H_4NMe_2 \end{array}\right.$$

Instead of a chloride of phosphorus many factories replace the ketonic oxygen atom by using excess of carbonyl chloride. The reaction takes place readily at about 50° C. and is complete after about six hours.[10]

(*d*) *Methyl Violet Process.*—This consists in oxidizing dimethyl aniline, and is probably really to be regarded as a modification of the new fuchsine process, the formaldehyde being formed *in situ* from one of the methyl groups. The product is pentamethyl rosaniline :



$$3C_6H_5N(CH_3)_2+3O = C\begin{cases} C_6H_5{=}N\begin{cases}CH_3\\ H\\ Cl\end{cases} \\ (C_6H_5N(CH_3)_2)_2\end{cases} +3H_2O$$

Methyl Violet.

The oxidation is brought about by heating to 40–60° C. with cupric chloride, or a mixture of cupric nitrate or sulphate and common salt, in the presence of acetic acid or phenol, the copper being subsequently precipitated by the addition of sodium sulphide.[11]

When methyl violet is boiled with benzyl chloride and alkali in alcoholic solution, benzyl pentamethyl rosaniline is formed.[12] This dyes in rather bluer shades than methyl violet, and finds application under the name of methyl violet 6B.

When rosaniline is methylated by treatment with methyl chloride, not more than three methyl groups can be introduced, but a hexamethyl rosaniline can be prepared by indirect methods, and this hexamethyl compound occurs in commerce as crystal violet. It is manufactured from dimethyl aniline by the phosgene process, or by condensing tetramethyl diaminobenzhydrol with dimethylaniline in the presence of concentrated sulphuric acid at 100° C. After neutralizing the acid the excess of dimethyl aniline is blown off by steam, and the leuco base oxidized with lead dioxide in the usual way: [13]

$$(Me_2NC_6H_4)_2CH\boxed{OH\quad H}C_6H_4NMe_2 \rightarrow (Me_2NC_6H_4)_3CH$$

Leuco Crystal Violet.

As stated on page 117 hexamethyl rosaniline is capable of uniting with a seventh molecule of methyl chloride to give a quaternary ammonium salt. The manufacture is carried out by heating methyl violet base in alcoholic solution in an autoclave to 95° C. and then pumping in methyl chloride, alkali being simultaneously added so as to keep the solution neutral. The resulting dyestuff is used for dyeing silk green under the name of methyl green.[14]

Ethyl derivatives corresponding to the above polymethyl rosanilines have also been prepared, but do not call for special notice.

Acid Triphenylmethane Dyes.—Acid dyestuffs are obtained from magenta and its derivatives by the introduction of sulphonic acid groups. Magenta itself on treatment with four parts of 20 per cent. oleum at 120–170° C. yields a trisulphonic acid known as acid magenta.[15] When sulphonation is complete the melt is dissolved in water, limed out, and the calcium salt of the dyestuff converted into the sodium salt by double decomposition with sodium carbonate. The sulphonation products of methyl and crystal violet are of no value as dyestuffs, but valuable acid dyes are obtained by sulphonating phenyl and tolyl rosanilines. These phenyl and tolyl rosanilines are too insoluble in water to be used as dyestuffs although they can be applied in alcoholic solution, but their sulphonic acids are readily soluble and have been used to a considerable extent.[16]

The unsulphonated bases are manufactured by heating rosaniline with aniline or toluidine in the presence of an organic acid or a salt of an organic acid. The part played by the organic acid is purely catalytic, and when the reaction is finished the acid can be recovered unchanged. Technically, acetic acid and benzoic acids are the only ones used, but salicylic, stearic and oleic acids function in a similar way. Dicarboxylic acids, on the other hand, do not seem to have the same effect.

The most important of these arylrosanilines is the triphenyl derivative, usually known as aniline blue, spirit soluble, or spirit blue. In its manufacture 25 parts of rosaniline and two parts of benzoic acid are heated to 180° C. with 250 parts of aniline. One part of benzoic acid is then slowly added, the temperature being maintained at 180° C. and the melt well agitated. Torrents of ammonia gas are evolved and after about 8–9 hours the condensation is complete. The melt is then allowed to cool, and when cold emptied into sufficient hydrochloric acid to dissolve the aniline and precipitate the dyestuff as its insoluble hydrochloride. In order to obtain pure blue shades almost chemically pure aniline, free from toluidine, must be used. Such qualities of aniline are known in commerce as "aniline or blue."

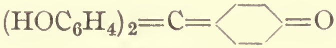
On treating aniline blue with ten parts of concentrated sulphuric acid at 35° C. it is converted into a monosulphonic acid, which is easily isolated by simply running the melt into water, as the free acid is insoluble. The sodium salt, however, dissolves readily, and is used for wool and silk under the name of Nicholson's blue or alkali blue.

Sulphonation at 100° C. leads to a trisulphonic acid (water blue) which is used for dyeing cotton on a tannin or tin mordant.

Diphenyl naphthyl methanes have been obtained by methods similar to those used in the manufacture of triphenyl methanes. Thus, Michler's ketone condenses with phenyl-*α*-naphthylamine to form Victoria blue, and with *p*-tolyl-*α*-naphthylamine to form night blue. This latter forms insoluble compounds with certain dyes and is used in their estimation.

3. Aurines or Rosolic Acids.

The aurines or rosolic acids are the hydroxyl analogues of rosaniline :



Pararosolic Acid.

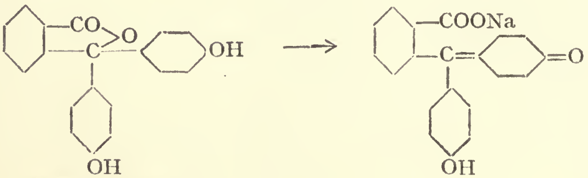
They can be manufactured by condensing formaldehyde with phenols in a manner exactly analogous to the new fuchsine process, or by condensing phenols with oxalic acid in the presence of sulphuric acid, the decomposition of the oxalic acid furnishing the methane carbon atom.[17]

They have but little affinity for the fibre and are almost useless as dyestuffs, although some of their lakes were at one time used for colouring paper.

About the most important is chrome violet R, obtained by condensing formaldehyde with salicylic acid, the leuco compound of which is regarded as trioxytriphenyl methane tricarboxylic acid.

4. THE PHTHALEINS AND RHODAMINES.

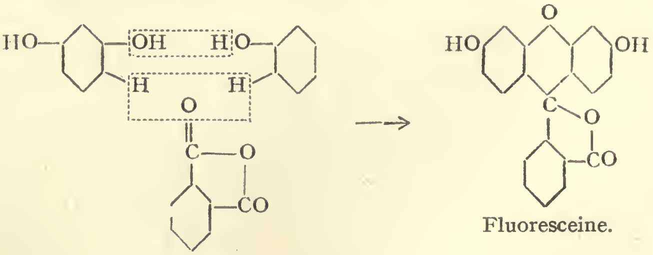
Phenols condense with phthalic anhydride with loss of water and formation of triphenyl methane derivatives. In the case of phenol itself the product (phenolphthalein) is colourless, but forms intensely coloured salts, salt formation probably being accompanied by an opening of the lactone ring :



Phenolphthalein.

Phenolphthalein itself finds no application as a dyestuff, but is used as an indicator and as a mild purgative.[18]

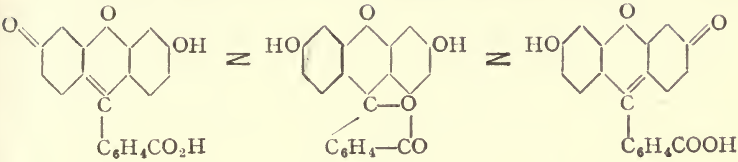
If instead of phenol, resorcinol is condensed with phthalic anhydride, a phthalein is formed, and in addition a molecule of water is split out between two hydroxyl groups with the formation of a heterocyclic ring : [19]



Fluoresceine.

Compounds containing this ring system are known as pyronines, of which the fluoresceins are the hydroxyl derivatives and the rhodamines the amino derivatives.

As a class these dyes are notable for the beauty and brilliance of their shades, and the majority exhibit fluorescence, probably owing to their undergoing double symmetrical tautomerism,[20] *e.g.* :



The condensation of phthalic anhydride with resorcinol can be brought about simply by heating the two together for some hours to 180–200° C., but takes place more readily in the presence of a condensing agent such as zinc chloride or sulphuric acid.

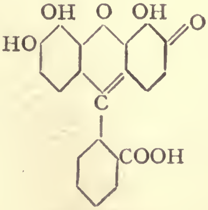
Fluorescein itself is scarcely used as a dyestuff, although its sodium salt occurs under the name uranine, but its bromo and iodo substitution products meet with considerable application. The tetrabrominated product is eosine, the bromination being brought about at the ordinary temperature in aqueous or alcoholic solution.[21]

Diiodo and tetraiodo fluoresceins are obtained when fluorescein is dissolved in dilute caustic soda and treated with the calculated amount of iodine in the same solvent. They find application for photographic purposes under the name of erythrosine.

Phloxine is tetrabromdichlorfluoresceine, prepared by condensing dichlorphthalic acid with resorcinol and then brominating, and Rose Bengal is the corresponding tetraiodo compound.

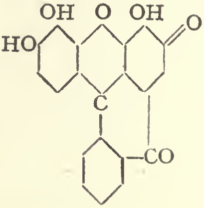
Nitrobromo fluoresceins have also been described.

Two important colours also belonging to this class are galleïne and cœruleïne, which are derived from pyrogallol.[22] The condensation is brought about by heating phthalic anhydride and gallic or pyrogallic acid and sulphuric acid to 200° C.:



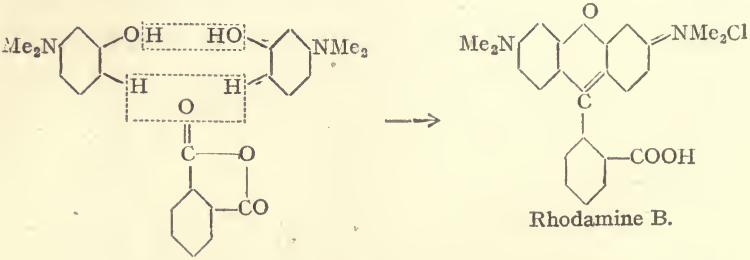
Galleine.

Galleïne produces red-violet shades on a chrome mordant and finds considerable application in printing. On further heating with 20 parts of concentrated sulphuric acid it loses a molecule of water, forming cœruleïne :



This produces olive-green shades on a chrome mordant.

The rhodamines are the amino analogues of fluoresceine, and are derived from *m*-aminophenol. They are manufactured by condensing phthalic anhydride with dimethyl or diethyl-*m*-aminophenol : [23]



Rhodamine B.

or by replacing the hydroxyl groups in fluoresceine by chlorine by means of phosphorus chloride and then heating the fluoresceine chloride thus produced with alkylamines.

The former process is the more convenient, and is carried out by heating 10 parts of dimethyl-*m*-amino phenol with 12 parts of phthalic anhydride for five hours at 170° C. out of contact with the air. On cooling the melt sets solid, and consists chiefly of the phthalate of the dye base. This is too insoluble for use as a dyestuff, and must be converted into the more readily soluble chloride, sulphate, or oxalate. This can be done by digesting with cold aqueous ammonia, and then extracting the free base with benzole or other solvent, the chloride being subsequently obtained from the benzole extract by treatment with hydrochloric acid, or the phthalate can be digested with hot concentrated soda solution, and the residual free dye base converted into a soluble salt by treatment with acid. Technically the latter is the more convenient process, as it avoids the use of organic solvents, but the former gives the purer product.

The rhodamines give blue-red shades on silk and wool which are strongly fluorescent.

When fluoresceine chloride is heated with aniline or toluidine, phenyl and tolyl rhodamines are formed. On sulphonation these yield valuable violet acid dyes, the phenyl derivative being violamine B and the tolyl derivative violamine R.

REFERENCES AND LITERATURE.

[1] *B*. **33**, 303.
[2] *B*. **11**, 1236; **12**, 1462; **13**, 610, 2222; **15**, 232. D.R.P. 4,332.
[3] *B*. **12**, 796.
[4] D.R.P. 46,384; 48,525; 50,286; 50,293; 50,440; 55,621; 64,736; 66,791; 69,199; 71,156; 74,014.
[5] *B*. **13**, 2204.
[6] *Dingl*. **266**, 455, 503, 547.
[7] *B*. **6**, 25. D.R.P. 16,750; 67,128; 68,464.
[8] D.R.P. 53,937; 55,565; 55,848; 61,146; 87,934; 96,762.
[9] D.R.P. 59,775.
[10] D.R.P. 27,789; 29,943.
[11] *B*. **6**, 352.
[12] *B*. **16**, 2904.
[13] D.R.P. 26,016; 27,032; 27,789; 29,943; 29,962.
[14] B. **6**, 352, 363; **16**, 2904.
[15] D.R.P. 2096, 8764.
[16] *Dingl*. **162**, 297; *C.r*. **54**, 428; **56**, 945; **57**, 1131. *Jahr*. 1862, 347, 696; 1863, 417. *B*. **5**, 417.
[17] *A*. **194**, 119; **202**, 184.
[18] *B*. **202**, 68.
[19] *A*. **183**, 1; **202**, 68; **212**, 347. *B*. **4**, 558, 662; **7**, 1211.
[20] *B*. **28**, 44.
[21] B. **7**, 143; **8**, 62, 146. *A*. **183**, 38. *Dingl*. **263**, 49.
[22] *B*. **4**, 457, 555, 663; **14**, 1326. *A*. **209**, 249, 272.
[23] D.R.P. 44,002; 48,367.

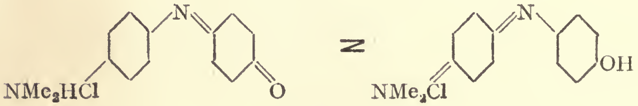
See also O. Mühlhäuser, " Teckhnik der Rosanilinfarbstoffe." (Stuttgart, 1889.)

The application of the triphenyl methane dyes is treated by Whittaker in "Dyeing with Coal Tar Dyestuffs," this series, Sections II., III., and VII.

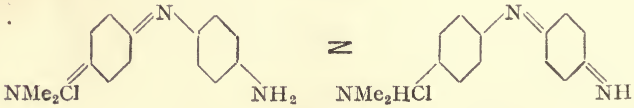
SECTION VI.—THE INDAMINES AND INDOPHENOLS

THESE are all derivatives of quinone imides or quinone diimides, the indophenols differing from the indamines by containing two amino- and one phenolic residue, whereas the indamines contain three amino residues.

Both series of compounds are capable of tautomerism :

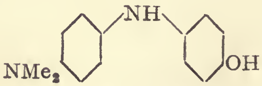


Indophenol.

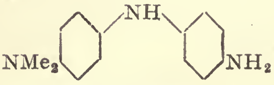


Indamine.

and both on reduction pass into soluble *leuco*-compounds which are readily oxidized back to the dyestuff by atmospheric oxygen :

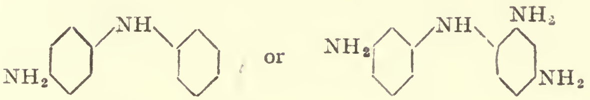


leuco-Indophenol.



leuco-Indamine.

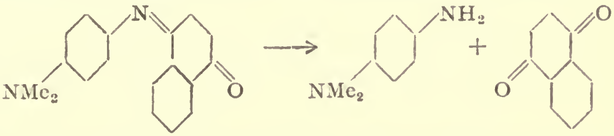
As will be seen, these *leuco*-compounds are diamino-, dioxy-, or amino-oxy-diphenylamines, and it is notable that they cannot be oxidized to the corresponding quinonoid compounds unless there is a hydroxyl or an amino-group in both para-positions with reference to the diphenylamine nitrogen atom. Thus neither of the compounds



gives an indamine on oxidation.

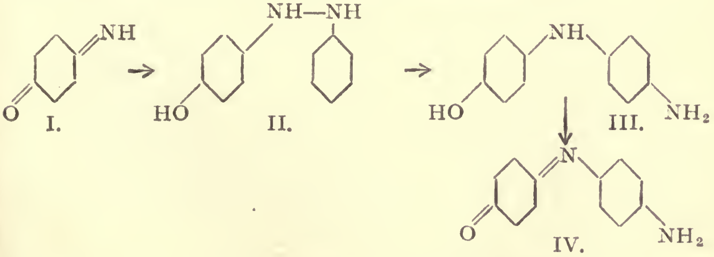
The indamines and indophenols are insoluble substances, and hence this property of giving soluble reduction products can be made use of in dyeing with them, the dyeing being carried out in a hydrosulphite vat and the fabric subsequently exposed to the air, exactly as is done in the case of the indigoid and anthraquinonoid vat dyes.

All the indamines and indophenols are either green or blue in colour, but the shades obtained are very loose as the dyes are rather unstable and in the presence of acids readily decompose into the quinone and the diamine :



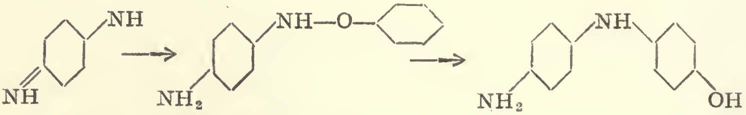
The indamines and the indophenols can be prepared by two methods, viz.—

I. A quinone imide or quinone diimide is condensed with an amine or a phenol having a free para-position.[1] Here probably the first action of the amine is an addition to the quinonoid with the production of a hydrazine (II), which then undergoes a semidine rearrangement :



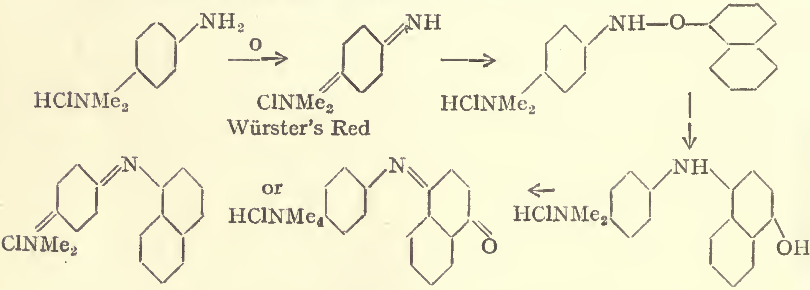
the diamino- or amino-oxy-diphenylamine (III) then being oxidized to the dyestuff (IV) either by the air or at the expense of another molecule of the quinonoid.

With phenols the reaction is probably analogous, a hydroxylamine derivative being first formed instead of a hydrazine:



the latter step being similar to the rearrangement of phenyl-*β*-hydroxylamine, C_6H_5NHOH, into *p*-amino-phenol.

In carrying out the above process it is not usual to isolate the quinone imide or quinone diimide, but simply to oxidize a *p*-amino-phenol, or a *p*-diamine in which at least one of the amino-groups is primary, in the presence of an amine or a phenol with a free para-position:



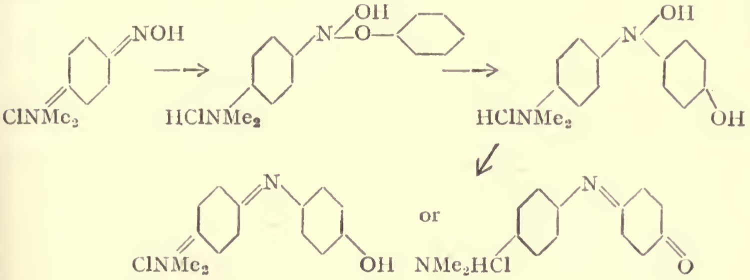
Frequently it is not even necessary to isolate the *p*-diamine, this being prepared by reducing the corresponding nitro- or nitroso-amine, and the solution thus obtained oxidized in the presence of a suitable amine or phenol.

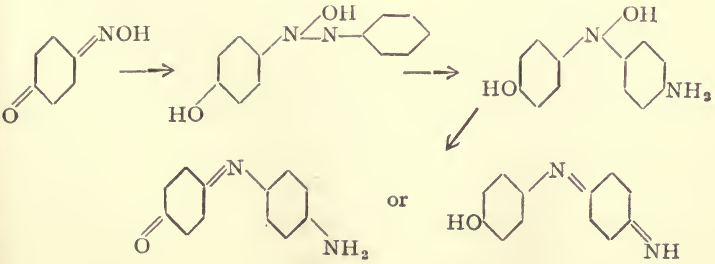
Since the indamines and indophenols are rather sensitive to acids (see above) the oxidation is best carried out in alkaline solution by means of sodium hypochlorite or potassium ferricyanide, or in neutral or faintly acid solution with sodium bichromate and acetic acid or zinc chloride. This latter salt acts like an acid towards bichromate:

$$Na_2Cr_2O_7 + ZnCl_2 + 4H_2O = 2NaCl + 2Cr(OH)_3 + Zn(OH)_2 + 3O$$

In manufacturing naphthol indophenol, for example, by this method the process is carried out by dissolving 10 parts of nitroso-dimethyl aniline in 100 parts of water at 50° C. and then reducing the solution by the addition of 10 parts of sifted zinc dust. The colourless solution of the diamine is then filtered from unchanged zinc dust and added to 12 parts of α-naphthol dissolved in 25 per cent. caustic soda solution, and the whole oxidized by an aqueous solution of 10 parts of sodium bichromate followed by the slow addition of acetic acid of 30–40 per cent. strength. Good agitation is required during the addition of the acetic acid, and sufficient should be added to produce a faintly acid reaction. The dyestuff separates out, but as it is very difficult to filter it is best washed by decantation and preserved as a paste.

II. The indamines and indophenols can also be prepared by condensing the *p*-nitroso-phenols or the salts of the *p*-nitroso amines with phenols or amines having a free para-position. Here again the reaction is probably essentially addition to the labile quinonoid form of the nitroso compound, followed by an intramolecular rearrangement :

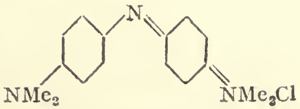




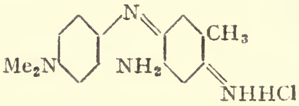
Carbazole indophenol is readily prepared by this method by dissolving 20 kilos of carbazole in 200 kilos of R.O.V. and then adding a solution of 16 kilos of *p*-nitrosophenol in 150 kilos of R.O.V. Efficient agitation is required, and the temperature must not be allowed to exceed 30° C. The indophenol is precipitated by running the melt on to ice, and serves for the manufacture of hydrone blue.[2]

Owing to the fugitive character of the shades the indophenols and indamines are of very little value as dyes. Their chief use is as intermediate products, *e.g.* in the preparation of the azines and sulphide colours.

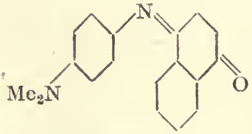
Of theoretical interest are :



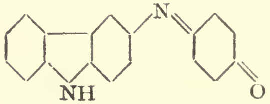
Bindschedler's Green.[3]



Toluylene Blue.



Indophenol.

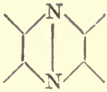


Carbazole Indophenole.[4]

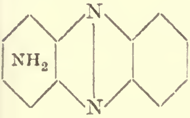
REFERENCES AND LITERATURE

[1] *B.*, **16**, 2843. D.R.P. 15,915.
[2] D.R.P. 218,317.
[3] *B.*, **13**, 208 ; **16**, 865.
[4] D.R.P. 218,317.

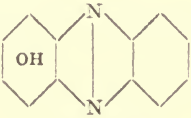
SECTION VII.—THE AZINES

IN these dyes the chromophore is the azine group 

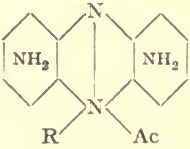
They can be divided into two classes, viz. the azines proper and the azonium compounds, in the latter of which an alkyl or aryl group is attached to one of the cyclic nitrogen atoms. They can be further subdivided into the following classes :



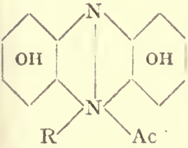
Eurhodines.



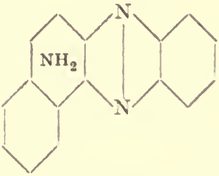
Eurhodoles.



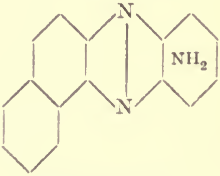
Safranines.



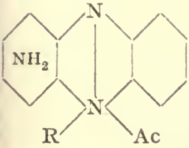
Safranoles.



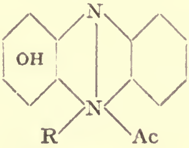
Rosindulines



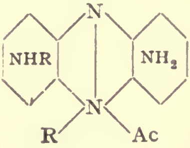
Isorosindulines.



Aposafranines.

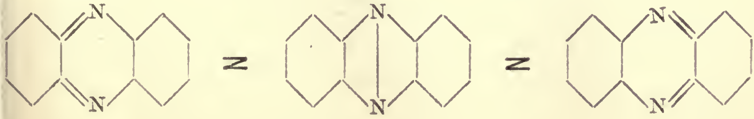


Safraninones.

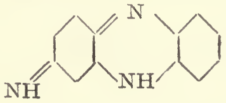


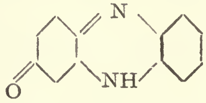
Indulines.

All the azines are capable of double symmetrical tautomerism, and therefore, as would be expected, are all strongly fluorescent :

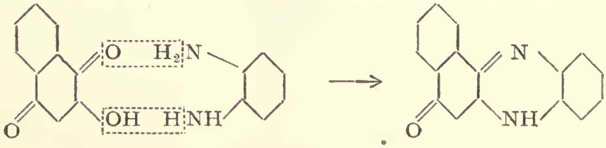


This capacity for forming tautomers becomes still more complicated in the case of amino- and oxy-azines :

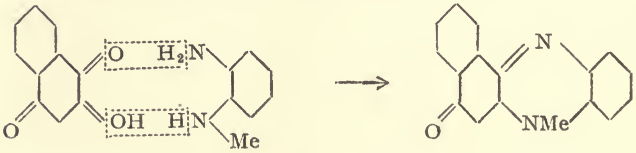




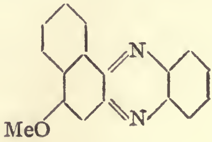
That such isomers are actually formed is shown by the study of the eurhodoles.[1] Thus β-oxy-α-naphthoquinone condenses with *o*-phenylene diamine to form an azine :



This on methylation with methyl iodide gives two methyl derivatives, one of which is identical with the methyl rosindone obtained by condensing β-oxy-α-naphthoquinone with monomethyl *o*-phenylene diamine :



The other is obviously derived from the ortho-quinonoid form :

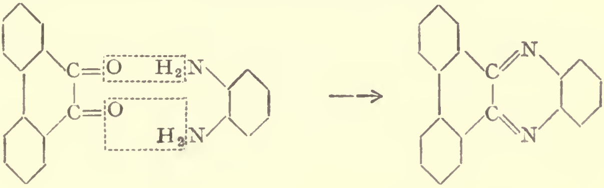


The Simple Azines

The simple azines are of but minor importance as dyes, but the reactions by which they are obtained will be described, as they throw some light on the methods used in preparing the more complicated and technically valuable products.

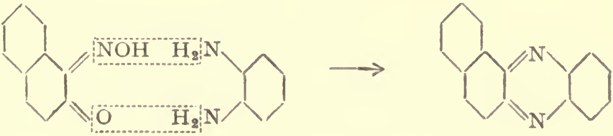
(i) Laurent [2] obtained dinaphthazine by heating α-nitronaphthalene with lime, and Wohl obtained diphenazine by heating nitrobenzene with caustic soda.

(ii) Hinsberg [3] obtained azines by condensing α-diketonic compounds such as glyoxal, phenanthraquinone β-naphthoquinone, etc., with ortho-diamines :

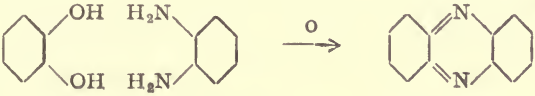


The reaction takes place very readily by simply heating the components in some suitable solvent such as glacial acetic acid or in sodium bisulphite solution. Such compounds are known as quinoxalines and are of great service for identifying ortho-diamines.

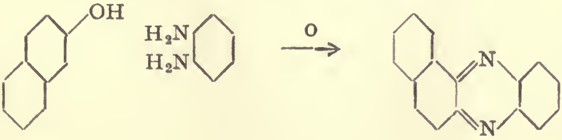
Instead of α-diketones, α-nitroso-β-naphthol [4] can be used :



(iii) Merz [5] found that azines are formed when orthodioxy phenols are heated in the air with ortho-diamines :

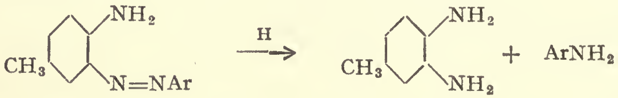


(iv) Witt [6] found that azines are formed when a phenol which is substituted in the para-position is carefully oxidized in the presence of an ortho-diamine :

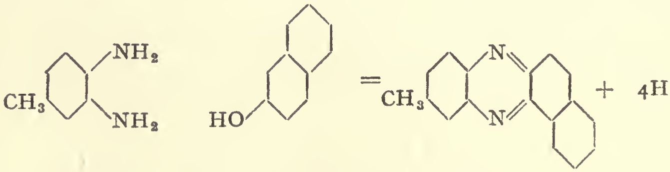


The presence of a substituent in the para-position to the phenolic group is essential, as otherwise an indophenol would be formed (see p. 130).

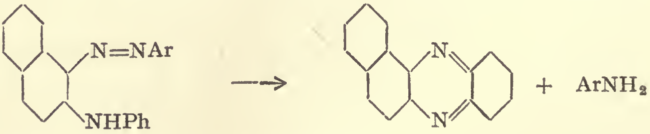
A neat modification of this method is due to Ullmann and Ankersmit,[7] who have found that azines are formed when β-naphthol is heated with ortho-amino-azo-compounds. Probably the first step consists in the reduction of some of the amino-azo-compound to the corresponding ortho-diamine:



This then reacts with the naphthol, the hydrogen shown in the equation not being liberated but reducing more of the azo-compound:



(v) Witt [8] has shown that the ortho-azo derivatives of secondary amines, especially those containing a β-naphthyl group, are decomposed when heated with acids into an azine and a primary amine:

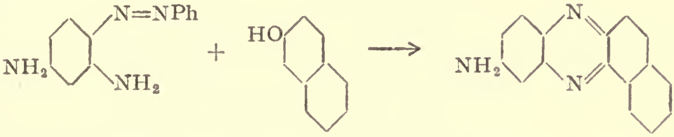


The yields are usually excellent.

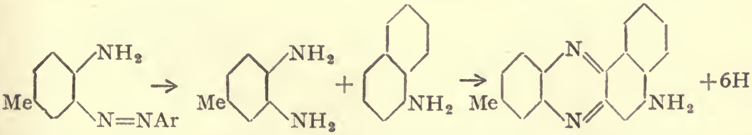
In the free state the simple azines are almost colourless. They are very stable and as a rule distil unchanged at a high temperature, sometimes over 400°. The mono-acid salts are intensely coloured, but are only stable in the absence of water or in the presence of excess of acid. The diacid salts cannot be isolated, but apparently exist in the presence of concentrated acid. The simple azines have no tinctorial properties, affinity for the fibre only being acquired by the entrance of hydroxyl or amino- groups into the molecule. The hydroxyl derivatives are weak acids, but the tinctorial properties are usually very feeble.

THE EURHODINES

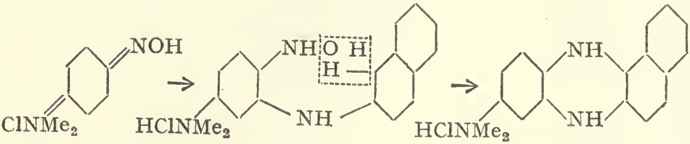
These are the amino-azines and can be obtained by the same means as the simple azines. Thus if an α-diketone is condensed with an aromatic triamine[9] in which two of the amino groups are in the ortho-position to one another, a monamino-azine is formed. A similar compound is obtained if a diamino-azo-compound, such as chrysoidine, is heated with β-naphthol :



The amino-azines can also be obtained when any *o*-amino-azo-compound is heated with the hydrochloride of certain aromatic monamines, such as α-naphthylamine, best in phenol solution.[10] During the reaction it is probable that the azo-compound first becomes reduced to the corresponding ortho-diamine and that this then condenses with the monamine, the hydrogen split off during the condensation reducing a further quantity of the azo-compound :

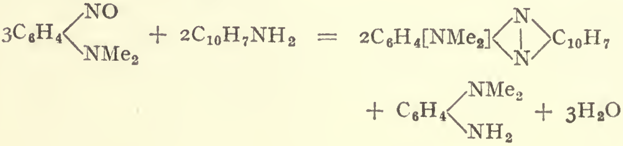


A very general method of obtaining eurhodines consists in heating *p*-nitroso-amines[11] (or quinone dichlorimides) with monamines which are substituted in the para-position, such as β-naphthylamine. Here it is probable that the nitroso-amine reacts in the quinonoid form and adds on a molecule of the monamine in the usual way.[12] Water then splits out and the *leuco*-azine is finally oxidized at the expense of more of the nitroso-compound :



Leuco-azine.

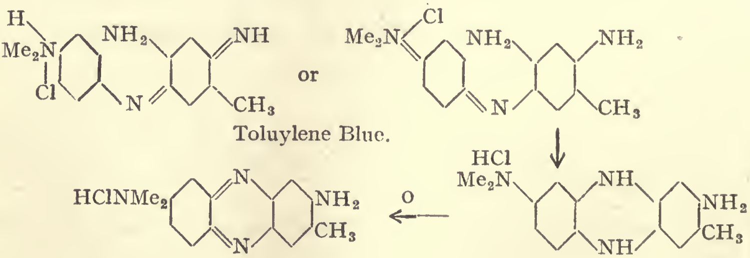
Hence three molecules of nitroso-compound condense with two molecules of the amine :



$$3C_6H_4\left\langle\begin{matrix}NO\\NMe_2\end{matrix}\right. + 2C_{10}H_7NH_2 = 2C_6H_4[NMe_2]\left\langle\begin{matrix}N\\|\\N\end{matrix}\right\rangle C_{10}H_7 + C_6H_4\left\langle\begin{matrix}NMe_2\\NH_2\end{matrix}\right. + 3H_2O$$

This method usually gives excellent results and is employed on the large scale. It is best carried out by boiling the constituents in glacial acetic acid solution.

Finally, eurhodines are obtained when certain ortho-amino indamines are boiled with dilute acids. Thus toluylene red or neutral red extra is obtained by boiling toluylene blue with dilute acids.[13] Here, again, the reaction is probably the addition of a primary amine to a quinonoid group, but in this case the condensation is intramolecular :



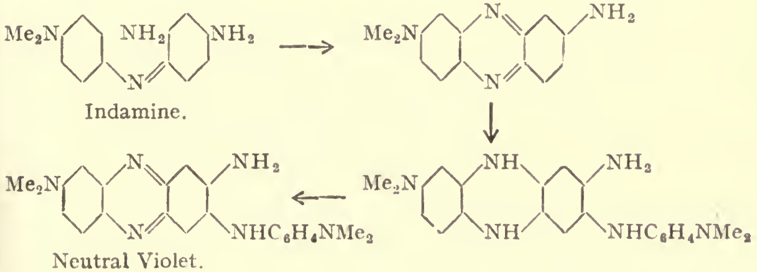
Toluylene Blue.

Neutral Red Extra.

The last step depends upon atmospheric oxygen, and if large quantities are being dealt with air should be blown through the solution, as if this is not done, considerable quantities of the indamine will be reduced.

The manufacture is an extremely simple matter, as it is only necessary to mix solutions of nitrosodimethyl aniline hydrochloride and *m*-phenylene diamine and warm gently. On standing toluylene blue separates, and on boiling this with dilute acid, and at the same time blowing air through the solution by means of a perforated pipe, it is converted into neutral red extra.

Neutral violet [14] is obtained by the oxidation of a mixture of dimethyl-*p*-phenylene diamine and *m*-phenylene diamine. Here the indamine is first formed, which then passes into the diamino-azine, as in the case of neutral red. This is then allowed to add on another molecule of the para-diamine, the *leuco*-azine being then oxidized to the dye :

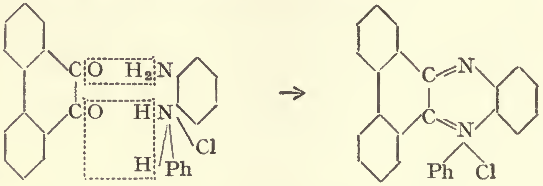


The Azonium Compounds (Safranines and Indulines)

The azonium compounds are vastly more important than the azines proper. They are all highly coloured, but have but poor tinctorial properties unless an amino-group is present. The commercial dyes are all azonium salts, and the free bases as a rule cannot be isolated in a state of purity.

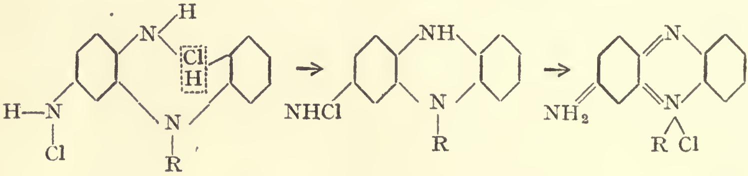
The simple azonium compounds can be obtained by condensing the α-diketones with *o*-amino secondary amines.[15]

Thus flavinduline is prepared by condensing *o*-aminodiphenylamine with phenanthraquinone : [16]

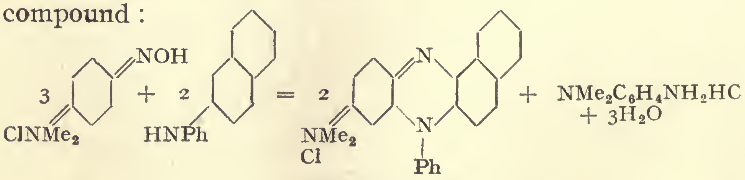


Flavinduline is the only commercial dye made by this process, the other azonium compounds being made by one of the following methods :—

(i) By condensing quinone dichlorimides with secondary amines which are substituted in the para-position.[17] This method is of no technical importance. The reaction consists in the addition of the amine to the quinone, loss of hydrochloric acid and then tautomeric change :



(ii) By condensing the hydrochlorides of para-nitroso tertiary amines, such as nitroso dimethyl aniline, with secondary amines such as phenylnaphthylamine.[18] The course of the reaction is exactly analogous to the condensation of the nitroso bases with primary amines which was discussed on page 138. Here also the oxidation is brought about at the expense of part of the nitroso-compound :



Neutral Blue.[19]

The condensation is best brought about by heating to 100° C. in glacial acetic acid solution. The acetic acid is then distilled off *in vacuo*, the residue dissolved in water and the dyestuff salted out.

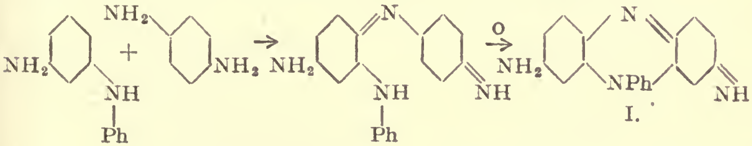
(iii) Diamino-azonium bases are formed when an indamine is oxidized in the presence of a monamine, and this very important process is capable of several variations, viz.:

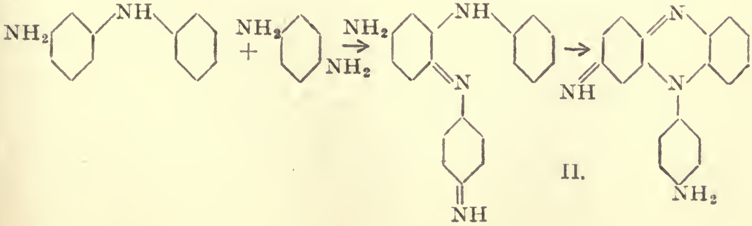
(*a*) The indamine is prepared from the corresponding nitroso-compound.

(*b*) The indamine is not isolated but is formed as an intermediate product, the azine being formed in one operation by the joint oxidation of one molecule of a diamine and two molecules of a monamine. In order that this method may be successful it is necessary for at least one of the amino-groups of the diamine to be primary, as otherwise no indamine could be formed. Instead of using two molecules of one monamine, one molecule each of two different monamines can be used. In this case one of the monamines must have an unsubstituted para-position so as to allow of indamine formation, and the other monamine must be primary.

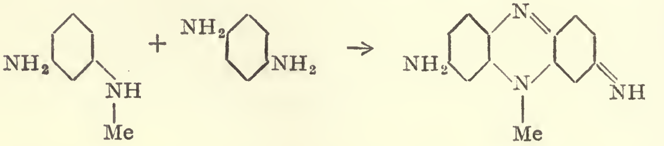
(*c*) A meta-amino secondary amine is oxidized in the presence of a diamine. This modification is of theoretical importance, as it has led to the proof of the symmetrical constitution of the safranines as follows:—

When meta-amino-diphenylamine is oxidized in the presence of para-phenylene diamine, safranine formation might take place in two directions, leading to a symmetrical compound (I) or to an unsymmetrical compound (II):



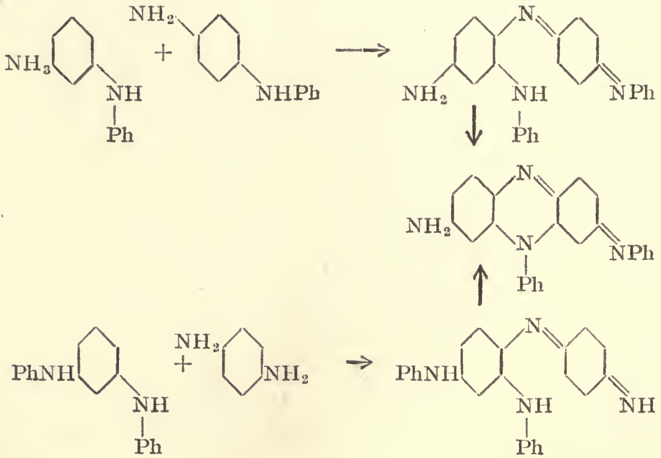


Now, methyl-meta-phenylene diamine, when oxidized in the presence of *p*-phenylene diamine, gives a safranine :



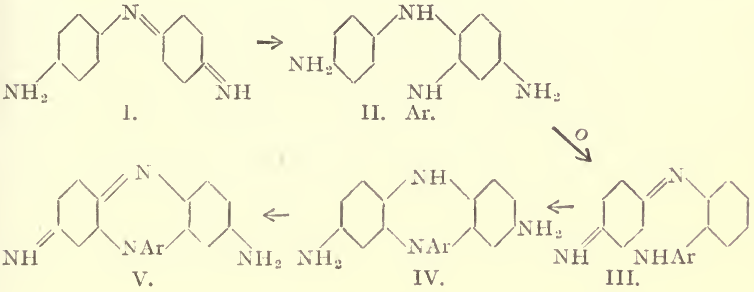
This would be impossible if the reaction took place according to II.

Again, Nietzki [20] has shown that the same compound is obtained by oxidizing a mixture of *m*-amino-diphenylamine and *p*-amino-diphenylamine as is obtained by oxidizing a mixture of *m*-phenyl-amino-diphenylamine and *p*-phenylenediamine. This is only explicable on the assumption that the reaction takes the course I :



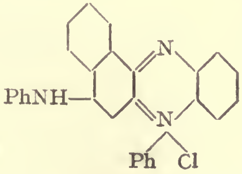
(*d*) Finally, azonium compounds are formed when amino-azo-compounds are heated with the hydrochloride of a monamine. In this case probably part of the azo-compound becomes reduced to the diamine, which then condenses with the monamine to form the indamine, the oxidation being brought about by the reduction of more of the azo-compound.

In all cases the formation of the azine from the indamine (I) and monamine is due to the condensation of the monamine with the quinonoid indamine to form a complex diarylamine (II), oxidation to a quinonoid compound (III), and then intramolecular condensation (IV) followed by oxidation (V):



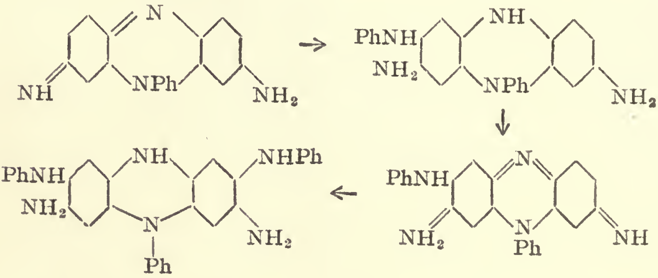
In preparing azines by the joint oxidation of a *p*-diamine and a monamine, the diamine is usually prepared by the reduction of a suitable azo-compound or nitroso-amine. The oxidation is best carried out with sodium bichromate or manganese dioxide.

One of the best known dyes of this group is azo carmine G. It is obtained by heating benzene-azo-α-naphthylamine hydrochloride with aniline and aniline hydrochloride at 130° C. After cooling the melt is ground up and purified by extraction with boiling dilute hydrochloric acid and toluol. The residue is then sulphonated by heating with 4 parts of 23 per cent. oleum at 100° C. The dyestuff is the sulphonic acid of

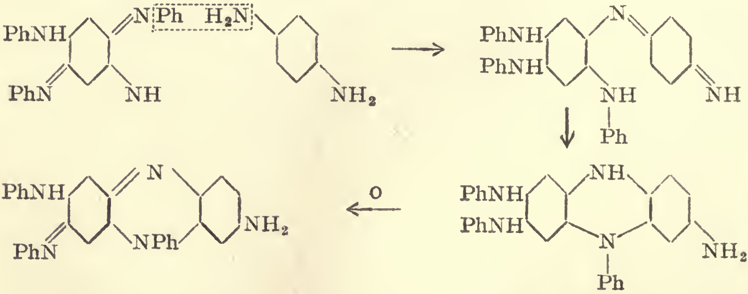


Azo carmine B is the sodium salt of the trisulphonic acid.

The name *Induline* is usually given to those dyes which are obtained by heating an amino-azo-compound with aniline and aniline salts. The reactions which take place are extremely complicated and depend on the conditions under which the melt is carried out. Probably some safranine is formed by the series of reactions described on pages 142, 143. This, being a quinonoid compound, is capable of condensing with another molecule of the amine. On oxidation this again passes into a quinonoid compound which can then condense with another molecule of the amine, and so on :

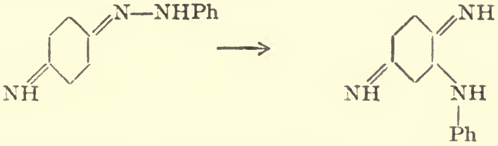


Witt[22] has investigated the reaction and finds that when amino-azo-benzene is heated with aniline and aniline hydrochloride to 100° azophenine is formed. At a higher temperature this condenses with the p-diamine formed simultaneously to form induline B or 3B :

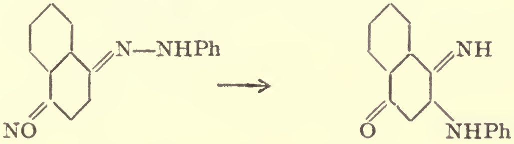


On further heating this passes into still bluer products, either by the ordinary quinonoid condensation or by the phenylation of the amino group, this latter reaction being exactly analogous to the formation of diphenylamine by heating aniline with aniline hydrochloride.

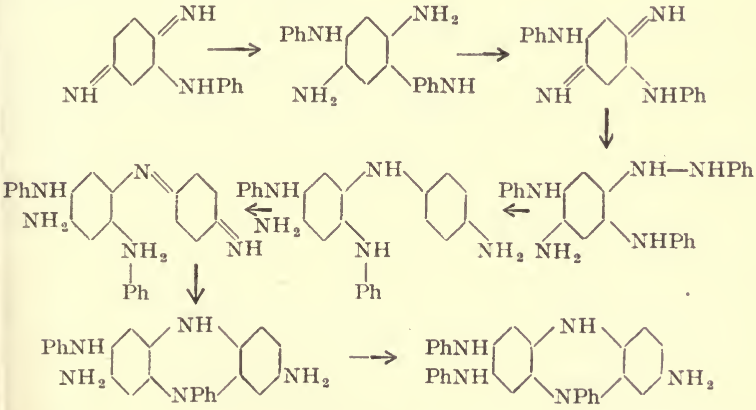
Another possible explanation of the reaction is that the amino-azo-compound reacts in the quinonoid form and first undergoes a semidine change :



and in confirmation of this it has been pointed out that benzene-azo-α-naphthol, on prolonged boiling with acetic acid, passes into an analogous compound :

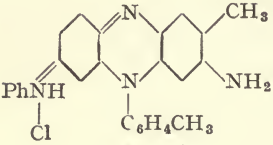


This quinone di-imide might then condense with aniline to form the azine as follows :



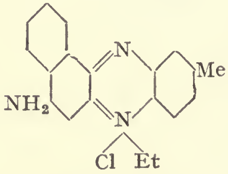
Which of these reactions takes place it is impossible to say until the reaction has been investigated much more fully. The indulines obtained by the amino-azo melt are usually spirit soluble colours. They are converted into water soluble dyes by sulphonation.

The following are a few of the most important azonium colours :



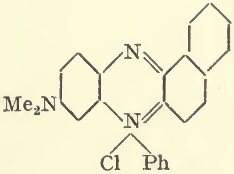
Mauveine.

Joint oxidation of aniline and toluidine Interesting as the first artificial dye prepared commercially.



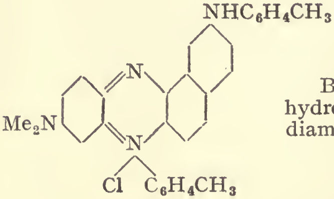
Induline Scarlet.

By fusing azo-derivatives of ethyl-*para*-toluidine with α-naphthylamine. D.R.P. 77226.



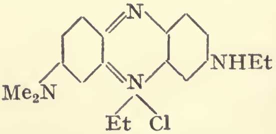
Neutral Blue.

By condensing nitroso-dimethyl aniline with phenyl-β-naphthylamine. D.R.P. 19224.



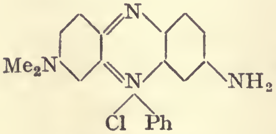
Basle Blue.

By condensing nitroso-dimethyl-aniline hydrochloride with 2.7-ditolyl-naphthylene diamine. D.R.P. 40886.



Fast Neutral Violet C.

By condensing nitroso-dimethyl-aniline with diethyl-*m*-phenylenediamine. D.R.P. 59063.

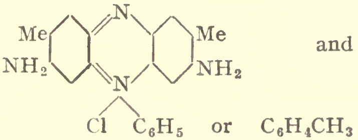


Methylene Violet.

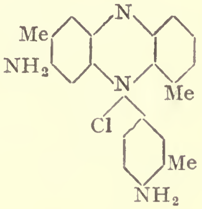
BN
RRW
RRA
3RA Extra

By the oxidation of a mixture of *p*-amino-diphenylamine, *o*-toluidine and aniline. D.R.P. 49853.

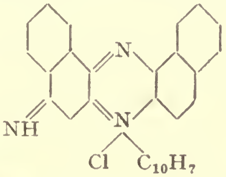
Safranine (various marks) is obtained by the oxidation of a mixture of toluylene diamine and ortho toluidine and subsequent condensation with aniline or ortho-toluidine. It consists of a mixture of :



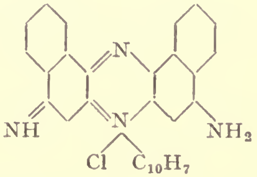
and



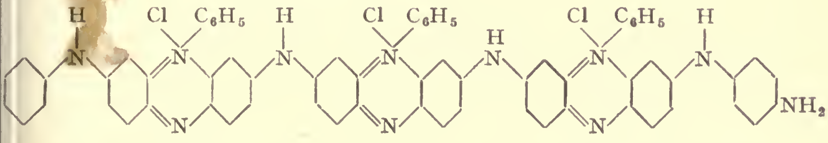
Magdala red or fast pink for silk is obtained by fusing α-naphthyl-azo-α-naphthylamine with α-naphthylamine. It consists of a mixture of :



and



Aniline Black[23] is obtained by the oxidation of aniline and has been ascribed the formula :



although this cannot be said to be proved. It is always developed on the fibre, although the dyestuff itself is made to some extent for use as a pigment.

REFERENCES AND LITERATURE.

[1] *B.*, **24**, 2167.
[2] *A. Ch.*, **59**, 384.
[3] *B.*, **17**, 319 ; **18**, 1228.
[4] *B.*, **42**, 4263.
[5] *B.*, **19**, 725.
[6] *B.*, **19**, 917.

[7] *B.*, **38**, 1811.
[8] *B.*, **20**, 571.
[9] *B.*, **19**, 445.
[10] *B.*, **18**, 1119 ; **19**, 441.
[11] *B*,, **21**, 719, 1598.
[12] *A.*, **287**, 56 ; **336**, 112.
[13] D.R.P. 15,272. *B.*, **12**, 933.
[14] D.R.P. 15,272
[15] *B.*, **20**, 1183.
[16] D.R.P. 79,570.
[17] *B.*, **21**, 1598.
[18] *B.*, **21**, 719.
[19] *B.*, **21**, 723. D.R.P. 19,224.
[20] *B.*, **29**, 1442.
[21] D.R.P. 45,370.
[22] *B.*, **16**, 1102.
[23] *B.*, **40**, 3412 ; **44**, 2570. *Soc.*, **97**, 2388.

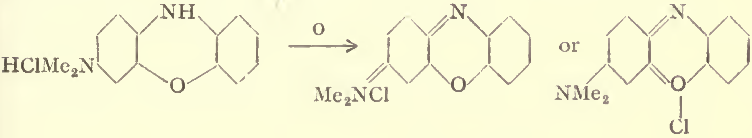
A detailed description of the manufacture of safranine is given in Walter, " Aus der Praxis der Anilinfarbenfabrikation," 1903.

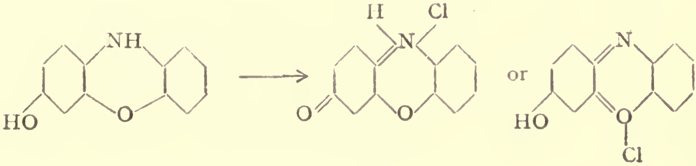
Aniline Black is treated by Noelting and Lehne in a book entitled " Anilinschwarz," of which an English translation appeared in 1909.

A description of aniline black dyeing is also given by Whittaker in Section XI. of his volume on "Dyeing with Coal Tar Dyestuffs" in this series.

SECTION VIII.—THE OXAZINES

THESE are similar in structure to the thiazines, but in them the sulphur has been replaced by oxygen. Like the corresponding thiazines, the oxy- and amino-derivatives are not dyes, but *leuco*-compounds which pass into the dyes on oxidation :

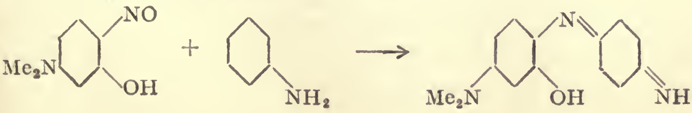


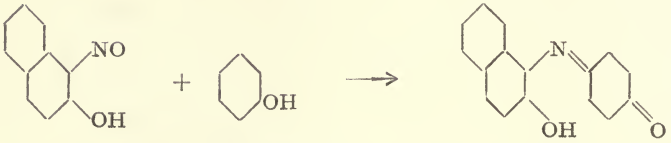


Sometimes the amino-compounds are denoted as oxazimes and the oxy-derivatives as oxazones, but this nomenclature is not universal.

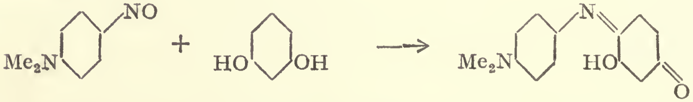
The first colouring matter of this series was obtained by Meldola[1] in 1879 by heating nitroso-dimethyl aniline hydrochloride with β-naphthol in glacial acetic acid solution.

The oxazines are almost invariably prepared by heating nitroso-amines or nitroso-phenols with suitable phenols or bases. In preparing oxazines by this method it is necessary to chose the components so that an *o*-oxy-indamine or *o*-oxy-indophenol can be formed as an intermediate product. In order to fulfil this condition either a suitable oxy-nitroso-compound, such as nitroso-dimethyl-*m*-amino-phenol, can be condensed with a phenol or a base :

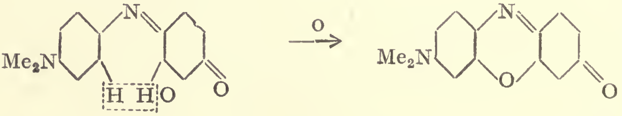




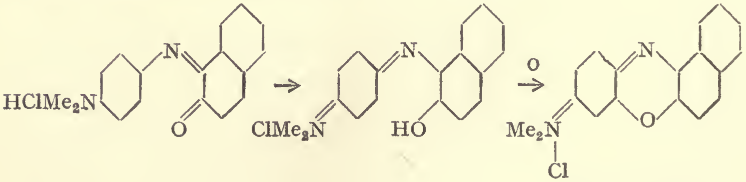
or a nitroso-phenol or nitroso-base can be condensed with a phenolic compound of such a nature that condensation must take place in the ortho- position to a hydroxyl group, *e.g.* resorcinol :



The oxy-indophenol or oxy-indamine then passes into the oxazine by oxidation :

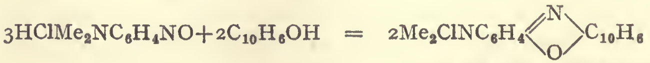


If, however, the phenol is β-naphthol, the mechanism of this oxidation is somewhat different, and probably takes place in the following steps :



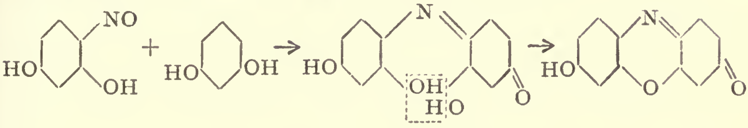
Meldola's Blue.

In all cases the oxidation takes place at the expense of some of the nitroso-compound, the equation being :

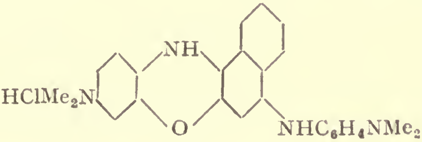


$$3HClMe_2NC_6H_4NO + 2C_{10}H_6OH = 2Me_2ClNC_6H_4 \overset{N}{\underset{O}{\lessgtr}} C_{10}H_6 + Me_2NHClC_6H_4NH_2 + 2H_2O$$

Again, the components can be selected so that the indamine or indophenol contains two hydroxyl groups, both of which are in the ortho-position to the nitrogen atom, and which are attached to different nuclei. In this case ring formation takes place by simple loss of water :

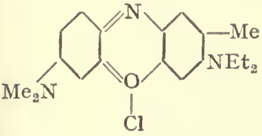


In carrying out the preparation of oxazines by the above method the components are merely boiled together in some suitable solvent, such as water, alcohol, or glacial acetic acid. Care must be taken not to prolong the boiling more than necessary, as the amino-compound formed as a side product will then condense with the oxazine. Thus in the preparation of Meldola's blue dimethyl-*p*-phenylenediamine is formed as a side product, and on prolonged heating this condenses with the dyestuff, just as primary amines always condense with quinoid compounds, giving :



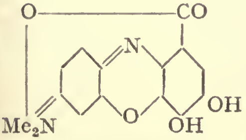
Also, in order to avoid decomposition of the nitroso-compound it is advisable to add it slowly. The condensation is very simply brought about by boiling in alcoholic or acetic acid solution.

Other dyes of this group are :



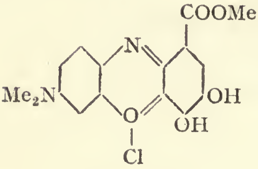
Capri Blue.

By condensing nitroso-dimethyl aniline hydrochloride with diethyl-*m*-amino-*p*-cresol. D.R.P. 62,367.



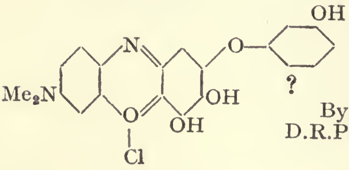
Gallocyanine.

By condensing nitroso-dimethyl-aniline hydrochloride with gallic acid D.R.P. 19,580. It dyes cotton on a chrome mordant.



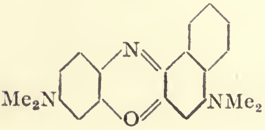
Prune Pure.

By condensing nitroso-dimethyl-aniline with the methyl ester of gallic acid. D.R.P. 45,786. It is used both with a chrome mordant and with tannin.



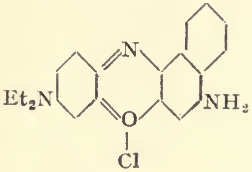
Phenocyanine. VS, R and TC.

By condensing gallocyanine with resorcinol. D.R.P. 77,452.



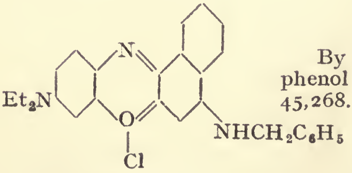
New Methylene Blue, GG.

By the action of methylamine on Meldola's Blue, and subsequent oxidation. D.R.P. 54,658.



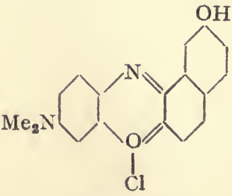
Nile Blue A.

By condensing nitroso-diethyl-*m*-aminophenol with *a*-naphthyl-amine. D.R.P. 45,268.



Nile Blue 2B.

By condensing nitroso-*m*-diethylamino phenol with benzyl-*a*-naphthylamine. D.R.P. 45,268.

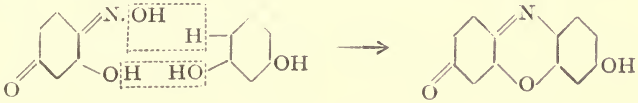


Muscarine.

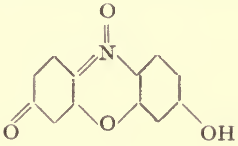
By condensing nitroso-dimethyl-aniline hydrochloride with 2.7-dioxynaphthaline. *B.*, **29**, 2994.

RESORUFIN AND RESAZURIN.

By the action of nitrous acid on resorcinol, Weselsky [2] obtained two compounds. These were investigated by Nietzki,[3] who named them resazurin ($C_{12}H_7O_4N$) and resorufin ($C_{12}H_7O_3N$). He found that resazurin on reduction gives resorufin, and this on further reduction passes into a *leuco*-compound, $C_{12}H_9O_3N$, which is very readily oxidized back to resorufin. He further showed that resorufin is a monohydric phenol, and synthesized it by heating mono-nitroso-resorcinol with resorcinol and concentrated sulphuric acid :



He further found that resazurine was formed when this condensation took place in the presence of manganese dioxide, and therefore denoted this compound as :



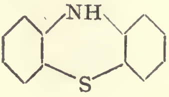
On bromination resorufin gives a tetrabrom compound which is placed on the market as Iris Blue.

REFERENCES AND LITERATURE.

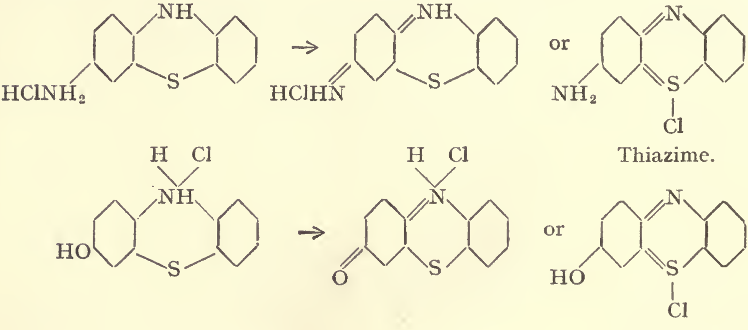
[1] *B.*, **12,** 2065. *Soc.*, **39,** 37.
[2] *A.*, **162,** 273.
[3] *B.*, **22,** 3020 ; **23,** 718 ; **24,** 3366.

SECTION IX.—THE THIAZINES

THESE are all derived from thiodiphenylamine :



Thiodiphenylamine itself and its amino- and hydroxy-derivatives are colourless or pale yellow compounds. The amino- and oxy- derivatives, however, are *leuco*- compounds and rapidly absorb oxygen from the atmosphere and pass into the dyes, the thiazimes and thiazones :



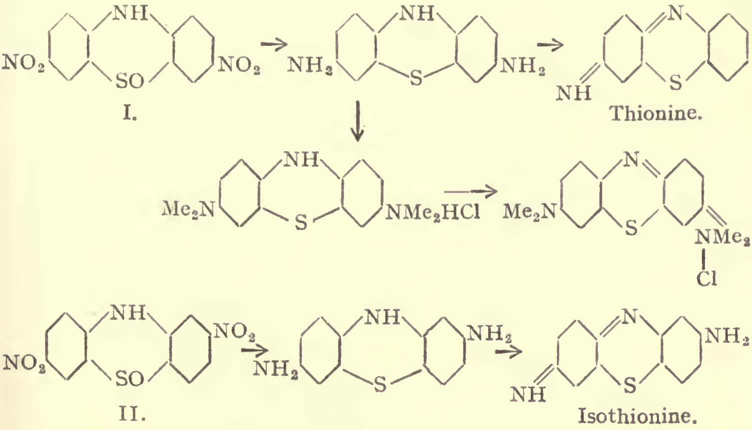
Thiazone.

It will be seen that the thiazines are really indamines and indophenols in which the ring has been closed by sulphur. This closing of the ring increases the stability, and although the thiazines are not very fast colours they are much faster than the corresponding indamines and indophenols.

The first thiazine dye was obtained by Lauth,[1] in 1876, by oxidizing *p*-phenylenediamine in the presence of sulphuretted hydrogen.

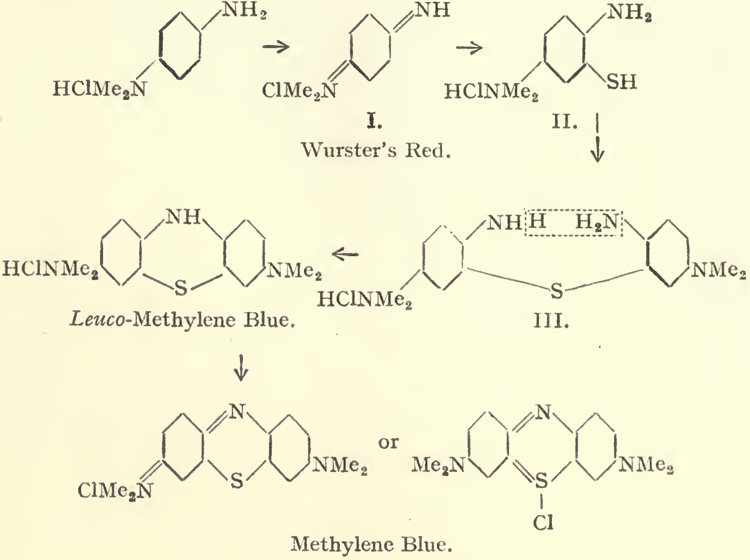
He named the blue dye he obtained Lauth's Violet or Thionine, but it was not a commercial success owing to the poor yield—about 20 per cent. In the same year Caro [2] applied Lauth's reaction to dimethyl-*p*-phenylenediamine, obtained by the reduction of nitroso-dimethyl aniline, and obtained a tetramethyl thionine in much better yield. This was manufactured by the Badische Company and placed on the market under the name of Methylene Blue. It is interesting to notice that this was the first patent for the production of an artificial dyestuff to be granted by the German Patent Office.

The constitution of thionine and methylene blue were elucidated by Bernthsen.[3] He found that when thiodiphenylamine is nitrated it gives two dinitro-sulphoxides, I. and II. Both these on reduction and subsequent oxidation gave blue dyes, that from the α-compound (I.) being identical with Lauth's thionine. On methylating the ***leuco-*** derivative of this he obtained a tetramethyl thionine which proved to be identical with methylene blue :

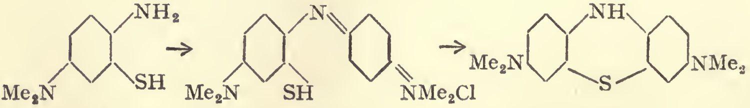


These reactions have never been used for the technical production of the thionines.

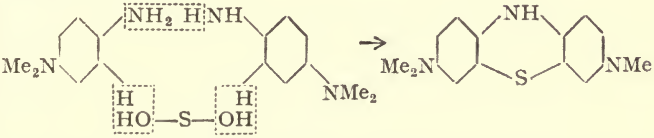
In the preparation of thionines by Lauth's method, the oxidizing agent first converts the *p*-diamine into a quinone imide (I.), which, like other *p*-quinones, then condenses with sulphuretted hydrogen to give the mercaptan (II.). This then condenses with another molecule of the quinone diimide to form III., which passes into the *leuco*- dye by loss of ammonia. This in turn becomes oxidized to the dyestuff proper :



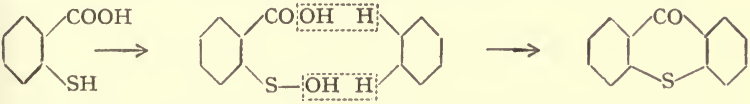
Instead of using two molecules of the diamine, the preparation can be carried out by oxidizing an equimolecular mixture of the diamine and dimethyl aniline.[4] In this case the mercaptan is formed as before and then undergoes indamine formation with the dimethyl aniline. The quinonoid indamine then undergoes intramolecular condensation with the mercaptan group to form *leuco*-methylene blue :



Oehler has patented a process for producing methylene blue by treating nitrosodimethyl aniline with concentrated sulphuric acid and zinc sulphide.[5] Here the first step is probably the reduction of the nitroso- compound to the diamine. The sulphuretted hydrogen is probably simultaneously oxidized to the unknown sulphoxylic acid, HO—S—OH, which then condenses with the diamine with loss of water :

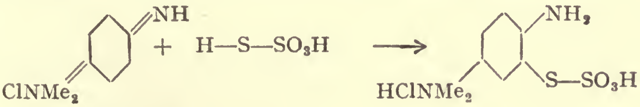


In support of this it may be pointed out that Smiles and his students have shown that mercaptans condense with aromatic compounds in the presence of strong sulphuric acid to form sulphides.[6] Thus, thioxanthones are obtained in excellent yield when thiosalicylic acid is heated with an aromatic compound in the presence of concentrated sulphuric acid :



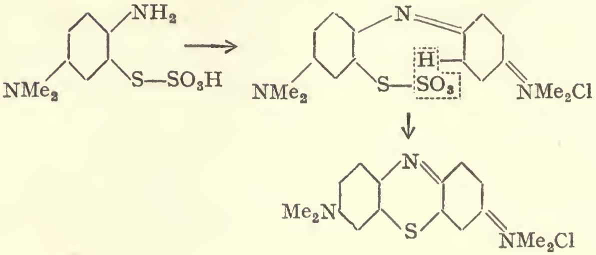
A similar reaction takes place between thiosalicylic acid and malonic ester (see p. 167).

The manufacture of methylene blue is now always carried out by the thiosulphate process.[7] In this dimethyl-*p*-phenylene-diamine is oxidized in the presence of sodium thiosulphate, when the quinone imide at once condenses with the thiosulphuric acid to form the thiosulphonic acid :



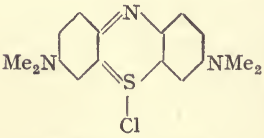
Würster's Red.

This can be converted into methylene blue by two processes, viz. it can be reduced to the mercaptan and this then oxidized in the presence of dimethyl aniline, when indamine formation, etc., takes place ; or, more usually, the thiosulphonate is oxidized directly in the presence of dimethyl aniline to the corresponding indamine, which on heating loses sulphurous acid with the formation of methylene blue :



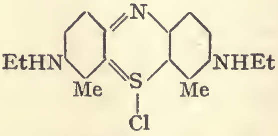
The manufacture of methylene blue is carried out as follows. Dimethylaniline (12 kilos) is dissolved in 40 litres of water and 65 kilos of strong hydrochloric acid and converted into its nitroso compound by the addition of 7·1 kilos of sodium nitrite (see p. 81). The nitroso compound is not isolated but immediately reduced to the diamine by the addition of zinc dust, of which sufficient must be added to neutralize the whole of the hydrochloric acid. After diluting to 500 litres 16 kilos of dimethyl aniline hydrochloride and 50 kilos of sodium thiosulphate are added, and then a concentrated solution of 25 kilos of sodium dichromate run in and the whole boiled for two hours. Sufficient sulphuric acid to convert the whole of the chromium and sodium into sulphate is next added and the solution boiled free from sulphur dioxide. The leuco base is then oxidized by the addition of 8 kilos of neutral sodium chromate and the dyestuff finally salted out.

Other dyes of this series are :



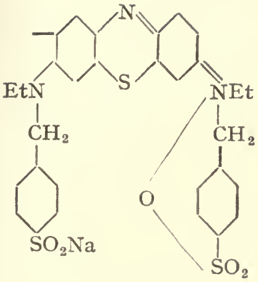
Methylene Green.

By the action of nitrous acid on Methylene Blue. D.R.P. 38,979.



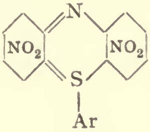
New Methylene Blue.

From amino-methyl ethyl aniline by the thiosulphate process. D.R.P. 54,658.



Thiocarmine R.

An interesting series of dyes, which have not yet found application, is obtained when dinitro- or tetranitro-diphenylamine-*o*-sulphoxide is condensed with an aromatic compound:[8]



Condensation takes place very readily at the ordinary temperature in the presence of concentrated sulphuric acid, and most aromatic compounds react. Benzene, however, does not, and as thiophene does, this forms a very convenient test for thiophene. Soluble products are only obtained when sulphonic acid groups are present.

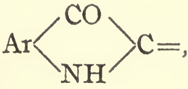
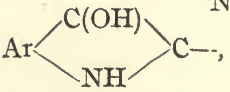
REFERENCES AND LITERATURE.

[1] *B.*, **9**, 1035.
[2] D.R.P. 1886.
[3] *A.*, **230**, 73.
[4] D.R.P. 38,573; 39,757; 45,839.
[5] D.R.P. 24,125.
[6] *Soc.*, **97**, 1290; **99**, 640.
[7] D.R.P. 38,573.
[8] *Soc.*, **93**, 145, 1687; **94**, 1253; **95**, 186, 362, 980.

SECTION X.—THE INDIGOID DYESTUFFS

THESE are all vat dyes and from the point of view of chemical constitution can be divided roughly into two classes, viz. the indigos and the thioindigos. This division is not a very sharp one, for, as will be seen, some of the dyes contain both an indigo and a thioindigo group.

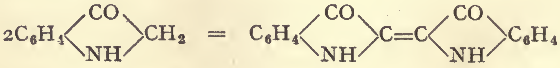
THE INDIGOS

These all contain the group  $\mathrm{Ar}\left\langle\begin{matrix}\mathrm{CO}\\ \mathrm{NH}\end{matrix}\right\rangle\mathrm{C}=$, which on reduction passes into  $\mathrm{Ar}\left\langle\begin{matrix}\mathrm{C(OH)}\\ \mathrm{NH}\end{matrix}\right\rangle\mathrm{C}-$, the reduction products being soluble in alkali and being rapidly oxidized by the air to the original substance.

Indigo itself is by far the most inportant member of the series, and is in fact the most important dye on the market at present. It has been used since prehistoric times, certain Egyptian mummy cloths having been found to be dyed with it.

Until comparatively recently the whole of the dyestuff used was obtained from natural sources, but during the last few years the synthetical product has displaced the natural.

Natural Indigo.—Indigo occurs in the indigo plant as a glucoside of indoxyl (Indican), which on hydrolysis is split up into indoxyl and glucose, the indoxyl on exposure to the air being at once oxidized to indigo :



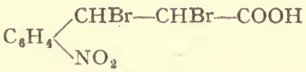
$$2\mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{CO}\\ \mathrm{NH}\end{matrix}\right\rangle\mathrm{CH_2} = \mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{CO}\\ \mathrm{NH}\end{matrix}\right\rangle\mathrm{C}=\mathrm{C}\left\langle\begin{matrix}\mathrm{CO}\\ \mathrm{NH}\end{matrix}\right\rangle\mathrm{C_6H_4}$$

The indigo plant (*Indigofera tinctoria*) was formerly cultivated in Europe, but at present is chiefly grown in

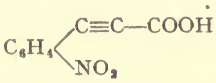
South America and Bengal, although the area under cultivation is rapidly decreasing owing to the use of the synthetic dye. In order to extract the dyestuff the plants are covered with water and allowed to ferment in large vats (" steeping vats ") for about fifteen hours. The yellow liquid is then drawn off from the debris and beaten, either mechanically or by hand, so as continually to expose a fresh surface to the air. By this means the indoxyl is oxidized to indigo, which, being insoluble in water, settles out as a fine mud. This is then boiled up with water in order to destroy the ferments, collected by filtration through cloth, pressed and dried.

Syntheses of Indigo.—The great fastness of the shades and the enormous demand for the dyestuff led at an early date to many attempts at its synthesis. The first success was achieved in 1870 by Baeyer and Emmerling, who obtained small quantities of indigo by heating isatine with phosphorus trichloride and acetyl chloride and then oxidizing the product with air.

The next important step was the preparation of the dyestuff by Baeyer from *o*-nitro-cinnamic acid. This he effected by first saturating the double bond with bromine and then treating the brominated compound with alcoholic potash, so as to form *o*-nitro-phenyl propiolic acid : [1]

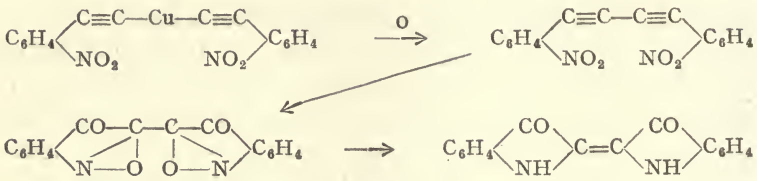


$$\mathrm{C_6H_4}\!<\!\begin{matrix}\mathrm{CHBr{-}CHBr{-}COOH}\\ \mathrm{NO_2}\end{matrix}$$



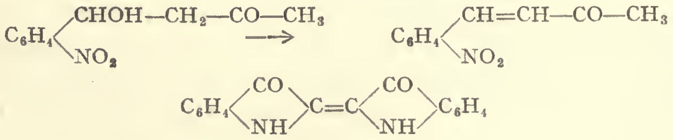
$$\mathrm{C_6H_4}\!<\!\begin{matrix}\mathrm{C{\equiv}C{-}COOH}\\ \mathrm{NO_2}\end{matrix}$$

This was then converted into indigo by two methods, viz. (*a*) it was converted into isatine by boiling with caustic soda, and this then converted into indigo by reduction with an alkaline solution of glucose ; or (*b*) it was boiled with water, when loss of carbon dioxide took place with the formation of *o*-nitro-phenyl acetylene. The copper salt of this on oxidation with ferricyanide gave the corresponding diacetylene, which when treated first with concentrated sulphuric acid and then with ammonium chloride passed successively into diisatogen and indigo : [2]



Neither of these methods was successful commercially, although nitro-phenyl propiolic acid was used to a small extent for producing indigo directly on the fibre.[3]

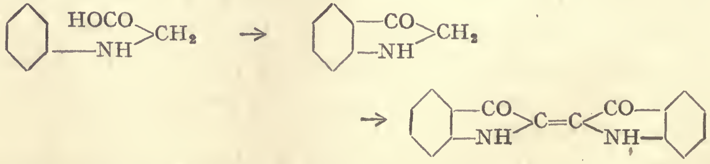
The next series of syntheses started from *o*-nitro-benzaldehyde and were due to Baeyer and Drewson. They found that the condensation product of *o*-nitro-benzaldehyde and acetone readily loses water to form *o*-nitro-aceto-cinnamone, which passes into indigo on treatment with caustic alkali :[4]



The bisulphite compound of the condensation product of acetone and *o*-nitro-benzaldehyde is used to a small extent for calico printing under the name of indigo salt. In this process the colour is developed on the fibre by treatment with strong caustic alkali solution.

None of the above syntheses have been commercially successful owing to the high price of toluene.

The commercial preparation of indigo is now exclusively carried out by Heumann's process. This consists in fusing phenyl glycine, or phenyl glycine-*o*-carboxylic acid, with caustic alkali and then oxidizing the indoxyl formed with air :



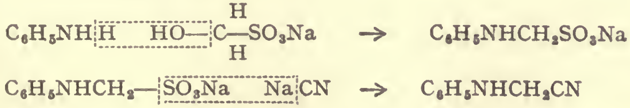
As originally proposed the method did not appear at all promising, as the yields did not exceed 8 per cent. ; but the difficulties have now been surmounted and the yields are excellent.[5] This improvement in the yield has been largely brought about by the addition of substances to the alkali melt. The addition of a very large number of substances such as metallic sodium, magnesium, lime, sodamide, etc., has been patented, but it is believed that the addition of sodamide is the method actually used at the present.[6] In order that the process may be a commercial success it is necessary to recover the alkali, but the method by which this is done is preserved as a trade secret.

The phenyl glycine can be obtained in two ways, viz. by condensing aniline with chloracetic acid, or from aniline and formaldehyde by Bucherer's process.

The condensation of aniline with chloracetic acid is not so simple as would seem at first sight, as there is a great tendency to form the diglycine, $C_6H_5N(CH_2COOH)_2$. This can be overcome by using ethyl chloracetate instead of the free acid, but unfortunately the ester thus obtained can only be hydrolysed with alcoholic potash. The amyl ester can be saponified with aqueous alkali, but the cost is very high.

Another method of overcoming the difficulty is to condense chloracetic acid with aniline in the presence of common salt and ferric hydroxide. Under these circumstances the ferric salt of the glycine is formed, and as this is insoluble in brine it separates out and is thus protected from further action of the chloracetic acid.

Phenyl glycine is very readily obtained according to Bucherer's method by condensing aniline with the bisulphite compound of formaldehyde and then treating the product with sodium cyanide :[7]



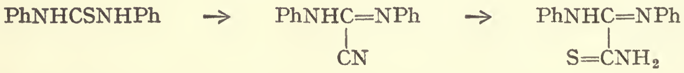
$$C_6H_5NH\boxed{H\quad HO-}\overset{H}{\underset{H}{C}}-SO_3Na \rightarrow C_6H_5NHCH_2SO_3Na$$

$$C_6H_5NHCH_2-\boxed{SO_3Na\quad Na}CN \rightarrow C_6H_5NHCH_2CN$$

The nitrile thus obtained on saponification yields phenyl glycine.

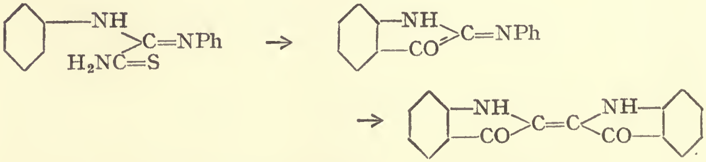
The glycine of anthranilic acid is obtained by condensing anthranilic acid, prepared from naphthalene as described on pages 41, 80, with chloracetic acid, or according to Bucherer from anthranilic acid and formaldehyde as described above.

A very interesting synthesis of indigo, which however has not proved successful on the large scale, is due to Sandmeyer.[8] In this case the starting out substance is aniline, which is first converted into thiocarbanilide by heating it with carbon bisulphide. This is then treated with potassium cyanide and the nitrile thus obtained converted into the corresponding thioamide by treatment with yellow ammonium sulphide :



$$\mathrm{PhNHCSNHPh} \rightarrow \underset{\displaystyle \mathrm{CN}}{\mathrm{PhNHC{=}NPh}} \rightarrow \underset{\displaystyle \mathrm{S{=}CNH_2}}{\mathrm{PhNHC{=}NPh}}$$

This, on treatment with concentrated sulphuric acid, passes into α-isatine anilide, which on reduction with ammonium sulphide loses aniline and forms indigo :



Of the homologues of indigo only two have proved to be of commercial value. The dimethyl indigo obtained from the phenyl glycine derived from *o*-toluidine [9] is indigo T or G, and the dibromo- product of that derived from the glycine of β-naphthylamine [10] is ciba green G.

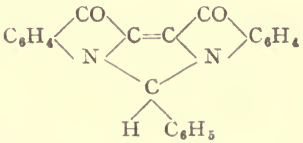
Of the substitution products of indigo, the sulphonic acid has long been known, and at one time was used to a considerable extent as an acid dye for wool and silk under the name of indigo carmine. Its use is now almost obsolete as, unlike indigo itself, the shades obtained are very fugitive.

The halogenated indigos are of comparatively recent introduction and are of very great importance. Those halogenated in the para- position to the nitrogen atoms are very like indigo in shade, but rather brighter, whereas those in which the halogen atoms are in the para- position with regard to the carbonyl groups are much redder. Thus, Friedlander has shown that 6-6′-dibromo-indigo is identical with Tyrian Purple, a dyestuff extracted from oysters and snails and much prized by the ancients. It is readily obtained from bromo-anthranilic acid by the glycine method, but is not regarded as sufficiently valuable to place on the market.[11]

Of the technically valuable halogen indigos may be mentioned indigo 2R (5-bromo-indigo), indigo RB or 2B (5.5′-dibromo-indigo), ciba blue 2B or indigo 4B (5.7.5-tetrabromo-indigo). Pentabromo- and hexabromo- indigo (indigo 5B and 6B) are also known, but the slight solubility of their reduction products militates against their success.

All the above dyestuffs are usually mixtures of the different bromo-derivatives. As stated above, they dye in rather brighter shades than indigo itself, and are considerably faster.

A very interesting vat dye has been placed on the market under the name of ciba yellow.[12] It is prepared by boiling indigo with benzoyl chloride and copper powder in nitrobenzene solution, and is usually given the formula :

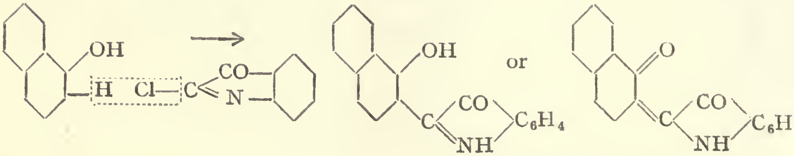


although apparently without any sufficient reason.

An isomer of indigo occurs in the indigo plant. It has received the name indirubin and has been synthesized by condensing indoxyl with istaine :

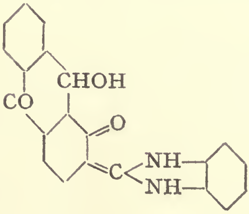
It cannot be used as a dye, as on reduction it passed into indoxyl which on oxidation gives indigo. Its tetrabromo-derivative, however, is more stable and has been placed on the market as ciba heliotrope. It is prepared by condensing dibromisatine with dibromindoxyl.[13]

Very closely related to the indigos is a series of dyes obtained by condensing α-isatine chloride or α-isatine anilide with phenols having a free ortho-position : [14]



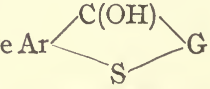
Alizarine Indigo 3R.

In the same way helindon blue 3GN is obtained from α-oxy-anthranol : [15]



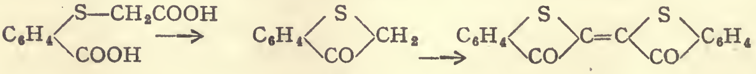
THE THIOINDIGOS.

These are very similar to the indigos in structure, but in them one or both of the imino- groups have been replaced by a sulphur atom. Like the indigos they are all vat dyes, and on reduction give compounds of the structure



$\mathrm{Ar}{<}\begin{matrix}\mathrm{C(OH)}\\ \mathrm{S}\end{matrix}{>}\mathrm{G}$

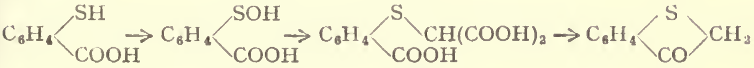
The first member of the series to be prepared was discovered by Friedlander in 1905.[16] He obtained it by fusing *o*-carboxy-phenyl thioglycollic acid (I.) with caustic alkali :



$\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{S{-}CH_2COOH}\\ \mathrm{COOH}\end{matrix} \longrightarrow \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{S}\\ \mathrm{CO}\end{matrix}{>}\mathrm{CH_2} \longrightarrow \mathrm{C_6H_4}{<}\begin{matrix}\mathrm{S}\\ \mathrm{CO}\end{matrix}{>}\mathrm{C{=}C}{<}\begin{matrix}\mathrm{S}\\ \mathrm{CO}\end{matrix}{>}\mathrm{C_6H_4}$

I. II. III.

The first action of the caustic potash is to condense the aryl thioglycollic acid (I.) to 1-oxy-3-thionaphthene (II.), which then undergoes oxidation to form the dyestuff (III.). A very ingenious modification of this process is due to Prescott, Hutchison and Smiles.[17] They found that when thiosalicylic acid is condensed with malonic acid in the presence of sulphuric acid or chlorsulphonic acid, first oxythionaphthene (IV.) and then thioindigo is formed. This process depends on the formation of a sulphoxylic acid (II.) which then condenses with the malonic acid : [18]



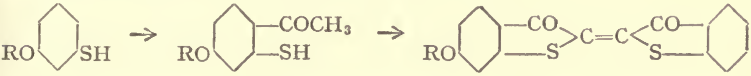
$$C_6H_4{<}\begin{matrix}SH\\COOH\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}SOH\\COOH\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}S\\COOH\end{matrix}{\diagdown}CH(COOH)_2 \rightarrow C_6H_4{<}\begin{matrix}S\\CO\end{matrix}{>}CH_2$$

I. II. III. IV.

A third synthesis consists in condensing thiosalicylic acid with dichlorethylene and then heating the product with dehydrating agents : [19]

$$C_6H_4{<}\begin{matrix}S\\COOH\end{matrix}{\diagdown}CH{=}CH{\diagup}\begin{matrix}S\\HOCO\end{matrix}{>}C_6H_4 \rightarrow C_6H_4{<}\begin{matrix}S\\CO\end{matrix}{>}C{=}C{<}\begin{matrix}S\\CO\end{matrix}{>}C_6H_4$$

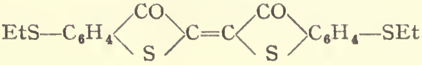
Finally, the alkoxy-thioindigos can be obtained by condensing the alkoxy-mercaptans with acetyl chloride in the presence of aluminium chloride and then oxidizing the mercapto-aceto-phenone thus obtained : [20]



The influence of substituents on the colour of the thioindigo dyes is important, and the following rules are fairly general : Alkyl groups have a powerful influence. When at 4 or 6 they render the shade more blue ; when at 3 or 5 they render it redder. The influence of halogen atoms is similar but not so strongly marked. Substituents at 4 have a greater effect than those at 6.

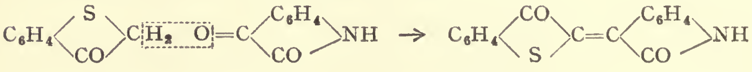
Alkoxy- groups have a very powerful effect. They blue the shade when at 4 or 6 and redden it when at 3 or 5. A methoxy- group at 3 or 5 reddens the shade even when there is a chlorine atom at 4, and a methoxy- group at 4 or 6 blues the shade even when there is a methyl group at 3 or 5.

Thioindigo itself (thioindigo red B) dyes from an alkaline hydrosulphite vat in blueish-red shades which are remarkable for their extraordinary fastness, especially towards chlorine. So fast are the shades in fact that the whole of the cotton can be dissolved away with bleach without affecting the dye. Of its halogen substitution products the most important are ciba bordeaux or 5.5′-dibromothioindigo [*] and thioindigo red BG or helindon red B, which is the corresponding chlorine compound. Of the alkoxy-thioindigos, helindon orange R is the 5.5′-diethoxy- compound, which passes into helindon scarlet R on the entrance of halogen atoms. The corresponding thiethoxy compound,

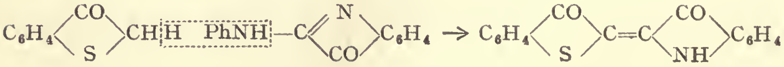


is helindon scarlet S or thioindigo scarlet S.

An important class of dyes, the hemithioindigos, is obtained by condensing oxythionaphthene with α-diketones. The most important member of this series is thioindigo scarlet R or ciba red B, and is obtained by condensing oxythionaphthene with isatine : [21]



Its dibromo derivative is thioindigo scarlet G or ciba red G. An isomeric compound is obtained by condensing oxythionaphthene with α-isatine anilide and is placed on the market as ciba violet A :



Finally, an interesting dyestuff, ciba scarlet G, is obtained

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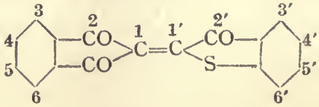
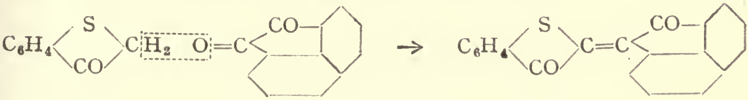
[*] The atoms in thioindigo are usually numbered as follows:—



by condensing oxythionaphthene with acenaphthenequinone.[22] On bromination it gives ciba scarlet R.



REFERENCES AND LITERATURE.

[1] *B.*, **3,** 514.
[2] *B.*, **15,** 50. D.R.P. 19,266.
[3] D.R.P. 15,516.
[4] *B.*, **15,** 2856 ; **16,** 2205. D.R.P. 19,768.
[5] *B.*, **23,** 3043. D.R.P. 54,526 ; 85,071.
[6] D.R.P. 63,331 ; 137,955 ; 138,903 ; 179,933.
[7] D.R.P. 157,710 ; 157,909 ; 158,090 ; 158,346. *B.*, **37,** 4059, 4073, 4087 ; **39,** 989, 2796.
[8] D.R.P. 192,872 ; 200,914.
[9] *B.*, **24,** 978 ; **42,** 3641, 4218.
[10] D.R.P. 193,970.
[11] *B.*, **42,** 765.
[12] E.P. 29,368^{10}.
[13] D.R.P. 192,682
[14] D.R.P. 237,199 ; 241,825–6–7.
[15] D.R.P. 242,053.
[16] D.R.P. 177,345-6 ; 188,702 ; 192,075 ; 194,237 ; 194,254. *B.*, **39,** 1060.
[17] *Proc.*, **27,** 317. *Soc.*, **101,** 570.
[18] *Soc.*, **97,** 1290 ; **99,** 840.
[19] D.R.P. 205,324.
[20] D.R.P. 198,509.
[21] D.R.P. 182,260.
[22] D.R.P. 205,377 ; 210,813 ; 211,696.

A critical survey of indigo and its competitors is given by Felsen in "Indigo u. seine Konkurrenten." 1909.

The application of the indigoid vat dyes is treated by Whittaker in "Dyeing with Coal Tar Dyestuffs," this series, Section IX.

SECTION XI.—THE ANTHRAQUINONOID DYES

THE anthraquinone dyes can be divided into three classes, viz. (i) Mordant Dyes, (ii) Acid Dyes, (iii) Vat Dyes.

THE ANTHRAQUINONOID MORDANT DYES.

These consist of polyoxy-anthraquinone derivatives, and although they are almost insoluble in water they are sufficiently soluble to unite with metallic oxides to form highly coloured salts ("lakes"). The colour of these lakes often depends on the metallic atom present, and hence the dyes are frequently polygenic in nature. Alizarine, for example, dyes in red shades on an alumina mordant and in violet shades on a stannic or chrome mordant.

It was formerly believed that only those oxy-anthraquinones which contained two hydroxyl groups in the 1 and 2 positions were capable of acting as mordant dyes[1] (Rule of Kostanecki and Liebermann). Although fairly general this rule is not absolutely correct, but all the commercially valuable oxy-anthraquinones do contain such hydroxyl groups.

The preparation of the oxy-anthraquinones can be carried out by two methods, viz. by inserting the hydroxyl groups into anthraquinone or by building up the anthraquinone nucleus from phenolic compounds.

Hydroxylation of Anthraquinone.—Hydroxyl groups can be inserted into the anthraquinone nucleus by the same methods as are used for preparing phenols and naphthols, the most important of which is the fusion of the corresponding sulphonic acids with caustic alkali. As stated on page 66, however, hydroxyl groups can also be inserted by direct oxidation. This oxidation can be brought about by a variety of reagents, and can frequently be carried out simultaneously with the replacement of a sulphonic acid group, as, for example, in the preparation of alizarine.

The direct oxidation of anthraquinone leads to a variety of products according to the condition of the experiment and according to the oxidizing agent employed. Thus, when oxidized with nitroso-sulphuric acid (chamber crystals) with the addition of boric acid, quinizarine (1.4-dioxy-anthraquinone) is the chief product,[2] whereas when oleum is used the hydroxyl groups first enter the 1.5 positions giving anthrarufin,[3] which on further oxidation passes into a hexa-oxy-anthraquinone. Further information will be found in the discussion of the individual dyes.

Alizarine (1.2-dioxy-anthraquinone).—This is by far the most important mordant dye and is one of the most used dyes on the market. It was originally obtained from madder, the root of a plant (*Rubia tinctorum L.*) growing in the south of France, in the Orient, Bengal, and Japan, in which the dyestuff occurs in the form of a glucoside. It is now solely obtained from anthraquinone, the synthetic product having completely replaced that obtained from natural sources.

The proof of the constitution of alizarine rests on the following facts :—

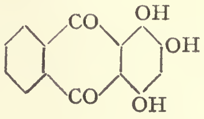
(i) Distilled over zinc dust it yields anthracene.

(ii) Heated with acetyl chloride it gives a diacetyl derivative and hence contains two hydroxyl groups.

(iii) On methylation it gives only a mono-methyl ether, and hence probably one hydroxyl group is in the ortho-position to a carbonyl group, it being well known that hydroxyl groups in such positions can only be methylated with the utmost difficulty.

(iv) On oxidation it yields phthalic acid, and hence the two hydroxyl groups must be attached to the same benzene ring.

(v) Phthalic anhydride condenses with hydroquinone to give a dioxy-anthraquinone (quinizarine [4]) in which the hydroxyl groups must be in the para- position to one another. This, on oxidation with manganese dioxide and sulphuric acid, gives a trioxy-anthraquinone (purpurin), which on further oxidation gives phthalic acid. Hence in purpurin the three hydroxyl groups must be attached to the same benzene nucleus, and consequently its formula must be:



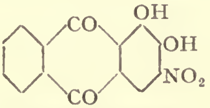
But purpurin is also formed by the oxidation of alizarine, and hence alizarine must be 1.2- or 1.3-dioxy-anthraquinone. As alizarine is formed when phthalic anhydride is condensed with pyrocatechol,[5] the hydroxyl groups must be in the ortho- position to one another. Hence alizarine must be 1.2-dioxy-anthraquinone.

The first process for the synthetic production of alizarine was patented in 1869 almost simultaneously by Perkin [6] in this country and by Caro, Graebe, and Liebermann in Germany. They obtained it by fusing anthraquinone-2-sulphonic acid with caustic potash, oxidation taking place simultaneously with the replacement of the sulphonic acid group. In this process the oxidation was brought about partly at the expense of some of the anthraquinone sulphonic acid, which was thereby reduced to anthracene, and partly by atmospheric oxygen. In modern practice an oxidizing agent, such as potassium chlorate or sodium nitrate, is added and the melt carried out under pressure. As a rule 100 kilos of anthraquinone yield about 105 to 110 kilos of alizarine.

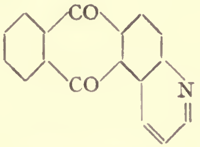
The process is carried out as follows. Sodium nitrate (250 lbs.) is dissolved in 5000 lbs. of 40 per cent. caustic soda solution heated to 125° C. A paste of silver salt containing 66·6 per cent. of the salt is then added, the usual charge being 1250 lbs. The autoclave is then closed and the temperature raised to 180° C. and maintained at this point for 36–48 hours. After cooling the charge is acidified with dilute acid and the alizarine filtered off and washed. For this purpose water *absolutely* free from iron must be used or the shade will be spoilt.

On sulphonation under ordinary conditions the sulphonic group enters the 3-position, giving alizarine red S,[7] a dyestuff sometimes used in volumetric work as a substitute for methyl orange. When the sulphonation is carried out in the presence of mercury salts the sulphonic group enters the α-positions of the ring which does not contain the hydroxyl groups, and a mixture of alizarine-5- and alizarine-8-sulphonic acids is obtained. This mixture forms the commercial erweco acid alizarine red BS.[8]

When alizarine is nitrated either in glacial acetic acid solution or dissolved or suspended in some neutral solvent, such as nitrobenzene or ligroin, or in sulphuric acid solution in the presence of boric acid,[9] 3-nitro-alizarine (alizarine orange A or N) is formed. This on reduction gives the corresponding amino-alizarine which, when heated with glycerine, sulphuric acid and nitro-benzene (Skraups reaction), gives the corresponding quinoline (alizarine blue) which dyes cotton in remarkably fast shades.[10]

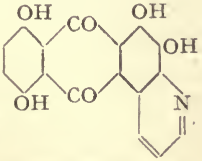


Alizarine Orange.

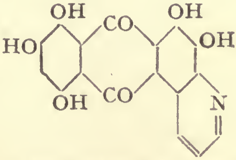


Alizarine Blue.

This last, on oxidation with oleum, passes first into quinalizarine quinoline (alizarine green X),[11] and then into pentaoxy-anthraquinone quinoline (alizarine indigo blue S).[12]



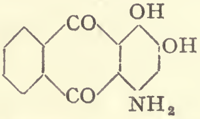
Alizarine Green X.



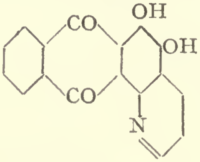
Alizarine Indigo Blue S.

Both these dyes are usually placed on the market as their bisulphite compounds.

If, on the other hand, the diacetyl or dibenzoyl derivative of alizarine is nitrated,[13] the nitro- group enters the α-position and, on splitting off the acyl groups, 4-nitroalizarine is obtained. This is of no importance as a dye, but on reduction passes into the amino-compound [14] (alizarine garnet), which is capable of dyeing unmordanted silk in violet-red shades. Treated by Skraup's method it yields the corresponding quinoline (alizarine green S).[15]



Alizarine Garnet.

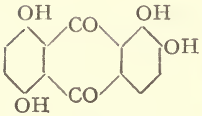


Alizarine Green S.

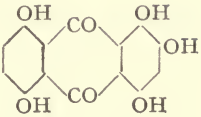
This latter dye, it will be noticed, only differs from alizarine blue in the position of the quinoline nitrogen atom. It is quite remarkable that such a slight difference in the structure should cause a change in colour from blue to green. As will be seen later, however, the anthraquinone acridones show a similar change in colour when the positions of the imino- and carbonyl groups are reversed.

On oxidation alizarine yields a variety of products according to the conditions of the experiment. When the oxidation is carried out with manganese dioxide and sulphuric acid the chief product is purpurin (1.2.4-trioxyanthraquinone), a dyestuff found together with alizarine in madder but very little used. The shades are similar to those obtained from alizarine.

When the oxidation is carried out with oleum, the chief product is quinalizarine [16] (1.2.5.8-tetraoxy-anthraquinone), which is placed on the market as alizarine bordeaux. This, on oxidation with manganese dioxide, passes into alizarine cyanine R),[17] which gives blue shades on an alumina mordant.

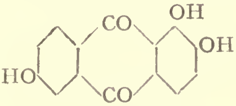


Alizarine Bordeaux.

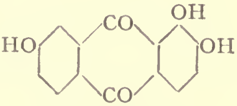


Alizarine Cyanine R.

When anthraquinone-2.6-disulphonic acid is fused under pressure with caustic alkali and potassium chlorate, 1.2.6-trioxy-anthraquinone (flavopurpurin, alizarine GI,RG, SCD or X) is obtained. This dyes in very similar shades to alizarine. A similar compound, 1.2.7-trioxy-anthraquinone (isopurpurin, alizarine GD, RX or SX Extra), is obtained in the same way from the 2.7-disulphonic acid. In both cases the reaction is exactly analogous to that which takes place in the preparation of alizarine :



Flavopurpurin.



Isopurpurin.

If 1.5-dinitro-anthraquinone is heated with 40 per cent. oleum with or without the addition of a reducing agent, 1.3.4.5.7.8-hexaoxy-anthraquinone (anthracene blue WR) is formed. The same compound is formed when anthrarufin or anthrachrysone is oxidized with oleum.[18]

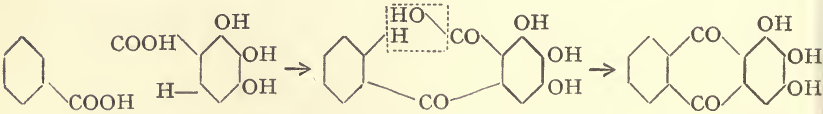
As stated on page 170, oxy-anthraquinones can also be formed by building up the anthraquinone nucleus from suitable phenolic compounds. This can be done in three ways—

(i) Phthalic anhydride is condensed with a phenol in the presence of aluminium chloride and the resulting *o*-benzoyl benzoic acid then heated with sulphuric acid or other dehydrating agent.[19] This reaction is very general and is not confined to the phenols. Thus anthraquinone itself can be obtained by condensing phthalic anhydride with benzene :

The yields are usually excellent, but a whole (double) molecule of aluminium chloride must be used. Were it not for this disadvantage the synthesis of anthraquinone by this method might be a commercial success.

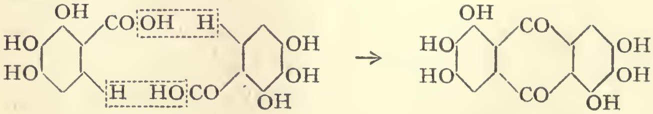
(ii) Phthalic anhydride is condensed with a phenol in the presence of sulphuric acid or zinc chloride. Here pyronines are apt to be formed simultaneously, and with the simpler phenols are the main product (see p. 124). With the polyhydric phenols, however, the method is often quite satisfactory. Thus phthalic anhydride and pyrogallol yield anthragallol[20] (anthracene brown or alizarine brown W, WG, etc.).

(iii) By heating an oxy-benzoic acid, or a mixture of an oxy-benzoic acid and a benzoic acid derivative. This reaction consists in a simple loss of water between the carboxyl groups and the hydrogen atoms of the benzene ring. Since, as a rule, it is only those hydrogen atoms which are in the para- position to a hydroxyl group which react in this way, it follows that only meta-oxy-benzoic acids can be used. Thus, if a mixture of gallic acid and benzoic acid is heated with sulphuric acid, anthracene brown is obtained:[21]



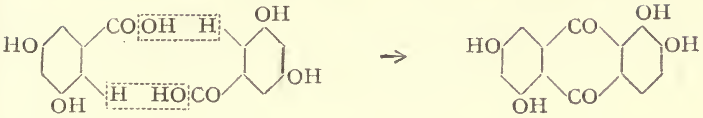
Anthracene Brown.

a small quantity of hexaoxy-anthraquinone being formed at the same time. This latter compound (rufigallic acid) is the sole product when gallic acid is heated with sulphuric acid:[22]

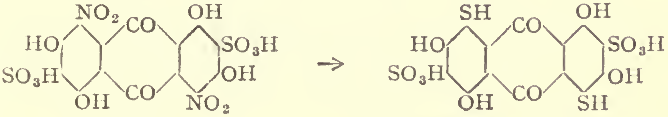


Rufigallic Acid.

In exactly the same way 3.5-dioxy-benzoic acid gives anthrachrysone:[23]

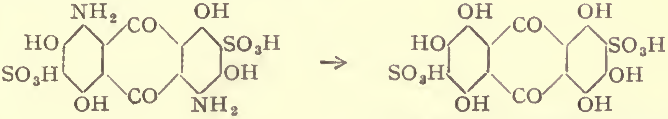


This, on nitration and sulphonation, passes into a dinitrodisulphonic acid. If this is treated with sodium sulphide the nitro- groups are replaced by mercaptan groups, yielding the dyestuff acid alizarine green B and G, which gives green shades on a chrome mordant : [24]



Acid Alizarine Green B and G.

If, on the other hand, the nitro- groups are reduced with nascent hydrogen the diamino-compound is obtained, which, when treated with caustic alkali, loses ammonia and forms a hexaoxy-anthraquinone disulphonic acid (acid alizarine blue BB and GR).[25]



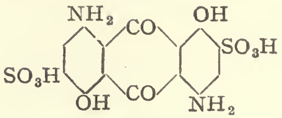
Acid Alizarine Blue BB and GR.

This dyes in red shades from an acid bath, which become blue on after-treatment with chromium fluoride.

THE ANTHRAQUINONOID ACID DYES.

These are usually sulphonic acids of amino-anthraquinone derivatives, and are used for dyeing wool from an acid bath. As a rule they dye in very level shades, which are extremely fast to light.

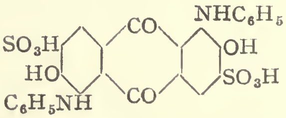
The oldest, and one of the most valuable dyes of this series, is alizarine saphirol,[26] which is obtained by nitrating and then reducing anthrarufin disulphonic acid :



Alizarine Saphirol.

It dyes in very pure shades of blue.

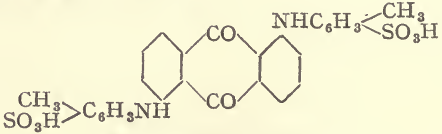
Somewhat similar to this in constitution is erweco acid alizarine red R, obtained by condensing dinitro-anthraflavic acid disulphonic acid with aniline :[27]



Erweco Acid Alizarine Red R.

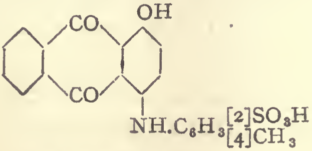
It dyes wool red from an acid bath, the colour passing into deep blue on after-treatment with chromium fluoride.

Anthraquinone violet is obtained by condensing anthrarufin or 1.5-dinitro-anthraquinone with *p*-toluidine and then sulphonating the product :[28]

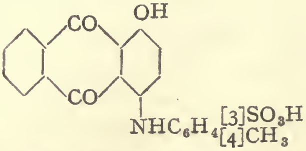


Anthraquinone Violet.

Most of the anthraquinone acid dyes, however, are derivatives of quinizarine. Thus, if quinizarine is heated with one molecule of *p*-toluidine and the product sulphonated we obtain alizarine irisol D,[29] which gives blue-violet shades becoming greenish blue on after-chroming. An isomeric compound is obtained by condensing *leuco*-quinizarine with *p*-toluidine-2-sulphonic acid, and is placed on the market as alizarine direct violet R or alizarine cyanol R :

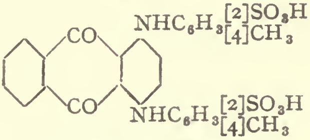


Alizarine Irisol D.



Alizarine Direct Violet R.

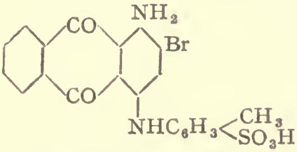
By condensing one molecule of quinizarine with two molecules of *p*-toluidine and sulphonating the product we obtain alizarine cyanine green E,G Extra or K, formerly known as quinizarine green :[30]



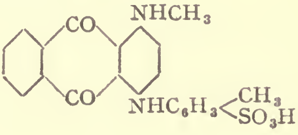
Alizarine Cyanine Green.

An isomeric compound only differing from the above in the position of the sulphonic acid groups is obtained from *leuco*-quinizarine and *p*-toluidine-2-sulphonic acid. It is placed on the market as alizarine direct green G or alizarine brilliant green G.

Alizarine pure blue B is obtained by condensing 2.4-dibrom-1-amino-anthraquinone with *p*-toluidine and then sulphonating the product. Alizarine astrol is obtained when a molecule of quinizarine is condensed with a molecule of methylamine and a molecule of *p*-toluidine, and the product sulphonated. It dyes in greenish shades of blue :



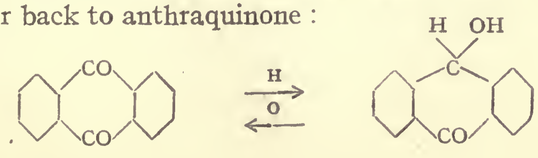
Alizarine Pure Blue B.



Alizarine Astrol.

The Anthraquinonoid Vat Dyes.

All compounds containing an anthraquinone ring pass on reduction in alkaline solution into water soluble products which are readily oxidized by atmospheric oxygen back to the original substance. Athraquinone, for example, on reduction passes into oxy-anthranol, which is readily oxidized in the air back to anthraquinone :



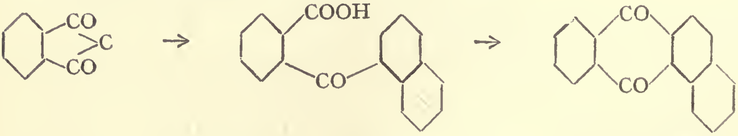
If the soluble reduction product has affinity for animal or vegetable fibres, then if the original product is insoluble in water we have a vat dye. The reduction of the dyestuff is almost invariably carried out with an alkaline solution of sodium hydrosulphite, and the oxidation brought about by exposing the fabric to the air.

The anthraquinonoid vat dyes are almost exclusively used for dyeing cotton, the vats being too strongly alkaline for wool or silk. As a rule the cotton is dyed as yarn, as it is almost impossible to dye piece goods in even shades. They are also used to a considerable extent for printing.

In chemical composition the anthraquinonoid vat dyes differ very much, some of them being extremely simple and others very complex. They are noted for their extraordinary fastness, especially to light.

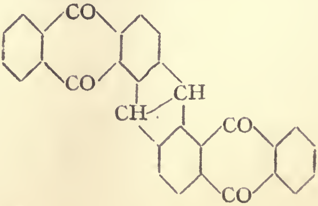
Considered from the point of view of chemical structure the anthraquinonoid vat dyes can be divided into eight classes.

(i) **Homologues of Anthraquinone.**—Anthraquinone is too weakly coloured to be used as a dyestuff, but naphthanthraquinone has been placed on the market under the name of sirius yellow G. It is prepared by condensing naphthalene with phthalic anhydride in the presence of aluminium chloride and then heating the resulting *o*-naphthoyl benzoic acid with concentrated sulphuric acid : [31]

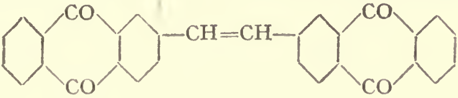


Sirius Yellow G.

Of much greater importance is anthraflavone G, which is obtained by fusing β-methyl anthraquinone with caustic potash.[32] It was originally believed to have the structure :

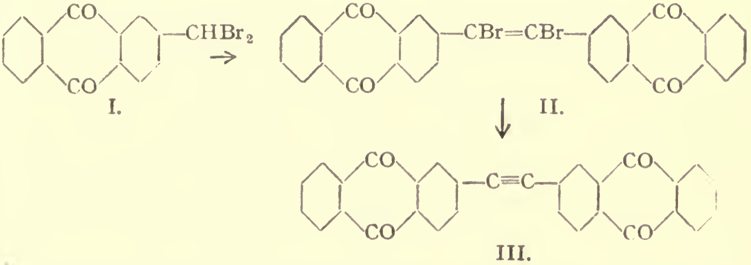


but has now been proved to be a stilbene derivative :

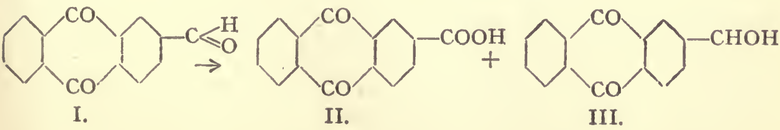


Anthraflavone G.

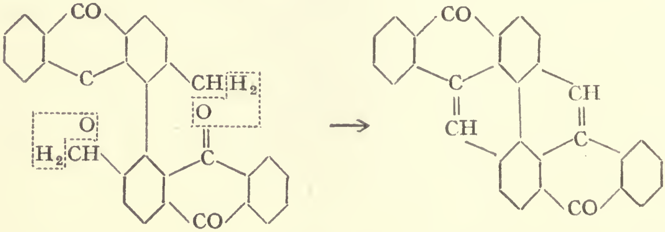
This latter formula is based on the fact that anthraflavone is obtained when ω-dibrom-β-methyl anthraquinone is heated with copper powder, or with tertiary bases such as dimethyl aniline. In this connection it is interesting to notice that if ω-dibrom-β-methyl anthraquinone (I) is heated alone to 240°–250°, torrents of hydrobromic acid are evolved and dibromanthraflavone (II) is formed. From this the corresponding acetylene derivative (III) can be obtained, which on reduction gives anthraflavone :



As regards the mechanism of the formation of anthraflavone by fusing β-methyl anthraquinone with caustic potash, it is extremely probable that first of all the aldehyde (I) is formed, and that this then undergoes intermolecular oxidation and reduction to form the carboxylic acid (II) and the alcohol (III), just as benzaldehyde under the influence of caustic alkali gives a mixture of benzoic acid and benzyl alcohol. The anthraflavone would then be formed by the loss of two molecules of water from two molecules of the alcohol :

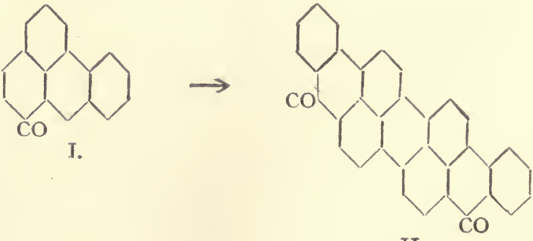


(ii) **The Benzanthrones.**—These contain two anthraquinone residues fused together in a more or less complicated manner, but only two carbonyl groups. The simplest member of the series is pyranthrone [33] or indanthrene golden orange G, which is obtained by the loss of two molecules of water from 2.2′-dimethyl-1.1′-dianthraquinonyl :



On halogenation the depth of the colour is increased, the chlorinated compound [34] being indanthrene golden orange R and the brominated compound [35] indanthrene scarlet G.

Of more complicated structure are the blue and violet dyes of this class. Thus, when anthraquinone is heated with glycerine and concentrated sulphuric acid, benzanthrone (I) is formed,[36] which on fusion with caustic potash passes into violanthrene BS or indanthrene dark blue, which probably has the structure II and dyes cotton in very fast red-violet shades.[37]

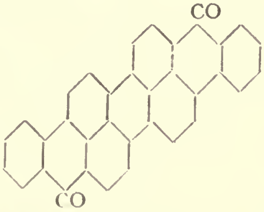


I.

II.

On halogenating [38] this gives indanthrene violet RT, and on nitrating [39] viridanthrene or indanthrene green B. It is rather remarkable that a compound containing a nitro-group should be satisfactory as a vat dye, as one would expect reduction of this to take place in the vat.

Of very similar structure is violanthrene R Extra or indanthrene violet R Extra, which is obtained by fusing halogen derivatives of benzanthrone with caustic alkali.[40] It is generally given the constitution :



Its chloro-derivative [41] (indanthrene violet 2R) is rather redder in shade.

(iii) **The Acyl-Amino-Anthraquinones.**—The amino-anthraquinones have very feeble tinctorial properties, but some of their acyl derivatives are valuable dyestuffs. The simplest of these is algol yellow WG or benzoyl α-amino-anthraquinone.[42] Helio fast yellow 6GL is the corresponding salicyl derivative and is very similar in shade.

Algol pink R is the N-benzoyl derivative of 1-oxy-4-amino-anthraquinone. On methylating the hydroxyl group we get algol scarlet G. The dibenzoyl derivative of 1.4-diamino-anthraquinone is algol red 5G, and that of 1.5-diamino-anthraquinone is algol yellow R.

Although the benzoyl derivatives have proved to be far the most valuable as dyestuffs, one or two derivatives of dibasic acids have also been placed on the market. Thus the succinyl derivative of α-amino-anthraquinone [43] is algol yellow 3G.

Here must also be mentioned the urea derivatives such as helindon yellow 3GN, obtained by the action of one molecule of phosgene on two molecules of β-amino-anthraquinone.[44] In this connection it is interesting to notice that, unlike most primary aromatic amines, the amino-anthraquinones do not give thioureas when heated with carbon bisulphide and sulphur. These thioureas can be obtained by other means and are vat dyes, although they are not of sufficient value to place on the market.

The position and nature of substituent groups has a considerable influence on the shade of the benzoyl amino-anthraquinones, and the following rules are fairly general.

The benzoyl-amino-group being at 1:

(*a*) Substituents at 2 have very little effect.

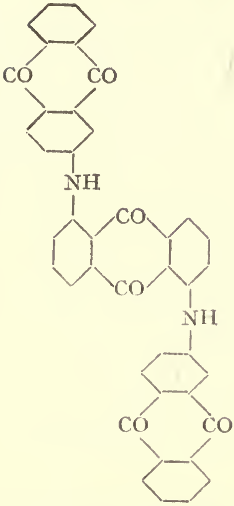
(*b*) Substituents at 4, other than halogen atoms or alkoxy-groups, have a great effect in shifting the shade towards the blue end of the spectrum. A second benzoyl amino-group in this position produces a yellow-red dyestuff, whereas an amino-group produces a still greater effect, monobenzoyl-1.4-diamino-anthraquinone dyeing in corinth shades. The influence of the hydroxyl group is still more marked, 4-oxy-1-benzoyl amino-anthraquinone dyeing in blue-red shades. As would be expected, the nitro-group shifts the colour right into the violet.

(*c*) Most substituents at 5 have little effect, a nitro-group merely producing orange shades. The influence of primary, secondary, and tertiary amino-groups, however, is more marked, the entrance of these groups leading to red or bordeaux colours.

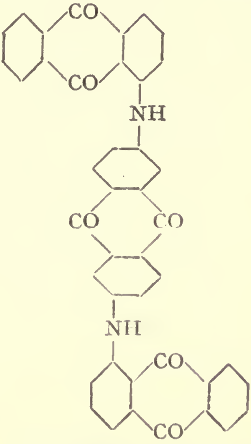
(*d*) Although but little data is available, substituents at 8 seem to exert much the same effect as those at 4. If there are active substituents at both 4 and 8, then blue or violet dyes are obtained. Thus, 4.8-dihydroxy-1.5-dibenzoylamino-anthraquinone dyes in blue shades, 4-hydroxy-1.8-dibenzoylamino-anthraquinone in violet shades, and 1.4.5.9-tetrabenzoylamino-anthraquinone in red-violet shades.

The manufacture of the acyl amino-anthraquinones is very simple. They are invariably formed by boiling the corresponding amino-anthraquinone with the acid, or better with the acid chloride, in solution in some neutral solvent of high boiling-point, such as nitro-benzene.

(iv) **The Anthraquinone Imides.**—The secondary amino-anthraquinones are usually red or bordeaux dyes, and are readily obtained by condensing an amino-anthraquinone with a chloro-anthraquinone in the presence of sodium carbonate or acetate and either copper powder or cuprous chloride.[45] Most of the dyes contain three anthraquinone residues. The most important members of the series are:



Indanthrene Bordeaux B.



Indanthrene Red G and R.

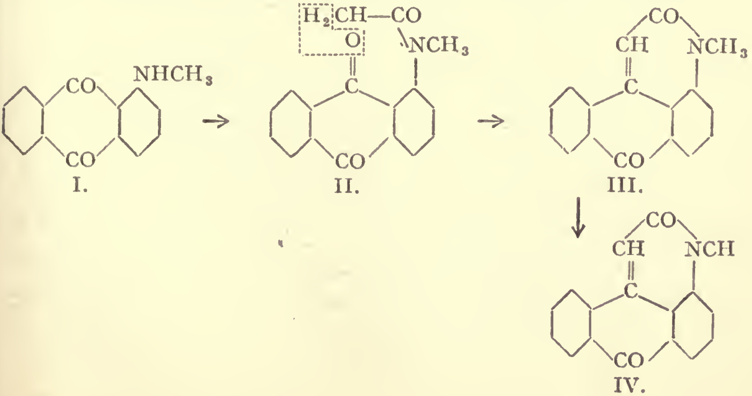
$Cl[6]C_{14}H_6O_2[1]NH[2]C_{14}H_6O_2[7]NH[1]C_{14}H_6O_2[7]Cl$

Indanthrene Bordeaux B Extra.

$MeO[4]C_{14}H_6O_2[1]NH[2]C_{14}H_6O_2[6]NH[1]C_{14}H_6O_2[4]OMe$

Algol Bordeaux 3B.

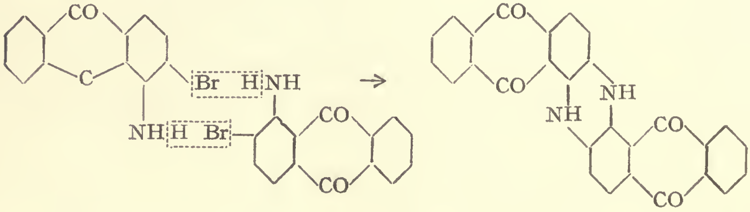
Algol red B is also an anthraquinone imide, but in addition contains a pyridine ring.[46] It is obtained by condensing α-brom-anthraquinone with methylamine and then acetylating the product (I). This acetyl derivative (II) on loss of water passes into III, which when brominated and then condensed with β-amino-anthraquinone gives the dyestuff (IV):



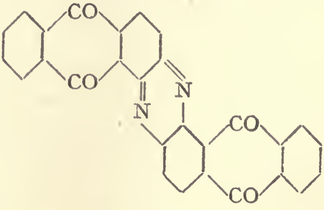
I. II. III. IV.

(v) **Cyclic Hydrazines.**—These are also anthraquinone imides, but contain two imino- groups which form part of a ring. To this class belongs the most important of all the anthraquinone vat dyes, viz. indanthrene blue R or RS, discovered by Bally in 1901 by fusing β-amino-anthraquinone with caustic alkali.[47] In order to obtain a good yield of the dyestuff it is necessary to add an oxidizing agent, such as potassium nitrate, to the melt. The same dye is also obtained when α-amino-anthraquinone is heated under pressure with certain neutral salts, such as copper sulphate, ferric chloride or aluminium chloride, but the yields by this latter method are very poor.[48]

The constitution of the dyestuff was established by Scholl,[49] who obtained it by heating 2-brom-1-amino-anthraquinone with copper powder :



It forms a blue powder which gives a blue vat from which cotton is dyed in very beautiful shades of blue which are very fast to light and soap, although rather loose to chlorine. This looseness to chlorine is due to the oxidation of the cyclic hydrazine to the azine :



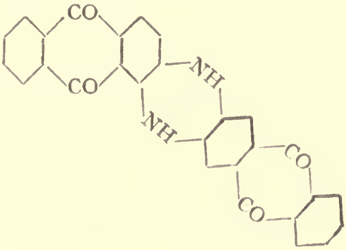
This azine is yellow in colour and is very easily reduced to the hydrazine, so that the colour of a fabric which has been bleached by chlorine can be restored by treating it with a reducing agent.

The entrance of halogen atoms into the indanthrene molecule produces dyestuffs of a rather greener shade, but at the same time renders the oxidation to the azine less easy. Hence the halogenated indanthrenes are faster to chlorine than indanthrene itself. The most important of them are the dichloro- derivative [50] (indanthrene blue CCD) and the dibromo- derivative [51] (indanthrene blue GC).

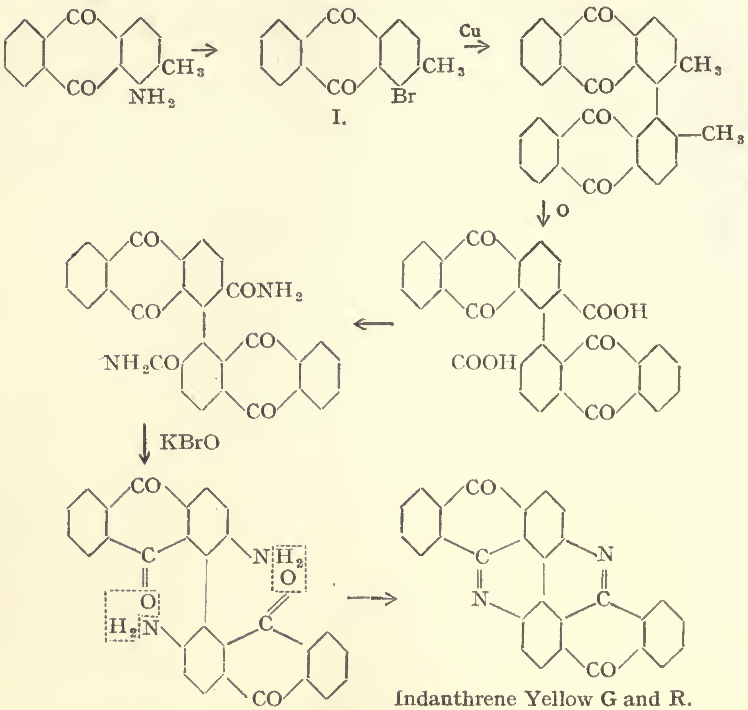
The oxidation of the cyclic hydrazine to the corresponding azine could obviously also be prevented by replacing the two imino-hydrogen atoms by alkaly radicles. This has been done by Bayer and Co., who place the di-N-methyl derivative [52] on the market as algol blue K. This dyestuff is prepared by heating 2-brom-1-methylamino-anthraquinone with sodium acetate and cuprous or cupric chloride.

A dihydroxy compound [53] (algol blue 3G) is made by heating 1-amino-2-brom-4-oxy-anthraquinone with caustic soda and copper powder.

An isomer of indanthone has been described.[54] It is prepared by condensing 2.3-diamino-anthraquinone with alizarine and has the formula :

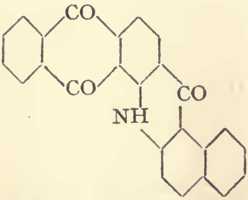


(vi) **The Flavanthrenes.**—These consist of highly condensed dianthraquinonyl derivatives containing only two carbonyl groups. The best known member of the series is flavanthrene itself (indanthrene yellow G and R). This appears as a side product in the manufacture of indanthrene blue RS, but is best obtained by heating β-amino-anthraquinone with antimony pentachloride in nitro-benzene solution.[55] The constitution of the dye was proved by Scholl,[56] who synthesized it as follows :

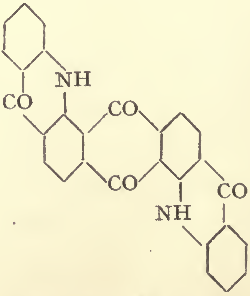


Indanthrene Yellow G and R.

(vii) **The Anthraquinone Acridones.**—These are usually prepared by condensing 1.2-chloro-anthraquinone carboxylic acids with aromatic amino-compounds and then treating the resulting secondary amine with concentrated sulphuric acid. The most important members of the series are indanthrene red BN Extra [57] and indanthrene violet RN :

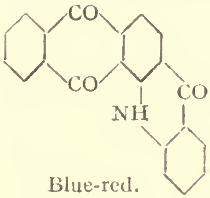


Indanthrene Red BN Extra.

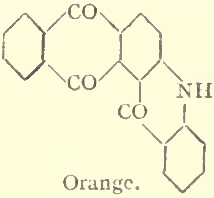


Indanthrene Violet 2R.

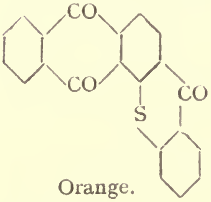
It is interesting to notice the difference in colour of the isomeric acridones and to compare it with the colour of the corresponding thioxanthones and xanthones.[58] In every case it is found that the colour is nearer the violet end of the spectrum when the carbonyl group is in the β-position than when it is in the α-position.



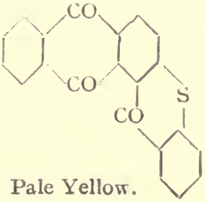
Blue-red.



Orange.



Orange.



Pale Yellow.

As will be seen, the thioxanthones are paler in colour than the corresponding acridones. The xanthones are less highly coloured than the thioxanthones, and differ from them by having no affinity for the fibre.

(viii) **Dyes of Unknown Constitution.**—Under this heading must be classed a variety of anthraquinone derivatives the constitution of which has not yet been elucidated. For example, if 1.5- or 1.6-diamino-anthraquinone is condensed with formaldehyde and the product fused with caustic potash, indanthrene maroon R is obtained. Indanthrene grey B and indanthrene brown B are obtained by fusing amino-anthraquinones with caustic potash; and by treating the acetyl amino-anthraquinones with phosphorus oxychloride indanthrene copper R is obtained.

REFERENCES AND LITERATURE.

[1] *B.*, **8,** 631; **18,** 2145; **20,** 3144; **34,** 1562; **35,** 1490.
[2] D.R.P. 81,245; 153,129.
[3] D.R.P. 101,220; 156,960.
[4] *B.*, **7,** 972; **11,** 2501.

[5] *B.*, **7,** 972.

[6] E.P. 1936^{69}, 1948^{69}.

[7] D.R.P. 3565.

[8] D.R.P. 205,965, 210,863.

[9] D.R.P. 74,562 ; *B.*, **12,** 584 ; A.P., 186,032.

[10] *B.*, **28,** 62 ; **29,** 708. D.R.P. 87,334.

[11] D.R.P. 46,654.

[12] D.R.P. 47,252.

[13] *Soc.*, **2,** 578 ; *B.*, **12,** 586.

[14] D.R.P. 66,811 ; 67,470. *B.*, **24,** 1610.

[15] *Mon. Sci.*, 1874. 1149. F.P. 104,146.

[16] D.R.P. 60,885.

[17] D.R.P. 62,018.

[18] D.R.P. 67,102.

[19] *Z. ang.*, **19,** 670. *A.*, **291,** 9. *C.r.*, **19,** 139.

[20] *B.*, **10,** 38.

[21] *B.*, **10,** 39.

[22] *A.*, **19,** 204.

[23] *B.*, **19,** 754 ; **35,** 2305.

[24] D.R.P. 73,684.

[25] D.R.P. 75,490.

[26] D.R.P. 96,364 ; 100,136 ; 103,395 ; 108,362.

[27] D.R.P. 235,776.

[28] D.R.P. 108,274.

[29] D.R.P. 86,150.

[30] D.R.P. 86,150.

[31] D.R.P. 193,961 ; 229,401.

[32] D.R.P. 179,893 ; 199,756. *B.*, **46,** 709, 712.

[33] D.R.P. 174,494 ; 175,067 ; 212,019.

[34] D.R.P. 218,262.

[35] D.R.P. 218,262.

[36] D.R.P. 176,018.

[37] D.R.P. 185,221.

[38] D.R.P. 177,574.

[39] D.R.P 185,222.

[40] D.R.P. 194,252.

[41] D.R.P. 217,570.

[42] D.R.P. 225,232.

[43] D.R.P. 210,019 ; 212,436.

[44] D.R.P. 232,739.

[45] D.R.P. 174,699 ; 184,905 ; 197,554 ; 206,717 ; 216,668.

[46] D.R.P. 194,253.

[47] D.R.P. 129,845–6–7–8 ; 158,287 ; 210,233 ; 216,891.

[48] D.R.P. 186,636.

[49] *B.*, **36,** 3410, 3427, 3710 ; **40,** 320, 326, 390, 395, 924, 933.

[50] D.R.P. 155,415.

[51] D.R.P. 138,167.

[52] D.R.P. 158,287.

[53] D.R.P. 193,121.

[54] D.R.P. 178,130.

[55] D.R.P. 133,666 ; 136,015 ; 138,119.

[56] *B.*, **40,** 1619 ; **41,** 2304.

[57] D.R.P. 234,977 ; 237,236.

[58] *B.*, **44,** 3125.

A critical survey of alizarine and its competitors is given by Felsen in "Turkisrot u. seine Konkurrenten." 1909.

For the application of the mordant dyes see Whittaker, "Dyeing with Coal Tar Dyestuffs," this series, Section IV. ; acid dyes, *ibid.*, Section III. ; vat dyes, *ibid.*, Section IX.

SECTION XII.—THE QUINOLINE DYES

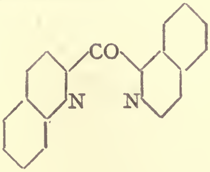
THERE are a few compounds derived from quinoline which have tinctorial properties, although all of them are of very minor importance.

Cyanine.—This was discovered by Williams in 1856, and is obtained by heating equimolecular proportions of quinoline and lepidine (γ-methyl quinoline) with alkyl iodides (two molecules) in the presence of alkali. The mono-acid salts are blue, but the diacid salts are colourless. As the mono-acid salts are strongly basic and are capable of absorbing carbon dioxide from the air to form the colourless diacid salts, the substance is useless as a dye. Some of the cyanines are used for preparing orthochromatic photographic plates.

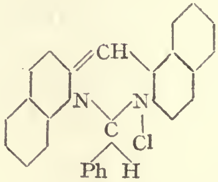
Their constitution is not known, but they are probably triphenyl methane derivatives.

Quinoline Red.—This is probably also a triphenyl methane derivative. It has the formula $C_{26}H_{19}N_2Cl$. It is prepared by condensing crude coal tar quinoline with benzotrichloride. According to Hoffmann it consists of two dyes, one formed by the union of a molecule of benzotrichloride with a molecule of quinoline and one of quinaldine, and the other by the union of benzotrichloride with isoquinoline and quinaldine. It dyes silk and wool red, and the shades are strongly fluorescent, but very loose to light. Like the cyanines it finds application in the preparation of orthochromatic plates.

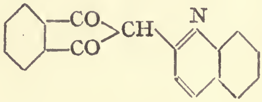
Vongerichten[1] has shown that on oxidation it gives α-quinolyl-α-isoquinolyl ketone :



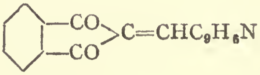
which on treatment with caustic potash gives isoquinoline and quinaldinic acid. On reduction he obtained benzyl mercaptan. He therefore considers the structure of the dyestuff to be :



Quinoline Yellow.[2]—This is the most important of the quinoline dyes, and is obtained by condensing quinaldine with phthalic anhydride in the presence of zinc chloride. The resulting product has no basic properties, but is capable of dyeing silk and wool yellow. In practice, however, it is always sulphonated and used as an acid wool dye. The shades are remarkably pure and very fast to light. The dyestuff, however, only finds limited application on account of its high price. It is believed to have the structure :



or

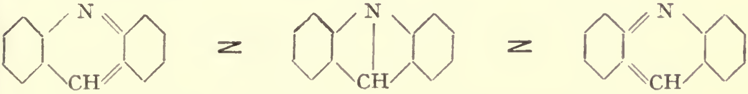


REFERENCES AND LITERATURE.

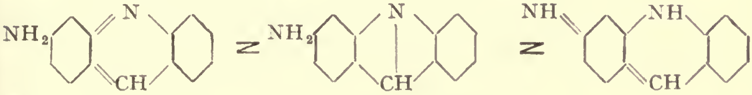
[1] *B.*, **43**, 128 ; **45**, 3446.
[2] D.R.P. 158,761 ; 204,255. *Ch. Ztg.*, 1904, 1206.

SECTION XIII.—THE ACRIDINE DYES

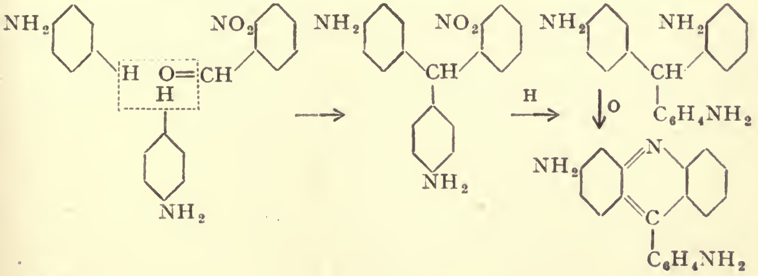
THE simple acridines are pale yellow compounds which are noted for the strong fluorescence they exhibit. They may be regarded as desmotropic substances exhibiting double symmetrical tautomerism :



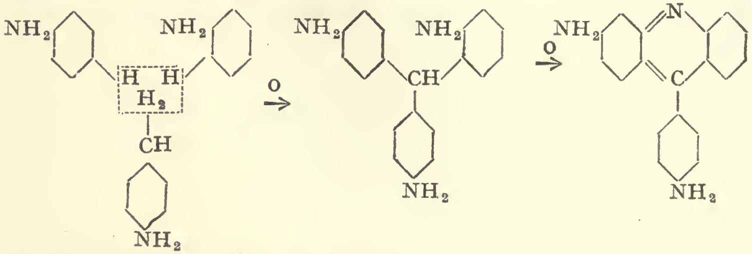
The entrance of the amino-group increases the colour and at the same time confers tinctorial properties on the acridines. The commercial dyes all contain an amino-group in the para-position to the *ms*-carbon atom, and the increase in colour may be due to this rendering a third desmotropic form possible :



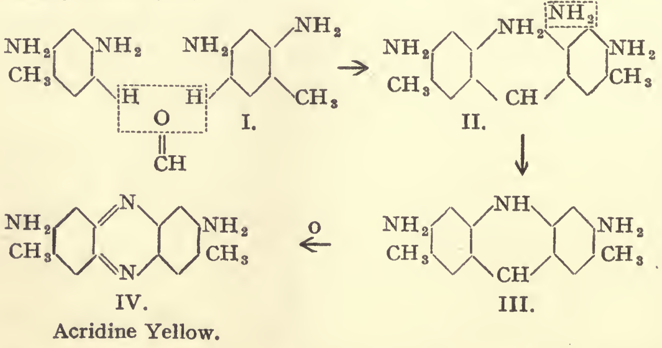
The first acridine dye was obtained by Nicholson in 1863 from the mother liquors from the manufacture of magenta. The constitution of this compound was discovered by Fischer and Koerner,[1] who prepared it by condensing *o*-nitro-benzaldehyde with aniline and then reducing the nitro-group. The triamino-triphenyl methane thus obtained passed into the acridine on oxidation :



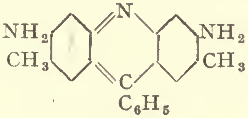
The dye is still used to a considerable extent, especially for colouring leather, under the names of chrysaliline, leather yellow, phosphine, etc. The commercial article is a mixture of the above acridine and the corresponding toluene homologue. Its formation as a bye-product in the manufacture of magenta is obviously due to part of the condensation taking place in the ortho-position :



But few acridine compounds are of any importance as dyes. They are obtained by condensing aldehydes with meta-diamines in acid solution and then closing the acridine ring by loss of ammonia (heating with hydrochloric acid under pressure). Thus, when formaldehyde is condensed with *m*-toluylene diamine, a tetramino-ditolyl methane is formed (II). This when heated with hydrochloric acid under pressure gives the dihydroacridine (III), which on oxidation (air or ferric chloride) passes into the dyestuff, acridine yellow (IV) :

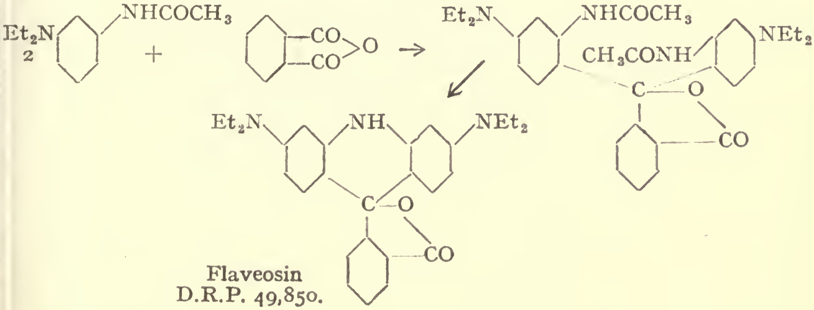


Benzoflavine [2] is formed in the same way from *m*-toluylene diamine and benzaldehyde. It has the formula :



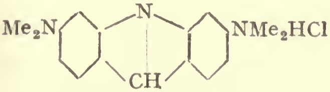
Benzoflavine.

A few acridine dyes have been obtained by fusing the acetyl derivatives of asym.-dialkyl-*m*-diamines with phthalic anhydride and then hydrolysing the product, when simultaneous loss of ammonia takes place :[3]

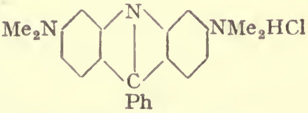


Flaveosin
D.R.P. 49,850.

Other acridine dyes are :



Acridine Orange.
D.R.P. 59,179.



Acridine Orange R Extra.
D.R.P. 68,908.

REFERENCES AND LITERATURE.

[1] *B.*, **17**, 203. D.R.P. 52,324.
[2] *B.*, **32**, 2352. D.R.P. 43,714.
[3] *B.*, **42**, 3631.

SECTION XIV.—THE SULPHUR OR SULPHIDE COLOURS

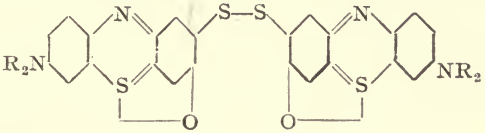
THE composition of this important class of dyes is quite unknown, and they are manufactured by empirical methods, details being preserved very strictly as trade secrets. The first dyestuff of this class was obtained in 1873 by Croissant and Bretonièrre, who, by heating various organic waste products such as bran, wood chips, straw, etc., with sulphur and sodium sulphide, obtained a substance which was soluble in sodium sulphide solution and capable of dyeing cotton in brown or brown-black shades. This they named Cachou de Laval. Since then the sulphur melt has been enormously extended, it being the general routine in the dye factories to submit every new aromatic compound obtained to the sulphur melt under various conditions.

The sulphide dyes are only applicable to cotton, which they dye from a bath containing sodium sulphide, although recently sulphide colours have been introduced which require a hydrosulphite vat. They dye in very fast shades of yellow, brown, blue, violet, and black, although the colours are usually rather dull. True reds have not yet been obtained.

The condition of the dye in the dye bath is uncertain, but it is probably present as a reduction product, as many of the dyes require subsequent oxidation on the fibre, although this is not always the case.

The chemical composition of the dyes is still quite unknown, but they probably consist chiefly of very complicated thiazine compounds containing a large number of thiazine rings and probably also mercaptan groups. At the same time it is likely that many of them also contain thiazole groups, thus resembling primuline.

It is worthy of notice that blue sulphide dyes of the type :



have been obtained by synthetic means, although their cost is too great for them to find any sale for tinctorial purposes.[1] It must be borne in mind that technical sulphide dyes are by no means pure products, such as might possibly be obtained by exhaustive sulphuration. On the contrary, the melt is closely watched and interrupted as soon as the desired shade is obtained, as if carried beyond this point the product has different tinctorial properties. Further, the conditions as regards amount of sulphur and/or sodium sulphide, temperature, etc., have a great influence on the character of the product, and can only be fixed by the arbitrary means of trial and failure. Finally, the presence of catalysts such as copper and zinc salts has a great effect.[2]

The temperatures usually employed are from 150–200° C., but in some cases 100° C. is sufficient. Water, alcohol or other solvents are sometimes added, and in some cases the fusion may be carried out in the presence of caustic soda or sodium thiosulphate.[3]

As torrents of ammonia and sulphuretted hydrogen are evolved the fusion pot must be connected with a suitable flue. As the dyes cannot be classified according to their chemical composition it will be most convenient to consider a few of the more important members according to colour.

Yellows and Browns.—*m*-Toluylene diamine gives immedial yellow,[4] orange shades being obtained at higher temperatures.

Acet-*p*-phenylene diamine or *p*-nitroacetanilide gives a brown dye (thiocatechin),[5] although that obtained from the unacetylated base is greenish black.

Cotton brown[6] is obtained from nitrodiphenylamine with sodium sulphide and sulphur. Eclipse brown from two molecules of toluylene diamine, one molecule of oxalic acid, sulphur and sodium sulphide.[7]

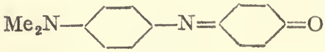
Thion brown is derived from aniline-azo-*m*-toluylene diamine by fusing with sulphur alone, whereas kryogen brown is obtained when 1.8-dinitronaphthalene is reduced with sodium sulphide and sulphite and the product fused with sulphur.

Blues.—These are almost invariably obtained from indophenols at a low temperature. As the indophenols are at once reduced to the corresponding diphenylamine derivative, these latter can also be used as starting-out points.

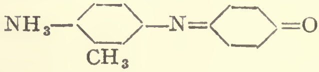
Blues on further treatment with sulphur usually pass into blue-blacks.

The following are typical sulphide blues :

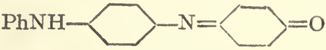
Immedial Pure Blue[8] from



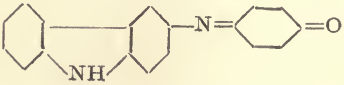
Immedial Indone from



Kyrogen Indigo[9] from



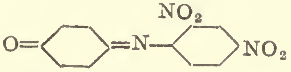
The most important blue, however, is derived from the indophenol obtained by condensing nitrosophenol with carbazole :



This fused with sodium polysulphide gives blue sulphide colours of no great importance, but when the fusion is carried out with excess of sulphur dyes are obtained which can no longer be dyed from a sodium sulphide bath, but which when applied from a hydrosulphite vat dye in pure blue shades which are remarkably fast. These blues are placed on the market as hydrone blue,[10] and are serious competitors of indigo.

Other blue, yellow, brown, and black dyes are also derived from carbazole.[11]

Blacks.—The first black sulphide colour was obtained by Vidal[12] from *p*-aminophenol or *p*-phenylene diamine, and was named Vidal's black after its discoverer. It, however, gives rather brownish shades, and the first deep black (immedial black FF) to be obtained was derived from dinitroindophenol:

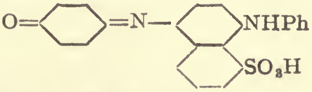


or rather the corresponding diphenylamine derivative, obtained by condensing chlordinitrobenzole with *p*-aminophenol.[13]

The most important black, however, is derived from 1.2.4.-dinitrophenol[14] by fusing with sulphur and sodium sulphide. This is placed on the market by almost all the important firms under various trade names, such as sulphur black, katigen black, immedial black N, etc. It is one of the most important black dyes, the annual consumption being upwards of 5000 tons.

The details of the fusion employed vary widely in different works, but a good black is obtained by dissolving 4 parts of crystallized sodium sulphide and 1½ parts of sulphur in 5 parts of water, and then adding 1 part of dinitrophenol little by little, and finally boiling the whole for 24 hours.

Greens.—Green sulphide colours are usually only obtained when copper sulphate is added to the melt. Thus, when *p*-nitrophenol is melted with sulphur and sodium sulphide a black (Vidal's black) is obtained, but in the presence of copper sulphate a green dye (Italian green)[15] results. In the same way the indophenol:



gives immedial green C.[16]

REFERENCES AND LITERATURE.

[1] R.G.M.C., 1912, 212. D.R.P. 167,012 ; 178,940 ; 179,225.
[2] F.P. 345,307. D.R.P. 101,577 ; 125,583.
[3] D.R.P. 134,704 ; 147,862 ; 141,970.
[4] D.R.P. 139,430.
[5] D.R.P. 82,748 ; 84,632 ; 85,330 ; 88,392 ; 91,719 ; 91,720 ; 94,501
[6] D.R.P. 102,821.
[7] D.R.P. 125,586.
[8] D.R.P. 134,947.
[9] D.R.P. 132,212 ; 134,947 ; 141,752 ; 150,546 ; 150,553.
[10] D.R.P. 218,371 ; 221,215 ; 224,590 ; 224,591.
[11] D.R.P. 224,951.
[12] D.R.P. 85,330 ; 88,392.
[13] D.R.P. 103,801 ; 113,893.
[14] D.R.P. 98,437.
[15] D.R.P. 101,577 ; 148,024.
[16] D.R.P. 162,156.

A comprehensive account of the sulphide dyes will be found in "Die Schwefelfarbstoffe : Ihre Herrtellung u. Verwendung," by Otto Lange. Leipzig, 1912.

The application of the sulphide colours is treated by Whittaker in "Dyeing with Coal Tar Dyestuffs," this series, Section VIII.

CONCLUSION

To what extent a synthetic dyestuff industry can be established on a paying basis in Great Britain is a question on which there is considerable difference of opinion. It is certain that we have a vast amount of leeway to make up before we can compete on equal terms with the large continental firms and combines, and a handicap of some forty years cannot be made up in a day. That the country suffers from no physical disabilities is certain, as the raw materials with the exception of pyrites are all abundant, and the import of pyrites should be cheaper than to central Europe owing to our extensive seaboard. The high cost of transport has been a severe handicap in the past; but possibly, if nationalization does not bring down the railway rates, it may lead to the re-opening of inland waterways and coasting harbours, many of which have been acquired by the railway companies, and then closed down in order to compel merchants to send their goods by rail, a procedure which, however desirable from the point of view of the railway shareholders, cannot be said to be in the interests of the general public.

Without entering into political controversy on the relative merits and demerits of tariff reform, it is difficult to see how a new industry can be nursed into a state of efficiency if not for a time protected from unfair competition, by unfair competition being understood the dumping of goods at a price below manufacturing cost in order to squeeze out competitors with less capital to expend, with the intention, of course, of subsequently raising prices. This seems to be generally recognized, and most political parties agree that at least temporary protection must be offered to the "key" industries, and the future of the dyestuff industry is no doubt largely dependent on the intelligent application of this principle.

The Government, recognizing the national importance of establishing a dyestuff industry, have decided to give financial assistance to manufacturers, and have recently published details of their proposals.* These provide for financial aid of two kinds, viz. A. Loans, and B. Grants-in-Aid of (1) Buildings and Plant; (2) Research.

Loans.—Loans are to be made chiefly to further the production of special classes of dyes, either not hitherto manufactured in this country, or only manufactured to an insufficient extent, and which entail abnormal expenditure on plant.

Grants-in-Aid.—Grants-in-aid are to be made to meet abnormal depreciation and capital cost of plant due to the war, and will not exceed 40 per cent. of the total cost of the plant and buildings on account of which they are made. They will also be made for Research, by which term is to be understood specialized technical research conducted in close connection with the actual manufacture of dyes and intermediates. The grants must not exceed 40 per cent. of the actual cost of any extensions of laboratory buildings and equipment, and 40 per cent. of the maintenance costs of such buildings.

The general conditions for the granting and administration of loans and grants-in-aid may be summarized as follows:—

(1) The recipient must apply them to develop in the shortest possible time the manufacture of colours which are in short supply, the nature and quantity of which are to be determined or approved by the Board of Trade.

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* "Memorandum by the Board of Trade on the Scheme for the Allocation and Administration of the Funds provided by Parliament for the Development of the Dye Industry by means of Financial Assistance to Companies and Firms in Aid of Developments, Extensions, and Research" (Cd. 9194). 1918. Price, 1*s.* 2*d.*—Abstracted in *J.S.C.I.*, 1918, p. 428 (Review).

(2) Applicants must furnish such particulars of their businesses as the Board may desire.

(3) No loan shall exceed 50 per cent. of the total net value of the material assets of the applicant.

(4) The company shall not disburse dividends exceeding 8 per cent. until the terms of the loan or grant have been fulfilled.

(5) Loans to be repayable within twenty years, and may be secured by mortgage, the rate of interest to be 1 per cent. above bank rate, with a minimum of 5 per cent.

(6) After allowing for depreciation, debenture interest, excess profits, and other levies (if any), 10 per cent. of the remainder of the profit to be applied to the repayment of loan. If over 8 per cent. has been earned, half of this surplus to be allocated to repayment.

(7) Manufacturers must undertake to supply all their products at reasonable prices, and to distribute them in an equitable manner; the Board reserving to itself the right to fix prices and arrange distribution.

(8) Contracts and agreements with foreign manufacturers are to be approved by the Board, and foreign participation must not exceed 25 per cent., either in capital or voting power.

As regards these conditions, manufacturers will not be willing to disclose full particulars of their businesses, and the rate of interest charged seems decidedly on the high side. It would have been better to have based interest on profit. The clause referring to depreciation is likely to give rise to friction or abuse, judging by what has taken place under this head when assessing the Excess Profits Duty. The fixing of reasonable prices and equitable distribution is also likely to lead to dispute, as no basis is given on which these are to be calculated. The last clause is to provide against foreign control, and although it will no doubt be effective with small or single concerns, it will be very difficult to apply to large combines and groups, where one company has a large or controlling interest in another, and may be itself controlled by a third, which is perhaps controlled from abroad.

The scheme is to be administered by a "Dyes Commissioner," assisted by (1) a Loans and Grants-in-Aid Committee, (2) a Trade and Licensing Committee, (3) an Inspector of Research, (4) an Inspector of Accounts. This seems a somewhat cumbersome control, and may probably lead to delays and red-tape. As regards the constitution of the Trade and Licensing Committee it is to consist of nine members with the Dyes Commissioner, the members to be elected as follows:—

(1) A chairman elected by the Board of Trade.

(2) Four representatives of dye consumers, of which three are to be elected by the Colour Users Committee and one by the National Federation of Associations of Paint, Colour and Varnish Manufacturers.

(3) Four representatives of the dyestuff manufacturers, of which two will be nominated by Levinsteins and British Dyes, Ltd. (British Dyestuffs Corporation), and one each by the Dye and Intermediate Section of the British Chamber of Commerce and the Board of Trade.

The function of this Committee is to advise on the dyes which should be imported, and on the dyes and intermediates the manufacture of which should be specially encouraged. Producers of primary materials, such as benzole, etc., are specifically excluded from the whole scheme.

Manufacturers are to be asked to submit, amongst other things, details of their scientific and technical staffs and laboratories and complete financial accounts, information which they will hardly care about placing at the disposal of a Government department, especially when that department contains their rivals in the trade, and reserves to itself the power to fix prices.

The success of the whole scheme is very questionable, and no manufacturing concern will care about having their progress examined by an "Inspector of Research." Of course, if the Committees are "packed" with members of the same group of companies, that group would not object to submitting information to what would practically be a family party, but outside firms most certainly would.

Probably a better scheme would have consisted in the establishment of a central "Board of Chemical Industry," on the same lines as the United States "Bureau of Chemistry." The function of such a Board would be to ascertain what chemical manufactures it was desirable to establish in this country, and then work out the processes concerned, not merely on a laboratory scale, but also on a semi-manufacturing scale in plant dealing with quantities of say 100 lbs. Its scope would not be limited to the dyestuff industry only, but would embrace the whole field of chemical manufacture. The data it would provide would comprise all information requisite both from a chemical and from an engineering point of view for the erection of manufacturing scale plant. This information would probably be best published in the form of Bulletins. Certainly this would place the information at the disposal of foreign competitors; but if the information was circulated in the form of confidential reports it would be sure to filter through. The Board would of course be a Government department, and in no way under the influence of manufacturers, although these, together with the users, would be asked to suggest products which in particular should be of home production.

The success of such a scheme would naturally depend very largely on the person chosen to administer it, technical manufacturing experience being *sine qua non*, as otherwise the work carried out might degenerate into research of purely academic interest. One of the smaller national factories might be converted into the necessary research laboratory and experimental works, the junior staff being recruited from the products of our universities and colleges, thus enabling the chemist who wishes to enter industrial life to get first-rate experience of technical difficulties and problems.

In addition to carrying out work on manufacturing processes, the proposed Board might well do most valuable work in determining general chemical engineering data, such as the optimum composition of acid-proof and acid-resisting alloys for various purposes, standardization of sizes, etc.

Apart from all schemes of Government aid the future of the dyestuff industry cannot be said to be clear. The combination of the two leading firms in this country will leave the supply of dyestuffs more or less in the hands of the combine, and however desirable this may be from the point of view of avoiding wasteful competition, and from the point of view of the shareholders, its desirability from the consumer's point of view is not so clear. It is true that the Government intend to prevent artificial prices being maintained by granting importation licences, but agreements of some sort seem to have been arrived at between the combine and French and American producers. The contents of these agreements have not been published, but if they include arrangements for fixing prices it would seem that the only safeguard would lie in the importation of dyes from Germany; and if, at some future date, the British combine were to make similar arrangements with the German combine, the dyer would be reduced to buying what was offered, and at the price at which it was offered. Such an arrangement may never, of course, be brought about, but with the trade more or less concentrated in the hands of one firm the danger is always present.

From a purely economic point of view the cost of production would probably be at a minimum if the benzole and toluol producers converted their products into intermediates and then sold these to the actual dye-makers.

Owing to the excellent transport facilities enjoyed by most coke-oven undertakings, and to the fact that heat is available free of cost in the form of surplus gas from the ovens, or in the form of blast-furnace gas, the production of intermediates could be carried out by such firms at a minimum cost. Another advantage of this scheme would be that the free sale of intermediates would allow the smaller dye-makers to compete on more even terms with the large undertakings, whereas, at present, they must either make their own intermediates—an expensive operation where comparatively small quantities of a large number of products are required,—or alternatively they must buy them from their competitors. Such schemes have for some time been under discussion both in this country and in America, but war conditions have so far caused them to be shelved. The arrival of peace may, however, see their realization.

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