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THE MANUFACTURE OF ORGANIC DYESTUFFS

THE MANUFACTURE OF ORGANIC DYESTUFFS

AUTHORISED TRANSLATION, WITH ADDITIONS,
FROM THE FRENCH OF

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PREFACE.

AFTER the second edition of Benedikt's *Chemistry of the Coal-tar Colours* had gone out of print, the only other text-book on the subject which appeared in the English language was Collin and Richardson's translation of Nietzki's *Chemistry of the Organic Dyestuffs.* Both these works are now hopelessly out of date, and would have to be entirely rewritten to be of any use. The excellent works of A. G. Green (*Tabular Survey*) and of Cain and Thorpe (*Synthetic Dyestuffs*) are rather too compendious and expensive as class-books, and there has been for some years a demand for a really reliable text-book for the use of students, and also for others who merely wish to obtain a general idea of the subject. When Dr. Wahl's work, *L'Industrie des matières colorantes organiques*, appeared as one of the numerous volumes of Derômes's *Bibliothèque des industries chimiques*, I was at once convinced that this excellent little book, written by a chemist who is a recognised authority, and has also had considerable practical experience, would constitute a worthy successor to that of Benedikt, and would supply a real want. I therefore suggested to Mr. Atack that he should undertake the translation, and, when he communicated this to the author, Dr. Wahl not only gave his immediate consent, but undertook to collaborate in bringing the English edition up to date. Much new matter has been added as a consequence of the rapid development of this industry from a commercial as well as from a theoretical point of view during the comparatively short time that has elapsed between the issue of the French and the English editions. The writer has also taken some personal interest in the publication in reading the proof-sheets and making certain suggestions.

In two points the new book differs materially from that of Benedikt. In the first place, practically no attempt is made to educate the reader in organic chemistry up to the point of his being able to comprehend the intricate chemistry of the dyestuffs. It should therefore be clearly understood that anyone seeking to derive any benefit from the book must of necessity possess a good knowledge of organic chemistry. In the second place, the *application* of the dyestuffs is very superficially dealt with, and for information on this point other books or manuals must be consulted. While keeping the subject-matter within the compass of a text-book, it has thus been possible to introduce considerably more matter directly concerned with the history, chemistry and manufacture of the colouring matters than was the case with Benedikt's textbook.

The work is not intended as a compendium. It deals concisely with raw products, intermediate products, and finished dyestuffs in sufficient detail to give the reader a complete survey of the subject. In most cases the chapters contain short historical accounts of great interest, and numerous reliable examples taken from practice are introduced. It is obviously impossible to detail in a volume of this size the thousand and odd colouring matters on the market, but the examples given are typical of the groups, and represent the most important individuals, or those which are best suited for illustration purposes.

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September, 1914.

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ABBREVIATIONS.

(*The date given is the first year of publication.*)

Ann. Liebig's Annalen der Chemie. Leipzig. 1832. Four volumes per annum.

Ber. Berichte der deutschen chemischen Gesellschaft. Berlin. 1868.

Bull. Soc. chim. Bulletin de la Société chimique de France. Masson, Paris. Two volumes per annum. 1864. 4th series, 1907.

Bull. Soc. ind. Mulhouse. Bulletin de la Société industrielle de Mulhouse. Bader, Mulhouse. 1831.

B.F. Brevet français. (French patent.)

Chem.-Ztg. Chemiker-Zeitung. Cöthen. 1887.

Chem. Ind. Chemische Industrie. Berlin.

Compt. Rend. Comptes-rendus de l'Académie des Sciences. Gauthier-Villars, Paris. 1835.

D.R.P. Deutsches Reichs Patent. (German Patent.)

Dingler. Dingler's polytechnisches Journal. Augsburg.

E.P. English Patent.

F. Friedländer, " Fortschritte der Teerfarbenfabrikation."

Färb.-Ztg. Färber-Zeitung. Springer, Berlin. 1890.

J.C.S. Transactions of the Chemical Society. London. 1848. Two volumes per annum.

Journ. f. prakt. Chem. Journal für praktische Chemie. 1834.

J. Soc. Chem. Ind. Journal of the Society of Chemical Industry. London. 1882.

Journ. Soc. Dyers and Col. Journal of the Society of Dyers and Colourists. Bradford. 1885.

Monatsh. f. Chem. Monatshefte für Chemie. Vienna. 1880.

Mon. sci. Montieur scientifique. Dr. Quesneville, Paris. 1857.

Rec. trav. ch. P.-B. Recueil des travaux chimiques des Pays-Bas.

Zeitsch. angew. Chem. Zeitschrift für angewandte Chemie. Leipzig. 1888.

Zeitsch. f. Farben- und Textilchemie. Zeitschrift für Farben- und Textil-Chemie. Dr. Buntrock. Vieweg, Braunschweig. 1892.

LIST OF PRINCIPAL FIRMS.

[A.] *Aktiengesellschaft für Anilinfabrikation*, Berlin. (Berlin Aniline Co.)

[B.A.S.F.] *Badische Anilin- und Soda-Fabrik*, Ludwigshafen a/Rhein. (Badische Co.)

British Alizarine Co., London.

Basler chemische Fabrik, Basle.

Brooke, Simpson and Spiller, Hackney Wick, London, E.*

[By.] *Farbenfabriken vorm. Bayer & Co.*, Elberfeld. (Bayer Co.)

[C.] *Cassella & Co.*, Frankfurt a/Main.

Chemische Fabriken Griesheim Elektron, Griesheim, near Frankfurt.

[C.A.C.] *Clayton Aniline Co.*, Manchester.

[C.I.B.] *Société pour l'industrie chimique* or *Society of Chemical Industry* (*Ges. f. chem. Ind.*), (formerly *Bindschedler & Busch*), Basle.†

Claus & Co., Clayton, Manchester.

Colne Vale Chemical Works, Milnes bridge, Huddersfield.

[D.] *Dahl & Co.*, Barmen.

[D.H.] *L. Durand, Huguenin & Co.*, Basle and Hüningen.

[G.] *J. R. Geigy & Co.*, Basle.

[H.] *Read Holliday & Sons, Ltd.*, Huddersfield.

Carl Jäger, Düsseldorf-Derendorf.

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* This firm has been taken over by Messrs. Claus & Co.

† This company has purchased the Basler chemische Fabrik, and recently the Clayton Aniline Co., Manchester.

[K.] *Kalle & Co.*, Biebrich a/Rhein.

Kinzlberger & Co., Prague.

[L.] *Farbwerke Mühlheim* (formerly *A. Leonhardt & Co.*, Mühlheim, near Frankfurt a/M.).

Leipziger Anilinfabrik (Beyer & Kegel, Lindenau-Leipzig).

Leitch & Co., Milnes bridge, Huddersfield.

[Lev.] *Levinstein, Ltd.*, Blackley, Manchester.

[M.L.B.] *Farbwerke vormals Meister, Lucius und Brüning*, Höchst a/Main. (Höchst Farbwerke.)

H. N. Morris, Ardwick, Manchester.

Niederländische Farben- und Chemikalienfabrik, Delft.

[O.] *K. Oehler*, Anilin- und Anilinfarben-Fabrik, Offenbach a/Main.*

Pick, Lange & Co., Amsterdam.

[P.] *Société anonyme des matières colorantes et produits chimiques de Saint-Denis* (Poirrier and Dalsace), Paris.

Schöllkopf Aniline & Chemical Co., Buffalo, U.S.A.

[S.] *Sandoz & Co.* (formerly *Kern & Sandoz*), Basle.

[S.U.R.] *Société chimique des Usines du Rhône* (formerly *Gilliard, Monnet & Cartier*), Lyon.

[T.M.] *Fabriques de produits chimiques de Thann et Mulhouse*, Mulhouse (Alsace).

[W.] *Weiler-Ter Meer*, Chemische Fabrik, Uerdingen a/Rhein.

Wiescher & Co., Haeren.

Williams Bros., London.

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* Now the property of the Chemische Fabriken Griesheim-Elektron.

THE MANUFACTURE OF ORGANIC DYESTUFFS.

INTRODUCTION.

THE colour industry commenced with the discovery of *Mauveine* in 1856 by William Henry Perkin, then assistant to Hofmann at the Royal College of Chemistry in London. Two years later this dyestuff was manufactured by Perkin senior and junior in their works at Greenford Green, and met with considerable success under the trade names of *Tyrian purple*, *Perkin's violet*, *Mauve* or *Mauveine*. The year 1859 is not less memorable, being the date when Verguin, chemist at the dye-works of Messrs. Renard Brothers and Franc in Lyons, discovered *Aniline red*. The process became the property of the "Fuchsine" Company with a capital of four million francs. Discoveries followed with astonishing rapidity, Magenta (Fuchsine) itself being converted by chemists into *Imperial violet*, *Lyons blue*, *Paris violet*, etc.

The wonderful development of this new industry, almost exclusively in French hands, gave splendid promise; but the complex mechanism of the reactions giving rise to these new products was not at all understood. The percentage composition and exact arrangement of the molecular structures of these dyestuffs were unknown, and the French scientists did not foresee, or pretended not to see, what the industry, as well as pure science, could gain by such determinations. Even if at the beginning, chance and empiricism have played the greater part in the first stages of a discovery, this state of things was destined to become rapidly modified. Owing to the impetus caused by the adoption of the theories of valency and of radicles, and hence of structural formulae, by which the characteristic properties of carbon compounds were diagrammatically represented by simple symbols, organic chemistry passed through a period of rapid development, of which no parallel can be found in the history of other sciences. (See A. Haller, *Report of the Paris Exhibition*, 1900.)

Unfortunately these theories met with great opposition in France. This was all the more difficult to overcome as it was supported by eminent scientists who united in refusing to recognise such novel theories. Whereas Gerhardt, Würtz and others, in France, continued their efforts in a hopeless struggle, which finally ended in a triumph for these theories, in Germany the application of these views by Kekulé, Hofmann, V. Meyer, Graebe and Liebermann, Baeyer, and others, was so productive that these theories were accepted with enthusiasm, and found favourable conditions for their successful application.

These advances of organic chemistry immediately had their effect on the German colour industry, causing its rapid development. It borrowed its methods, views, symbols and language from science. The chemist engaged in the industry thus found a firm scientific basis, an aid and reliable guide with which he did not hesitate to launch out resolutely in the way which led him to his great discoveries.

Thus, this industry, after having undergone a period of expansion in France as well as in England, gradually crossed the frontier and established itself in Germany and Switzerland, where it has developed so rapidly that to-day their supremacy cannot be disputed.

Nothing will illustrate the economic importance of this industry better than the following statement relating to the prosperity of the main German firms :

FIRM.	Number of Chemists.	Number of Employees.	DIVIDENDS PAID PER CENT.					
			1897	1900	1908	1909	1910	1911
	1900	1900						
Badische Anilin- und Sodafabrik, Ludwigshafen	148	8,640	24	24	22	24	24	25
Farbwerke vormals Meister, Lucius, & Brüning, Höchst a/Main	120	3,555	26	26	27	27	27	30
Farbenfabriken Bayer, Elberfeld	145	7,889	18	18	24	24	—	29
Aktiengesellschaft für Anilinfabrikation, Berlin	55	1,800	12½	15	18	18	—	20
Leopold Cassella, Frankfurt	60	1,800	—	—	—	—	—	—
Kalle & Co., Biebrich a/Rhein	—	—	—	—	4	10	10	10

In 1908, of the various smaller colour firms: *Weiler-Ter Meer*, paid 7 per cent.; *Grünau, Landshoff und Meyer*, 10 per cent.; *Chemische Fabrik Griesheim Elektron*, 14 per cent.

On the 1st of January, 1905, an association of the *Badische Anilin- und Sodafabrik*, *Farbenfabriken Bayer*, and *Berlin Aktiengesellschaft* was formed for a period of fifty years. This combine owns the Augusta-Victoria coal-mine, and has large interests in the new Norwegian works for the electro-synthetic manufacture of nitric acid. The firms *Kalle*, *Leopold Cassella*, and *Meister, Lucius und Brüning* have also formed a similar combine.

In this small volume the author proposes to illustrate the numerous and varied reactions by which the chemical industry has succeeded in converting comparatively simple substances extracted from coal-tar, such as benzene, naphthalene, anthracene, phenol, etc., into innumerable dyestuffs, the formulae of which are generally very complex.

Having briefly indicated the processes by which the principal constituents can be isolated from tar, some of the principal methods of converting the raw materials into other compounds, which are conveniently called *intermediate products*, will be examined. It would be difficult to bring all the methods at the disposal of the chemist for attaining his object into such a limited space, and it has therefore been necessary to make a selection. The author has been guided in his choice by the aim of presenting facts to the reader in as connected a chain as possible, and in such a manner that, starting with simple reactions, the complex reactions involved in the production of colouring matters are reached in progressive stages.

Having outlined the methods of preparation and constitutional formulae of the hydrocarbons and phenols, there will be considered in order :

1. *Sulphonation*, which gives mono-, di-, tri- or polysulphonic acids of benzene, naphthalene, phenol, etc.

2. *Alkaline fusion*, which constitutes a general method for the synthesis of the phenols, starting with the sulphonic acids, of which the preparation has just been given. Fusion with alkalies of mono-, di- or polysulphonic acids yields new phenols or naphthols, polyphenols or hydroxynaphthols, and by more careful treatment hydroxy-sulphonic acids.

3. *Nitration*, which yields nitro-compounds with the original hydrocarbons, whereas nitration of sulphonic acids or hydroxy-sulphonic acids gives a number of new intermediate products : nitro- and hydroxy-nitro-compounds, and nitro- and hydroxy-nitro-sulphonic acids.

4. *Reduction* converts all these nitro-compounds into amines, which are more or less complex according to the original nitro-compound.

5. On *alkylation*, amines or phenols yield secondary or tertiary amines, or phenolic esters.

Hence, commencing with some four or five substances of simple composition, an enormous number of intermediate products is obtained by suitable application of these reactions. It will be understood that here again it will be necessary to limit the number of substances mentioned. Being limited to the general rules which apply to these various processes, several typical examples have been chosen to illustrate the manufacture of the more important intermediate products which should be considered in connection with the study of dyestuffs.

The study of the dyestuffs themselves forms the third part of this book. As it is necessary to distinguish between substances which are merely coloured and those which possess tinctorial properties, it has appeared advisable to outline Witt's chromophore theory, and also the different methods of dyeing by which dyestuffs are fixed on textile fibres. In order to simplify the study of the chemistry of colouring matters, they have been divided into fifteen groups which will be examined in order.

This book has not been written with the object of stating the various theories which have been put forward with regard to the constitution of organic dyestuffs, but is intended for the thoughtful reader who wishes to understand the various treatments to which the raw materials are subjected, and the manner in which they are carried out in practice in the manufacture of colouring matters. As the study of these changes is so intimately connected with organic chemistry, of which it constitutes one of the most attractive chapters, it has appeared not only interesting, but absolutely essential to show by what particular series of reactions, analytical and synthetical, chemists have succeeded in determining the structure of the principal colouring matters, such as *Magenta*, *Alizarin*, *Indamine*, *Indigo*, etc.

To facilitate further reading, it has been considered advisable to give some of the original references. The restricted character of this volume does not allow a complete bibliography to be given, and only recent references have been mentioned, as it is always easy to obtain the earlier references from more detailed treatises.

A. WAHL.

NANCY,
15*th May,* 1911.

FIRST PART.

RAW MATERIALS.

CHAPTER I.

COAL TAR.

In the manufacture of organic dyestuffs, a considerable number of products obtained from coal tar are used as raw materials, and it is for this reason that these dyestuffs are sometimes given the name "Coal-tar Colours."

The tar is obtained by the dry distillation of coal, which yields three kinds of products: gases, liquids (ammoniacal liquor and tar), and a solid residue of coke. This process is carried out in different apparatus, according to whether the distillation is carried out with a view to manufacturing illuminating gas, or coke for metallurgical purposes. In gas-works, the carbonisation is carried out in retorts. Closed brick chambers, arranged in parallel in series of 12, 18 or 24, are used as coke-ovens. In gas-works, retorts are at present being replaced by chambers similar to coke-ovens. The coke-ovens are usually erected in the immediate neighbourhood of the mine.

In the original apparatus the gases and condensable products which escaped from these ovens were not collected, but were sent into pipes placed in the walls of the chambers, where their combustion gave the heat necessary to maintain the distillation. In 1866, a French engineer, Knab, erected coke-ovens at Commentry in which the condensable products could be recovered, only the gases being burnt. Since that time these processes have been perfected, and the use of coke-ovens suitable for the recovery of the bye-products is now general. Although they were only adopted in Germany in 1881, the amount of tar which they have produced has increased rapidly. The yield of tar from coke-ovens in Germany alone was :

In 1897,	52	thousand	tons.
,, 1898,	78	,,	,,
,, 1900,	93	,,	,,
,, 1902,	190	,,	,,
,, 1904,	273	,,	,,

In 1908, 800 thousand tons of tar, worth about a million sterling, were produced : 585 thousand tons from coke-ovens, 204 thousand tons from gas-works, 3,050 tons from water-gas works, and 8,000 tons from oil-gas works.

The yield of tar depends on the nature of the coal, the temperature, and the time of carbonisation ; average gas-coal yields 4·7 to 6·7 per cent., and coal for coke-manufacture only 1·3 to 4·0 per cent. of tar, as it is not so rich in volatile constituents.

Composition of Tar. Coal-tar is a thick black liquid of density varying from 1·1 to 1·3. It is a mixture of a large number of substances, containing aromatic hydrocarbons from the simplest, such as benzene, to the more complex, such as retene, picene, chrysene, etc. It contains nitrogen, oxygen and sulphur compounds, such as the pyridine bases, phenols, etc., and also particles of carbon which give it the black colour.

Treatment of Tar. The separation of these various products is effected by a series of operations, partly physical, partly chemical, of which a full description cannot be given in this book, but will be found in Leroide's book on the gaseous fuels and their bye-products (published by Doin et fils, Paris).* Only a résumé of the process will be given.

After the tar has been freed from ammoniacal liquor, it is fractionally distilled from direct fired iron boilers, the products being separated into either four or five fractions, according to the works. In this separation, the temperature and sometimes also the density of the distillate are used as a guide. The various fractions collected have the following names :

I. Fraction 105-110°, *Crude Naphtha.*
II. ,, 110-210°, *Light oil.*
III. ,, 210-240°, *Carbolic oil.*
IV. ,, 240-270°, *Heavy or Creosote oil.*
V. ,, Above 270°, *Anthracene oil.*

or only four fractions may be collected :

I. Up to 150°, *Light oil* (density less than 1).
II. From 150 to 210°, *Medium oil* (density greater than 1).
III. From 210° to 280°, *Heavy oil.*
IV. Above 300°, *Anthracene oil.*

The residue remaining after distillation is a thick mass called pitch. The naphtha is separated from the water by decantation ; the liquid is first shaken with dilute sulphuric acid to remove basic substances, and then with concentrated sulphuric acid to resinify the unsaturated hydrocarbons and sulphur compounds (thiophen). Finally, after washing twice with caustic soda and with water, the product is again fractionally

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* See also G. Lunge, *Coal Tar and Ammonia.*

distilled, giving benzols and solvent naphtha. On redistilling these give more or less pure hydrocarbons: benzene, toluene, xylenes, etc., which have still to be further purified.

The light oils are distilled and separated into two portions: the fraction up to 170° is added to the naphtha and treated as described later, the other fraction is added to the carbolic oil. The latter contains phenols and naphthalene, which are separated by shaking with caustic soda, when the phenols dissolve, whereas the naphthalene and other hydrocarbons are insoluble. On acidifying the alkaline solution, crude carbolic acid separates and is fractionally distilled, giving phenol and cresols. The insoluble hydrocarbons are distilled to give naphthalene. The heavy oils are used for lubricating, impregnating wood, etc.; they are also used in the manufacture of illuminating gas, being decomposed by heat; the gaseous products formed are collected. On leaving to crystallise, anthracene oil gives crude anthracene, and on redistilling the oil gives a further yield of anthracene. (For details see Rispler, *Chem.-Ztg.*, 1910, **34**, 261, 279, 286, 349, 407).

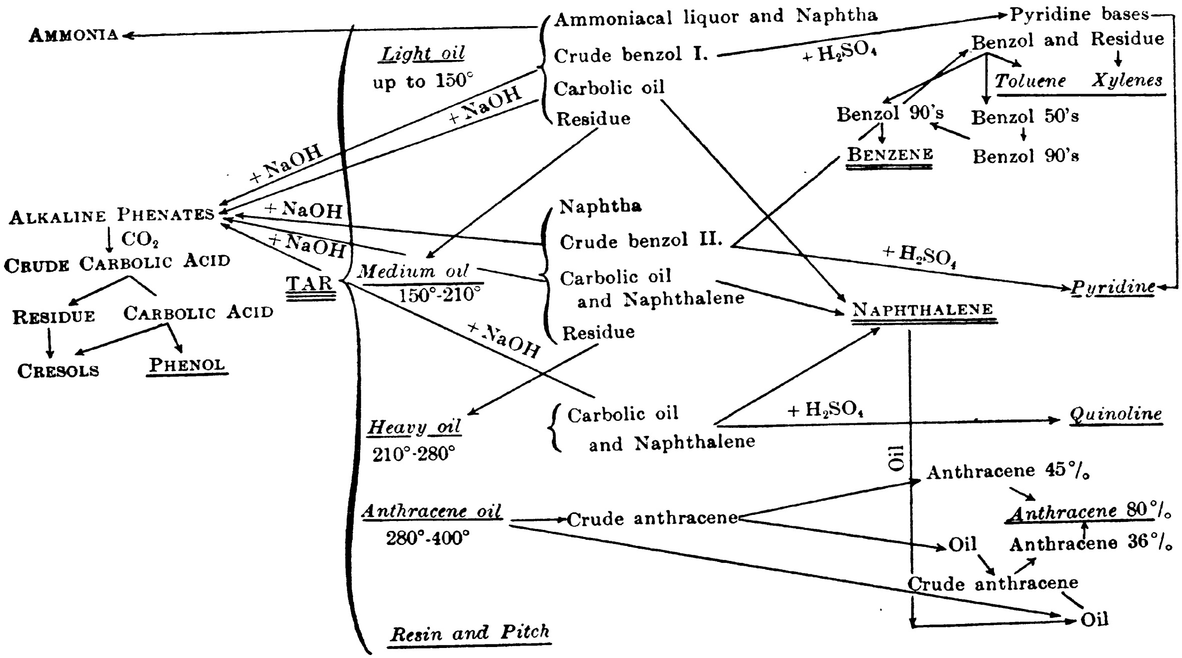
According to Lunge, the distillation of one ton of coal-tar yields on an average:

Ammoniacal liquor - -	3·0 gallons.
Naphtha - - - -	6·3 ,,
Light oils - - - -	13·4 to 15·0 gallons.
Heavy oils - - -	68 gallons.
Pitch - - - -	0·54 ton.

The relative amounts of the various fractions obtained naturally vary with the nature of the coal, the temperature of carbonisation and the apparatus in which it is effected. If the temperature is low, the yield of tar is greater, and it is then richer in light hydrocarbons (benzene, toluene, etc.). If the temperature is higher,

TREATMENT OF COAL TAR.

(*From "Farbenchemisches Praktikum" by Möhlau and Bucherer. Leipzig*, 1908.)



the volatile products are submitted to the decomposing effect of the heated parts of the carbonising apparatus, and the amount of light hydrocarbons diminishes, whilst that of the more condensed products (naphthalene, anthracene, etc.) is increased. This occurs in coke-ovens.

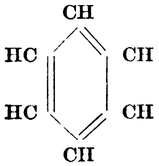
The treatment of the tar is outlined in the diagram on the previous page.

CHAPTER II.

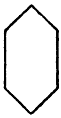
HYDROCARBONS.

Benzene, C_6H_6, is a colourless liquid, of high refractive power, possessing a characteristic smell. It boils at 80·5° and solidifies at 4° C. Its empirical formula calculated from the percentage composition is CH, but vapour density determinations show that it has the molecular formula C_6H_6.

It has been shown that all the six hydrogen atoms are equivalent (Franchimont, Nölting), and should therefore be symmetrically arranged. A number of structural formulae have been suggested which would account for the chemical properties of benzene, the one generally adopted being that of Kekulé. In this, benzene is represented by a regular hexagon, each corner being occupied by a CH group; the carbon atom being tetravalent, these atoms are linked alternately by single and double bonds:



or

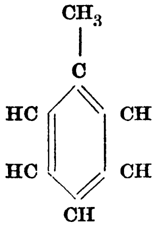


The bonds and the carbon and hydrogen atoms are often omitted, and benzene represented by a hexagon. Amongst the experimental proofs supporting this formula may be mentioned the well-known synthesis of benzene carried out by Berthelot by heating acetylene to a dull red heat, when it polymerises, giving, amongst other hydrocarbons, benzene :

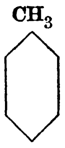
$$3C_2H_2 = C_6H_6.$$

The acetylene having been obtained by direct combination of hydrogen and carbon in the electric arc, Berthelot's synthesis is a complete synthesis from the elements.

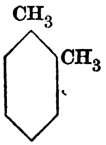
Toluene, C_7H_8, is a colourless liquid, of B.P. 111°, and only solidifies at a much lower temperature than in the case of benzene. Its density at 15° is 0·872. Its properties are analogous to those of benzene. It has the formula C_7H_8, and its constitution is established by the fact that careful oxidation gives benzoic acid, $C_6H_5.COOH$, the calcium salt of which decomposes on heating with soda-lime to give benzene. Toluene is therefore methyl benzene, its formula being $C_6H_5 . CH_3$:



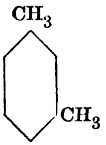
or



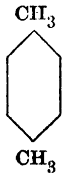
Xylene, C_8H_{10}, is present in the *light oils* in the fractions boiling at about 140°. The xylene so obtained is not one substance, but a mixture of the three isomers possible according to theory ;



ortho-xylene.



meta-xylene.

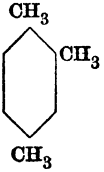


para-xylene.

These substances cannot be separated by distillation, as their boiling points do not differ sufficiently; the *para*-compound is easily isolated by treating the mixture with concentrated sulphuric acid, when the *ortho*- and *meta*-xylenes are attacked, whilst the *para*-xylene remains unchanged. All the three compounds are liquids, the crude xylene extracted from tar being a mixture of the three isomers in the following proportions:

ortho-xylene	(B.P. 142-143°)	10-25	per cent.
meta-xylene	(B.P. 137-138°)	60	,,
para-xylene	(B.P. 136-137°)	10-25	,,

Cumene, C_9H_{12}, extracted from tar, is also a mixture, in which the most important isomer is ψ-(*pseudo*-)cumene:



Commercial products:

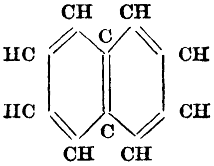
The properties of the hydrocarbons which have just been outlined are those of the pure substances. Commercial samples, called *benzols*, generally consist of a mixture of several hydrocarbons and have different names according to the proportions in the mixture. In addition to commercially pure benzene, there are 90's (known as "nineties benzol"), 30's, 10's, and 0's benzols, that is, 90, 30, 10 or 0 per cent. of the product distils below 100° C. (with the thermometer in the liquid). Such samples of benzene contain toluene and xylenes which can be separated by careful distillation. There are other impurities which it is impossible to remove by distillation, such as carbon disulphide and sulphur compounds (thiophen). It is then necessary to resort to chemical processes, which are very numerous. Carbon disulphide can be eliminated by saturating the benzene with moist ammonia, which requires about 0·25 per cent. of the gas (Schwalbe, *Zeitschr. f. Farben- und Textil.-Ind.*, 1904, **3**, 462). Haller and Michel (*Bull. Soc. chim.*, 1896, **15**, 390) have outlined a process for removing sulphur compounds which consists of treating the benzene with aluminium chloride, this being the subject of a patent of the *Société des matières colorantes de Saint-Denis* (*D.R.P.*, 79,505). Agitation of the hydrocarbon with sulphuric acid also removes thiophen, but at the same time a small quantity of the hydrocarbon is sulphonated and becomes soluble in water. This may be avoided by first passing in a current of nitrous fumes to resinify the thiophen, which is then removed by rapid shaking with concentrated sulphuric acid (*Mon. sci.*, 1905, 499).

The following table gives the composition of some commercial products :

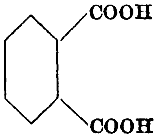
	Benzene.	Toluene.	Xylenes.	Cumenes.	Naphthalene.
90's Benzol - -	84	13	3	0	0
50's Benzol - -	43	46	11	0	0
0's Benzol - -	15	75	10	0	0
Solvent naphtha I.	0	5	70	25	0
,, ,, II.	0	0	35	60	5
Heavy naphtha -	0	0	5	80	15

Test for thiophen in benzene. Several drops of concentrated sulphuric acid are taken in a test-tube, a small crystal of isatin added, and a small amount of the benzene added. If thiophen is present, an intense blue colour will be obtained on shaking the sulphuric acid.

Naphthalene, $C_{10}H_8$, is the hydrocarbon present to the largest extent in coal-tar ; whereas 100 kgm. of tar only give on an average 2 kgm. of benzene, ½ kgm. of toluene, and ½ kgm. of phenol, some 5 to 6 kgm. of naphthalene are obtained. It is a white solid substance, with a characteristic odour. It melts at 80°, and boils at 218°. Naphthalene sublimes very readily, and this property is used in its purification. The constitution of naphthalene is represented by two condensed benzene nuclei:

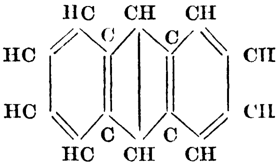


The formula is established by the fact that on oxidation naphthalene yields the dibasic acid, phthalic acid, which has the following constitution:



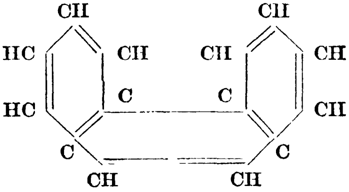
On oxidising nitronaphthalene, a mixture of phthalic and nitrophthalic acids is obtained: the naphthalene molecule is therefore symmetrical, and formed by the fusion of two benzene rings.

Anthracene, $C_{14}H_{10}$, was discovered in coal-tar by Dumas and Laurent in 1832. It is a white crystalline solid, of M.P. 216·5° and B.P. 351°. The anthracene deposited from the anthracene oil is very impure, and does not contain more than 30 to 32 per cent. of anthracene. It is purified by treating with solvents in which it is only slightly soluble, such as pyridine (*D.R.P.* 42,053, April 15th, 1887), liquid sulphur dioxide (Bayer Co., *D.R.P.* 68,484; *F.P.* 220,621), acetone (Bayer Co., *D.R.P.* 78,861), and other substances (*D.R.P.* 111,359, 113,291, 122,852, 164,508, 178,764 (1906)). Finally it is sublimed (Rispler, *Chem. Ztg.*, 1910, **34**, 261 *et seq.*). Anthracene has the constitution :



If solutions of anthracene are exposed to the action of light, a less soluble polymeride of anthracene, paraanthracene, of M.P. 244°, is deposited. Anthracene is found in tar together with methylanthracenes, of which there are two isomerides, α and β.

Phenanthrene, $C_{14}H_{10}$, is an isomeride of anthracene having the formula :

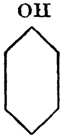


It has M.P. 99°, and B.P. 340°.

CHAPTER III.

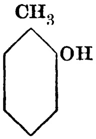
THE PHENOLS.

Phenol or *Carbolic acid*, C_6H_5OH. Pure phenol forms colourless prismatic needles of characteristic odour. It has M.P. 42° and B.P. 182°. In contact with air it slowly becomes pink. Phenol dissolves in alkalies, from which solution it is reprecipitated by acids; it forms true salts with alkalies in which an atom of hydrogen in the phenol is replaced by an atom of a monovalent metal. Phenol corresponds to the formula C_6H_5OH, its salts or phenates to $C_6H_5(OX)$, as will be detailed later (see p. 35); phenol is easily synthesised from benzene by way of benzene sulphonic acid, and from this it is obvious that phenol contains the benzene nucleus. It is hydroxybenzene:

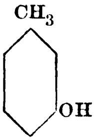


Phenol gives a violet coloration with ferric chloride.

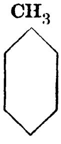
Cresols, $CH_3 . C_6H_4OH$. The cresols, which are present together with phenol in crude carbolic acid, are hydroxytoluenes; there are three isomers:



ortho-cresol.
M.P. 30°, B.P. 188·5°.



meta-cresol.
M.P. 4°, B.P. 200°.



para-cresol.
M.P. 36°, B.P. 199°.

They are present in the following proportions :

ortho	35 per cent.
meta	40 ,,
para	25 ,,

The cresols are used as raw material in the manufacture of certain dyestuffs and as antiseptics. The mixed cresols are on the market as a colourless liquid, boiling at 185° to 285°, under such names as "tricresol," "enterol," etc. The slight solubility of cresol in water (2 per cent.) is a disadvantage for its use as an antiseptic, although its bactericidal power is much greater than that of the more soluble mixture of phenol and soap ("sapocarbol").

SECOND PART.

INTERMEDIATE PRODUCTS.

WITH comparatively few exceptions the raw materials described in the preceding chapter cannot be directly converted into dyestuffs. It is first of all necessary to convert them into intermediate products which differ in properties from the raw materials due to the introduction of new groups. These intermediate substances are obtained by a number of very simple general reactions, of which the main ones can be referred to five types which will be described in the following order :

1. Sulphonation.
2. Alkaline fusion.
3. Nitration.
4. Reduction of nitro-compounds.
5. Alkylation.

Only the general principles relating to these different operations will be indicated, with an outline of the manner in which they are used in practice.

CHAPTER IV.

SULPHONATION.

SINCE 1834 it has been known that, on heating certain aromatic hydrocarbons with concentrated sulphuric acid, they become soluble in water and alkalies. This reaction has since been made of a general character, and may be applied to a very large number of organic substances, which are converted in this way into *sulphonic acids.* The readiness with which substances sulphonate varies considerably. Some, such as benzene and toluene, are converted into sulphonic acids even by ordinary cold acid; others require the use of monohydrated (100 per cent. H_2SO_4), or fuming acid containing more or less sulphuric anhydride. It is sometimes even necessary to work at a high temperature with an acid which contains a large amount of anhydride. Under these conditions it is often difficult to limit the action to the formation of monobasic acids, and there result disulphonic, trisulphonic or polysulphonic acids.

Constitution of the sulphonic acids. The mechanism of sulphonation is very simple. In the case of benzene the reaction is:

$$C_6H_6 + H_2SO_4 = C_6H_6SO_3 + H_2O.$$

The benzene sulphonic acid thus obtained gives well-defined salts with bases; the sodium salt has the composition $C_6H_5SO_3Na$, one atom of hydrogen in the original acid being replaced by an atom of sodium. As there is only one hydrogen atom which possesses this property, the formula $C_6H_6SO_3$ is written as $C_6H_5.SO_3H$.

The complex SO_3H has been given the name "sulphonic acid group," and *sulphonation may be regarded as an operation by which an atom of hydrogen in an organic compound is replaced by the sulphonic acid group.* If this substitution is repeated two, three, or more times, di-, tri- or polysulphonic acids are obtained. According to the relative positions which these groups take up in the molecule, a greater or less number of isomers can exist. Amongst the factors which exert the greatest influence on the orientation of the sulphonic group or groups may be mentioned the temperature, concentration of the sulphuric acid, the duration of the reaction, and the presence of substituted groups before sulphonation. The addition of small quantities of mineral inorganic substances, such as mercury salts and boric acid, exerts a peculiar catalytic influence on the rate of sulphonation, causing a different orientation of the sulphonic acid group (Iljinsky, *Ber.*, 1903, **36**, 4194; Schmidt, *Ber.*, 1904, **37**, 66; Liebermann and Pleus, *ibid.*, 646; Farbenfabriken Bayer, *D.R.P.* 149,801; Iljinsky, *E.P.* 25,738 (1903)).

The sulphonic acids are also obtained by the action of chlorsulphonic acid on organic compounds, thus:

$$R\text{-}H + ClSO_3H = R . SO_3H + HCl,$$

where R is an organic radicle. This method is not of frequent application.

Practical Details of Sulphonation.

If sulphonation is to be carried out with fuming sulphuric acid of a certain concentration, it is first necessary to prepare the acid by mixing ordinary sulphuric acid with the necessary amount of fuming acid, which is at present sold in commerce with 75-90 per cent. SO_3 content. Formulae exist from which it is easy to calculate the proportions of the mixture. For example, if a is the percentage of anhydride to be contained in the required acid, b the strength of the fuming acid available, and c the concentration of the ordinary acid, then the amount x of this acid which it will be necessary to add to 100 parts of fuming acid is given by the formula :

$$x = \frac{22(b-a)}{100 + 0{\cdot}22(a-c)}.$$

Recently Prats (*Chem. Ztg.*, 1910, **34**, 264) has given a modified formula ; thus, to prepare an amount a of fuming acid, containing h per cent. of SO_3, from an amount x of a fuming acid containing k per cent. SO_3 and an amount y of an ordinary acid containing s per cent. H_2SO_4 :

$$x = a\frac{9h + 40(100-s)}{9k + 40(100-s)}.$$

$$y = a - x.$$

The substance to be sulphonated is often dissolved in the ordinary sulphuric acid and the calculated amount of fuming acid added.

Apparatus. The sulphonation is carried out in cast-iron vessels ; in case ordinary sulphuric acid is used without addition of fuming acid, it is preferable to have a lead-lined apparatus. The cover is provided with a certain number of holes (Fig. 1).

A is for introducing the fuming acid and the substance to be sulphonated.

B is for the axis of the stirrer.

C is a cast-iron pipe passing to the bottom of the vessel to which a pipe *F* can be joined for emptying the vessel.

D is the thermometer.

After having introduced the necessary amount of sulphuric acid of the desired concentration, the substance to be sulphonated is added in small portions through the opening *A*. The readings of the thermometer enable the progress of the operation to be followed, and, according to whether the process is to be effected at a low or high temperature, cold water or steam is circulated through the outer jacket which surrounds the vessel.

For higher temperatures the vessel is placed in an oil-bath.

The progress of the sulphonation is followed by taking a small sample from time to time, and examining its solubility in water or in alkalies, according to the substance being prepared. When the reaction is finished, the opening *A* is closed by a clamp plate, the stirrer is stopped, the tube *F* connected to *C*, and compressed air passed into the apparatus.

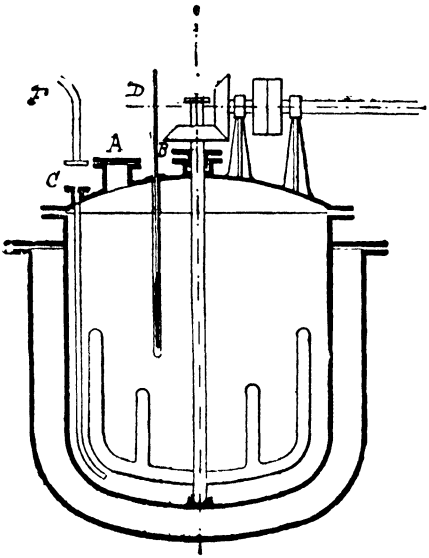


FIG. 1.—Apparatus for Sulphonation Process.

For this purpose the axis of the stirrer is generally made hollow, and it is only necessary to connect it with the compressed air supply. The sulphonated product flows out by pipe *F*, and is collected in a large lead-lined wooden vat containing cold water or ice. The sulphonic acid may be insoluble or soluble in water. In the first case, the precipitated sulphonic acid is removed by using a filter-press, after having diluted sufficiently with water. In the second case, two methods are available for isolating the sulphonic acid from its solution. Sometimes the addition of common salt causes the precipitation of the sodium salt of the sulphonic acid, which is then readily filtered off. If this method is not successful, the sulphuric acid is neutralised by slaked lime, the calcium sulphate formed being removed by using a filter-press, when the calcium salt of the sulphonic acid passes through into the filtrate. This solution is then treated with sodium carbonate, giving a solution of the sodium salt of the sulphonic acid, which is often used as such for further operations.

Details of the plant used for the manufacture of sulphonic acids are given in Fig. 2.

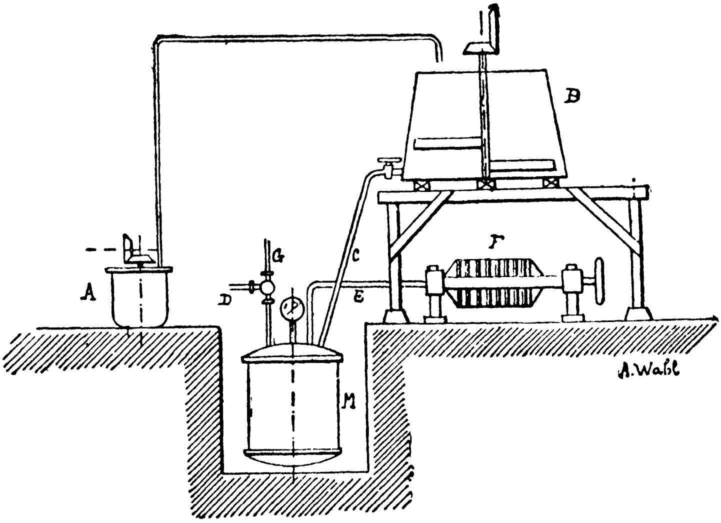


FIG. 2.—Manufacture of Sulphonic acids.

A is the vessel in which the sulphonation is effected. When the process is finished, the product is conveyed into the vat *B*, which is lined with lead and contains sufficient water to finally dilute the solution to 5 per cent. acid content. If the acid is soluble, common salt or lime is added to *B*, and then the contents of the vat are run into an underground reservoir *M*, which is a compressor. This apparatus is provided with a number of fittings in its upper portion as indicated in the figure. *C* communicates with the vat *B*. *D* is used to connect the compression apparatus with the atmosphere, *E* is a pipe passing to the bottom for leading the product into the filter press *F*, *G* is the entrance for compressed air.

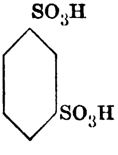
When the content of the vat *B* has been discharged into the vessel *M*, the taps *C* and *D* are closed and *E* and *G* opened. The liquid with the precipitate which it retains in suspension is forced into the filter press, which retains the precipitate and allows the liquid to pass.

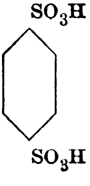
Principal Sulphonic Acids of the Hydrocarbons.

Derivatives of Benzene.

Benzene monosulphonic acid, $C_6H_5 . SO_3H$, is obtained by boiling equal volumes of benzene and concentrated sulphuric acid for twenty-four hours, under a reflux condenser ; or by heating one part of benzene and five parts of concentrated sulphuric acid for two days in an autoclave at 100°. The product is poured into water, saturated with lime, and the filtrate from the calcium sulphate concentrated.

Benzene disulphonic acid, $C_6H_4(SO_3H)_2$. If benzene or its monosulphonic acid is treated with an excess of fuming sulphuric acid, a mixture of the two isomeric disulphonic acids (*meta* and *para*) is formed :





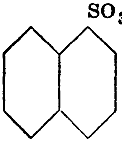
Larger quantities of the *meta*-acid are formed at lower temperatures and when the reaction is of short duration. The following is an example of a commercial preparation (*Mon. sci.*, 1878, 1169). Fifty parts of benzene are stirred with 200 parts of concentrated sulphuric acid at a temperature of 40°, rising gradually to 100°; when all the benzene has disappeared, the liquid is heated for one or two hours at 275°, allowed to cool, and then poured into 1,000 parts of cold water and neutralised by lime. The liquid which flows out of the filter-press is decomposed by potassium carbonate and the solution filtered from the calcium carbonate and evaporated until its SP. GR. is 1·275. On cooling, the potassium salt of the *m*-disulphonic acid crystallises out, whilst that of the isomer remains in solution.

Derivatives of Toluene.

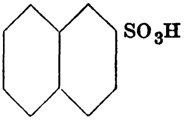
On treating toluene with concentrated sulphuric acid or fuming acid which does not contain much anhydride, a mixture of the three isomers (*ortho*, *meta*, and *para*) is obtained. Of these acids, the *ortho*- and *para*- are the most important; the first is used in the preparation of saccharin, and the second gives *p*-cresol on fusion with alkali. There are a number of processes (*D.R.P.*, 35,211, 57,391) available for isolating these acids from their mixture.

Derivatives of Naphthalene.

On sulphonation naphthalene gives two isomeric monosulphonic acids, termed naphthalene α- and β-monosulphonic acids, of the following constitutions:

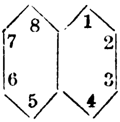


α-acid.

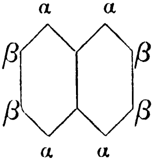


β-acid.

In the case of the di- and tri-sulphonic acids, the isomers become more numerous, and it is necessary to have a definite nomenclature This is done by distinguishing the carbon atoms of the naphthalene nucleus by numbers or Greek letters, commencing at the top of the right-hand ring :



or



Naphthalene Monosulphonic Acids.*

When naphthalene is treated with concentrated sulphuric acid, a mixture of the α- and β-monosulphonic acids is obtained in varying proportion according to the temperature. Thus at 100° the mixture contains 80 per cent. of the α-acid and 20 per cent. of the β-acid, whilst at 170° it contains 75 per cent. of the β-acid and only 25 per cent. of the α-acid. This shows that the α-acid is not stable at high temperatures, and to obtain it the preparation must be carried out at a low temperature. According to the recent researches of Euwes (*Rec. trav. ch. P.B.*, 1908, **18**, 298) the pure α-acid is obtained by treating naphthalene with the equivalent amount of sulphuric acid at a temperature of 80°. On heating the naphthalene with double its weight of concentrated sulphuric acid at a temperature lower than 80°, only the α-acid is produced in appreciable quantities ; by using the same proportions of the reacting substances, but heating for six to eight hours at 180°, the β-acid is formed almost exclusively.

The acids may be separated by making use of the different solubilities of their calcium, barium, lead,

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*See G. Schultz, *Die Chemie des Steinkohlenteers,* Braunschweig, 1900, vol. i., 186.

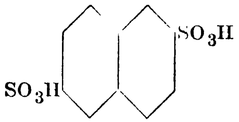
etc., salts ; the salts of the β-acid are less soluble than those of the α-acid.

α-Monosulphonic Acid. This acid is prepared commercially by heating 150 to 175 kilograms of concentrated sulphuric acid to about 40°-50° in a cast-iron vessel (Fig. 1), and then adding 100 kilograms of finely powdered naphthalene in small portions. The sulphonation commences immediately, and, when almost all the naphthalene has disappeared, the liquid is poured into water, neutralised with lime and filtered. The filtrate is decomposed by sodium carbonate, filtered, and the liquor concentrated until the sodium salts crystallise out, when they are separated by fractional crystallisation.

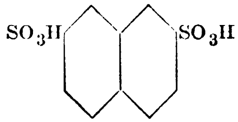
β-Monosulphonic Acid. 100 kilograms of naphthalene are added to 100 kilograms of warm concentrated sulphuric acid ; the mixture is heated at 160° for three hours, then raised to 170°, and finally heated for one hour at 180°. The product is then allowed to cool and is poured into salt solution, when the sodium salt of the naphthalene β-sulphonic acid crystallises out, whilst the small quantity of the α-isomer and of the disulphonic acid remain in solution.

Naphthalene Disulphonic Acids.

The further sulphonation of the two naphthalene monosulphonic acids yields different mixtures of the isomeric disulphonic acids according to the experimental conditions. *The second sulphonic acid group never enters the ring to which the first group is attached.* Hence naphthalene α-sulphonic acid gives a mixture of the 1 : 5- and 1 : 6-disulphonic acids, and the β-acid a mixture of the 2 : 6- and 2 : 7-acids. These two acids are very important and may be obtained direct from naphthalene. Thus, on heating one part of naphthalene with five parts of sulphuric acid for four hours at 160° no monosulphonic acid is obtained, but there is produced a mixture of the 2 : 6- and 2 : 7-disulphonic acids :



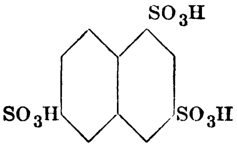
and



The first of these acids is often called naphthalene β-disulphonic acid, the second being known under the incorrect name of naphthalene α-disulphonic acid. If the sulphonation is carried out at a higher temperature for twenty-four hours, the 2 : 7-acid disappears and the 2 : 6-acid is the main product; the same result can be obtained by sulphonating naphthalene β-monosulphonic acid. To separate the two disulphonic acids, they are converted into their calcium salts; that of the 2 : 7-acid is the most soluble. Use may also be made of the fact that the calcium salt of the 2 : 6-acid is insoluble in a saturated salt solution, whereas the calcium salt of the 2 : 7-acid dissolves in this solution on heating. (Ebert and Mertz, *Ber.*, 1876, **9**, 609; Baum, *D.R.P.* 61,730; Grünau, Landshoff and Meyer, *D.R.P.* 48,053.)

Naphthalene Trisulphonic Acids.

Of these acids, one of the most important is the 1 : 3 : 6 acid:



This acid was discovered by Gürcker and Rudolph (*D.R.P.* 38,281), who obtained it by the following method: one part of naphthalene is added to eight parts of fuming sulphuric acid containing 24 per cent. of anhydride, and the mixture heated for several hours at 180°. Another method is to add one part of naphthalene to six parts of fuming sulphuric acid containing 40 per cent. of anhydride, taking care to keep the temperature below 80° C., the heating being continued on a water-bath until all the anhydride has disappeared, when the liquid is poured into water, neutralised with lime, and treated as usual.

Sulphonic Acids of the Phenols.

Phenol sulphonic acids. Kekulé (*Ber.*, 1869, **2**, 330) showed that sulphuric acid acts on phenol even in the cold, giving a mixture of the *ortho-* and *para-*sulphonic acids ; the latter acid is formed as the principal product when the reaction is carried out at higher temperatures. The separation of these acids is a matter of considerable difficulty ; according to Obermiller (*Ber.*, 1908, **41**, 696), the most convenient method is the fractional crystallisation of their barium or magnesium salts.

CHAPTER V.

ALKALINE FUSION.

In 1867, Würtz and Dusart in France and Kekulé in Germany discovered simultaneously that, on fusing benzene monosulphonic acid with caustic potash, potassium phenate and sulphite are produced:

$$C_6H_5SO_3K + 2KOH = C_6H_5OK + K_2SO_3 + H_2O.$$

This reaction may be applied to the greater number of the sulphonic acids, which are converted in this manner into phenols. *Alkaline fusion is hence a process by which the sulphonic acid group* SO_3H *may be replaced by the hydroxyl group* OH.

Other methods are available for the synthetic preparation of the hydroxy-hydrocarbons: for example, the amido-derivatives may be converted into diazo-compounds and these decomposed by water, or the amido-compounds may be heated under pressure with water. The conversion of an amine into phenol or naphthol can be effected by treatment with an excess of a solution of sodium bisulphite (sp. gr. 1·32 to 1·38), and subsequently saponifying with aqueous alkali:

$$R\,.\,NH_2 + NaHSO_3 = ROSO_2Na + NH_3$$

$$ROSO_2Na + 2NaOH = R\,.\,ONa + Na_2SO_3 + H_2O.$$

Alkaline fusion of the di-, tri- or poly-sulphonic acids under certain conditions causes the successive replacement of one, two or more sulphonic groups by hydroxyl groups, giving hydroxy-sulphonic acids or polyphenols. Hence this constitutes a very general and important synthetic process. It has recently been extended by Sachs (*Ber.*, 1906, **39**, 3006; *D.R.P.* 173,522 (1904), *B.F.* 359,064 (1905), *D.R.P.* 181,333 (1905)), who, noting the analogy between the formulae of caustic soda and sodamide: Na(OH), Na(NH_2), has fused the sulphonic acids with sodamides. In this manner the sulphonic group is replaced by the amido-group:

$$C_6H_5SO_3Na + NaNH_2 = Na_2SO_3 + C_6H_5NH_2.$$

Alkaline fusion may also be applied to halogenated derivatives.

Practical Details of the Alkaline Fusion Process.

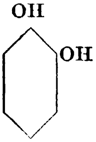
The alkali generally used is caustic soda, the action of which is not always the same as that of caustic potash. The solid alkali is heated in an iron vessel fitted with a stirrer with a small amount of water until the mass is completely liquid, and to this is added the sulphonated derivative. The temperature and length of the reaction vary with the nature of the product. The fusion requires a high temperature which sometimes greatly alters the organic substance. In such cases it is convenient to replace the fused alkali by a more or less concentrated solution, carrying out the operation in a closed vessel capable of standing the pressure (an autoclave); the more dilute the alkaline solution the higher the temperature at which the process may be carried out. Substances may also be added to lower the melting point, for example, a mixture of alkalies (caustic soda and potash, alkalies and alkali alcoholates) may be used. It is to be noted that in the case of the complex polysulphonic acids, the concentration of the alkali exerts an important influence on the nature of the compound formed, as the sulphonic group eliminated by concentrated or fused alkali is not always the same as that which is eliminated by dilute caustic alkali. (*D.R.P.* 68,721).

Whichever method is used, when the reaction is finished, the product is poured into water, acidified with a mineral acid, boiled to free from sulphur dioxide, and allowed to cool. If the phenol is insoluble, it is easily separated ; in case it is soluble, it is separated by steam distillation, or shaking with a suitable solvent, or, when dealing with a phenol sulphonic acid, it is isolated as in the case of a sulphonic acid.

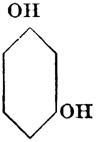
Phenols Derived from Benzene.

Synthesis of Phenol. 100 parts of sodium benzene sulphonate are fused with 75 parts of caustic soda, the temperature being raised to 300°, and then gradually to 330°, this temperature being maintained until the mass has become liquid. The melt is poured into water, acidified, and the phenol separated. The yield is about 80-90 per cent. of the weight of sulphonate used. (G. Schultz, *Die Chemie des Steinkohlenteers*, 1900, vol. i., 139.)

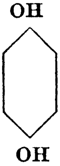
Dihydroxybenzenes, $C_6H_4(OH)_2$.



Pyrocatechol.



Resorcinol.



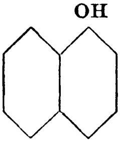
Quinol (hydroquinone).

All three isomers are important ; they are obtained by very different methods. The only one of interest at present is the one for which alkaline fusion is used, *meta*-dihydroxybenzene or resorcinol.

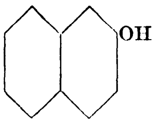
Preparation of Resorcinol. Sixty kilograms of sodium benzene disulphonate are heated at 270° with 150 kilograms of caustic soda in an iron vessel fitted with a stirrer. The resulting mass is dissolved in 500 litres of water, acidified with sulphuric acid, filtered, and the sodium sulphate allowed to crystallise out. The resorcinol is extracted by repeatedly shaking with ether in closed vessels ; after distilling off the ether, the white residue is purified by distillation or sublimation. Resorcinol forms rhombic crystals of M.P. 118°, B.P. 276·5°.

Hydroxy-Derivatives of Naphthalene.

By alkaline fusion the naphthalene monosulphonic acids are converted into phenolic compounds called "naphthols." The naphthols are related to naphthalene in the same way that the phenols are to benzene. Just as there are two naphthalene monosulphonic acids, so two naphthols are known, α and β :



α-naphthol.

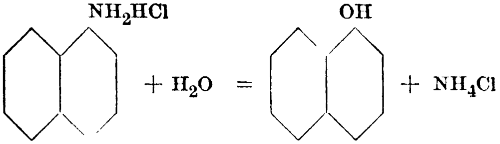


β-naphthol.

Preparation of the Naphthols.

β-Naphthol. Two parts of caustic soda, to which has been added a small amount of water, are fused in an iron vessel provided with a stirrer, and one part of dry, powdered sodium naphthalene β-sulphonate added, the temperature being gradually raised to 300°. When the reaction has finished, the product is dissolved in water and decomposed with acid ; the precipitated β-naphthol is dried and purified by distillation *in vacuo*. In this preparation the fused caustic soda may be replaced by a concentrated solution, the heating being carried out in an autoclave at 270°-290°.

α-*Naphthol* may be prepared by fusing naphthalene α-sulphonic acid with caustic soda, but it is preferable to use the method which involves the substitution of OH for the amido-group in α-naphthylamine. This replacement can be carried out in a very simple manner by heating the sulphate or hydrochloride of α-naphthylamine in an autoclave with water at 200° for three or four hours, when α-naphthol and the corresponding ammonium salt are produced. (Meister, Lucius & Brüning, *D.R.P.* 74,879.)



Another method is to convert α-naphthylamine into the diazo-compound (see p. 98), and from this into α-naphthol by boiling.

Properties of the Naphthols. α-Naphthol is a solid crystalline substance, colourless when pure, but becomes brown on exposure to air. It is insoluble in water, very soluble in alcohol, ether, and other organic solvents; it melts at 96° and boils at 278-280°. β-Naphthol is similar to the α-compound, but has a slightly different smell; it melts at a higher temperature, 122°, and may hence be distinguished from α-naphthol, which melts in boiling water; it boils at 285-286°. Like the phenols, the naphthols are weak acids, being soluble in caustic alkalies, but not in alkaline carbonates.

Naphthol Sulphonic Acids.

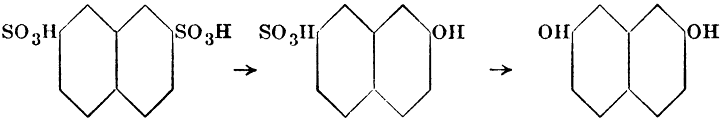
The naphthol monosulphonic acids can be obtained in different ways:

1. By alkaline fusion of the disulphonic acids;
2. By sulphonation of the naphthols.

The naphthol di-, tri- or poly- sulphonic acids can be similarly prepared by alkaline fusion of the naphthalene polysulphonic acids, but it is better to sulphonate the naphthols, as alkaline fusion of the polysulphonic acids often yields dihydroxy-naphthalene sulphonic acids.

1. Formation by Alkaline Fusion.

Naphthalene 2 : 7-disulphonic acid can be converted into β-naphthol monosulphonic acid and then into 2 : 7-dihydroxynaphthalene.



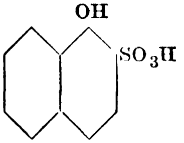
2 : 7-Naphthol sulphonic acid or " F acid " is prepared as follows (*D.R.P.* 42,112 and 45,221) : 100 kilograms of sodium naphthalene disulphonate are made into a paste with 400 kilograms of a 50 per cent. solution of caustic soda, and heated at 200-250° until an acidified sample gives traces of 2 : 7-dihydroxynaphthalene on extraction with ether. The mixture is then poured into 1,000 litres of water, acidified with hydrochloric acid, freed from sulphurous acid by boiling, and allowed to cool, when the sodium salt of F acid crystallises out.

2 : 7-*Dihydroxynaphthalene.* One part of sodium naphthalene-2 : 7-disulphonate is fused with two and a half parts of caustic soda at a temperature of 290-300° in an atmosphere of hydrogen. On acidifying and extracting with ether, evaporation of the ethereal solution gives crystals of the dihydroxynaphthalene (Ebert and Mertz, *Ber.*, 1876, **9**, 609).

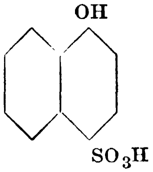
1-*Naphthol*-3 : 6-*disulphonic acid* is obtained by heating the naphthalene trisulphonic acid with caustic soda at 170-180° (*D.R.P.* 38,281).

2. Sulphonation of the Naphthols.

Derivatives of α-naphthol. (Friedländer and Taussig, *Ber.*, 1897, **30**, 1456). α-Naphthol sulphonates readily ; on heating with concentrated sulphuric acid at 50-60° C. it yields a mixture of the 1 : 2- and 1 : 4-monosulphonic acids and a small amount of disulphonic acid. By carrying out the operation at 40° with a slight excess of concentrated sulphuric acid, the sulphonation may be limited to the production of a mixture of the monosulphonic acids :



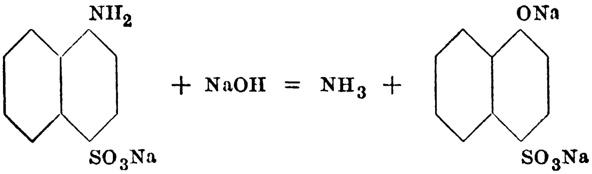
1 : 2-acid.



1 : 4-acid.

The **1** : 4-acid is the most important and is called Nevile and Winther's or N.W. acid. To separate it from the 1 : 2-isomer, the property of diazo-compounds to react with the two acids at different velocities is used, the 1 : 2-acid reacting first. When the reaction is completed the azo-dyestuff formed is precipitated by salt and separated, when the filtrate is a solution of N.W. acid, which is generally employed directly. The yield is 80 to 85 per cent. of the theoretical.

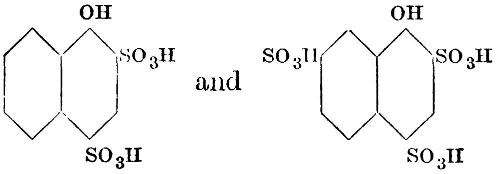
Nevile and Winther's acid may also be obtained by diazotising 1 : 4-naphthylamine sulphonic acid, usually termed *naphthionic acid* (see later, p. 62), and then boiling with water (Nevile and Winther, *Ber.*, 1880, **13**, 1940 ; *D.R.P.* 26,012) ; or heating naphthionic acid with caustic soda (*D.R.P.* 46,307), thus :



Finally, on heating 1 : 4-chlornaphthalene sulphonic acid with caustic soda, N.W. acid is obtained (*D.R.P.* 77,446).

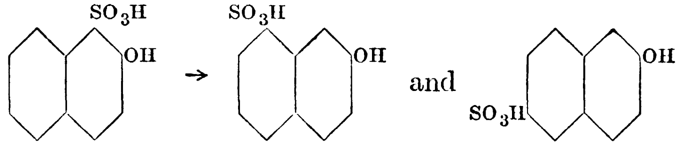
Naphthol di- and tri-sulphonic acids. Of these acids, the most important are those which may be obtained directly by sulphonation of α-naphthol ; these are **1-naphthol-2 : 4**-disulphonic acid and **1**-naphthol-**2 : 4 : 7-**

trisulphonic acid (*D.R.P.* 10,785 and 77,996), which are used for the preparation of nitro-dyestuffs.



Derivatives of β-naphthol. The sulphonated derivatives of β-naphthol are more important than those of α-naphthol.

On treating β-naphthol with concentrated sulphuric acid at the ordinary temperature, there is first formed an unstable 2-naphthol-1-sulphonic acid, which, on continuing the reaction in presence of an excess of sulphuric acid, is converted into a mixture of the two acids, 2-naphthol-8-sulphonic acid, or crocein acid, and 2-naphthol-6-sulphonic acid, or Schäffer acid.



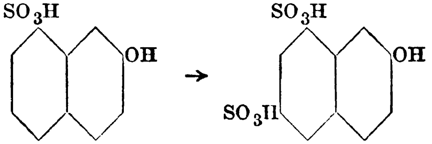
2-Naphthol-1-sulphonic acid. Crocein acid (2 : 8). Schäffer acid (2 : 6).

The relative proportions of 2 : 8 and 2 : 6 acids obtained depends on the temperature, amount of acid, and length of the reaction. On sulphonating β-naphthol with twice its weight of sulphuric acid at a temperature of 40-60°, there is formed almost as much 2 : 8-acid as 2 : 6-acid. Crocein acid (2 : 8) is obtained in larger quantity by carrying out the sulphonation in the cold, and allowing to stand for several days ; on the other hand, Schäffer acid is formed in larger amount at 100°.

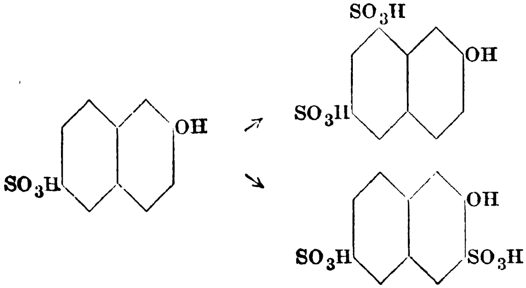
The disulphonic acids are produced on sulphonating with a larger amount of sulphuric acid at a temperature of 110°; with fuming sulphuric acid the trisulphonic acid is formed.

Crocein or *Bayer acid*, when prepared, contains some of its isomer, from which it can be separated in several ways. One part of finely powdered β-naphthol is added to two parts of warm sulphuric acid (168° Tw.), and the mass heated, the temperature being kept between 50° and 60°. When the naphthol has disappeared, the liquid is poured into water, neutralised with lime, and the monosodium salts, $C_{10}H_6(OH)SO_3Na$, isolated as usual. To separate these, they are converted into neutral salts, which are then treated with alcohol. The salt of crocein acid dissolves, whereas that of Schäffer acid is insoluble. There are other methods available for this separation (*D.R.P.* 26,231, 30,077, and 33,857. See also G. Schultz, *Ber.*, 1884, **17**, 461; Claus and Voltz, *Ber.*, 1885, **18**, 3155; Schäffer, *Journ. f. prakt. Chem.*, 1869, **106**, 449).

Disulphonic acids. By further sulphonation the 2 : 8 and 2 : 6 monosulphonic acids are converted into disulphonic acids. Thus, crocein acid gives 2-naphthol-6 : 8-disulphonic acid, generally called "G acid":



On sulphonation Schäffer acid gives a mixture of the 2 : 6 : 8-acid and an isomer 2 : 3 : 6, called "R acid":



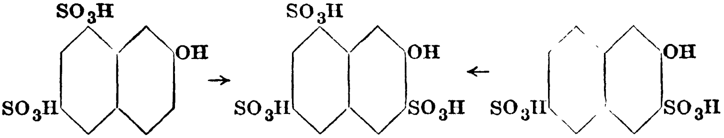
G acid.

R acid.

From this it will be easily understood that on energetic sulphonation β-naphthol will give rise to a mixture of these two acids. They are separated by using difference in the solubility of their sodium salts in alcohol or in a saturated salt solution. The sodium salt of G acid dissolves in alcohol, whilst that of R acid is insoluble (*D.R.P.* 3,229); also the salt of G acid is more soluble in a saturated salt solution than the salt of R acid (*D.R.P.* 33,916 (1886)). Finally, they may be separated by combining with a diazo-compound, this taking place more slowly with G acid, which may hence be isolated (*D.R.P.* 26,491).

The 2-naphthol-3 : 7-disulphonic acid, obtained by sulphonation of 2-naphthol-7-sulphonic acid (*D.R.P.* 44,079; and Weinberg, *Ber.*, 1887, **20**, 2906; see p. 38), is called δ-acid.

Trisulphonic acids. Sulphonation of R and G acids yields the same acid, 2-naphthol-3 : 6 : 8-trisulphonic acid.



This acid is more easily obtained by sulphonating β-naphthol with fuming acid at about 140-150° (*D.R.P.* 22,038).

CHAPTER VI.

NITRATION.

COLD concentrated nitric acid reacts with most aromatic compounds, converting them into nitro-derivatives. This reaction is generally accompanied by the development of a considerable amount of heat, and it is necessary to keep this within certain limits so that the reaction is not too vigorous. Under these conditions, the nitration yields a nitro-derivative and water. Thus, in the case of benzene, the reaction may be expressed by the equation :

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$

Thus, *nitration may be considered as a process by which a hydrogen atom from the ring of an aromatic compound is replaced by the nitro-group* (NO_2).

Nitration may be effected by using the theoretical amount of acid, but the water formed in this reaction exerts a retarding action owing to the resulting dilution of the acid. Sometimes this dilution is reduced by using a large excess of nitric acid, but in this case it becomes difficult to limit the nitration to the formation of a mono-nitro-derivative, and di-, tri- or poly-nitro-derivatives may be produced by the substitution of nitro-groups for 2, 3, or more, hydrogen atoms. The most convenient method for avoiding the diluting effect of the water is to remove it as fast as it is formed. This is easily done by carrying out the nitration in presence of concentrated sulphuric acid ; for this, a mixture of sulphuric acid with the required quantity of concentrated nitric acid, known as "mixed acid," is used.

In certain cases when it is essential to use nitric acid free from water, the mixed acid is prepared by dissolving dry powdered potassium nitrate in sulphuric acid, the acid potassium sulphate formed remaining in solution.

Recently a mixture of fuming nitric acid and acetic anhydride has been used for the nitration. This mixture has somewhat peculiar properties, and the products which it yields are often different from those given by mixed acid or fuming nitric acid (Orton, *J.C.S.*, 1902, **81**, 806; Marquis, *Bull. Soc. chim.*, 1903, **29**, 276; Bouveault and Wahl, *ibid.*, 1904, **31**, 847; Witt., *Ber.*, 1906, **39**, 3901). Possibly this mixture contains the mixed anhydride of acetic and nitric acids recently isolated by Pictet and Khotinsky (*Ber.*, 1907, **40**, 1163).

Practical Details of the Nitration. The compound to be nitrated is placed in a cylindrical cast-iron vessel, fitted with a stirrer, and closed by a cover which has an opening for the gradual introduction of the mixed acid. Another opening is fitted with an iron tube, in which is placed the thermometer. The vessel is put into another larger one, in which water can be circulated to regulate the rise in temperature. A tap is provided at the bottom of the apparatus for drawing off the contents. When the reaction is complete, the product is run into water; nitro-compounds are generally insoluble in water, some being liquids, others crystalline. After standing for a sufficient length of time, the nitro-derivative is separated by decantation if it is liquid, or by filtration if solid, is shaken several times with water to free from acid, and then purified by distillation or crystallisation.

With regard to the acid solution from which the nitro-derivative has been separated, it only contains a small amount of nitric acid, as only the theoretical quantity of acid is used, and moreover the reaction is generally quantitative. On the other hand, the solution contains all the sulphuric acid, and this is recovered by concentrating in lead-lined vessels; this treatment destroys any organic substances present, and eliminates the nitric acid.

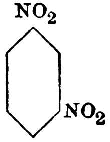
Nitro-Derivatives of the Hydrocarbons.

Derivatives of Benzene.

Nitrobenzene, $C_6H_5NO_2$, was discovered by Mitscherlich in 1834, by treating synthetic benzene with nitric acid; in 1847, Mansfield prepared the same product by nitrating benzene obtained from coal-tar. At present nitrobenzene is a very important commercial product, the apparatus used permitting the nitration of several hundreds of kilograms at the same time. The mixed acid necessary for the nitration of 100 kilograms of benzene, made by mixing 115 kilograms of nitric acid (90° Tw.) and 180 kilograms of sulphuric acid, is poured slowly into the benzene. At the commencement of the reaction, the liquid is cooled by a current of water passing through the apparatus, but towards the end the temperature is allowed to rise to 90-100°. If the process is carried out carefully, the yield is almost theoretical: 100 parts of benzene give 150 parts of nitrobenzene, the theoretical yield being 157. According to the *D.R.P.* 221,787 (1907) of the Fabriques de Saccharine, late Fahlberg, List and Co., of Salbke-a./Elbe, a theoretical yield of nitrobenzene is obtained by adding concentrated sulphuric acid to a mixture of benzene and an alkaline nitrate at a suitable temperature.

Properties. Nitrobenzene is generally a light yellow liquid, but when pure is a colourless, highly refractive liquid of B.P. 206-207°, which on cooling crystallises in long needles of M.P. 7°; its density at 15° C. is 1·208. Nitrobenzene is slightly soluble in water, and is miscible in all proportions with organic solvents. It is volatile in steam, six parts of water being necessary for the separation of one part of nitrobenzene in this manner. Pure nitrobenzene or a mixture with nitrotoluenes is obtained, according to whether the benzene used for the nitration was pure or contained toluene. Nitrobenzene is used mainly for the manufacture of aniline ; it is also used in perfumery under the name of "oil of mirbane."

Dinitrobenzene is obtained when nitrobenzene or benzene itself is nitrated with hot mixed acid in the apparatus used for the preparation of nitrobenzene. Under these conditions a mixture of the three dinitrobenzenes is formed, but the main product is *meta*-dinitrobenzene,



the *ortho*- and *para*-isomers only being formed in small quantities.

m-Dinitrobenzene crystallises in slightly yellow needles, of M.P. 89·8°, and B.P. 297°. It is somewhat soluble in boiling water. The *ortho*-isomer has M.P. 118°, the *para*-compound, M.P. 171°. *m*-Dinitrobenzene is used for the preparation of *m*-nitraniline, *m*-phenylenediamine, and in the manufacture of explosives.

Derivatives of Toluene.

The nitration of toluene yields a mixture of the three isomeric nitro-toluenes which consists mainly of the *ortho*- and *para*-varieties ; *meta*-nitrotoluene is only formed in small amounts. The relative proportions in which the *ortho*- and *para*-compounds are obtained varies with the conditions of the nitration, the concentration of the acid, and the temperature. Whereas with concentrated nitric acid about 66 per cent. of *para*-nitrotoluene is obtained, with the mixed acid from 60 to 66 per cent. of the *ortho*-derivative is formed (Girard and de Laire, Nölting and Forel). According to Friswell (*J. Soc. Chem. Ind.*, 1908, 258), who has studied the influence of varying conditions, the proportion is to be considered fixed in practice as 35 to 40 per cent. of the *para*-derivative and 60 to 65 per cent. of the *ortho*-derivative. When the nitration is carried out with nitric acid and acetic anhydride, the proportion of *o*-nitrotoluene formed is considerably increased, 88 per cent. of the *ortho*- and 12 per cent. of the *para*-compound being obtained (Pictet and Khotinsky, *Ber.*, 1907, **40**, 1163) ; finally, by the action of nitrous fumes on toluene vapour at 300-400°, 11 per cent. of the *meta*- and 89 per cent. of the *ortho*-nitrotoluene is obtained (*Chem. Fabrik Grünau*, Landshoff and Meyer, *D.R.P.* 207,170).

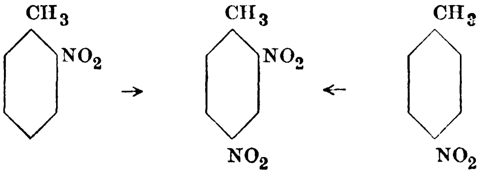
Toluene is nitrated as in the case of benzene, and in similar apparatus. The product is transferred to vessels cooled with ice, when the *para*-nitrotoluene crystallises out. The crystals are separated, and the oil remaining is fractionally distilled *in vacuo*. This oil is a mixture of *ortho*- and *para*-nitrotoluene, and the difference in the boiling points of these two substances—218° for the *ortho*-, 238° for the *para*-variety—is not sufficient in itself to obtain a complete separation. The first and last fractions contain practically pure *ortho*- and *para*-nitrotoluene respectively, but a large middle fraction is obtained which contains considerable amounts of the *para*-derivative. Hence, this is cooled, giving further crystals of *para*-nitrotoluene and an oil which is added to the distillation from the next operation. Other processes exist for the separation (*D.R.P.* 78,002 and 92,991), but they are not practicable commercially.

o-Nitrotoluene, obtained as above, is an amber-coloured liquid of B.P. 218-219° which solidifies on cooling and melts at 10·5°. The pure *o*-nitrotoluene of commerce contains as impurities some *m*-, and a small amount of *p*-nitrotoluene. On cooling to −5° to −10°, it crystallises partially, and the pure crystals of *o*-nitrotoluene formed melt at −4° ; this process has been used for its purification (Höchst Farbwerke, *D.R.P.* 158,219, Nov. 1903 ; *B.F.* 350,020 ; *F.*, viii., 88).

p-Nitrotoluene crystallises in yellow prisms of M.P. 54° and B.P. 238°. It is insoluble in water.

The two nitrotoluenes may be separated from the diluted nitration mixture by steam distillation, 3 parts of the *ortho*-compound or 2 parts of the *para*-compound passing over with 100 parts of water.

Dinitrotoluene. On nitrating toluene with hot mixed acid, 1 : 2 : 4-dinitrotoluene is obtained. The same product results from the nitration of either the *o*- or *p*-nitrotoluene :



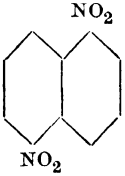
1 : 2 : 4-dinitrotoluene is a crystalline substance of M.P. 71°. It is used for the preparation of *m*-toluylenediamine, and in the manufacture of certain explosives.

Naphthalene Derivatives.

Naphthalene can yield two mono-nitro-derivatives : *α*- and *β*-nitronaphthalene ; only the first one is formed by the nitration of naphthalene, the *β*-isomer being prepared by indirect methods.

α-Nitronaphthalene was discovered by Laurent in 1835. Its commercial preparation was described by O. Witt (*Chemische Industrie*, 1887, **10**, 216). A mixture of 200 kilograms of nitric acid (76° Tw.), 200 kilograms of concentrated sulphuric acid, and 600 kilograms of the acid remaining from the previous operation, is placed in a cast-iron vessel, which can be cooled, and which is fitted with a stirrer provided with arms. 250 kilograms of powdered naphthalene are added through an opening in the cover, the addition taking one day for its completion in such a manner that, by cooling with water flowing through the outer chamber, the temperature of the mass is kept between 45° and 50°. When the process is finished, the liquid is allowed to run out by the lower tap into a lead-lined wooden vat ; on allowing to cool, the nitronaphthalene solidifies and forms a solid cake on the surface of the acid. The liquid underneath is separated. The nitronaphthalene is purified by boiling with water, which dissolves the excess of acid and frees from naphthalene, and then cooling rapidly by a stream of cold water, which precipitates the nitro-compound as a granular solid. Pure nitro-naphthalene may be obtained by dissolving these lumps in cumene or solvent naphtha, filtering, drying over calcium chloride, and cooling in a freezing mixture. In this way satisfactory crystals may be obtained, and these are separated by a hydraulic filter press (Wagner, Fischer, and L. Gautier, *Traité de chimie industrielle*, vol. ii., 236. Masson, 1903). α-Nitronaphthalene is insoluble in water, but soluble in benzene, carbon disulphide, ether, and warm alcohol. It forms long needles of M.P. 61° and B.P. 304°.

Dinitronaphthalenes. Ten dinitronaphthalenes should exist according to theory. On nitrating α-nitro-naphthalene under ordinary conditions, a mixture of 1 : 5- and 1 : 8-dinitronaphthalene is obtained :



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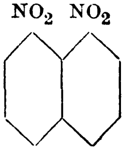


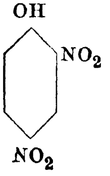
α-dinitronaphthalene. β-dinitronaphthalene.

These two products are important intermediate products for the manufacture of certain dyestuffs. They are easily obtained by treating naphthalene with cold nitric acid, then adding sulphuric acid to the mixture, and heating the resulting mass to complete the nitration. The product is washed with water, shaken with carbon disulphide to free from α-nitronaphthalene, and then with acetone to remove the 1 : 8-dinitro-compound. This treatment is continued until the M.P. has been raised to 210-212°. 1 : 5-dinitronaphthalene forms yellow needles which melt at 217° ; 1 : 8-dinitronaphthalene crystallises in rhombic plates of M.P. 170°.

Derivatives of Phenol.

Phenol reacts with warm dilute nitric acid, giving a mixture of *ortho-* and *para*-nitrophenol. The proportion of the *para*-derivative is much greater at lower temperatures.

Nitration of Phenol. One part of phenol is mixed with sufficient water to give a liquid ; the liquid so obtained is slowly added to a mixture of two parts of commercial nitric acid with four parts of water, keeping the temperature at about 35°. After one or two hours, the oil is separated, washed with water, and the isomers separated by steam distillation, the *ortho*-derivative only passing over with steam, leaving a residue of the *para*-compound. The yield of nitrophenol is 36 to 44 per cent. of the weight of the phenol. *o-Nitrophenol* crystallises in long yellow needles of M.P. 45° and B.P. 214°. Its salts are highly coloured. *p-Nitrophenol* forms almost colourless needles of M.P. 114°. Its salts are yellow. The nitration of both these isomers yields the same dinitrophenol, whose constitution must therefore be represented as that of a 1 : 2 : 4-derivative :

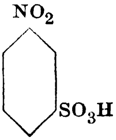


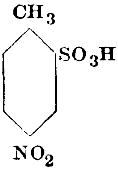
It is prepared by heating phenol with " mixed acid " at 130° to 140°. It crystallises in plates of M.P. 114°.

Nitrosulphonic Acids.

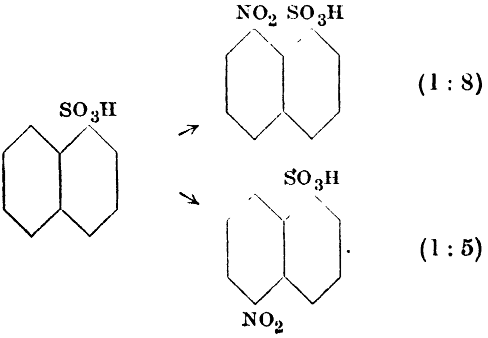
Nitrosulphonic acids may be obtained by two methods : (1) sulphonation of the nitro-derivatives, or (2) nitration of the sulphonic acids. These two methods may yield identical products or isomers, and the method adopted will depend on the compound to be prepared.

On treating nitrobenzene with fuming sulphuric acid, it is converted into nitrobenzene *m*-sulphonic acid, whilst on sulphonation *p*-nitrotoluene yields *p*-nitrotoluene *m*-sulphonic acid:



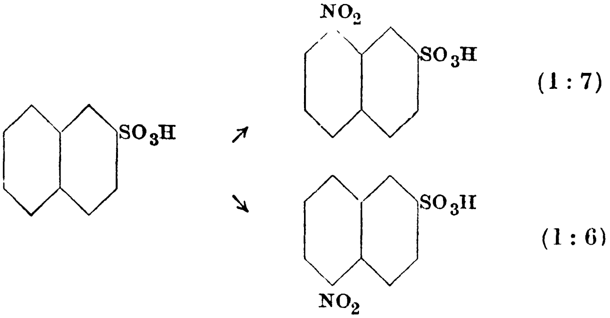


From these two examples it will be seen that in the benzene hydrocarbons the sulphonic acid and nitro-groups tend to take up *meta*-positions to one another. This is not the case in the naphthalene series. The α- and β-naphthalene monosulphonic acids yield on nitration isomeric nitrosulphonic acids in which the nitro-group occupies the α-position. The α-sulphonic acid gives a mixture of the 1 : 8-, 1 : 5- and 1 : 4-nitrosulphonic acids, containing 60 to 70 per cent. of the 1 : 8-acid, 20 per cent. of the 1 : 5-acid, the 1 : 4-acid only being formed in small amounts.



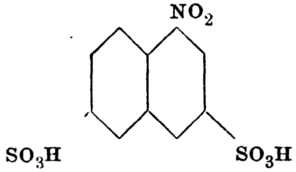
These acids are not generally separated, but are converted by reduction into the naphthylamine sulphonic acids, which are more readily isolated.

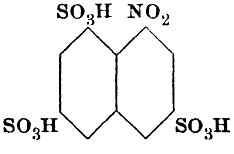
The nitration of the β-sulphonic acid yields a mixture of equal amounts of the 1 : 6- and 1 : 7-acids :



These acids were prepared by Cleve (*D.R.P.* 67,017 ; *Ber.*, 1886, **19**, 2179), and are used in the preparation of the corresponding α-naphthylamine sulphonic acids.

The di- and tri-sulphonic acids may be nitrated in a similar manner, the most important derivatives being the 1 : 3 : 6-nitrodisulphonic acid and the 1 : 3 : 6 : 8-nitro-trisulphonic acid :





which are produced by the nitration of the 2 : 7-disulphonic and 1 : 3 : 6-trisulphonic acids respectively.

CHAPTER VII.

REDUCTION OF NITRO-COMPOUNDS.

THE term "reduction" is applied to those reactions which take place between any chemical compound and hydrogen, which may be free or liberated in the nascent state by the interaction of suitable substances or is represented by other "reducing agents." In the case of aromatic compounds, reduction may lead to the addition of hydrogen to, or elimination of oxygen from, the compound, or both reactions may occur at the same time, as in the case of nitro-compounds.

The reduction of nitro-compounds leads to very different products, according to the character of the reducing agent employed and the conditions under which the reaction is carried out; thus there are *acid*, *neutral*, and *alkaline* reducing agents.

The most common acid reducing agents are metals, such as iron, zinc, or tin, in presence of a mineral or organic acid, the hydrogen liberated reacting with nitro-compounds as follows :,

$$R.NO_2 + 6H = R.NH_2 + 2H_2O.$$

The product obtained in this way contains an NH_2 or *amido*-group in place of the nitro-group, the compound formed being known as an *amine*. Under the same conditions a dinitro-derivative would give a *diamine*, and, generally, a polynitro-compound would give a polyamine. In case tin and hydrochloric acid are used, the reduction is sometimes accompanied by chlorination (von Braun, *Ber.*, 1912, **45**, 1274, 2910).

Neutral reducing agents include substances, such as zinc powder and aluminium amalgam, which decompose water, yielding an insoluble oxide, thus :

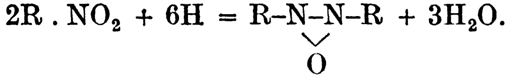
$$Zn + H_2O = ZnO + H_2.$$

In this case, reduction of the nitro-compounds yields substituted hydroxylamines :

$$R\,.\,NO_2 + 4H = R\,.\,NHOH + H_2O.$$

Certain neutral salts, such as the alkali sulphites, convert nitro-compounds into amines, introducing at the same time an SO_3H group.

Alkaline reducing agents do not all act in the same way. Thus zinc powder and caustic soda convert nitro-derivatives into *azoxy-* (I.) or *hydrazo-* (II.) compounds.

(I.)


$$2R\,.\,NO_2 + 6H = R\text{–}\underset{O}{\underbrace{N\text{–}N}}\text{–}R + 3H_2O.$$

$$\text{(II.)}\ 2R\,.\,NO_2 + 10H = R\text{–}NH\text{–}NH\text{–}R + 4H_2O.$$

Other alkaline reducing agents, such as ferrous oxide (ferrous sulphate and ammonia), exert a more energetic action, yielding amines. Finally, the alkali sulphides and hydrosulphides exert a selective reducing action on polynitro-compounds, and enable the reduction to be limited to only one of the nitro-groups.

Catalytic reduction processes have been discovered by Sabatier and Senderens, in which the vapour of the substance to be reduced, mixed with hydrogen, is passed over finely divided metals. (Senderens, d'Andoque and de Chefdebien, *D.R.P.* 139,407.)

Electrolytic Reduction. The electrolysis of water yields hydrogen at the negative plate, and this can serve as the reducing agent. The conditions under which the electrolysis is to be carried out, *viz.* the medium, the temperature, the nature of the cathode, and the presence of certain salts, exert a great influence on the character of the products obtained. (Elbs, *Zeitsch. f. Electrochemie,*

5, 108; *D.R.P.* 100,233, 100,234, 100,610, 121,835, 121,899, 121,900, 150,800, etc.) For details, the specialised treatises on electrochemistry must be consulted.

The amines may also be obtained from hydroxy-derivatives by heating in an autoclave with ammonia and a condensing agent. The condensation is more or less difficult to effect according to the hydroxy-derivative in question. The condensing agents used are zinc chloride, calcium chloride, and, recently, ammonium sulphite. This last compound is particularly suitable for converting a naphthol into naphthylamine, an intermediate compound being formed, which, in presence of ammonia, regenerates the ammonium sulphite and yields the amine:

$$R.OH + (NH_4)_2SO_3 = R{-}O{-}SO_2{-}NH_4 + NH_3 + H_2O$$

$$RO{-}SO_2{-}NH_4 + 2NH_3 = R.NH_2 + (NH_4)_2SO_3.$$

(See also Bucherer's method, *Journ. f. prakt. Chem.*, (2) 1904, **69**, 88; **70**, 349; **71**, 433; *D.R.P.* 117,471.)

In the case of naphthalene derivatives, these reactions are carried out at about 100°. In order to avoid loss of ammonia, the process is conducted in an autoclave, fitted with a stirrer, in case the original phenol or amine is insoluble in dilute ammonia.

Amido-Derivatives of the Hydrocarbons.

Derivatives of Benzene.

Aniline or *Phenylamine*, $C_6H_5.NH_2$. Aniline was discovered by Unverdorben in 1826 in the products of the dry distillation of Indigo. In 1835 Runge isolated it from coal-tar, but it was not until 1842 that Zinin prepared aniline by reducing nitrobenzene with ammonium sulphide. Béchamp first suggested the commercial preparation of aniline by reduction of nitrobenzene with iron turnings and acetic acid; this method is used at the present time, the acetic acid being replaced by the cheaper hydrochloric acid. In 1860 aniline was sold at over ten shillings a pound; at present a much purer article is sold at less than sixpence a pound (G. F. Jaubert, *Histoire de l'industrie suisse des matières colorantes*).

The amount of hydrochloric acid used for the reduction of the nitrobenzene by means of iron is much lower than that which is necessary according to the following equation:

$$C_6H_5NO_2 + 3Fe + 6HCl = C_6H_5NH_2 + 3FeCl_2 + 2H_2O.$$

This is explained by the ferrous chloride formed acting as a reducing agent, giving ferric chloride, which latter is then reduced again to the ferrous condition by solution of more iron:

$$2FeCl_3 + Fe = 3FeCl_2.$$

Manufacture of Aniline. The vessels used are made of boiler-plate, and are about six feet in height and one to four and a half feet in diameter. (Fig. 3.) An opening at the bottom allows of the vessel being emptied. The cover contains several openings: *A* is used for the axis of the stirrer, *B* for introducing the iron turnings, being closed by a cast-iron plate or wooden block, *C* is attached to a worm condenser. The axis of the stirrer is hollow, so that steam may be introduced by this means during the operation. 160 litres of water, 100 kilograms of iron, and 30 to 40 kilograms of hydrochloric acid are first placed in the apparatus, and then 400 kilograms of nitrobenzene added with constant stirring. To accelerate the reaction, steam is passed in, and then 300 kilograms of iron added in small amounts. The process lasts for eight hours, and is so arranged that the vapours which escape are cooled by a reflux condenser. When the process is finished the acid is neutralised with lime, and the aniline produced separated by steam distillation. The vapours are cooled in a worm condenser, when the liquid obtained forms two layers which may be separated. One layer is aniline, the other is water containing about 2 to 3 per cent. of dissolved aniline. This water is used for producing the steam necessary for the next operation, thus recovering the aniline which it contains in solution.

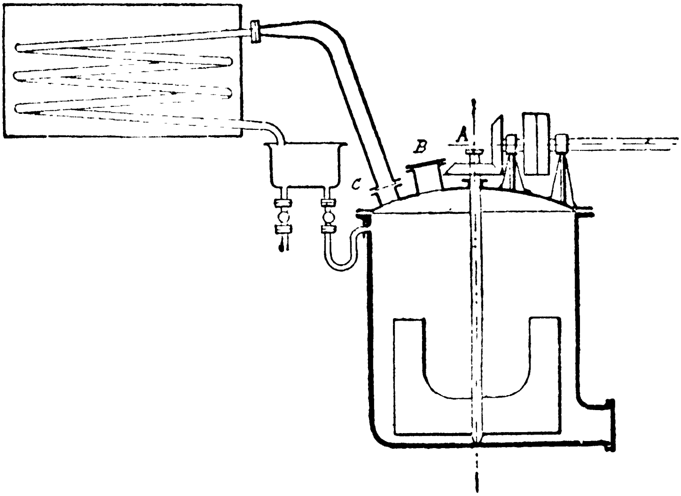


Fig. 3.

The aniline is purified by distillation, the yield being about 67 per cent. of the weight of nitrobenzene used (theoretical, 76 per cent.).

Properties. Pure aniline is a colourless liquid of B.P. 182°, M.P. −8°. It is heavier than water, having SP. GR. 1·026 at 15° ; it is soluble in water to the extent of 3 per cent. On exposure to air, aniline slowly becomes brown. In commerce a distinction is made between "aniline oil for blue," which is pure, and "aniline oil for red," which is a mixture of aniline and the toluidines in the following proportions : aniline, 10 to 20 per cent. ; *o*-toluidine, 30 to 40 per cent. ; *p*-toluidine, 25 to 40 per cent.

Pure aniline or its hydrochloride ("aniline salt") is used in dyeing for producing *Aniline black*. The hydrochloride forms white crystals of M.P. 192°, which become greenish-black on exposure to air.

Phenylenediamines or *Diamidobenzenes*. Three isomers exist, *o*-, *m*- and *p*-phenylenediamines, the last two being the most important.

m-Phenylenediamine is obtained by reducing *m*-dinitrobenzene with iron and hydrochloric acid. It forms crystals of M.P. 63°, and boils without decomposition at 277°. When pure it is white, but becomes brown in air.

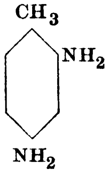
p-Phenylenediamine may be obtained by the reduction of *p*-nitraniline, but is actually manufactured by the reduction of amidoazobenzene (see p. 104). It forms white crystals of M.P. 147°, and B.P. 267°.

Derivatives of Toluene.

Reduction of nitro-derivatives of toluene yields the corresponding toluidines, or the bases formed by reducing crude nitrotoluene may be separated. For this purpose, it has been proposed to effect the reduction with alkali sulphides, which only attack the *para*-derivative and leave the *o*-nitrotoluene unaffected (Lösner, *D.R.P.* 78,002; Clayton Aniline Co., *D.R.P.* 92,991). The mixture may also be reduced with iron and hydrochloric acid, the *p*-toluidine being partially separated by cooling. In this case it is preferable to isolate the base in the form of the hydrate which it forms on shaking the crude product with somewhat less than its weight of crushed ice; the hydrate is then melted, and the *p*-toluidine purified by distillation (Friswell, *J. Soc. Chem. Ind.*, 1908, 258). There are also separation processes which depend on the difference in solubility of certain salts of the toluidines, such as the phosphates, oxalates, etc. (Lewy, *D.R.P.* 22,139), and on the action of nitrous acid (Wülfing, *D.R.P.* 37,932).

The most important toluidines are *ortho-* and *para*-toluidine. *o*-Toluidine is a colourless liquid which boils at 199° ; it becomes brown in air, and is slightly soluble in water. *p*-Toluidine crystallises in colourless plates of M.P. 45° and B.P. 198°.

Toluylenediamines. The only important one is *m*-toluylenediamine, which is obtained by the reduction of 1 : 2 : 4-dinitrotoluene. It forms crystals of M.P. 99°.

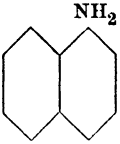


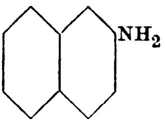
Derivatives of the Xylenes.

The xylidine obtained by the reduction of commercial nitroxylene is a mixture of four isomers, the separation of which is rather difficult and may be carried out in several ways (*D.R.P.* 39,947, 71,969, 87,615. See also Friedländer, *Monatsh. f. Chem.*, 1898, **29**, 639).

Derivatives of Naphthalene.

Two mononitronaphthalenes are known, and yield on reduction *α*- and *β*-naphthylamine :





As already mentioned (p. 48), *α*-nitronaphthalene is easily obtained by nitration of the naphthalene, whereas *β*-nitronaphthalene can only be prepared with difficulty by indirect means. Hence, the *β*-nitro-compound cannot be used for the manufacture of *β*-naphthylamine, and it is better to commence with β-naphthol, which is easily prepared by the alkaline fusion of naphthalene β-sulphonic acid.

α-*Naphthylamine* is manufactured by reducing α-nitronaphthalene with iron and hydrochloric acid, the rather vigorous reaction being kept in hand by adding the nitro-derivative in such a manner as to keep the temperature at about 50°. When the reaction is finished, the liquid is neutralised with lime, and the base separated by passing in a current of superheated steam. It is purified by distillation *in vacuo*, when it crystallises in white plates, M.P. 50° and B.P. about 100°. Commercial α-naphthylamine generally contains a small amount of the β-isomer (Reverdin and Nölting, *Sur la constitution de la naphtaline*, 1888, 35). The isomers may be separated by treating with xylene (Weiler-Ter-Meer, *D.R.P.* 209,076).

β-*Naphthylamine* is prepared commercially by heating ten parts of β-naphthol and 7·5 parts of a concentrated solution of ammonia in an autoclave for one day at 200°. The excess of β-naphthol is extracted by means of caustic soda. The β-naphthylamine is purified by distillation *in vacuo*, when it crystallises to form plates of M.P. 112° and B.P. 294°.

Sulphonated Derivatives of the Amines.

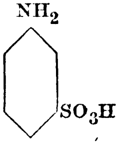
The amido-sulphonic acids may be obtained by several general methods :

1. By the reduction of nitro-sulphonic acids ;
2. By the sulphonation of amines ;
3. By heating the naphthol sulphonic acids with ammonia.

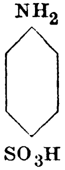
In certain cases it is possible to bring about the reduction and sulphonation at the same time by treating a nitro-derivative with a neutral sulphite (Piria, *Ann.*, 1851, **78**, 34).

Derivatives of Aniline.

The two most important derivatives are the *meta-* and *para*-amidobenzene sulphonic acids, or *metanilic* (I.) and *sulphanilic* acids (II.) :



(I.)



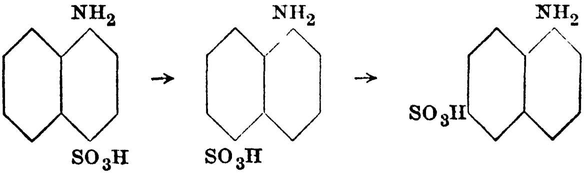
(II.)

The first is prepared by reducing *m*-nitrobenzene sulphonic acid. Sulphanilic acid is obtained by sulphonating aniline at 190°, or, better, heating aniline sulphate for several hours at 200-205°, the latter being the commercial method.

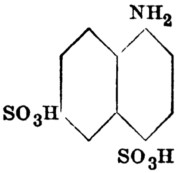
Derivatives of the Naphthylamines.

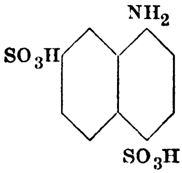
Derivatives of α-Naphthylamine.

All the seven isomeric α-naphthylamine monosulphonic acids predicted by theory are known. The sulphonation of α-naphthylamine has been studied by Erdmann (*Ann.*, 1893, **275**, 193), who found that, on treatment with five parts of the ordinary sulphuric acid at 130°, it yields almost exclusively the 1 : 4 or *naphthionic acid* if the reaction is only allowed to proceed for a short time. If the action of the sulphuric acid is prolonged, the 1 : 4-acid disappears, and the 1 : 5- and the 1 : 6-isomers are successively produced :



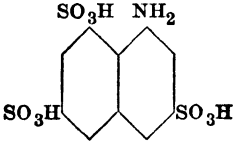
Naphthionic acid (1 : 4) is produced by sulphonating α-naphthylamine, but it is prepared commercially by heating α-naphthylamine sulphate at 170-180° for eight hours (Nevile and Winther, *Ber.*, 1880, **13**, 1940). Better results are obtained if a certain amount of oxalic acid is added to the sulphate. On sulphonating with three and a half parts of fuming sulphuric acid containing 25 per cent. SO_3, at 30° C., a mixture of the α-naphthylamine 4 : 6- and 4 : 7-disulphonic acids is obtained, and these are called " Dahl's acids " (*D.R.P.* 41,957).





Naphthylamine 1 : 6- *and* 1 : 7-*sulphonic acids* are prepared by the reduction of the corresponding nitrosulphonic acids, using the mixture formed on nitrating naphthalene β-sulphonic acid (see p. 52), the mixture obtained being known as " Cleve's acids " (Cleve, *Ber.*, 1887, **20**, 74).

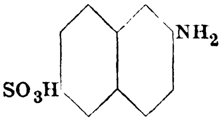
Trisulphonic acids. Of these, the most important is the 1 : 3 : 6 : 8-acid, formed by reduction of the corresponding nitronaphthalene trisulphonic acid (Koch, *D.R.P.* 56,058).



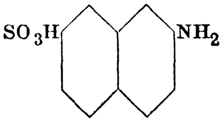
Derivatives of β-Naphthylamine.

On sulphonating β-naphthylamine with three times its weight of concentrated sulphuric acid at a temperature of about 100°, a mixture of four monosulphonic acids is produced, the sulphonic acid group again attaching itself to the ring which does not contain the NH_2 group. The main products are the 2 : 8- and 2 : 5-acids, the 2 : 6- and 2 : 7-acids only being obtained in small amounts ; the relative proportions vary with the experimental conditions (Green, *Ber.*, 1889, **22**, 721 ; Dahl, *D.R.P.* 29,084, 32,276).

Sulphonation by means of ordinary sulphuric acid at 15-20° yields almost exclusively the 2 : 5-acid, whilst on heating *β*-naphthylamine sulphate to 200-210°, the 2 : 6-acid is the main product. This acid, often called " Brönner's acid," is prepared in a pure state by heating Schäffer's *β*-naphthol sulphonic acid under pressure with ammonia (Liebmann, *Mon. sci.*, 1885, 1043). Under the same conditions, *β*-naphthol sulphonic acid (2 : 7), " F acid," yields *β*-naphthylamine sulphonic acid (Cassella, *D.R.P.* 43,740).

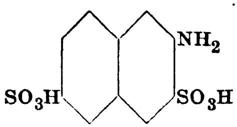


Brönner's acid (2 : 6).

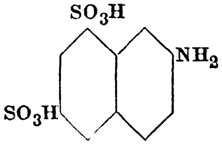


2 : 7-acid.

β-Naphthylamine disulphonic acids. The most important are the *β*-naphthylamine 3 : 6- and 6 : 8-disulphonic acids, called respectively " Amido R acid " and " Amido G acid."



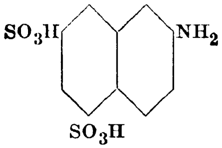
Amido R acid.



Amido G acid.

These acids are obtained by heating the corresponding *β*-naphthol disulphonic acids with ammonia under pressure.

β-Naphthylamine 5 : 7*-disulphonic acid* is obtained by the sulphonation of 2 : 5-naphthylamine sulphonic acid.



Hydroxy-Derivatives of the Amines.

These compounds include the amido-phenols and amido-naphthols, and may be obtained by the following processes :

1. By reducing the nitro-derivatives of the phenols or naphthols ;
2. Alkaline fusion of the amido-sulphonic acids ;
3. Heating a di- or a poly-phenol under pressure with ammonia ;
4. Reduction of the azo-derivatives of phenols or naphthols.

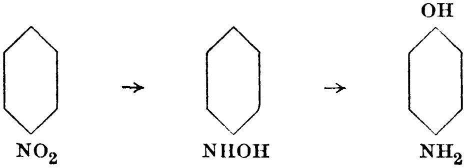
Benzene Derivatives.

Amidophenols. Three isomers are known, *meta, ortho* and *para.*

o-Amidophenol is prepared by reduction of the corresponding nitro-phenol with ammonium sulphide. It melts at 170°.

m-Amidophenol may be obtained by alkaline fusion of metanilic acid (*D.R.P.* 44,792), by reduction of *m*-nitrophenol, or by heating resorcinol with ammonium chloride at 200° in an autoclave for twelve hours (*D.R.P.* 49,060). It melts at 120°.

p-Amidophenol is obtained on the reduction of *p*-nitrophenol by means of zinc and hydrochloric acid. Another method of preparation has been outlined by R. Vidal ; nitrobenzene is reduced in sulphuric acid solution by means of zinc dust, when the phenyl-hydroxylamine first formed yields *p*-amidophenol in presence of acid :



On reduction, *p*-azophenol yields *p*-amidophenol (*D.R.P.* 82,426). This compound melts at 184°.

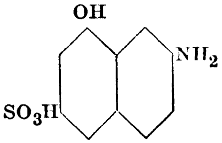
Sulphonated Hydroxy-Derivatives of the Amines.

These compounds contain an amido-group, a hydroxy-group and one or more sulphonic acid groups. They are prepared :

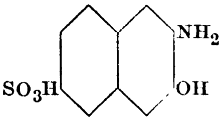
1. By alkaline fusion of the di- or poly-sulphonic acids of amines ;
2. By reduction of the azo-derivatives of naphthol sulphonic acid.

The compounds derived from naphthalene are of greatest interest.

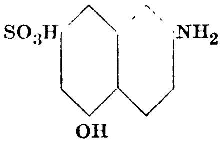
Amidonaphthol sulphonic acids. Of these, the 2 : 8 : 6, 2 : 3 : 6 and 2 : 5 : 7 are the most important.



Amidonaphthol sulphonic acid G, or γ-acid.



Amidonaphthol sulphonic acid R.

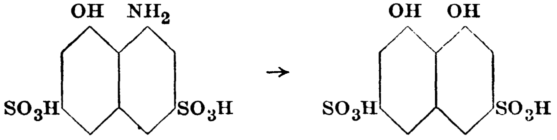


2 : 5 : 7 acid J.

The first two compounds are prepared by fusing the β-naphthylamine disulphonic acids G and R with caustic soda. The third is obtained by alkaline fusion of

2-naphthylamine-5 : 7-disulphonic acid, and is called "J acid."

Of the amidonaphthol disulphonic acids, the commonest is the 1 : 8 : 3 : 6, or "H acid," which is prepared by heating α-naphthylamine 3 : 6 : 8-trisulphonic acid with caustic soda at 180° (*D.R.P.* 69,722, 80,668). On heating with caustic soda, H acid itself undergoes a change, its amido-group being replaced by a hydroxyl-group, giving 1 : 8 : 3 : 6-dihydroxynaphthalene disulphonic acid, or *chromotropic acid*, which may also be obtained by heating α-naphthol or α-naphthylamine trisulphonic acids (1 : 8 : 3 : 6) with caustic soda (*D.R.P.* 67,563, 68,721, 69,190, 75,153).



H acid. Chromotropic acid.

Nitro-Derivatives of the Amines.

The nitro-amines may be prepared by two methods :

1. Partial reduction of the dinitro-compounds ;
2. Nitration of the amines.

The second method is the one generally used, and to avoid the nitric acid acting on the amido-group this group has to be protected by acylating the amine. The products resulting from the combination of an amine with an organic acid by the elimination of a molecule of water are termed acylated compounds. Thus, aniline and acetic acid give acetanilide :

$$C_6H_5NH_2 + CH_3COOH = H_2O + C_6H_5NH \,.\, COCH_3.$$

Nitration is then effected as usual, and gives the nitro-derivative of the acylated amine. This compound is easily converted into the nitro-amine by heating with dilute acids or alkalies to eliminate the acyl group.

Derivatives of Aniline.

Three nitranilines exist, the most important being the *meta-* and *para-*compounds.

o-Nitraniline is formed together with the *para-*compound (see below). It melts at 71·5°.

m-Nitraniline is prepared by partial reduction of the dinitrobenzene by means of iron and acetic acid (A. Wülfing, *D.R.P.* 67,018), or ammonium sulphide (Muspratt and Hofmann, *Ann.*, 1846, **57**, 215), or tin and hydrochloric acid in alcoholic solution (Anschütz and Heusler, *Ber.*, 1886, **19**, 2161). *m*-Nitraniline has M.P. 114° and B.P. 285°.

p-Nitraniline, $NO_2 . C_6H_4 . NH_2$, is obtained by the nitration of the acetyl derivative of aniline, acetanilide (see p. 66), with mixed acid. Finely powdered acetanilide is dissolved in concentrated sulphuric acid in an apparatus fitted with a stirrer, and the mixed acid gradually introduced, keeping the temperature at 40-50°. When the nitration has finished, the product is poured into water to precipitate the nitro-acetanilide. This is then separated and heated with caustic soda solution to eliminate the acetyl group; the *p*-nitraniline is precipitated on cooling, whilst the *o*-nitraniline formed remains in solution. Under these conditions about 60 per cent. of the *para-* and 25 per cent. of the *ortho-*derivative is obtained (Nölting and Collin, *Ber.*, 1884, **17**, 262).

p-Nitraniline is also obtained by nitrating benzylideneaniline (Farbenfabriken Bayer, *D.R.P.* 72,173), or by heating *p*-nitrochlorbenzene under pressure with ammonia. (See also Müller, *Chem. Ztg.*, 1912, **36**, 1049; Clayton Aniline Co., *D.R.P.* 148,749.) *p*-Nitraniline crystallises in yellow needles of M.P. 147°. Its principal use is in the production of Paranitraniline red ("Para red") on cotton fibre (see p. 108).

CHAPTER VIII.

ALKYLATION.

By this process, the acid hydrogen atom of a phenol or an organic acid, or a hydrogen atom of the amido-group in an amine, is replaced by an alkyl group. The alkylation of phenols and acids is sometimes called "esterification," but it is preferable to reserve this name for the alkylation of acids only.

Alkylation of Phenols.

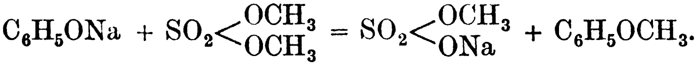
In order to alkylate a phenol, it is converted into the alkali salt, and then treated with certain substances, such as the halogenated derivatives of the saturated hydrocarbons, $C_nH_{2n+1}X$, where X is chlorine, bromine or iodine; methyl sulphate is also very convenient for alkylation, as its boiling point (187°) is high enough to allow of its use in open apparatus at the atmospheric pressure, whereas the alkylogens (halogen esters) have very low boiling points, and hermetically sealed apparatus (autoclaves) must be used, as the pressure attained is frequently very high. The alkyl nitrates may also be used for alkylation.

In the case of the simple alkyl esters, the reaction is expressed by the general equation:

$$C_6H_5ONa + C_nH_{2n+1}X = NaX + C_6H_5 . O . C_nH_{2n+1},$$

in which X may be chlorine, bromine, iodine, the nitrate radicle, etc.

If methyl sulphate is employed, the reaction is as follows :



$$C_6H_5ONa + SO_2\begin{smallmatrix}\diagup OCH_3\\ \diagdown OCH_3\end{smallmatrix} = SO_2\begin{smallmatrix}\diagup OCH_3\\ \diagdown ONa\end{smallmatrix} + C_6H_5OCH_3.$$

The phenol is converted into its sodium salt by means of alkali alcoholates in alcoholic solution, a slight excess of the alkylogen added, and the mixture heated in a closed vessel. In case methyl sulphate is used, the phenol is dissolved in a caustic alkali, the sulphate added and the mixture stirred. Treatment with water removes the mineral salts, and on shaking the product with caustic soda to dissolve the phenol, the alkylated derivative remains insoluble, and may then be purified by distillation or recrystallisation.

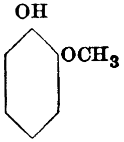
Derivatives of Phenol.

Anisole, $C_6H_5OCH_3$. It is a colourless liquid, boiling at 152°.

Phenetole, $C_6H_5OC_2H_5$. Colourless liquid of B.P. 172°.

Derivative of Dihydroxybenzene.

The most important is *guaiacol*, the monomethyl ether of pyrocatechol.



It is extracted from creosote, and crystallises in large prisms of M.P. 32°. It is used as a base for anti-tuberculous medicines.

Alkylation of Amines.

In an amine, the two hydrogen atoms of the amido-group may be successively replaced by alkyl radicles.

Thus, aniline can give monoalkylanilines and dialkylanilines :

$$C_6H_5NH_2 \rightarrow C_6H_5NHR \rightarrow C_6H_5N{<}^{R.}_{R.}$$

The name *primary* amine is given to amines which contain the NH_2 group ; if only one hydrogen atom of the NH_2 group has been replaced by an alkyl radicle, a *secondary* amine is obtained ; and if both hydrogen atoms are so replaced, the compound is termed a *tertiary* amine. The same nomenclature is used if the characteristic atoms of hydrogen in a primary amine are replaced by other than alkyl radicles, only the methods of preparation are different.

The alkylation of primary amines for the preparation of secondary amines is almost always accompanied by the formation of a tertiary amine. The separation of the two bases cannot as a rule be effected by fractional distillation, as the difference in their boiling points is not sufficiently great. The salts of the secondary amines are often solids, whereas those of the tertiary amines are oils.

The alkylating agents used in commerce are methyl and ethyl chlorides, produced at the moment when they are required by heating the amine in an autoclave with hydrochloric acid and the corresponding alcohol ; methyl sulphate may also be used.

Secondary Amines.

Monomethylaniline, $C_6H_5.NH.CH_3$, is prepared commercially by heating 55 parts of aniline hydrochloride and 16 parts of methyl alcohol in an autoclave at 180° for two to three hours, when the pressure first rises to twenty-five atmospheres and then falls again. The product is neutralised with lime, and the base separated by steam ; it then contains 90 per cent. of monomethylaniline and 6 to 7 per cent. of dimethylaniline. Monomethylaniline boils at 192°.

Monoethylaniline, $C_6H_5.NH.C_2H_5$, is prepared by heating 95 parts of aniline hydrochloride with 28 parts of alcohol at 180° in an enamelled autoclave. The hydrochloride of monoethylaniline crystallises out. The base is a colourless liquid of B.P. 204°.

Benzylaniline, $C_6H_5.NH.CH_2.C_6H_5$, is obtained by treating aniline with benzyl chloride. It is a solid, and has M.P. 33° and B.P. 310°.

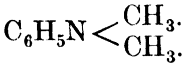
Diphenylamine, $C_6H_5.NH.C_6H_5$, is prepared commercially by the process of De Laire, Girard and Chapoteaut, in which aniline is heated with aniline hydrochloride in an autoclave at 220-230° :

$$C_6H_5NH_2 + C_6H_5NH_2.HCl = NH_4Cl + (C_6H_5)_2NH.$$

The product is poured into water, and hydrochloric acid added to dissolve the aniline, when the diphenylamine crystallises out, the yield being 60-70 per cent. It forms colourless crystals of M.P. 54° and B.P. 310°.

Tertiary Amines.

Dimethylaniline,



$$C_6H_5N{<}\begin{matrix}CH_3.\\CH_3.\end{matrix}$$

Commercial Preparation. Dimethylaniline was originally obtained by heating aniline hydrochloride (or aniline and hydrochloric acid) with methyl alcohol at 230-235°. At the present time sulphuric acid is used instead of hydrochloric acid, and aniline, which is cheaper, is used in place of aniline hydrochloride, when there is not so great a possibility of the autoclave (enamelled or otherwise) being attacked by the volatile acid. According to J. Walter (*Chem. Ztg.*, 1910, 641, *et seq.*), the practical details of the process are as follows : 80 kilograms of aniline, 78 kilograms of methyl alcohol and 8 kilograms of sulphuric acid (168° Tw.) are heated together in an autoclave at 230-235° ; the pressure rises to twenty-eight to thirty-two atmospheres, this pressure being maintained for three hours, and then the autoclave is allowed to cool. On opening a valve, the gases escape, and the alcohol carried forward is condensed in a worm-condenser. The product is then forced by means of compressed air into a distillation apparatus, neutralised with caustic soda, and the bases separated by steam distillation. The dimethylaniline is purified by redistillation. The yield is 92 per cent. of the theoretical.

Dimethylaniline is a colourless liquid of B.P. 198°. Commercial dimethylaniline often contains monomethylaniline and unchanged aniline. The presence of the latter may be detected by means of dilute sulphuric acid, which dissolves the alkylated bases, but gives a precipitate with aniline of the insoluble aniline sulphate. The monomethylaniline is detected by mixing the product with acetic anhydride, which would cause a rise in temperature, whereas with pure dimethylaniline the temperature would be lowered, due to its solution. The monomethylaniline may be detected and estimated by treating the product with nitrous acid in presence of hydrochloric acid, and then with ether, when only the nitroso-monomethylaniline dissolves.

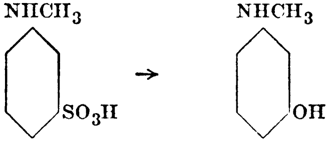
Methylbenzylaniline is obtained by the action of benzyl chloride on monomethylaniline. It is a liquid of B.P. 310°.

Ethylbenzylaniline boils at 285° (710 mm.).

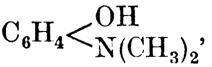
Alkylated Derivatives of the Amidophenols.

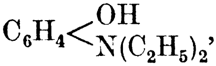
Of these, the only ones important in the manufacture of dyestuffs are those derived from *m*-amidophenol; they are obtained by the alkaline fusion of the *meta*-sulphonic acids of mono- and di-alkylated anilines.

Monomethyl-m-amidophenol,  $C_6H_4<\begin{smallmatrix}OH\\NHCH_3\end{smallmatrix}$. The properties and preparation of this compound are outlined in a patent of the B.A.S.F. (*D.R.P.* 48,151). Monomethyl-metanilic acid is fused with caustic soda. This sulphonic acid may be obtained either by sulphonating monomethylaniline or by methylating metanilic acid.



Monoethyl-m-amidophenol is obtained in a similar manner. It crystallises, and has M.P. 62°.

Dimethyl-m-amidophenol,  $C_6H_4<\begin{matrix}OH\\N(CH_3)_2\end{matrix}$, is prepared by several processes, for example, by fusing dimethylaniline sulphonic acid with alkalies (*D.R.P.* 44,792), or by heating resorcinol in an autoclave with dimethylamine (*D.R.P.* 49,060). Dimethyl-*m*-amidophenol forms small crystals which melt at 87°.

Diethyl-m-amidophenol,  $C_6H_4<\begin{matrix}OH\\N(C_2H_5)_2\end{matrix}$, is obtained in a similar manner to the dimethyl compound.

THIRD PART.

THE ORGANIC DYESTUFFS.

CHAPTER IX.

CLASSIFICATION AND APPLICATION OF DYESTUFFS.

THE classic experiment with Newton's prism showed that sunlight and white artificial light (from petrol, gas, incandescent and arc lamps) are formed by the superposing of coloured rays of light, the unequal refraction of which causes their separation on passing through the prism. The coloured image obtained in this manner with a pencil of white light is known as the "spectrum." Seven different shades may be distinguished: violet, indigo, blue, green, yellow, orange and red, called fundamental colours, as by admixture in suitable proportions all the various shades may be produced.

A body is said to be *transparent* when light can pass through it without being considerably diminished in intensity; on the other hand a body is termed *opaque* when it does not allow light to pass through in this manner. A body intermediate between these two is known as a *translucent* body. In nature, the majority of substances are opaque, and when light falls on them it is more or less completely reflected into space. The amount of reflection depends on the condition of the surface, being greater the more polished is the surface.

When light is reflected from a body, several things may occur: (1) The object may reflect the sunlight without altering the proportions of the different colours in the spectrum, and the object will appear to be white; (2) the object may absorb entirely all the light which it received, when it is called black; or (3) the object illuminated may only reflect a portion of the coloured rays which form the white light, and absorb the other portion. The object will then appear to be *coloured.* Newton employed the term *complementary colour* to denote the colour which together with the one to which it is complementary would produce the effect known as white.

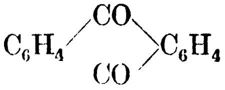
Coloured substances are met with amongst the chemical elements as well as in their compounds; thus iodine, sulphur, bromine, phosphorus, etc., are coloured; certain metals, for example, iron, chromium, copper, and nickel, yield coloured salts; others generally give colourless salts. Compounds of the so-called "organic" chemistry, that is to say, those which result from the combination of carbon with oxygen, hydrogen, nitrogen, or sulphur, are as a rule colourless or white substances. It is, hence, very curious indeed that there are many organic compounds which possess an intense and brilliant colour. By the detailed study of these cases, it has been found that analysis will only give a very small difference between the percentage composition of a colourless organic compound, and that of the highly coloured compound from which it is derived. Moreover, examples are known of coloured substances which have exactly the same composition as others which are perfectly colourless. Hence it is considered that the cause of these great differences is mainly the manner in which the atoms are bound to one another; briefly—*colour depends on the structure of the molecule.* To use a classic comparison, it is possible to construct several buildings of very different types with a number of bricks; and in the same way the atoms of carbon, hydrogen, nitrogen, oxygen, etc., may be combined as to give an almost unlimited number of compounds, the properties of which may be very different. Certain compounds will be colourless, others will be coloured, according to the relative arrangement of the atoms. These arrangements are represented by diagrams known as "constitutional formulae," which, amongst other things, illustrate clearly a relation between the colour of an organic substance and the manner in which its constituent atoms are linked. On examining the constitutional formulae of coloured substances, the presence of certain atomic groupings is noted, and consequently the colour is attributed to their presence.

In 1876, O. N. Witt (*Ber.*, **9**, 522; cf. *ibid.*, 1888, **21**, 325) endeavoured to state a general theory for these phenomena, and suggested that these special groups should be termed "chromophores." In order that a chromophore may be able to exert its influence, it must be present in an organic substance which contains a large number of carbon atoms, and it is hence that coloured substances are more frequently met with among the derivatives of hydrocarbons such as benzene, naphthalene and anthracene, the so-called aromatic hydrocarbons. If a chromophore is introduced into a molecule of an aromatic organic compound, a substance which is more or less coloured is obtained which Witt called a "chromogen." Thus azobenzene, anthraquinone, and quinone are chromogens, being coloured, due to the presence of the chromophores:

$$-N=N-,\ CO,\ \text{etc.}$$

$$C_6H_5—N = N—C_6H_5$$

Azobenzene.



$$C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}C_6H_4$$

Anthraquinone.

Chromogens yield colourless compounds on reduction. For example, azobenzene and quinone take up two atoms of hydrogen and are decolorised :

$$C_6H_5—N=N—C_6H_5 + H_2 = C_6H_5—NH—NH—C_6H_5,$$

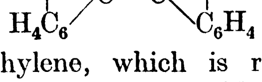
Azobenzene (coloured). Hydrazobenzene (colourless).

$$C_6H_4O_2 + H_2 = C_6H_4(OH)_2$$

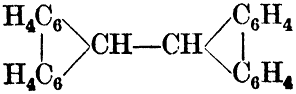
Quinone (coloured). Hydroquinone (colourless).

These conversions are reversible, as hydrazobenzene and hydroquinone yield on oxidation the coloured substances from which they were obtained. In most cases it is possible to convert a coloured substance in this manner into a colourless one and *vice versâ* ; such reduction products are known as "leuco-compounds." On the other hand, reduction sometimes completely decomposes coloured substances, and the colourless products do not yield the original substance on oxidation; such reduction products are no longer to be regarded as leuco-compounds.

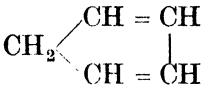
The disappearance of the colour, due merely to the taking up of hydrogen by the chromophore, shows that the relative affinities of the atoms which form it are not entirely saturated, these affinities being latent. In chemical language, this fact may be expressed by saying that chromophores are "unsaturated," and in the formulae the latent valencies are indicated by two or three lines called "double" or "triple" bonds. Unsaturated hydrocarbons are known which are coloured, for example,



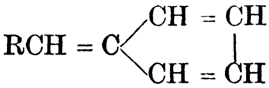
di-diphenylene-ethylene, which is red in colour. On reduction, it takes up two atoms of hydrogen, giving the colourless saturated hydrocarbon :



Cyclo-pentadiene



combines with aldehydes to give the highly coloured *fulgides*, which are compounds of the type:



the parent hydrocarbon of which is the coloured *fulvene*, an isomer of the colourless benzene.

As a rule, however, it is necessary for the compound to contain other elements than carbon and hydrogen, such as oxygen, sulphur, or nitrogen.

Dyeing. The conditions necessary for an organic substance to be coloured have been outlined above, but, if a substance is coloured, it is not of necessity a "dyestuff." Every coloured substance which can be fixed on the fibre in a more or less permanent manner by the processes used in dyeing or printing is called a dyestuff. The simplest way of dyeing fibre is to immerse it in a dilute solution of the dyestuff (for example, 0·02 or 0·1 per cent. aqueous solution), to which has been added an acid or suitable salts, and then heating almost up to the boiling point. In certain cases the dyestuff is precipitated on the fibre and dyes it uniformly; if the colour does not disappear on washing with water the fibre is said to be dyed. Dyed materials are more or less fast according to the nature of the dyestuff and its affinity for the fibre in question. This affinity varies considerably for different dyestuffs, and the same dyestuff often has very different affinities for different kinds of fibre. Whilst the majority of soluble dyestuffs dye animal fibres (wool and silk) under suitable conditions, there are only a comparatively small number which dye vegetable fibres (cotton, linen, jute, etc.) with equal facility. When the affinity of a dyestuff for a certain fibre is not sufficient to give fast shades the material is "mordanted." Mordanting consists of fixing on the fibre a substance, known as a *mordant*, which is capable of forming an insoluble coloured compound, called a *lake*, with the dyestuff at the time of dyeing, which hence remains fixed on the fibre. The insolubility of these lakes renders them very stable to the various mechanical and chemical treatments, and hence shades obtained by the use of mordants are very fast, and they are used whenever fast shades are required. The natural colouring matters, such as logwood, madder, and cochineal, which were used even in the earliest civilisations, are mordant dyestuffs.

Mordants may be divided into "metallic mordants" and "organic mordants." The former are the hydroxides of certain metals, of which the most important, owing to their frequent use, are ferric, aluminium, and chromium hydroxides. These are the common mordanting agents, others being the special mordants, such as the oxides of zirconium, lanthanum, glucinum, titanium, etc., studied by A. Scheurer and Brylinski. The same dyestuff gives very differently coloured lakes with different mordants; thus madder (Alizarin) gives a red lake on aluminium mordant, a garnet-coloured lake on chromium mordant, and a violet lake on iron mordant. Hence, the name "polygenetic dyestuffs" is sometimes given to those dyestuffs which are fixed by metallic mordants.

The organic mordants include the different tannins, and also fatty mordants, *e.g.* Turkey red oii, the exact action of which in fixing the dyestuff is not as yet definitely established. The principal organic mordant is tannin, which is used for mordanting vegetable fibres. Tannin possesses the property of forming lakes with a large number of dyestuffs which themselves have no affinity for vegetable fibres. It is therefore sufficient to mordant the fibre with tannin, and then dye it in order to cause the uniform precipitation of the coloured lake. If vegetable fibres are immersed in an aqueous solution of tannin for a sufficient time, the cells become impregnated with tannin; on subsequent immersion in the bath containing the dyestuff, this penetrates into the cellular membranes, forming an insoluble lake inside the fibre, which will then be dyed. The lakes so obtained are only comparatively insoluble, but very fast coloured lakes may be obtained by combining the dyestuff with both tannin and antimony oxide. For this purpose the fibre is passed through a tannin bath and then into tartar emetic; after washing, the antimony tannate remains on the fibre and acts as a mordant.

Soluble dyestuffs may be divided into two groups: those which dye textile fibres without the addition of mordants, the "substantive" dyestuffs, and those for which the use of mordants is essential, the "adjective" dyestuffs. The name "direct" or "substantive" dyestuffs has been reserved for dyestuffs which dye cotton and vegetable fibres without the use of a mordant. Whilst the dyeing of mordanted fibres is undoubtedly due to a chemical combination, the dyeing of the same fibres by means of substantive dyestuffs is a much more complex phenomenon. In this case, the physical phenomena of adhesion, capillarity, absorption and contact electrification, are to be taken into account in addition to the chemical phenomenon of combination between the dyestuff and the fibre.

With regard to insoluble dyestuffs, their use necessitates special methods which will be described when they are being considered. (See *Indigo, Sulphur colours, Aniline black.*)

The conditions which must be satisfied before a coloured substance will act as a dyestuff will now be considered. If the various dyestuffs which are soluble in water are examined, it will be found that they are all of the nature of salts; some are produced by the combination of an organic base with a mineral, or sometimes an organic, acid; others consist of a coloured organic acid combined with inorganic bases. The first-named are called "basic dyestuffs," the latter are termed "acid dyestuffs." In all dyestuffs one or other of these two characters is invariably more or less pronounced, and as a general rule it may be said that the tinctorial properties of a dyestuff will be the greater the more decided the acid or basic character. On the other hand a neutral compound, in which these two tendencies are balanced, will be a dyestuff of inferior character. Hence, if suitable groups are introduced into a coloured molecule, that is a chromogen, in order to give it an acid or basic character, the product may be expected to be a dyestuff. This has been found to be the case, and Witt has given such groups the name "auxochromes." Briefly: *The introduction of a chromophore into an organic molecule yields a coloured compound, a chromogen, and this will yield a dyestuff if suitably chosen auxochromes are introduced into certain positions in its molecule.*

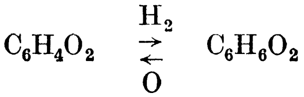
The auxochromes are groups which are capable of salt-formation, such as OH, SO_3H, $COOH$, which are acidic, and NH_2, NHR, NR_2, which are basic. Of these auxochromes, the $COOH$ and SO_3H groups introduced into a chromogen generally give it tinctorial properties without altering its shade. It has, however, been shown by Friedländer that the SO_3H group causes a great change in the shade of Indigoid dyestuffs if present in a certain position. On the other hand, the presence of the acidic OH group, or of the basic NH_2, NR_2 groups, has a very decided effect on both the tinctorial properties and on the shades of the product.

After what has been noted above, it does not seem impossible that textile fibres should also have a certain affinity for organic substances which are not coloured; in other words, it is possible to imagine that colourless substances might just as well be fixed on the fibre by "colourless dyeing." It has actually been found that cotton and vegetable fibres possess a very decided affinity for tannin, and also for the anilide of β-oxynaphthoic acid; on immersion in a warm, dilute solution of chromotropic acid, wool absorbs this compound as it would a dyestuff.

Chromophores.

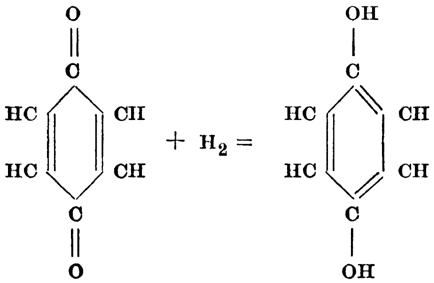
The chromophores are very numerous, and have a more or less pronounced effect on the colour. They are almost all unsaturated groups and consequently polyvalent; only the nitro-group, NO_2, is monovalent, and reduction completely destroys it without giving a leuco-compound.

One of the commonest chromophores is the carbonyl group, CO, present in quinone. Quinone, $C_6H_4O_2$, is a yellow compound which on reduction gives the colourless hydroquinone, $C_6H_6O_2$; the reaction is a reversible one, hydroquinone yielding quinone on oxidation in acid solution:



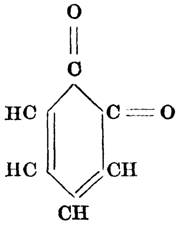
$$C_6H_4O_2 \underset{O}{\overset{H_2}{\rightleftarrows}} C_6H_6O_2$$

These reactions are supposed to be accompanied by a change in the linking of the atoms, expressed by:

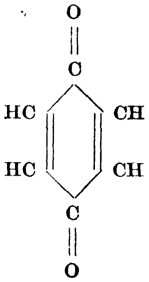


Thus hydroquinone is the "leuco-derivative" of quinone. An attempt has been made to classify the reduction of dyestuffs to leuco-compounds, and their production again on oxidation of the leuco-compounds, according to a method similar to the above example. That is to say, a group identical with or very similar to that in quinone is supposed to be present in coloured molecules. Two types of quinones are known: *ortho*-quinones and *para*-

quinones, dyestuffs being termed *ortho*-quinonoid or *para*-quinonoid, according to the grouping which is present.



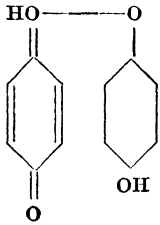
o-Benzoquinone.



p-Benzoquinone.

The Quinonoid theory of dyestuffs was suggested by Nietzki, but was first applied to coloured organic substances by Armstrong. It has the advantage of illustrating clearly the difference between the structure of a dyestuff and that of its leuco-derivative; it also illustrates the unsaturated character of the chromophores, and the influence exerted by the position occupied by the auxochromes in the molecule, these being generally *ortho* or *para*.

The recent researches of Willstätter, however, have shown that certain dyestuffs owe their colour to the combination of the quinonoid molecule with its reduction product, and hence belong to the "quinhydrones." Quinhydrone is the product obtained by the addition of one molecule of quinone to one of hydroquinone; it is highly coloured, and, admitting the tetravalence of oxygen, may be represented by the formula:



(Richter, *Ber.*, 1910, **43**, 3603).

The various dyestuffs have been classified according to the chromophore present :

Chap. X. Nitro-dyestuffs.
,, XI. Nitroso-dyestuffs or Quinone-oximes.
,, XII. Azo-dyestuffs.
,, XIII. Hydrazones.
,, XIV. Stilbene dyestuffs.
,, XV. Diphenylmethane dyestuffs.
,, XVI. Triphenylmethane dyestuffs.
,, XVII. Xanthene dyestuffs.
,, XVIII. Acridine dyestuffs.
,, XIX. Anthracene dyestuffs.
,, XX. Quinone-imide dyestuffs (Indamines, Indophenols, Oxazines, Thiazines, Azines).
,, XXI. Indigo and indigoid dyestuffs.
,, XXII. Thiazol dyestuffs.
,, XXIII. Sulphur dyestuffs.
,, XXIV. Aniline black.

CHAPTER X.

NITRO-DYESTUFFS.

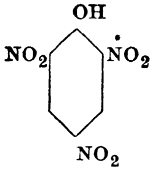
THE nitro-dyestuffs contain the chromophore NO_2; the mononitro-derivatives of the hydrocarbons are colourless or slightly coloured, but the intensity of the colour increases with the number of nitro-groups introduced. In order to convert these chromogens into dyestuffs, it is necessary to introduce auxochrome groups. The character of the groups to be introduced is readily decided by the following considerations.

The nitro-chromophore gives an acid character to molecules in which it is present, and it has been seen that the tinctorial properties of a dyestuff will be better the more pronounced its acid or basic character. Hence, it is preferable to introduce auxochromes such as OH, SO_3H, whose acid character will then be added to the effect of the chromophore itself. On the other hand, basic auxochromes, such as NH_2, NHR, NR_2, will have their influence opposed by the acidity of the NO_2 group, and the tinctorial power of the product will be diminished. In this case it is necessary to increase the acidity by introducing a sufficient number of nitro-groups. It is for this reason that the majority of the nitro-dyestuffs are nitro-derivatives of the phenols or naphthols, or their sulphonic acids. The mono-nitrophenols give coloured salts, but they do not behave as dyestuffs, tinctorial powers only appearing with the di- or tri-nitrophenols. The relative position of the OH and NO_2 groups has a great influence, being most favourable when they are in *ortho-* or *para*-position; thus these dyestuffs may be considered as derivatives of *ortho-* or *para*-nitrophenol.

Victoria orange is a mixture of the potassium salts of dinitro-*o*-cresol and dinitro-*p*-cresol, obtained by the nitration of the cresol sulphonic acids. It dyes wool and silk a yellow colour.

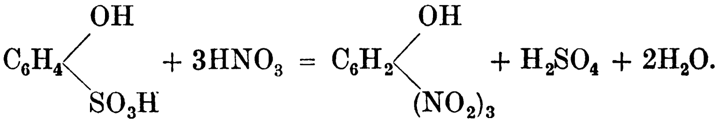
Flavaurine or *New yellow* is the 1 : 2 : 6 : 4-dinitrophenol sulphonic acid, obtained by the nitration of *o*-nitrophenol *p*-sulphonic acid.

Picric acid is the 1 : 2 : 4 : 6-trinitrophenol:



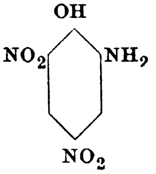
It is the oldest of the artificial dyestuffs. It is obtained by treating a large number of organic substances, such as hide, skin, aloes, etc., with nitric acid. Woulfe prepared it in 1771 by the action of nitric acid on Indigo, and noticed that it had the property of dyeing silk a yellow colour. In 1799, Welter prepared it in a crystalline condition by the action of nitric acid on wool and on silk. Its very bitter taste caused it to be given the name "Welter's bitter yellow" or "picric acid" (from πικρος, meaning "bitter"). Laurent showed in 1842 that it is a trinitrophenol.

Picric acid may be prepared by the nitration of phenol and of a large number of its derivatives, such as *o*-nitrophenol, *p*-nitrophenol, dinitrophenol, and phenolsulphonic acid. The last mentioned has been employed by Schmidt and Glutz (*Mon. Sci.*, 1878, 1115), and is used commercially. The apparatus employed is similar to that used in the manufacture of nitrobenzene. Equal parts of phenol and sulphuric acid (SP. GR. 1·84) are mixed and heated to 100°. Under these conditions, phenol *p*-sulphonic acid is produced, and to this an excess of nitric acid is added with constant stirring. On cooling, the product forms a crystalline mass, which is separated, washed with water, and purified by recrystallisation. The action of nitric acid on phenol sulphonic acid is as follows :



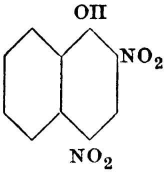
$$C_6H_4\left\langle\begin{matrix}OH\\SO_3H\end{matrix}\right. + 3HNO_3 = C_6H_2\left\langle\begin{matrix}OH\\(NO_2)_3\end{matrix}\right. + H_2SO_4 + 2H_2O.$$

Picric acid crystallises in yellow plates of M.P. 122·5°, which are slightly soluble in cold water, but are more soluble in warm water and in alcohol. It forms coloured salts, the potassium salt being remarkable for its slight solubility in water. On treatment with alkaline reducing agents, such as ammonium sulphide, picric acid readily gives picramic acid, dinitro-amidophenol, which is used for the manufacture of certain azo-dyestuffs.



On treating potassium picrate with a solution of potassium cyanide, an intense red coloration is produced, due to the formation of isopurpuric acid. The ammonium salt of this acid was for some time used under the name of *Grenat soluble* for dyeing wool and silk a reddish brown. Picric acid may also be used for dyeing wool and silk yellow, but the shades obtained are not very fast to washing or to light Hence, picric acid is rarely used except in small quantities in admixture with other dyestuffs. On the other hand, its explosive properties make it an important raw material for the preparation of explosives. It is introduced into shells in the molten state, being termed "melinite"; "lyddite," "roburite," etc., are similar products.

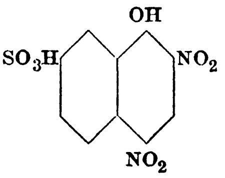
Martius yellow, or dinitro-α-naphthol,



This dyestuff has also been called *Manchester yellow*, *Naphthylamine yellow*, or *Naphthalene yellow*, and was prepared commercially by Martius (*E.P.* 2785 (1864)), by treating α-naphthol or α-diazonaphthalene with nitric acid. It is also formed on the nitration of α-naphthylamine, nitrosonaphthols, and 1 : 2 : 4-naphthol disulphonic acid. This last-mentioned process is the method used in commerce (Darmstätter and Wichelhaus, *Ann.*, 1869, **152**, 299); the sulphonic groups are replaced by nitro-groups, giving the dinitro-α-naphthol.

Martius yellow crystallises in yellow needles of M.P. 138°. Its alkali salts are very stable, as it is a strong acid, even decomposing carbonates. It dyes wool and silk a bright yellow, which is not very fast to washing or to heat on account of its volatility. Its main use was in the colouring of edible pastes (vermicelli and macaroni), for which purpose *Naphthol yellow S* is now used.

Naphthol yellow S.



This dyestuff is also known as *Acid yellow*, *Citronine A*, etc. It is the sulphonated derivative of Martius yellow, and is obtained by the nitration of α-naphthol trisulphonic acid (1 : 2 : 4 : 7), when the sulphonic groups occupying positions 2 and 4 are replaced by nitro groups (B.A.S.F., *D.R.P.* 10,785, Dec. 28th, 1879). Another method of preparation is to sulphonate α-naphthol in such a manner as to give a mixture of the 1 : 2 : 7 and 1 : 4 : 7 naphthol disulphonic acids, which is then treated with nitrous and nitric acid (*D.R.P.* 20,716). The salts of Naphthol yellow S have been described by Knecht and Hibbert (*Ber.*, 1904, **37**, 3475). The commercial product is the potassium salt, which dyes wool and silk a brilliant yellow.

Aurantia is the hexanitro-derivative of diphenylamine :

$$(NO_2)_3C_6H_2—NH—C_6H_2(NO_2)_3.$$

Hexanitro-diphenylamine was discovered in 1873 by Kopp, who called it "Kaisergelb." It crystallises from acetic acid in lemon yellow prisms of M.P. 238°.

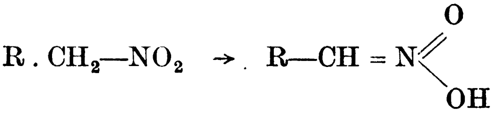
The basic character of the diphenylamine is overcome by the acidity of the six nitro-groups present in the molecule, and hence hexanitro-diphenylamine behaves as an acid in which the hydrogen attached to nitrogen is replaceable by metals to form salts. Its salts are highly coloured. The commercial product is the ammonium salt, which crystallises in brownish red needles. Aurantia dyes wool and silk an orange colour, but has not been used since the discovery of the azo-dyestuffs.

Constitution of the Nitro-Dyestuffs.

It is known that the introduction of a nitro-group into a hydrocarbon molecule gives acid properties to the atoms of hydrogen attached to the same carbon atom. It is for this reason that nitromethane, nitroethane, phenylnitromethane, etc., dissolve in alkalies to form true salts. V. Meyer first stated that in these salts the metallic atom is substituted for hydrogen and hence directly linked to carbon :

$$CH_3—CH_2—NO_2 \rightarrow CH_3—CHNa—NO_2.$$

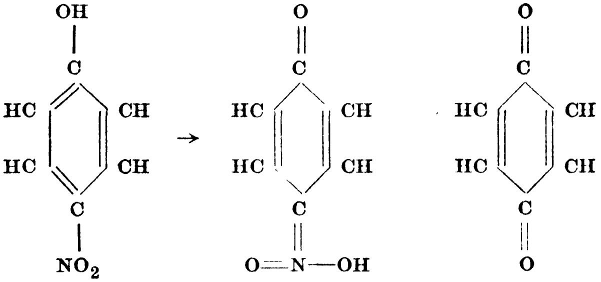
The study of these derivatives showed that the alkali salts are related to an isomeric form of the nitro-compound, which is formed when salt-formation occurs. These tautomeric forms were called "*iso*-nitro-" compounds, and a certain number of *iso*-nitro-compounds have since been isolated whose constitution is expressed by:



$$R\,.\,CH_2\text{—}NO_2 \rightarrow R\text{—}CH=N\Big<^{O}_{OH}$$

Nitro. *Iso*-nitro.

The nitrophenols form two series of salts with alkalies, a colourless series and a coloured series. Hantzsch (*Ber.*, 1906, **39**, 1084, 3072) has explained this fact by regarding the coloured salts as derivatives of *iso*-nitro-compounds, called "*aci*-nitrophenols."

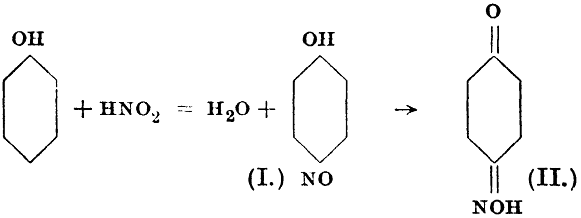


As will be seen from the third formula (quinone), *aci*-nitrophenols are derivatives of quinone. The same holds good for all the dyestuffs of this group.

CHAPTER XI.

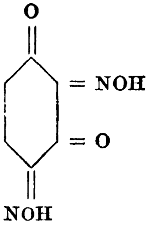
NITROSO-DYESTUFFS OR QUINONE-OXIMES.

WHEN nascent nitrous acid acts on phenol, a nitroso-derivative is formed in which the nitroso-group occupies the *para-* or *ortho*-position :



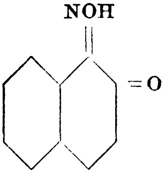
The nitrosophenols are also obtained by the action of hydroxylamine on the quinones, and hence nitrosophenols may be considered as oximes of the quinones ; hence the name quinone-oximes. The true nitrosophenol (I.) can change immediately into the oxime of quinone (II.). The fact that nitrosophenols are converted into dioximes by hydroxylamine, constitutes another proof in favour of formula II. There are, however, *p*-quinone oximes and *o*-quinone oximes ; these are coloured substances the salts of which possess an even more intense colour. The *o*-quinone oximes have the property of forming insoluble lakes with metallic oxides, *i.e.* they are dyestuffs which dye on metallic mordants, the commonest mordant being ferric hydroxide, which gives intense green shades. The most important dyestuffs of this group are :

Dinitroso-resorcinol, obtained by treating an aqueous solution of resorcinol with nascent nitrous acid. It crystallises in brown plates of M.P. 115°, and has the following constitution :

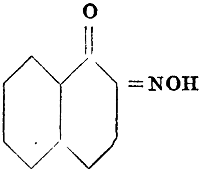


It gives olive green shades on iron mordant, and comes into commerce under the names *Fast green, Russian green, Alsace green.*

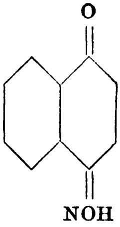
Nitrosonaphthols are produced on treating naphthols with nascent nitrous acid : β-naphthol gives α-nitroso-β-naphthol (I.) ; α-naphthol gives two nitroso-compounds, β-nitroso-α-naphthol (II.) and α-nitroso-α-naphthol (III.).



(I.)



(II.)



(III.)

Compound I. is called *Gambin G* or *Y*, and compound II. is known as *Gambin R* ; they are commercial in the form of pastes, and both give green shades on iron mordant. On treatment with nitrite, 2 : 7-dihydroxy-naphthalene gives *Dioxin. Naphthol green* is obtained in a similar manner from Schäffer's β-naphthol mono-sulphonic acid.

p-Nitrosodimethylaniline, $NO—C_6H_4—N(CH_3)_2$.

Tertiary amines also react with nascent nitrous acid to give nitroso-derivatives, which are not dyestuffs, but are important intermediate products. Nitrosodimethylaniline is prepared as follows: 200 grms. of dimethylaniline are dissolved in 500 cc. of hydrochloric acid diluted with 500 or 600 cc. of water, and a concentrated aqueous solution of 115 grm. of sodium nitrite added slowly from a tap-funnel immersed in the liquid. The vessel in which the reaction is carried out is immersed in a freezing-mixture of ice and salt, and it is advisable that the temperature should not rise above 5 to 10°. Nitrosodimethylaniline hydrochloride is precipitated in small yellow needles, which are separated, washed with a small amount of water, and dried at a low temperature. For almost all purposes, the hydrochloride may be used instead of the free base, which is obtained on decomposing with an alkali, and forms green crystals of M.P. 85°.

Dimethyl-p-phenylenediamine, $NH_2—C_6H_4—N(CH_3)_2$.

The hydrochloride of the above compound may be used directly for the preparation of this important diamine. Fifty grm. of nitrosodimethylaniline hydrochloride are added to a cooled mixture of 150 cc. of concentrated hydrochloric acid and 50 grm. of granulated tin. The nitrosodimethylaniline dissolves, and the solution, which is slightly coloured, or even colourless if the temperature has been kept sufficiently low, is left for twenty-four hours. The stannichloride of the diamine is precipitated in dense crystals, which are separated, decomposed with concentrated caustic soda, and allowed to cool. The diamine separates as an oil which rapidly turns brown on exposure to air; it is extracted with benzene, the benzene solution separated, washed, and concentrated. The residue is then distilled *in vacuo*, and yields dimethyl-*p*-phenylenediamine as a colourless liquid which solidifies to a white crystalline solid of M.P. 41°, B.P. 262-3°.

CHAPTER XII.

AZO-DYESTUFFS.

THE azo-compounds contain the chromophore

$$—N=N—.$$

On treating the salt of a primary aromatic amine with nascent nitrous acid, a "diazo-compound" is formed, as follows:

$$R—NH_2.HCl + HNO_2 = 2H_2O + R—N=N—Cl.$$

The diazo-compounds are generally colourless; they combine with amines and phenols derived from benzene and naphthalene or their substitution products (nitro-, sulphonated, halogenated, etc., compounds), giving rise to numerous intense dyestuffs of various shades.

Historical. The action of nitrous acid on primary amines is called "diazotisation" and was discovered by P. Griess, who showed, in 1864, that diazo-compounds combine with amines. Later it was shown by Kekulé and Hidegh that they also combine with phenols. Before Griess had recognised the wide application of his method, amidoazobenzene, *Aniline yellow*, had already been prepared by the action of nitrous acid on aniline (1859). In 1865 Martius applied the diazo-reaction to diamines, particularly *m*-phenylenediamine, which gives a brown dyestuff, *Bismarck brown*, which has been prepared commercially since 1866. In 1875, Caro and Witt combined the diazo-compounds of primary amines with diamines, and obtained the *Chrysoidines*. About the same time, Roussin in France, and Griess and Witt in

England, prepared *Orange I.* and *II.*, in which the naphthols, which were then much more difficult to obtain, were used for the first time.

From this time the number and variety of azo-dyestuffs rapidly increased; the sulphonic acids of various amines were diazotised and combined with the numerous isomeric sulphonic acids of the naphthols and naphthylamines. Thus, in 1878, there appeared the *Ponceaux* of the Höchst Farbwerke (Meister, Lucius and Brüning), the *Orchil substitutes* of Roussin and Poirrier, etc.

Azo-dyestuffs which contain an amido-group may be diazotised to yield new dyestuffs containing two $—N=N—$ chromophores; these are called "disazo-compounds," the first of which, *Biebrich scarlet*, was prepared by Nietzki in 1879. In this manner the possible number of compounds was considerably increased. A notable discovery was made in 1884 by Boettiger, who tetrazotised benzidine (produced by the molecular change of hydrazobenzene in presence of acid:

$$C_6H_5—NH—NH—C_6H_5 \rightarrow NH_2.C_6H_4—C_6H_4.NH_2),$$

and combined with naphthionic acid, when a red dyestuff was obtained which dyed cotton directly, whereas all the azo-dyestuffs known previously only dyed animal fibres. This dyestuff, called *Congo red*, was prepared by the Berlin Aktiengesellschaft. Benzidine and its various homologues yield innumerable dyestuffs on combining with naphthol sulphonic acids. In 1887 Green discovered a new series of substantive dyestuffs derived from *Primuline*. Certain of these dyestuffs may even be prepared directly on the fibre. This resulted in the introduction of a new practical process in dyeing, that of the "Ingrain" dyestuffs, which led to the direct production of insoluble azo-dyestuffs on the fibre, such as *Paranitraniline red*, *α-Naphthylamine bordeaux*, etc. By still further complicating the molecule of the azo-compound, trisazo- and polyazo-compounds, containing the chromophore three or four times, are obtained. Brown and black dyestuffs for wool and for cotton have also been prepared.

At present these complicated methods are being abandoned and the monoazo-derivatives of substituted *o*-amidophenols are again being largely used ; these yield mordant dyestuffs, which are applied in a particular manner. The wool is dyed as usual, and then treated with a solution of potassium dichromate, when the shade undergoes a remarkable change ; it darkens, and becomes very fast ; very resistant blacks may be obtained in this way. They are termed " chrome-developed " or " after-chromed " Azo-dyestuffs.

The azo-dyestuffs known at present number many thousands, but they only represent a small fraction of the number possible according to theory, Bülow having calculated that about 3,160,000 may exist.

Preparation of Azo-compounds.

The production of azo-compounds includes several operations :

1. The *diazotisation* of the primary amine ;
2. The combination of the diazo-compound with an amine or a phenol, often called *coupling* ;
3. The *precipitation* of the dyestuff from the solution in which it has been formed.

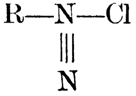
The conditions under which the various operations should be carried out were described in the English patent taken out by Griess on October 4th, 1877 (identical with *D.R.P.* 3224).

1. *Diazotisation.*

In this process the salt of an amine is converted into the corresponding salt of the diazo-compound by the action of nascent nitrous acid, produced by the decomposition of sodium nitrite with dilute hydrochloric acid :

$$R—NH_2 . HCl + NaNO_2 + HCl = NaCl + 2H_2O + R . N = N . Cl.$$

Compounds which are true salts contain pentavalent nitrogen, and are called "diazonium salts":



$$\begin{array}{c} \mathrm{R—\overset{}{N}—Cl} \\ \equiv \\ \mathrm{N} \end{array}$$

This reaction is generally quantitative and rapid, often instantaneous. When a simple amine, such as aniline or *o*-toluidine, is being diazotised, it is essential to add a large excess of mineral acid. If this precaution is not taken, a secondary reaction occurs, due to the combination of the diazo-compound produced with a portion of the original amine. In the case of aniline, diazoamidobenzene would be formed, thus:

$$C_6H_5 . N = N . Cl + H_2N . C_6H_5 \\ = HCl + C_6H_5 . N = N . NH . C_6H_5.$$

The presence of this compound is shown by the yellow colour of the solution and the formation of a yellow precipitate. This secondary reaction is avoided by keeping the solution sufficiently acid, by adding three or four equivalents of hydrochloric acid instead of the two theoretically necessary.

Diazotisation should take place at a low temperature, about 0°, as diazo-compounds are more or less decomposed on heating their solutions. Certain diazo-compounds decompose even at several degrees above 0°; others, on the other hand, are stable up to about 100° (*e.g.* the diazo-compound of Primuline). The decomposition takes place with liberation of nitrogen, and phenol is produced:

$$C_6H_5 . N = N . Cl + H_2O = HCl + N_2 + C_6H_5OH.$$

Hence this constitutes a method for preparing a phenol from an amine.

In actual practice, the dilute solution of the amine to be diazotised in the necessary amount of mineral acid (two, three or four equivalents) is poured into a tank fitted with a mechanical stirrer (Fig. 4). This solution is cooled with ice, or in more perfect plants by the circulation of brine, cooled to −10° by an ice-machine, in a coil immersed in the tank. When the temperature is low enough, the sodium nitrite solution is run in slowly, the process being followed by means of starch-iodide paper (zinc iodide is preferable to potassium iodide, as its antiseptic properties prevent the alteration of the starch). Excess of nitrite is detected by the production of a deep violet colour when a drop of the solution is placed on the paper.

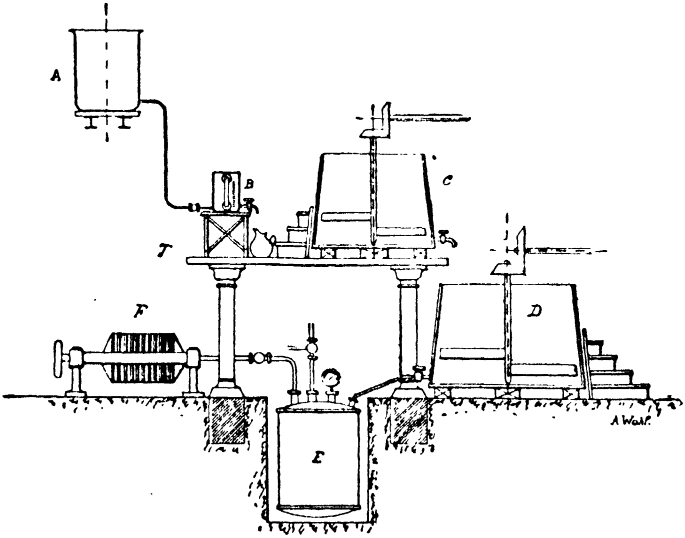


FIG. 4.

A. Sodium nitrite. *B*. Gauge for measuring the nitrite.
C. Diazotising vessel. *D*. Vessel for coupling.
E. Compressor. *F*. Filter press.

When amines, of which the salts are only slightly soluble, are to be diazotised, such as naphthylamines, benzidine, etc., they are finely powdered, and then suspended in dilute acid; addition of nitrous acid causes their solution, owing to the formation of the diazo-compound.

2. *Coupling.*

This process is carried out somewhat differently according to whether it involves combination with a phenol, a naphthol, or one of their sulphonic acids, or with an amine. In the first case (phenols, naphthols, and their sulphonic acids) coupling is carried out in alkaline solution. For this purpose the product is dissolved in an excess of caustic soda or sodium carbonate, and the diazo-solution prepared as above is added, the excess of alkali being sufficient to keep the liquid alkaline. In the case of an amine, it is dissolved in dilute acid, and coupling is effected in neutral or acid solution ; amido-sulphonic acids are dissolved in alkalies, and the reaction is carried out in neutral or acetic acid solution.

In commerce, the product to be coupled is dissolved in a suitable manner, and its solution placed in a vat situated at a lower level than that which contains the diazo-solution, to which it can be added. The vat is fitted with a mechanical stirrer which stirs the liquid throughout the process. The formation of the dyestuff commences immediately at a more or less rapid rate, and is often accompanied by the evolution of a considerable amount of heat. The mixture is allowed to stand for some time, and the reaction then completed by warming gently.

3. *Precipitation of the Dyestuff.*

The dyestuff does not often separate of itself, but is precipitated by addition of salt, the method recommended by Griess. Sometimes, when the free acid of the dyestuff is insoluble in water, it is precipitated by addition of mineral acid. These methods are general, and may be applied in all cases. In commerce, common salt is added to the warm solution of the dyestuff, and is dissolved rapidly by stirring ; the dyestuff soon separates in a more or less dense granular powder. The progress of the reaction is followed by spotting the liquid on filter-paper, when the precipitate is surrounded by a more or less coloured ring; when the intensity of this colour no longer decreases, the addition of salt is stopped. The stirring is continued until the liquid is quite cold, and then the liquid is treated in a filter-press as for the separation of the sulphonic acids (see p. 27). The cakes obtained are then placed in a drying-oven. These ovens are brick chambers, heated by steam coils; in them are placed the trays containing the dyestuff to be dried. This method of drying is rather long, and the use of vacuum ovens is now preferred. The trays containing the precipitate are placed in a pile in a horizontal cylinder, which can be hermetically sealed. Steam pipes arranged at the bottom may be used for raising the temperature of the inside of the vessel, which is evacuated by means of a pump.

After drying, the dyestuff is powdered in mills, of which there are many types. One of the simplest consists of a horizontal cast-iron cylinder, which can be rotated round its axis, and in which the dyestuff to be ground is placed. After rotating for one or two days, the dyestuff is reduced to an mpalpable powder. The final process consists in bringing the dyestuff to the "commercial standard," that is to say, the concentration desired for the market. For this purpose, comparative dye-trials are made, and the necessary dilution is made by adding the necessary amount of salt, sodium sulphate, dextrine, etc.

CLASSIFICATION OF AZO-DYESTUFFS.

According to whether an azo-compound contains one or more $—N=N—$ chromphores, it is called a monoazo-, disazo-, trisazo- or polyazo-compound.

MONOAZO-DYESTUFFS.

The simplest monoazo-compound is azobenzene:

$$C_6H_5—N=N—C_6H_5.$$

This is a red substance, but has no dyeing properties. It is a chromogen of great importance, and it is only necessary to introduce salt-forming groups (auxochromes) to obtain dyestuffs. Its sulphonic acid is a weak dyestuff, possessing a slight affinity for wool. The amido-, alkylamido- and hydroxy-derivatives of azobenzene are dyestuffs; they are prepared by the action of any diazo-compound on an amido- or hydroxy-compound. The monoazo-dyestuffs may hence be represented by the general formula:

$$X—N=N—Y$$

in which X represents the radicle of the amine used for the preparation of the diazo-compound and Y the radicle of the amine or phenol which has been coupled with this diazo-compound.

Properties. The monoazo-compounds have an acid or basic reaction according to the nature of the auxochromes present; those derived from phenols or their sulphonic acids are soluble in alkalies. The alkaline solution often has a different colour from that of the original substance; this property is applied in the use of indicators, *e.g. Methyl orange.* Concentrated sulphuric acid dissolves azo-compounds, yielding coloured solutions. Concentrated nitric acid decomposes azo-compounds, and this has been used to ascertain their constitution (Schmidt, *Ber.*, 1905, 38, 3201). Thus:

$$SO_3H \,.\, C_6H_4 \,.\, N=N \,.\, C_6H_4 \,.\, N(CH_3)_2 + 2HNO_3$$
$$= \underbrace{SO_3 \,.\, C_6H_4 \,.\, N=N}_{} + (NO_2)_2C_6H_3 \,.\, N(CH_3)_2 + 2H_2O.$$

Chlorine, bromine and hypochlorous acid also decompose azo-dyestuffs. In aqueous solution hydroxyazobenzene gives with chlorine 2 : 4 : 6-trichlorphenol and benzene diazonium chloride (Schmidt, *J. prakt. Chem.*, **89**, 239).

One of the most important reactions is that of reducing agents, which completely destroy the dyestuff, as follows :

$$X—N=N—Y + 4H = X.NH_2 + NH_2.Y.$$

The amine from which the diazo-compound was prepared is regenerated, and the compound Y, which was coupled with the diazo-compound, is converted into an amido-derivative. This reaction may serve for the determination of the composition or even the constitution of azo-dyestuffs (Witt, *Ber.*, 1886, **19**, 1719; 1888, **21**, 3471). The most convenient reducing agents are: zinc and hydrochloric acid, zinc and ammonia, zinc and caustic soda, tin and hydrochloric acid, stannous chloride, titanous chloride (Knecht and Hibbert, *Ber.*, 1905, **38**, 3318), and sodium hydrosulphite (Grandmougin, *Ber.*, 1906, **39**, 2494, 3561, 3929).

The monoazo-dyestuffs will be considered in two groups :

1. Those formed by the combination of the diazo-compound of any amine, X.NH_2, with a hydroxy- or amido-derivative of a benzene hydrocarbon. In this case Y will represent an amine, a phenol, or one of their derivatives.

2. Those formed by the combination of any diazotised amine with a hydroxy- or amido-derivative of naphthalene; in this case Y will represent a naphthylamine, a naphthol, or one of their sulphonic acid or other derivatives.

When Y is a hydroxy-compound, the azo-compound is called a hydroxyazo-compound; when Y is an amine, the azo-compound is called an amidoazo-compound.

Monoazo Derivatives of Benzene.

Constitution. The combination of a diazo-compound with an amine is governed by a certain number of rules :

I. Coupling takes place in the *para*-position to the auxochrome groups, OH, NH_2, NR_2, when this is free.

II. If the *para*-position is occupied, coupling occurs in the *ortho*-position.

III. If both *ortho*- and *para*-positions are occupied, coupling does not occur.

Note.—These rules have several exceptions. Cases are known in which the *para*-position is occupied, but coupling will not take place, although the *ortho*-position is free. Thus, dimethyl-*p*-toluidine, dimethyl-*p*-bromaniline, and dimethylsulphanilic acid do not combine with diazo-compounds (Scharwin and Kaljanow, *Ber.*, 1908, **41**, 2058). In other cases, when the *para*-position is occupied by an unstable group, this group may be eliminated during coupling, which then takes place in *para*-position. For example, *p*-hydroxybenzoic acid, dimethyl-*p*-amidobenzoic acid, and even tetramethyldiamidodiphenylmethane, combine in *para*-position with diazo-compounds, with elimination of carbon dioxide and formic acid (Limpricht and Fitze, *Ann.*, 1891, **263**, 236).

Hydroxyazo-compounds.

The simplest compound of this class is hydroxyazobenzene :

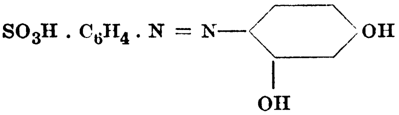
$$C_6H_5 . N = N . C_6H_4 . OH.$$

It is prepared by combining a diazonium salt with phenol in alkaline solution, or by condensing aniline with nitrosophenol. It crystallises in orange needles of M.P. 151°. On treatment with fuming sulphuric acid, it gives a monosulphonic acid :

$$SO_3H.C_6H_4 . N = N . C_6H_4.OH,$$

which may also be obtained by coupling diazo-sulphanilic acid with phenol. Its sodium salt is called *Tropæolin Y*, which dyes wool a rather dull brownish yellow.

Dihydroxyazobenzenes. Symmetrical dihydroxyazobenzene is known, being obtained by oxidation of the corresponding hydrazo-compound, but it is not of any importance. The asymmetrical dihydroxyazobenzene is obtained by combining a diazonium salt with resorcinol; fuming sulphuric acid converts it into the *p*-sulphonic acid :



which is also obtained by coupling diazo-sulphanilic acid with resorcinol. The sodium salt is called *Tropæolin O* or *Resorcin yellow*. It dyes wool a reddish yellow shade.

Amidoazo-compounds.

AMIDOAZOBENZENE, the first member of this series, is obtained by a peculiar reaction, namely the molecular change of diazoamidobenzene in presence of an excess of aniline. One equivalent of aniline hydrochloride is dissolved in five or six equivalents of aniline ; to this mixture, warmed to about 30-40°, is added a concentrated solution of a little more than one equivalent of sodium nitrite. After standing for two hours at 40°, and then for twelve hours at the ordinary temperature, an excess of hydrochloric acid is added. Amidoazobenzene hydrochloride is precipitated in black needles. It was used under the name of *Aniline yellow* from 1861-3 for dyeing wool. It is now used as the raw material for the preparation of *p*-phenylenediamine, which is obtained by reduction (see Schultz, *Chemie des Steinkohlenteers*, i., 87) :

$$C_6H_5 . N=N . C_6H_4 . NH_2 + 4H = C_6H_5NH_2 + C_6H_4(NH_2)_2.$$

On treatment with fuming sulphuric acid, this compound gives a mixture of the mono- and di-sulphonic acids, the sodium salts of which are known as *Acid yellow G*, *New yellow*, or *Fast yellow* (for details see Würtz, *Dictionnaire de chimie*, article on "Colorantes (matières)," p. 1313 in 2nd supplement).

Dimethylamidoazobenzene,

$$C_6H_5—N=N—C_6H_4—N(CH_3)_2,$$

is obtained by combining a diazonium salt with dimethylaniline ; the free base crystallises in yellow plates, and is used for colouring butter ; the hydrochloride forms violet needles. The sulphonic acid, produced by the combination of diazosulphanilic acid with dimethylaniline, is called *Helianthin.* Its alkaline salts are called *Orange III.* [P.], *Tropæolin D*, and *Methyl orange.* They dye wool yellow, and are used as indicators.

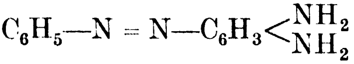
Phenylamidoazobenzene,

$$C_6H_5—N=N—C_6H_4—NH—C_6H_5.$$

The sulphonic acid of this compound was discovered almost simultaneously by Witt, Griess and Roussin (1876-7), by coupling diazo-sulphanilic acid with diphenylamine. The alkali salts have the names *Orange IV.* [P.], *Diphenylamine orange, New yellow*, etc. In the same manner, diazometanilic acid yields *Metanil yellow*, the shade of which is more yellow. By nitrating *Diphenylamine orange*, Knecht has obtained the nitro-derivatives : *Azo yellow, Azoflavine S, Indian yellow, Citronine*, etc.

DIAMIDOAZOBENZENE. Symmetrical and asymmetrical derivatives are known, the latter being the more important.

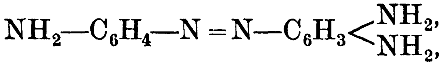
Chrysoïdine,



$$C_6H_5—N=N—C_6H_3<\begin{matrix}NH_2\\NH_2\end{matrix}$$

was discovered by Caro and Witt in 1875-6 by coupling diazobenzene chloride with *m*-phenylenediamine. The free base crystallises in yellow needles, and forms two series of salts, of which those containing one molecule of acid are stable. Commercial *Chrysoïdine* is the hydrochloride, which forms octahedral crystals, and dyes wool, silk, and cotton mordanted with tannin, orange shades.

TRIAMIDOAZOBENZENE,



$$NH_2—C_6H_4—N=N—C_6H_3<\begin{matrix}NH_2,\\NH_2,\end{matrix}$$

was first prepared by Martius in 1864 by treating *m*-phenylenediamine with nascent nitrous acid, and was manufactured in England by Dale in 1866. This reaction yields a mixture of triamidoazobenzene and a much larger amount of a disazo-compound (Täuber, *Ber.*, 1897, **30**, 2111, 2899; Möhlau and Meyer, *ibid.*, 2203) which forms the commercial product *Bismarck brown*, *Vesuvine*, *Phenylene brown*, or *Manchester brown*. It is a basic dyestuff, which gives brown shades on wool, leather, and cotton mordanted with tannin, and is still used. It has since been found (Täuber, *Ber.*, 1900, **33**, 2116) that nitrosophenylenediamine is also obtained on treating *m*-phenylenediamine with nitrous acid.

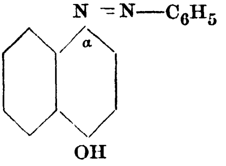
Monoazo Derivatives of Naphthalene.

Constitution. These dyestuffs are formed by the combination of any diazo-compound with a naphthol, a naphthylamine, or one of their derivatives. Here again this combination is governed by rules which are as follows :

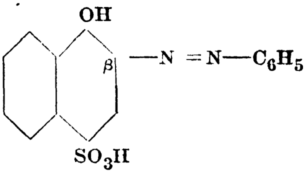
I. In the case of α-naphthol, α-naphthylamine and their sulphonic acids, coupling takes place in *para*-(α) position to the OH or NH_2 groups, providing this position and the adjacent β-position are both free. If either of these positions is occupied, coupling occurs in *ortho*-(β) position to the OH or NH_2 groups. In case this last-named position is itself also occupied, no coupling will occur. Examples of this are :

(*a*) Diazobenzene chloride combines with α-naphthol to give benzene azo α-naphthol (I.).

(*b*) Diazobenzene chloride unites with Neville-Winther's α-naphthol sulphonic acid to give the azo-compound (II.).

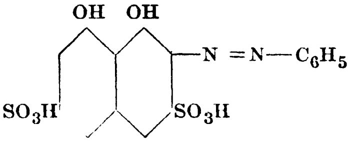


(I.)

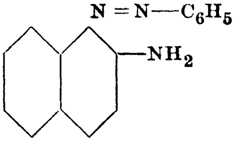


(II.)

(*c*) Diazobenzene chloride gives with chromotropic acid the dyestuff



II. In the case of β-naphthol, β-naphthylamine and their sulphonic acids, coupling occurs in the α-position adjacent to the OH or NH_2 group, and never in the β-position. If the adjacent α-position is not free, combination does not occur. Thus β-naphthylamine combined with diazobenzene chloride gives:



It follows that derivatives of α-naphthol and of α-naphthylamine can give rise to *para*-hydroxy- or *ortho*-amidoazo-compounds, according to whether the azo-group is placed in *para*- or *ortho*-position to the auxochromes; the derivatives of β-naphthylamine and β-naphthol will always be *ortho*-azo-compounds. The *ortho*-derivatives generally have greater tinctorial properties.

Hydroxyazo-compounds.

The azo-compounds which are formed by the combination of non-sulphonated diazo-compounds with naphthols are insoluble in water. Some have been used for colouring fats and soaps, and some may be fixed on the fibre by a special process. In order to obtain soluble dyestuffs, it is necessary to introduce into the molecule one or more sulphonic acid groups. Direct sulphonation gives mixtures of complex isomers, and it is preferable to proceed according to one of the following processes :

1. Combination of a diazo-sulphonic acid with a naphthol.
2. Combination of a diazo-compound with naphthol sulphonic acids.
3. Combination of a diazo-sulphonic acid with naphthol sulphonic acids.

Derivatives of α-naphthol.

DYESTUFF.	AMINE DIAZOTISED.	COUPLED WITH	SHADE ON WOOL.
Tropæolin 3O or *Orange I.*	Sulphanilic acid.	α-Naphthol.	Orange.
Tropæolin 4O or *Azococcine.*	Aniline.	N.W. acid.	Brick red.
Azococcine 2R.	Xylidine.	N.W. acid.	Red.
Soudan brown.	α-Naphthylamine.	α-Naphthol.	
Azorubine S.	Naphthionic acid.	N.W. acid.	Red.
Azoeosine.	o-Anisidine.	N.W. acid.	Reddish purple.

Certain insoluble azo-derivatives of β-naphthol have become of great importance ; they are *p*-nitrobenzene-azo-β-naphthol or *Paranitraniline red*, and naphthalene-azo-β-naphthol or *α-Naphthylamine bordeaux.* Dyeing with these insoluble dyestuffs is carried out by first impregnating (padding) the cotton with a solution of β-naphthol in caustic soda, and then, after drying, immersing the material in a solution of diazo-*p*-nitraniline or diazonaphthalene, when the dyestuff develops immediately. In place of β-naphthol, Naphthol AS. [Griesheim Elektron], the anilide of β-oxynaphthoic acid is now used to produce more brilliant shades of general fastness.

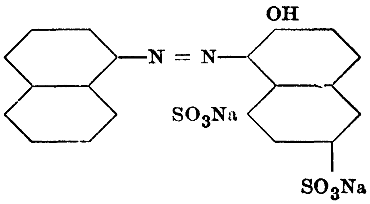
To obtain soluble products, the monosulphonic acid, crocein acid, and more frequently the disulphonic acids R and G are used. It is to be noted that the same diazo-compound gives dyestuffs of very different shades when combined with R acid or G acid, although these two derivatives only differ in the position of one sulphonic acid group (see p. 41). Generally, the shades obtained with R acid are more towards the violet portion of the spectrum; whilst G acid yields orange shades with diazo-compounds of the benzene series, R acid gives red shades. (This is the reason that these are called R and G acids, from the German words *Rot* (red) and *Gelb* (yellow)).

The dyestuffs so obtained are very numerous; to this group belong the *Ponceaux*, *Scarlets*, etc.

Derivatives of β-naphthol.

DYESTUFF.	AMINE DIAZOTISED.	COUPLED WITH	SHADE ON WOOL.
Ponceau 4GB [B.A.S.F.]. *Crocein orange*, *Brilliant orange*.	Aniline.	Schäffer's acid.	Orange.
Orange G [A.],[M.L.B.] [B.A.S.F.].	,,	G acid.	Orange.
Ponceau 2G [A.], [M.L.B.], [B.A.S.F.].	,,	R acid.	Reddish orange
Orange No. 3.	*m*-Nitraniline.	R acid.	Orange.
Ponceau G.	Toluidine.	G acid.	,,
Ponceau RT.	,,	R acid.	Orange.
Scarlet GR.	Xylidine.	Schäffer's acid.	Yellowish red.
Ponceau 2R [A.].	,,	R acid.	Red.
Ponceau G.	,,	G acid.	Orange.
Ponceau 3R [M.L.B.].	ψ-Cumidine.	R acid.	Red.
Bordeaux B [M.L.B.].	α-Naphthylamine.	,,	,,
Crystal Scarlet [C.].	α-Naphthylamine.	G acid.	,,
Orange II.	Sulphanilic acid.	β-Naphthol.	Orange.
Roccelline.	Naphthionic acid.	,,	Red.
Brilliant Ponceau.	,,	G acid.	,,
Azorubine 2B.	,,	R acid.	,,
Crocein 3BX [By.].	,,	Crocein acid.	,,

Preparation of Crystal Scarlet.

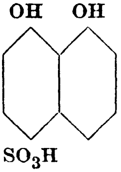


α-Naphthylamine may be diazotised by suspending it in dilute hydrochloric acid and adding a solution of sodium nitrite, but, if it is considered preferable to have the α-naphthylamine in solution before diazotising, α-naphthylamine hydrochloride must first be prepared. For this purpose, 100 grams of the base are dissolved in 400 to 500 grams of warm alcohol, and an excess of concentrated hydrochloric acid added; the hydrochloride is deposited in silver plates which are separated when cold. 18 parts of this hydrochloride are dissolved in 500 parts of water, to which have been added 200 parts of dilute hydrochloric acid (1 : 10), and, when all of it has dissolved, the solution is cooled to 0° with ice and diazotised by adding a solution of 7 parts of sodium nitrite in 50 parts of water. After about ten to fifteen minutes, the liquid is poured into a solution of 40 parts of G salt dissolved in 700 parts of water, to which 8 parts of caustic soda have been added. The dyestuff forms slowly, and is precipitated in a crystalline condition.

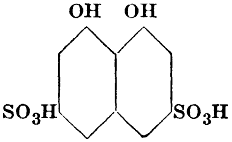
α-Naphthylamine hydrochloride may also be diazotised by suspending in 200 parts of dilute hydrochloric acid (1 : 10), cooling to 0°, and adding 100 parts of a solution of sodium nitrite (7 grams per litre), when the naphthylamine salt dissolves slowly, the remainder of the process being carried out as above.

Dihydroxyazo-compounds.

These compounds are obtained by coupling diazo-compounds with the dihydroxynaphthalenes or their sulphonic acids. The most important dihydroxynaphthalenes for this purpose are the 1 : 5 and 2 : 7 isomers ; the sulphonic acids most frequently used are those in which the OH groups are in the 1 : 8 or *peri*-position (*peri*-dihydroxynaphthalene sulphonic acids). Of the monosulphonic acids, " S acid," and of the disulphonic acids, chromotropic acid, are the most interesting.



S acid.



Chromotropic acid.

S acid is prepared from naphthalene *a*-sulphonic acid, which is nitrated and the product reduced, giving a mixture of 1 : 5 and 1 : 8 *a*-naphthylamine sulphonic acids, which are separated. The 1 : 8 or " Schöllkopf acid " is sulphonated, when it gives 1-naphthylamine-4 : 8-disulphonic acid (*D.R.P.* 40,571). The sodium salt of this acid is heated at 180° with water in an autoclave ; or diazotised, and the diazo-compound boiled with water (*D.R.P.* 57,388, 74,644). Finally, the *a*-naphthol-4 : 8-disulphonic acid so obtained is fused with caustic soda (*D.R.P.* 54,116).

On combining S acid with diazobenzene or diazotoluenes, or their sulphonic acids, it gives a series of dyestuffs called *Azomagentas.* Chromotropic acid gives the *Chromotropes* ; these dyestuffs dye wool, and the dyed fibre may be developed by chroming. The shade, which is at first red or violet, becomes an intense black or bluish black on treating with dichromate.

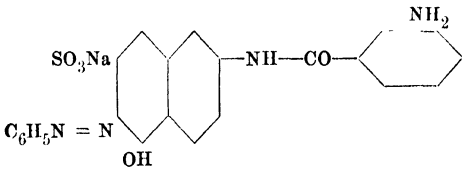
Amidoazo-compounds.

These are only of secondary importance, the only interesting one being the red dyestuff called *Orchil* *substitute*, prepared by Roussin and Poirrier in 1878 by combining diazo-*p*-nitraniline with naphthionic acid.

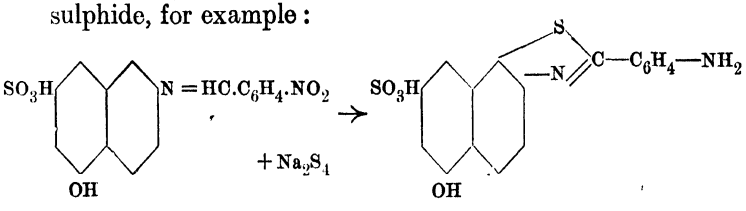
Hydroxy-amidoazo-compounds.

The mono-azo-dyestuffs derived from H acid and Gamma acid do not dye cotton, but some of the mono-azo-dyestuffs from J acid are direct dyestuffs; whereas the azo-compounds from amines of the benzene series do not possess any affinity for cotton, on coupling with α-naphthylamine, J acid gives a good direct colour.

The use of N-substituted J acid derivatives containing an external amido-group, or an amido-group attached to a heterocyclic nucleus, has led to a large number of valuable dyestuffs, mostly dyeing orange to red shades, the amido-group of which can be diazotised and developed with β-naphthol for the production of bright red colours. The Rosanthrene dyestuffs were the first of this series. The simplest one, *Rosanthrene O* [C.I.B.], is prepared by combining diazobenzene with the reduction product of the condensation of *m*-nitrobenzoyl chloride with J acid, and has the following constitution:



Thiazol derivatives of a similar character have been obtained by condensing J acid with nitrobenzaldehydes, and boiling the compound obtained with sodium poly-sulphide, for example:

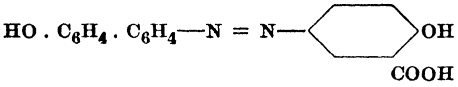


Benzylidene compound Thiazol derivative.

On combination with simple diazo-compounds, these substances give Azo-dyestuffs which form a part of the *Diazo Brilliant scarlet* series [By.].

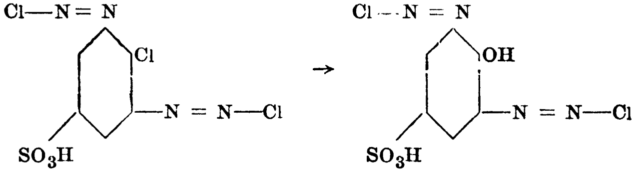
Mordant Monoazo-dyestuffs.

The combination of the diazo-derivatives of amido-carboxylic acids with amines and phenols, as well as the combination of diazo-compounds with these acids, yields monoazo-compounds which dye chrome-mordanted wool. This property of dyeing on mordants is possessed to a high degree by dyestuffs derived from salicylic acid. *Alizarin yellow R* and *GG* [M.L.B.] are produced by the combination of salicylic acid with *p*- and *m*-nitrodiazobenzene respectively ; the *Diamond yellows* are obtained by coupling the diazobenzoic acids with salicylic acid. *Diamond Flavine* [By.] has the following constitution :



and is prepared by tetrazotising benzidine, coupling with one molecule of salicylic acid, and boiling with water. The property of dyeing on a mordant may be attributed to the proximity of the OH group to the carboxyl group ; it is met with again in the monoazo-derivatives of α-naphthol-β-carboxylic acid and β-naphthol-α-carboxylic acid.

Chrome-developed Monoazo-dyestuffs. These dyestuffs are now of great importance for dyeing wool. They include the hydroxy-monoazo-compounds prepared from *o*-amidophenol or naphthol, or their substitution products. These dyestuffs dye wool rather dark shades from an acid bath, but are converted into very rich tones of fast deep brown, blue, or black, on treating the dyed fibre with a dilute solution of potassium dichromate, and heating. These dyestuffs are prepared by diazotising an *ortho*- or *para*-substituted *o*-amidophenol or *o*-amidonaphthol, and coupling, preferably with β-naphthol. In a similar manner there have been prepared the disazo-compounds of dihydroxydiamidophenol, which are obtained by a rather unexpected process discovered by the B.A.S.F. (*D.R.P.* 138,268, 139,327; *E.P.* 16,811, 20,551 (1901)). If diamidochlorbenzene sulphonic acid is diazotised and the tetrazo-compound obtained treated with an alkali, its chlorine atom is replaced by a hydroxyl group; coupling will then take place as usual.



The following are chrome-developed monoazo-compounds. (From Nietzki, *Chemie der org. Farbstoffe*, 1906 (5th edition), p. 69):

Acid Alizarin black R [M.L.B.].	Nitro-o-amidophenolsulphonic acid + β-naphthol.
Diamond black P.V. [By.].	o-Amidophenol sulphonic acid + dihydroxynaphthalene.
Anthracene Chrome black [C.]	Amidonaphthol sulphonic acid R + β-naphthol.
Palatine Chrome black [B.A.S.F.].	o-Amidophenol p-sulphonic acid + β-naphthol.

The chrome-fixed azo-dyestuffs appear on the market under numerous names, such as *Eriochrome* [G.], *Salicin* [K.], *Erachrome* [Lev.], *Chromanthrene* [Lev.], *Alizadine* [H.], and *Mercerol* [H.] colours.

Pigment Colours.

The majority of the artificial pigments are insoluble salts of monoazo-dyestuffs. The value of a pigment colour depends upon its brilliancy, its fastness to light, its covering power, and the insolubility of its calcium, aluminium, barium, etc., salts. It must also not be affected by lime, must be quite insoluble in water and in oil, and must not sublime at too low a temperature.

Very few pigments completely satisfy all these requirements, but the number has recently been considerably extended, although the range of colour is still rather restricted.

The following are examples of Azo-dyestuffs which are being manufactured for pigments :

	AMINE.	COUPLED WITH
Lithol red R [B.A.S.F.]	2-Naphthylamine 1-sulphonic acid.	β-Naphthol.
Lake bordeaux B.	do.	β-Hydroxynaphthoic acid.
Lake red D.	Anthranilic acid.	β-Naphthol.
Pigment orange R [M.L.B.].	*p*-Nitro-*o*-toluidine.	do.
Pigment Fast red HL. *Helio Fast red RL* [By.]. *Lithol Fast scarlet R* [B.A.S.F.].	*m*-Nitro-*p*-toluidine.	do.
Pigment purple [M.L.B.].	*o*-Anisidine.	do.
Lake red P [M.L.B.].	*p*-Nitraniline-*o*-sulphonic acid.	do.
Lithol Rubin B [B.A.S.F.]. *Permanent red* 4 *B.*	*p*-Toluidine-*o*-sulphonic acid.	β-Hydroxynaphthoic acid.
Pigment scarlet 3 *B* [M.L.B.]	Anthranilic acid.	R salt.

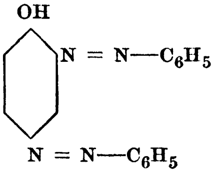
DISAZO-DYESTUFFS.

The disazo-compounds contain two azo-groups, —N=N—, as chromophores in their molecule. Those formed by the combination of two molecules of a diazo-compound with only one molecule of an amine or phenol are known as "primary" disazo-compounds. The characteristic feature of these compounds is that the two chromophores are linked to the ring to which the auxochromes are attached.

The "secondary" disazo-compounds have the chromophores and the auxochromes attached to different rings. They may be obtained: (*a*) by diazotising an amidoazo-compound and combining with a molecule of an amine or of a phenol, giving an *asymmetrical* secondary disazo-compound; (*b*) by tetrazotising a diamine and combining with two molecules of an amine or of a phenol, giving a *symmetrical* secondary disazo-compound.

Primary Disazo-compounds.

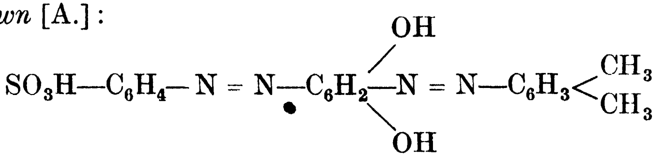
Phenolbisazobenzene.



This compound was discovered by Griess in the products obtained by the action of sodium or barium carbonates on diazobenzene nitrate. Later Griess obtained it by combining diazobenzene nitrate with benzene azophenol. It forms yellow plates of M.P. 131°.

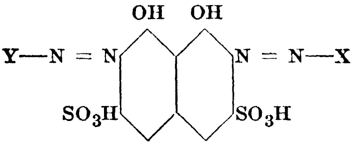
The diazotoluenes give homologous compounds.

Resorcinol, α-naphthol, and chrysoidine may all be combined with two molecules of a diazo-compound; these two molecules may be identical or different. Thus, resorcinol combined with one molecule of diazoxylene and one molecule of diazosulphanilic acid gives *Resorcin brown* [A.]:

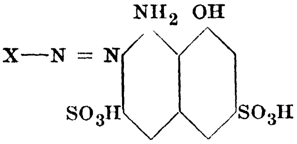


$$SO_3H-C_6H_4-N=N-\overset{OH}{\underset{OH}{C_6H_2}}-N=N-C_6H_3\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$$

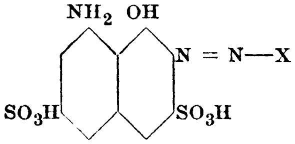
The *peri*-dihydroxy- and *peri*-amido-naphthol sulphonic acids give rise to an enormous number of disazo-compounds. Thus, chromotropic acid may be combined with two molecules of a diazo-compound to give dyestuffs of the type :



H acid behaves in a peculiar manner. When coupling is carried out in alkaline solution, the azo-group enters the naphthalene nucleus in the β-position adjacent to the hydroxyl-group ; whereas, if coupling takes place in acid solution, the azo-group goes into the β-position adjacent to the amido-group. Hence the same diazo-compound yields different dyestuffs with H acid according to whether the combination takes place in acid or alkaline solution.

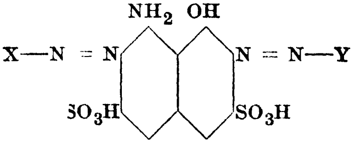


In acid solution.

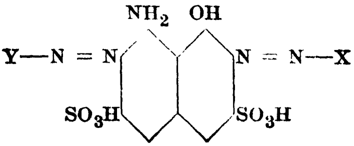


In alkaline solution.

Each of these monoazo-compounds may be combined with a fresh molecule of a diazo-compound, the first in alkaline solution, the second in acid solution. Hence two isomeric disazo-compounds may be obtained according to the order in which the groups are introduced :

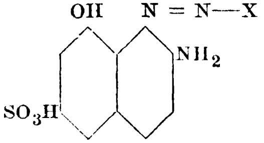


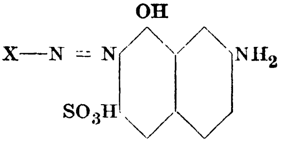
or



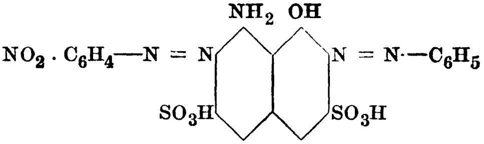
The shades of the isomers so obtained differ from one another.

Amidonaphthol sulphonic acid G behaves in a similar manner to H acid; in acid solution coupling occurs in *ortho*-position to the NH_2, in alkaline solution in *ortho*-position to the OH.



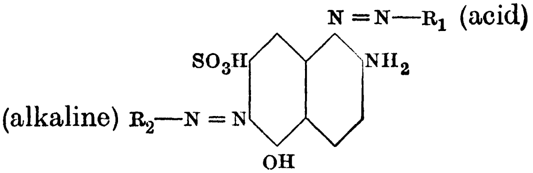


Naphthol blue-black [C.] is an important dyestuff of this class. It is obtained by coupling H acid with diazotised-*p*-nitraniline in acid solution, and then with a molecule of diazobenzene in alkaline solution:

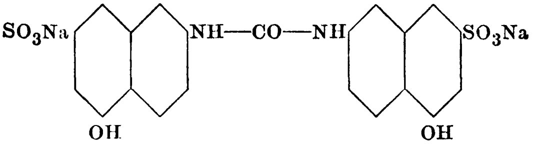


The *ortho*-sulphonic acid of this dyestuff is a black dyestuff, which is exceedingly fast to light.

The most important compound for the production of direct dyestuffs is the 2 : 5 : 7-amidonaphthol sulphonic acid, the so-called J acid. Like H acid it combines with two diazo-compounds, one in acid and the other in alkaline solution:



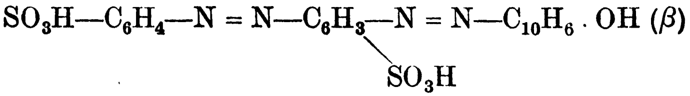
Many of the products are, however, too soluble or not soluble enough to be absorbed by cotton. The *Benzo Fast scarlets* [By.], introduced in 1900, are prepared from the urea derivative obtained by the action of carbonyl chloride on two molecules of J acid, a product which is capable of combining with two molecules of the same or different diazo-compounds, and has the constitution :



The *Azidine Fast scarlets* [Jäger] are prepared from the more complex urea obtained by passing phosgene into one molecule of *m*-toluylenediamine-4-sulphonic acid and two molecules of J acid.

Asymmetrical Secondary Disazo-Compounds.

These compounds are obtained by diazotising an amidoazo-compound and combining as usual with amines or phenols. The amidoazo-compounds of the benzene series yield reds, scarlets and bordeaux ; those of the naphthalene series give very intense browns, blues and blacks. It is to be noted that, of the amidoazo-compounds, only those which have the amido-group in the *para*-position can be diazotised ; the amido-group of *o*-amidoazo-compounds cannot be diazotised. All these dyestuffs are sulphonic acids of type of *Biebrich scarlet*, which was discovered by Nietzki in 1879, and was first manufactured by Kalle & Co. at Biebrich (Nietzki, *Ber.*, 1880, **13**, 1838 ; *D.R.P.* 18,027). This is produced by diazotising amidoazobenzene disulphonic acid and combining the product with β-naphthol :

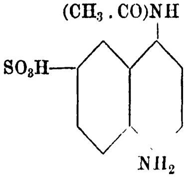


$$SO_3H—C_6H_4—N = N—\underset{\diagdown SO_3H}{C_6H_3}—N = N—C_{10}H_6 \cdot OH\ (\beta)$$

It dyes wool and silk bright scarlet shades.

Amidoazobenzene or its sulphonic acids may be replaced by other amidoazo-compounds, and β-naphthol by its sulphonic acids. In this manner an enormous variety of dyestuffs is obtained.

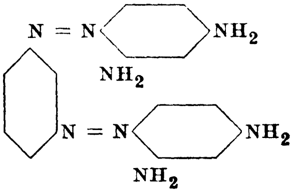
The azo-blacks are very important substances for the dyeing of wool; they are used in place of logwood, which was previously used exclusively for dyeing wool black. The first dyestuff of this class was the *Blue-black B* of the B.A.S.F. (1883), the next dyestuff prepared being the *Naphthol black* of Cassella.

DYESTUFF.	AMINE DIAZOTISED.	COUPLED WITH	RE-DIAZOTISED AND COUPLED WITH
Soudan III. [A.].	Amidoazobenzene.	β-Naphthol.	
Cloth red G [By.].	,,	N.W. acid.	
Brilliant Crocein [C.].	,,	G acid.	
Cloth red B [By.].	Amidoazotoluene.	R acid.	
Orchil red A [By.].	Amidoazoxylene.	,,	
Cloth scarlet G [K.].	Amidoazobenzene monosulphonic acid.	β-Naphthol.	
Biebrich scarlet [K.].	Amidoazobenzene disulphonic acid.	,,	
Orcelline [By.].	Amidoazotoluene sulphonic acid.	N.W. acid.	
Naphthylamine black D [C.].	α-Naphthylamine disulphonic acid.	α-Naphthylamine.	α-Naphthylamine.
Naphthol black [C.].	β-Naphthylamine disulphonic acid G.	,,	R acid.
Jet black [By.].	Amidobenzene disulphonic acid.	,,	Phenyl-α-naphthylamine.
Patent Biebrich black 4NA [K.].	Naphthionic acid.	Cleve's acids.	α-Naphthylamine.
Naphthalene Acid black [By.].	Metanilic acid.	,,	,,
Diaminogen black [C.].		α-Naphthylamine.	Amido-naphthol sulphonic acid G.

Symmetrical Secondary Disazo-Compounds.

These compounds are formed by combining two molecules of an amine or a phenol with the product obtained by diazotising a molecule of a diamine. Whereas a monamine yields a *diazo*-compound on diazotising, a diamine yields a *tetrazo*-compound.

The first *disazo*-compound known was the one which occurs with triamidoazobenzene in *Bismarck brown*, formed by coupling tetrazo-*m*-phenylenediamine with two molecules of *m*-phenylenediamine :

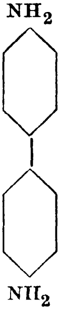


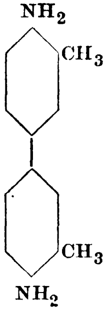
In case difficulty is experienced in tetrazotising a diamine, it may be avoided as follows : a nitro-monamine is diazotised and coupled with an amine or phenol, the nitro-monoazo-compound treated with an alkali sulphide, which only attacks the nitro-group, yielding an amido-group, and this is then diazotised and coupled with a further molecule. Another process is to diazotise the monoacetyl-compound of the amine, couple the diazo-compound with an amine or a phenol, and treat the monoacetylamidoazo-derivative so obtained with an alkali; the acetyl group is saponified, and coupled with an amine or a phenol. These processes have the advantage that they can give " mixed " compounds, that is to say, the two molecules coupled with the tetrazo-compound are different ; the general formula for these products is :

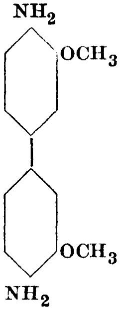
$$X—N{=}N—\text{Diamine}—N{=}N—Y.$$

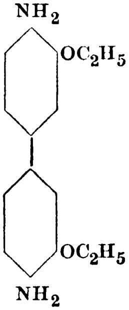
Direct Cotton Dyestuffs. Up to 1883, no azo-dyestuff was known which was capable of dyeing cotton or other vegetable fibres without mordanting. In this year, Böttiger discovered that on tetrazotising benzidine and combining with naphthionic acid, a red was obtained which dyed cotton direct; it is known as *Congo red.*

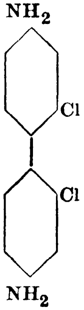
The property of giving substantive or direct cotton dyestuffs belongs to all azo-derivatives of benzidine and some of its substitution products such as: tolidine, obtained from *o*-nitrotoluene as benzidine is obtained from nitrobenzene; dianisidine, derived from *o*-nitroanisol; diphenetidine, derived from *o*-nitrophenetol. Their constitutional formulae are as follows:


Benzidine.

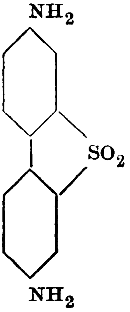

Tolidine.

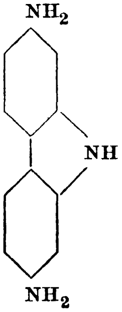

Dianisidine.

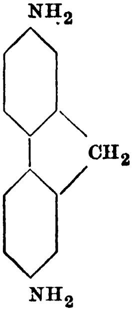

Diphenetidine.


m-Dichlorobenzidine.

It is very remarkable that *meta*-substituted derivatives of benzidine, such as *m*-dichlorbenzidine, etc., yield disazo-compounds which are *not substantive* dyestuffs.


Benzidine sulphone


Diamidocarbazol.


Diamidofluorene.

On the other hand, all dyestuffs prepared by means of *ortho*-substituted derivatives are substantive to cotton. The substantive character reappears if the *meta*-substituted group is divalent, as in benzidine sulphone, diamidofluorene, carbazol, etc. The bases are all *p*-diamines derived from diphenyl. It has been found that a large number of other *p*-diamines, such as the following, can also yield direct cotton colours :

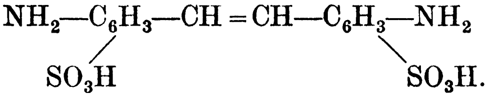
p-Phenylenediamine (*D.R.P.* 42,011, 42,814) :

$$NH_2—C_6H_4—NH_2.$$

Diamidostilbene (Bender, *Ber.*, 1886, **29**, 3234; *D.R.P.* 39,756) :

$$NH_2—C_6H_4—CH=CH—C_6H_4—NH_2.$$

Diamidostilbene disulphonic acid (*D.R.P.* 38,735) :



$$NH_2—\underset{SO_3H}{C_6H_3}—CH=CH—\underset{SO_3H.}{C_6H_3}—NH_2$$

Diamidodiphenylamine :

$$NH_2—C_6H_4—NH—C_6H_4—NH_2.$$

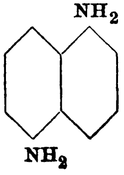
Diamidodiphenylurea (*D.R.P.* 46,737) :

$$NH_2—C_6H_4—NH—CO—NH—C_6H_4—NH_2.$$

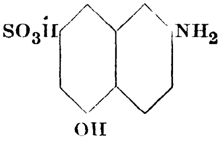
Diamidodiphenylthiourea :

$$NH_2—C_6H_4—NH—CS—NH—C_6H_4—NH_2.$$

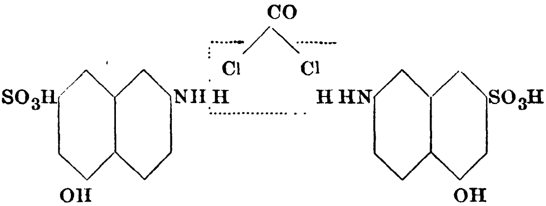
All the *p*-diamines do not yield substantive dyestuffs, for example, *p*-diamido-diphenylmethane and *p*-diamido-dibenzyl do not give them. On the other hand, 1 : 5 naphthalene diamine :



and its sulphonic acids give direct cotton colours. The factors which decide the substantive character are not thoroughly understood even at the present time; thus the dyestuffs obtained by combining J acid:



or its derivatives with diazo-compounds also have the property of dyeing cotton directly. The urea derivative obtained by condensing this acid with phosgene gas, thus



is the base of a numerous series of dyestuffs, among which are *Fast Benzo orange S*, the *Benzo scarlets*, etc. (Müller, *Zeitsch. angew. Chem.*, 1910, **23**, 1489).

Coupling of Tetrazo-compounds. Tetrazobenzidine, and the majority of the other *p*-diamines (such as diamidostilbene), do not immediately combine with two molecules of the amine or phenol with which they are mixed. In alkaline solution or in presence of acetic acid or sodium acetate, tetrazobenzidine first combines with one molecule of the amine or phenol; it is necessary to warm somewhat to obtain combination with the second molecule. Hence a large number of mixed disazo-compounds may be prepared of the type:

$$X—N=N—C_6H_4—C_6H_4—N=N—Y.$$

It is necessary to remember that coupling with amidonaphthol sulphonic acids takes place in a different manner according to whether the reaction occurs in alkaline or acid solution; this has been used principally in the case of symmetrical secondary disazo-compounds.

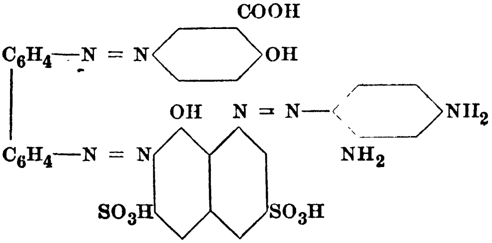
DYESTUFF.	BASE TETRAZOTISED.	COMBINED WITH
Congo red [A.].	Benzidine .	2 mol. naphthionic acid.
Congo Corinth G [A.].	”	1 mol. ” 1 mol. N.W. acid.
Diamine violet N [C.].	”	2 mol. amidonaphthol sulphonic acid G (in acid solution).
Diamine brown V [C.].	”	1 mol. amidonaphthol sulphonic acid G (in alkaline solution) + 1 mol. *m*-phenylenediamine.
Diamine scarlet [C.].	”	1 mol. G acid. 1 mol. phenol, and then ethylated.
Benzo orange R [By.].	”	1 mol. salicylic acid. 1 mol. naphthionic acid.
Diamine black RO [C.].	”	2 mol. amidonaphthol sulphonic acid G (in alkaline solution).
Diamine black BH [C.].	”	1 mol. γ-acid. 1 mol. H acid.
Diamine blue 2B [C.].	”	2 mol. H acid (in alkaline solution).
Diamine brown [M.L.B.]	”	1 mol. salicylic acid. 1 mol. amidonaphthol sulphonic acid G.
Benzopurpurine 4B [By.], [Lev.].	Tolidine.	2 mol. naphthionic acid.
Diamine blue 3B [C.].	”	2 mol. H acid.
Diamine blue BX [C.].	”	1 mol. H acid (in alkaline solution). 1 mol. N.W. acid.
Dianil blue G.	Dianisidine.	2 mol. chromotropic acid.
Diamine black 3O [C.].	Ethoxybenzidine.	2 mol. amidonaphthol sulphonic acid G (in alkaline solution).
Benzopurpurine 10B. [By.], [Lev.].	Dianisidine	2 mol. naphthionic acid.
Diamine sky blue.	”	2 mol. H acid.
Pyramine orange [By.].	Benzidine disulphonic acid.	2 mol. nitro-*m*-phenylene diamine.

TRISAZO-DYESTUFFS.

These compounds contain three —N = N— groups in the molecule. They are generally very intense dyestuffs of blue, dark green, or black shades, and may be obtained by several processes:

(1) A symmetrical secondary disazo-compound is prepared containing an NH_2 group which can be diazotised, that is not in *ortho*-position to the —N = N— chromophore; this is diazotised and the diazo-disazo-compound so obtained coupled with a suitable compound. For example:

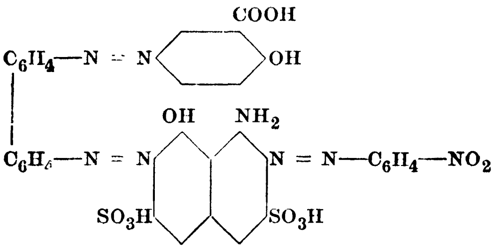
Diamine bronze G [C.]. Tetrazobenzidine is combined with one molecule of salicylic acid, and one molecule of amidonaphthol disulphonic acid H in alkaline solution, the product diazotised and coupled with *m*-phenylenediamine, giving:



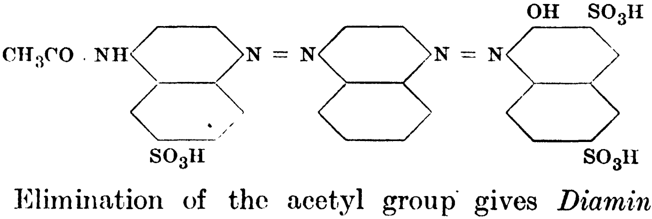
A large number of these dyestuffs are obtained by replacing the benzidine by other diamines, and H acid by α-naphthylamine or Cleve's acids.

(2) A mixed symmetrical secondary disazo-compound is prepared by combining a tetrazodiamine with a suitable compound in one part of the molecule, and also, in another part, with a phenol or an amine which can be coupled with another diazo-compound. For example:

Diamine green [C.]. Tetrazobenzidine is coupled with one molecule of salicylic acid and one molecule of H acid in alkaline solution. When the reaction is complete, the dyestuff produced is combined with a molecule of diazo-*p*-nitraniline in acid solution, giving:



It has already been mentioned that, if difficulties are experienced in the preparation of the necessary tetrazodiamine, an indirect method is used, which consists of diazotising the monoacetyl-derivative of the *p*-diamine, coupling with an amine, diazotising, and again coupling, and finally saponifying the acetyl group. The amidodisazo-compound obtained is then diazotised and suitably coupled. This method yields the *Diaminogens.* The acetylnaphthalenediamine sulphonic acids are diazotised, and coupled with *α*-naphthylamine; the dyestuff produced is diazotised, and combined with a naphthol sulphonic acid or an amidonaphthol disulphonic acid. With R acid, the following disazo-compound is obtained :



Elimination of the acetyl group gives *Diaminogen blue G* [C.], which may be diazotised, and again coupled. Dyestuffs of the Diaminogen class which contain a *p*-diamine are direct cotton colours, and these may be diazotised on the fibre and combined with phenols or naphthols, giving trisazo-dyestuffs. As a trisazo-compound still contains an NH_2 group which can be diazotised, it will yield a *tetrakisazo*-compound on diazotising and coupling. This last coupling process is often effected on the fibre.

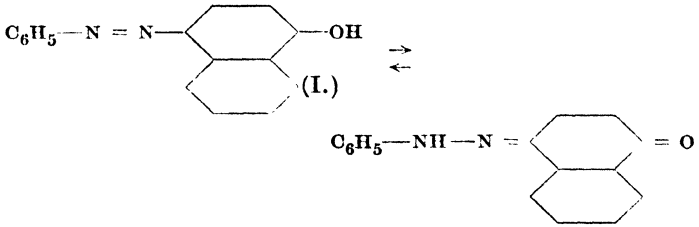
The following table gives some of the more important trisazo-dyestuffs :

Dyestuff.	Composition.
Benzo olive [By.].	Benzidine < salicylic acid. α-naphthylamine—H acid.
Benzo blue-black R [By.]	Tolidine < N.W. acid. α-naphthylamine—N.W. acid.
Diamine green B [C.].	Benzidine < H acid—*p*-nitraniline. salicylic acid.
Azocorinth [O.].	Tolidine < resorcinol—naphthionic acid. amidophenol sulphonic acid.

CHAPTER XIII.

HYDRAZONES.

THESE compounds are produced by the action of hydrazine or substituted hydrazines on aldehydes and ketones. The most important are the *phenylhydrazones* obtained by using phenylhydrazine and its nitro- and sulphonated derivatives; these are coloured substances, certain of which are true dyestuffs. There is a very close relationship between the phenylhydrazones and the azo-dyestuffs; thus benzene azo-α-naphthol (I.), is identical with the phenylhydrazone of α-naphthaquinone (II.), obtained by treating this quinone with phenylhydrazine.



(II.)

The identity of these two substances shows that in one case the reaction has been accompanied by a molecular change, either from left to right in the above formulae, or *vice versa*. At first it was thought that the azo-compounds had a quinonoid constitution. The differences which had been proved to exist between the *o*-hydroxy- and *o*-amidoazo-compounds and their *para*-isomers, had caused the *ortho*-derivatives to be classed with the hydrazones, whilst the *p*-hydroxy- and *p*-amidoazo-dyestuffs were considered to be true azo-compounds (Goldschmidt and Löw-Beer, *Ber.*, 1905, **38**, 1098). However, the researches of Goldschmidt and Löw-Beer, MacPherson, Willstätter and Veraguth, and R. Auwers, to mention only the most recent publications, have shown that the *ortho-* and *para*-hydroxyazo-compounds have a similar constitution, and in all probability are not quinonoid.

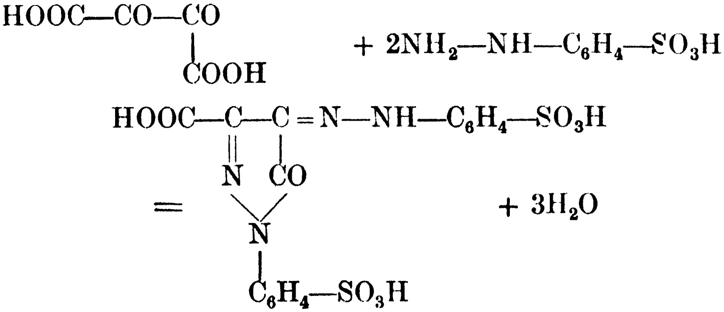
The hydrazones used as dyestuffs generally have a cyclic formula :

Isatin yellow is the sodium salt of the *p*-sulphonated phenylhydrazone of isatin.

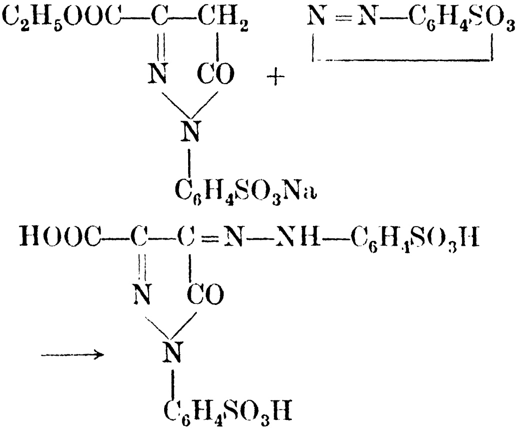
Phenanthrene red is the sodium salt of *p*-sulphonated diphenylhydrazone of phenanthraquinone.

Tartrazine.

This compound is the most interesting member of the Hydrazones. It was first prepared in 1884 by Ziegler and Locher (*Ber.*, 1887, **20**, 834 ; *D.R.P.* 34,294) by treating dioxytartaric acid with phenylhydrazine *p*-sulphonic acid. At first this dyestuff was considered to be a diphenylhydrazone, but the researches of Anschütz (*Ann.*, 1896, **294**, 219), and of Gnehm and Benda, have shown it to be a pyrazolone. It is prepared by heating phenylhydrazine sulphonic acid with sodium dioxytartrate and a small amount of water.



Tartrazine may also be obtained by commencing with oxalacetic ether, and treating with phenylhydrazine sulphonic acid to give a pyrazolone, which is then treated with diazosulphanilic acid, and the ethyl ester produced saponified :

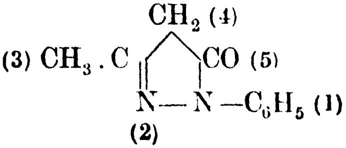


The azo-compound obtained apparently gives the isomeric hydrazone.

Commercial *Tartrazine* is the sodium salt, an orange yellow powder which dyes wool a brilliant greenish yellow shade, which is extremely fast to light.

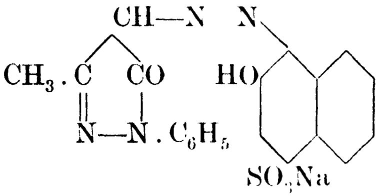
If the phenylhydrazine sulphonic acid is replaced by other derivatives and the oxalacetic ester by similar compounds, other dyestuffs of this group are obtained, such as the *Flavazines* [M.L.B.], the *Hydrazine yellows* [Griesheim], and the *Light Fast yellows* [By.]. They dye wool and silk, and are also used in the manufacture of pigment colours.

The *Xylene yellows* (Sandoz, *E.P.* 3373 (1908)) are dichlor-sulphonic acids of 1-phenyl-3-methyl-5-pyrazolone :



which is obtained by condensing phenylhydrazine with ethyl acetoacetate. *Radial yellows* [B.A.S.F.] are closely allied dyestuffs.

Eriochrome red B [G.] contains the *ortho*-hydroxy-azo-group essential for a chrome colour, and is produced by the combination of diazotised 1-amido-2-naphthol-4-sulphonic acid with the above phenylmethylpyrazolone:

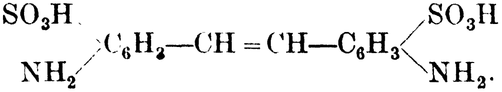


It gives dull red shades on wool, which change to bluish-red on after-chroming.

CHAPTER XIV.

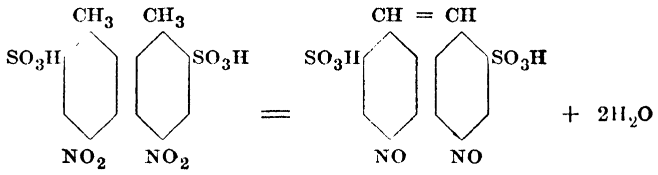
STILBENE DYESTUFFS.

STILBENE or diphenylethylene, $C_6H_5—CH=CH—C_6H_5$, is the parent substance of a number of dyestuffs which have been known for a considerable time. In 1883 Walter (*Bull. Soc. ind. Mulhouse*, 1887, 99) obtained an orange dyestuff by heating *p*-nitrotoluene sulphonic acid with caustic soda. Bender showed that this product is derived from stilbene, as on reduction it gives diamidostilbene disulphonic acid :

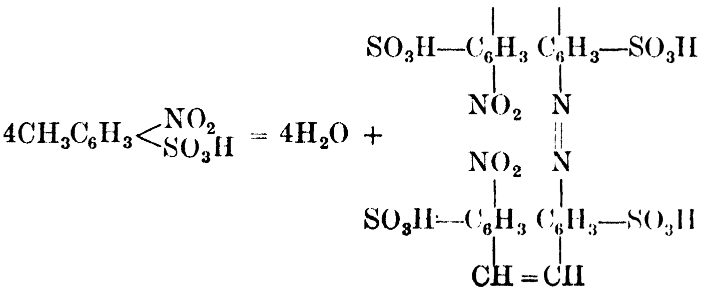


$$\begin{matrix} SO_3H \\ NH_2 \end{matrix} \!\!>\! C_6H_3—CH=CH—C_6H_3 \!<\!\! \begin{matrix} SO_3H \\ NH_2. \end{matrix}$$

According to the conditions under which the *p*-nitrotoluene sulphonic acid is treated with caustic soda the products are different. Dilute boiling caustic soda gives *Sun yellow* or *Heliochrysin* (G. Schultz and Bender. *Ber.*, 1886, **19**, 3234), whereas concentrated caustic soda at 80° gives *Direct yellow G.* [K.] (O. Fischer and Hepp, *Ber.*, 1893, **26**, 2233 ; 1895, **28**, 2281). All these products dye cotton directly an orange shade ; by the action of oxidising agents, greener shades are produced, such as *Mikado golden yellow* ; whereas on reduction the shade becomes redder, *Mikado orange* [L.], etc. (*D.R.P.* 46,252, 48,528). According to Fischer and Hepp, *Sun yellow* should be azoxystilbene disulphonic acid, and the *Direct yellow* dinitrosostilbene disulphonic acid. They result from the condensation of two molecules of *p*-nitrotoluene sulphonic acid by intramolecular oxidation:

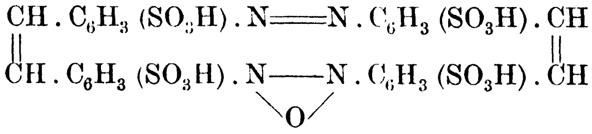


Oxidation should convert this derivative into dinitrostilbene disulphonic acid, and this should be *Mikado yellow*. This constitution is, however, incorrect, as the true dinitrostilbene disulphonic acid has been prepared by Green and Wahl (*Ber.*, 1897, **30**, 3101 ; 1898, **31**, 1078) by oxidising *p*-nitrotoluene sulphonic acid with sodium hypochlorite ; it is a pale yellow substance which does not dye cotton. In addition to dinitrostilbene disulphonic acid, oxidation in alkaline solution gives more or less dinitrodibenzyldisulphonic acid, according to the conditions, and both these oxidation products give dyestuffs with alkaline reducing agents. These dyestuffs appear to be identical with the *Mikado colours*, and are called *Stilbene yellow* and *Stilbene orange*. The constitution of these products has been established by Green and his co-workers (Green, Marsden and Schofield, *J.C.S.*, 1904, **85**, 1424, 1432 ; Green, Davies and Horsfall, *ibid.*, 1907, **91**, 2076 ; Green and Baddiley, *ibid.*, 1908, **93**, 1721) by the study of the various aldehydes formed by oxidising with permanganate. *Stilbene yellow 8G* contains two stilbene residues linked by an azo-group :



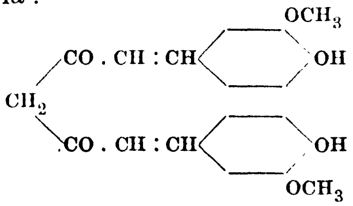
$$4CH_3C_6H_3{<}^{NO_2}_{SO_3H} = 4H_2O + \begin{array}{c} \mathrm{CH}=\mathrm{CH} \\ \mathrm{SO_3H{-}C_6H_3\quad C_6H_3{-}SO_3H} \\ \mathrm{NO_2}\quad\ \mathrm{N} \\ \qquad\ \, \| \\ \mathrm{NO_2}\quad\ \mathrm{N} \\ \mathrm{SO_3H{-}C_6H_3\quad C_6H_3{-}SO_3H} \\ \mathrm{CH}=\mathrm{CH} \end{array}$$

Direct yellow RT, *Afghan yellow*, and *Sun yellow* are considered to have the constitution :



$$\begin{array}{l} CH.C_6H_3(SO_3H).N{=\!=\!=}N.C_6H_3(SO_3H).CH \\ \| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ CH.C_6H_3(SO_3H).N{-\!-\!-}N.C_6H_3(SO_3H).CH \\ \qquad\qquad\qquad\qquad\quad \diagdown O \diagup \end{array}$$

Curcumin S is identical with *Sun yellow*, and is not to be confounded with true *Curcumin*, the colouring matter of turmeric, which, according to Mitobedzka, Kostanecki and Lampe (*Ber.*, 1910, **43**, 2163) probably has the formula :

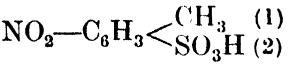


which would explain, by the symmetrical position of the two chromophores, the property of Curcumin of dyeing unmordanted cotton.

When *p*-nitrotoluene sulphonic acid is treated with caustic soda in presence of amido-compounds, such as *p*-amidophenol, *p*-phenylenediamine, benzidine, dehydrothiotoluidine, etc., new dyestuffs are obtained which are named respectively: *Polychromin Arnica yellow*, *Chicago orange*, *Curcuphenin*, etc.

Preparation of Direct Yellow.

p-Nitrotoluene Sulphonic acid.



$$NO_2—C_6H_3<\begin{array}{l}CH_3\ (1)\\SO_3H\ (2)\end{array}$$

2 kilograms of fuming sulphuric acid containing 30 per cent. of SO_3 are heated to 60-65°, and 500 grams of *p*-nitrotoluene added slowly with constant stirring,

the heating being continued until a drop of the liquid dissolves completely in water, and the smell of the original nitro-compound has disappeared. The mass is then poured slowly into 8 or 10 litres of cold water, and common salt added until the sodium salt of the sulphonic acid is precipitated. After cooling, the salt is separated, and dried. In order to obtain the pure sodium salt, it is necessary to recrystallise from water, but for conversion into the dyestuff this is unnecessary. The amount of pure salt in the product must be known, and this is determined by igniting a known weight of the product with concentrated sulphuric acid, and weighing the sodium sulphate formed.

Direct yellow. Five parts of caustic soda solution (27° Tw.) are heated to 80°, and one part of the above sodium sulphonate added; the mass thickens and becomes an orange brown colour, and after some time is poured into twenty times its weight of water, allowed to settle, and filtered.

CHAPTER XV.

DIPHENYLMETHANE DYESTUFFS.

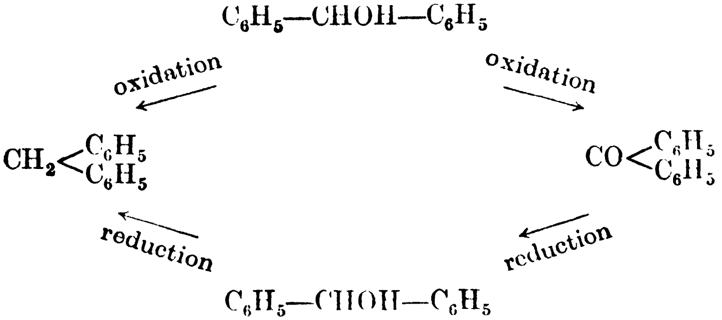
A CONSIDERABLE number of dyestuffs are more or less directly related to diphenylmethane :

$$C_6H_5—CH_2—C_6H_5.$$

On oxidation this hydrocarbon gives a ketone, benzophenone :

$$C_6H_5—CO—C_6H_5$$

and this on reduction first yields a secondary alcohol, diphenylcarbinol or benzhydrol, which, on further reduction, gives diphenylmethane :



$$C_6H_5—CHOH—C_6H_5$$

$$CH_2<^{C_6H_5}_{C_6H_5} \qquad CO<^{C_6H_5}_{C_6H_5}$$

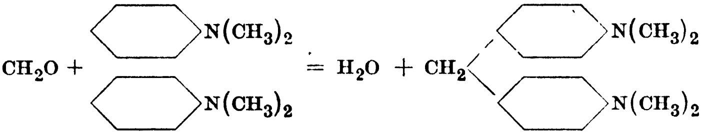
$$C_6H_5—CHOH—C_6H_5$$

These compounds are colourless, the dyestuffs being obtained from their amido- or alkylamido-derivatives, which can undergo the above series of reactions. The only amido-derivatives of interest are those in which the amido- or alkylamido-groups are in *para*-position, as, for example, tetramethyldiamidodiphenylmethane, tetramethyldiamidobenzophenone, tetramethyldiamidodiphenylcarbinol.

Tetramethyldiamidodiphenylmethane,

$$(CH_3)_2N—C_6H_4—CH_2—C_6H_4—N(CH_3)_2,$$

is prepared by a very simple reaction, a solution of dimethylaniline in dilute hydrochloric acid being treated with formaldehyde, when one molecule of aldehyde condenses with two molecules of the tertiary amine, combination taking place in *para*-position :

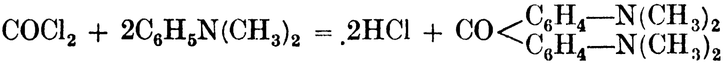


The product is purified by recrystallisation from alcohol, and forms plates of M.P. 90-91°.

Tetramethyldiamidobenzophenone, " ketone base,"

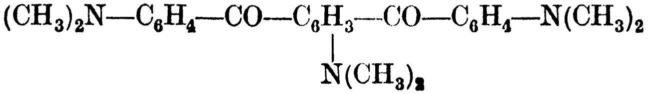
$$(CH_3)_2N—C_6H_4—CO—C_6H_4—N(CH_3)_2,$$

was prepared in 1876 by treating dimethylaniline with carbonyl chloride (W. Michler, *Ber.*, 1876, **9**, 715; Michler and Dupertuis, *ibid.*, 1900), and is still known as " Michler's ketone." The process is used at the present time, the gas being absorbed in dimethylaniline until the increase in weight corresponds to one molecule of carbonyl chloride for two molecules of dimethylaniline ; the product is then heated in an autoclave, poured into water, and the excess of dimethylaniline separated by steam distillation.



$$COCl_2 + 2C_6H_5N(CH_3)_2 = 2HCl + CO{<}\begin{matrix}C_6H_4—N(CH_3)_2\\C_6H_4—N(CH_3)_2\end{matrix}$$

Condensation only takes place in *para*-position to the nitrogen ; there are also formed as secondary products dimethylamidobenzoic acid and hexamethyltriamidodibenzoylbenzene :



$$(CH_3)_2N—C_6H_4—CO—\underset{\overset{|}{N(CH_3)_2}}{C_6H_3}—CO—C_6H_4—N(CH_3)_2$$

Michler's ketone crystallises in greyish plates of M.P. 179°. It is soluble in acids to a yellow solution, and gives light yellow shades on wool, silk, and cotton mordanted with tannin.

Tetramethyldiamidobenzhydrol.

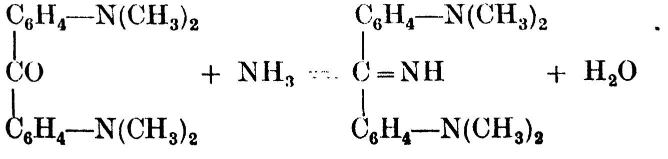
$$(CH_3)_2N-C_6H_4-CHOH-C_6H_4-N(CH_3)_2$$

This is often called "Michler's hydrol." It may be obtained by the oxidation of tetramethyldiamidodiphenylmethane, or by the reduction of Michler's ketone in alkaline solution. The first process has the advantage of avoiding the preparation of Michler's ketone, and hence the use of the poisonous carbonyl chloride. The oxidation of tetramethyldiamidodiphenylmethane is carried out in acetic acid solution by the theoretical amount of lead dioxide (*D.R.P.* 79,250). Michler's ketone is readily reduced by sodium amalgam in boiling alcoholic solution (Michler and Dupertuis, *loc. cit.*), by zinc powder and caustic soda in boiling amyl alcohol solution (B.A.S.F., *D.R.P.* 27,032); more recently calcium and alcohol have been suggested (Marschalk and Nicolajewski, *Ber.*, 1910, **43**, 641, 1701).

Michler's hydrol dissolves readily in alcohol and ether, and forms prisms of M.P. 96°; on heating in alcoholic solution, it is dehydrated. It dissolves in acids to give a magnificent bluish purple colour, which is unstable, and dyes wool and silk fugitive blue shades.

Auramine, $C_{17}H_{21}N_3$.

This is the only important diphenylmethane dyestuff. It was discovered by Kern and Caro in 1883 by fusing Michler's ketone with ammonium chloride and zinc chloride (B.A.S.F., *E.P.* 29,060, 31,936, 38,433 (1886)).



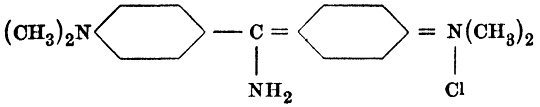
$$\begin{matrix} C_6H_4-N(CH_3)_2 \\ | \\ CO \\ | \\ C_6H_4-N(CH_3)_2 \end{matrix} + NH_3 = \begin{matrix} C_6H_4-N(CH_3)_2 \\ | \\ C=NH \\ | \\ C_6H_4-N(CH_3)_2 \end{matrix} + H_2O$$

In order to avoid the use of carbonyl chloride, Walter in 1887 (*Bull. Soc. ind. Mulhouse,* 1895, 82) and Sandmeyer in 1893 (Geigy, *D.R.P.* 53,614, 58,277) prepared *Auramine* by passing a current of ammonia into a fused mixture of dimethyldiamidodiphenylmethane and sulphur, when the thioketone formed reacts with the ammonia. *Auramine* is also prepared by treating the product obtained by the action of phosphorus oxychloride on *p*-dimethylbenzoylmethylaniline with dimethylaniline (Höchst Farbwerke, *D.R.P.* 41,751, 44,077).

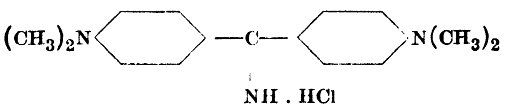
The free base of *Auramine* is colourless, but its salts are coloured, and are easily crystallised ; the commercial product is the hydrochloride. It is a basic dyestuff, dyeing wool, silk and tannin-mordanted cotton a yellow shade ; it is also used for colouring paper. It is reduced with difficulty to *leuco*-Auramine, $C_{17}H_{23}N_3$.

A series of *Auramines* is obtained from the homologues of Michler's ketone or the amidotolylmethane ; for example, *Auramine G* is obtained by using dimethylditolylmethane, sulphur, and ammonia (B.A.S.F., *D.R.P.* 67,478).

The constitution of the *Auramines* has been the subject of a number of researches (Graebe, *Ber.*, 1887, **20**, 3260 ; Fehrmann, *ibid.*, 2844 ; Stock, *Journ. f. prakt. Chem.*, 1893, **47**, 401 ; Semper, *Ann.*, **381**, 244) ; at the present time one or other of the following formulae is considered to express the constitution of ordinary *Auramine* :



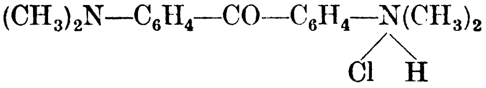
Stock's formula.



Graebe's formula.

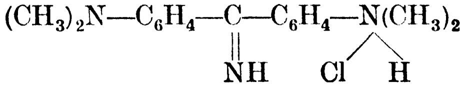
If Graebe's formula is correct, *Auramine* is the hydrochloride of tetramethyldiamidodiphenylimine. This formula appears to be correct by the readiness with which the dyestuff is hydrolysed on standing in aqueous solution, and more rapidly on boiling or by dilute acids, into ketone base and an ammonium salt. There are, however, certain reasons for which certain authors have considered it necessary to attribute to *Auramine* a quinonoid structure (see Nietzki, *Chemie der organ. Farbstoffe,* 5th edition, p. 131). There is perhaps still another method of representing the constitution of *Auramine* ; it has been stated that Michler's ketone is a weak dyestuff which becomes an intense yellow on addition of acids. It is, hence, probable that, in the case of the hydrochloride, this salt has the constitution (I.), and by analogy (II.) should represent the constitution of the corresponding imine, that is, of *Auramine* :

(I.)



$$(CH_3)_2N{-}C_6H_4{-}CO{-}C_6H_4{-}\underset{Cl\quad H}{\underset{/\ \backslash}{N}}(CH_3)_2$$

(II.)

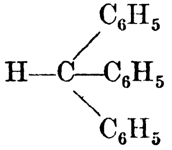


$$(CH_3)_2N{-}C_6H_4{-}\underset{NH}{\underset{\|}{C}}{-}C_6H_4{-}\underset{Cl\quad H}{\underset{/\ \backslash}{N}}(CH_3)_2$$

CHAPTER XVI.

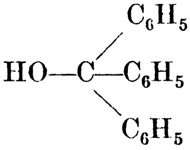
TRIPHENYLMETHANE DYESTUFFS.

Triphenylmethane and its higher homologues, diphenyltolylmethane, phenylditolylmethane, etc., are colourless, crystalline hydrocarbons which yield a large number of dyestuffs. These are derived from the products obtained by oxidising the hydrocarbons, which were called carbinols by Kolbe. Triphenylmethane (I.) yields triphenylcarbinol (II.), that is, methyl alcohol (carbinol) in which the three hydrogen atoms of the methyl group have been replaced by phenyl groups :



$$\mathrm{H{-}C(C_6H_5)_3}$$

(I.)



$$\mathrm{HO{-}C(C_6H_5)_3}$$

(II.)

Like the hydrocarbons, the carbinols are colourless substances, and in order to obtain dyestuffs it is necessary to introduce auxochromes into the carbinol molecule in *para*-position to the carbon atom of the methane residue. Hence there are two groups of these dyestuffs :

(1) The amido- or alkylamido-derivatives, in which the auxochromes are NH_2 and NR_2 groups ;

(2) The hydroxy-derivatives, in which the auxochromes are OH groups.

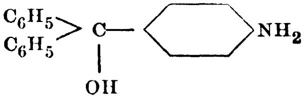
The amido-derivatives include : *Malachite green*, the *Magenta* series, and their substitution products.

The hydroxy-derivatives include the *Aurines*.

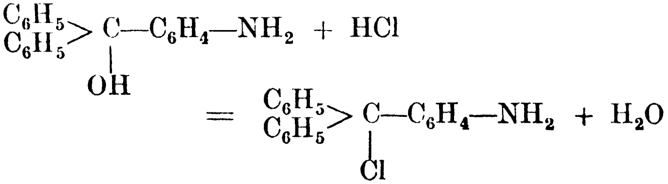
Finally, there are the dyestuffs derived from phthalic acid, the *Phthaleïns* and *Rhodamines*, which are also derived from triphenylmethane.

AMIDO-DERIVATIVES OF TRIPHENYLMETHANE.

If an amido-group is introduced into the triphenylcarbinol molecule in *para*-position to the carbon atom of the methane residue, *p*-amidotriphenylcarbinol is obtained :

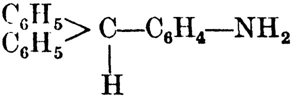


This compound is colourless, but with mineral acids, gives salts of an orange red colour which have a very feeble tinctorial power. These coloured salts are formed by the action of a molecule of the base on a molecule of acid, with elimination of a molecule of water. This reaction may be regarded in two ways, the simplest being represented by the following equation :



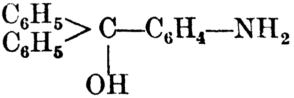
$$\left.\begin{array}{l}C_6H_5\\C_6H_5\end{array}\right> \underset{\displaystyle OH}{\underset{|}{C}}—C_6H_4—NH_2 + HCl = \left.\begin{array}{l}C_6H_5\\C_6H_5\end{array}\right> \underset{\displaystyle Cl}{\underset{|}{C}}—C_6H_4—NH_2 + H_2O$$

in which it will be seen that the hydroxyl group of the carbinol has been replaced by an atom of chlorine. This explanation was proposed by Rosenstiehl for all the coloured salts derived from triphenylmethane, but has been opposed and is now practically abandoned in spite of its apparent simplicity, on the grounds that the formulae of the hydrochloride, the carbinol and the hydrocarbon would be very similar :



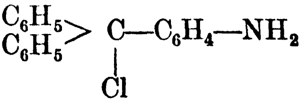
$$\left.\begin{array}{l}C_6H_5\\C_6H_5\end{array}\right> \underset{\displaystyle H}{\underset{|}{C}}—C_6H_4—NH_2$$

Colourless hydrocarbon.



$$\left.\begin{array}{l}C_6H_5\\C_6H_5\end{array}\right> \underset{\displaystyle OH}{\underset{|}{C}}—C_6H_4—NH_2$$

Colourless carbinol.

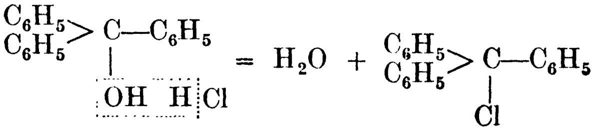


$$\left.\begin{array}{l}C_6H_5\\C_6H_5\end{array}\right> \underset{\displaystyle Cl}{\underset{|}{C}}—C_6H_4—NH_2$$

Coloured hydrochloride (Rosenstiehl).

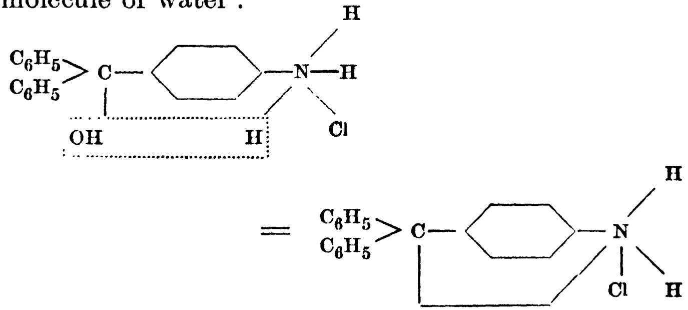
Thus, the colour of the hydrochloride would appear to be dependent merely on the replacement of hydrogen by chlorine, whereas if one or more hydrogen atoms of a hydrocarbon are replaced by chlorine, the derivative obtained is generally still colourless. Thus, benzene and toluene give colourless chlorine derivatives; methane is a colourless gas, and its mono-, di-, and tri-chloro-derivatives are colourless. Hence Rosenstiehl's formula appears to be insufficient.

Triphenylcarbinol and triphenylchloromethane, obtained by the action of dry hydrochloric acid on triphenylcarbinol,

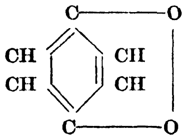


$$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\underset{\boxed{OH\ \ H}Cl}{\overset{}{C}}-C_6H_5 = H_2O + \begin{matrix}C_6H_5\\C_6H_5\end{matrix}\!>\underset{Cl}{C}-C_6H_5$$

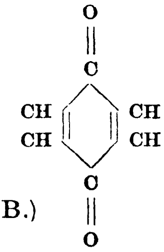
are both colourless substances, and the colour only appears when there is an amido-group in the molecules in the *para*-position. It would, therefore, appear that, as the amido-group is necessary for the formation of a coloured salt, it should take part in the reaction. It may be considered that the acid first combines with the basic amido-group to give a normal salt which then loses a molecule of water:



The coloured salt should then be the hydrochloride of a base $C_{19}H_{15}N$, differing in formula from carbinol by one molecule of water, but the base has not yet been isolated. This base has been called *fuchsonimine* by Baeyer and Villiger (*Ber.*, 1904, **37**, 597, 2848). This formulation (p. 144) was proposed by Fischer for all the amido-triphenylmethane dyestuffs, and has the advantage that these dyestuffs are considered to be derivatives of quinone. Since the researches of Fischer, the view held with regard to the constitution of quinone itself has been modified, and at present the formula B is accepted in place of the older formula A.

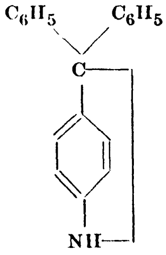


(A.)

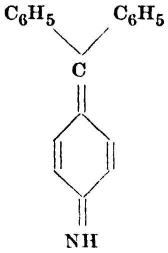


(B.)

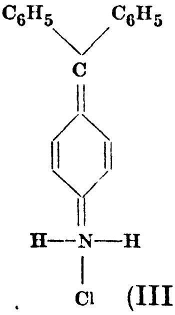
Nietzki has modified the constitutional formulae used to represent the triphenylmethane dyestuffs in a similar manner, and at the present time fuchsonimine is considered to be represented by (II.) in place of the older formula (I.), and its hydrochloride is called fuchsonimonium chloride (III.).



(I.)



(II.)

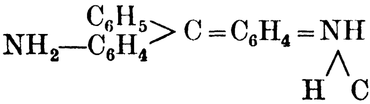


(III.)

This quinonoid notation represents the carbinols and their salts by entirely different formulae. It appears natural that, with the conversion of the colourless carbinol into a coloured salt, a very great change should occur in the linking of certain of the atoms and their relative positions in the molecule. This modification of the linkages is represented by the new formulae, which have the further advantage of bringing this group of dyestuffs into agreement with the quinonoid theory. (See Wahl, *Revue générale des Sciences*, 1905, p. 558 : "Les idées actuelles sur la constitution des colorants du triphenylmethane.")

Diamido-derivatives of Triphenylmethane.

Fuchsonimonium chloride is a very feeble dyestuff, but it is a chromogen, as, on introducing a further amido-group in *para*-position to the carbon atom of the methane residue, there is produced *Döbner's violet*, or amido-fuchsonimonium chloride :

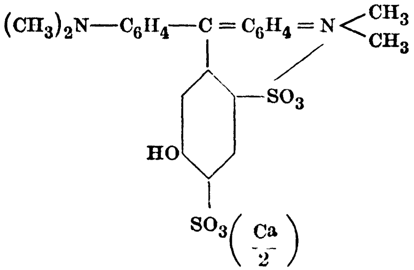


$$\left.\begin{array}{r}C_6H_5\\ NH_2{-}C_6H_4\end{array}\right> C=C_6H_4=\underset{H\ \wedge\ Cl}{NH}$$

This is the simplest diamido-derivative of triphenylmethane, and was discovered by Döbner in 1878 by heating benzotrichloride with aniline and nitrobenzene (*Ber.*, 1882, **15**, 234). It is no longer of any importance, but its tetramethyl derivative, *Malachite green*, is of very great interest.

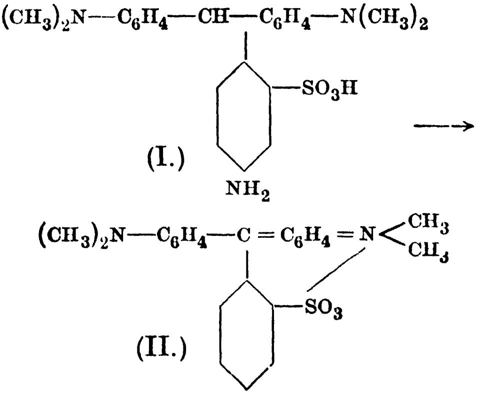
Malachite green.

This dyestuff was first prepared by O. Fischer in 1877 by heating benzaldehyde with dimethylaniline and zinc chloride, and oxidising the product obtained (E. and O. Fischer, *Ber.*, 1877, **10**, 1625 ; 1878, **11**, 950 ; 1879, **12**, 791, 796, 2348). In 1878 Döbner obtained the same dyestuff by heating benzotrichloride with dimethylaniline and zinc chloride (*Ber.*, 1878, **11**, 1236, 2274 ; *D.R.P.* 4322, 4988, 18,959). This last process has been replaced by the benzaldehyde process, which has itself been slightly modified.



Patent blue is an acid dyestuff which dyes wool and silk from an acid bath, giving greenish blue shades which are fast to soap and alkalies. *Cyanol*, or *Acid blue* 6 *G*, is obtained by using monoethyl-*o*-toluidine, and *Patent blue A* from ethylbenzylaniline.

At first, the fastness to alkalies and the change of shade was considered to be due to the presence of the hydroxy-group in the *meta*-position. In the years 1896-7, Suais in France and Sandmeyer in Switzerland showed independently, by different methods, that the fastness to alkalies is really due to the presence of a sulphonic acid group in *ortho*-position to the carbon atom of the methane residue (Sandmeyer, *J. Soc. Dyers and Col.*, 1896, 154). Suais condensed tetramethyldiamidobenzhydrol with metanilic acid, when combination occurs in *para*-position to the amido-group, giving (I.):

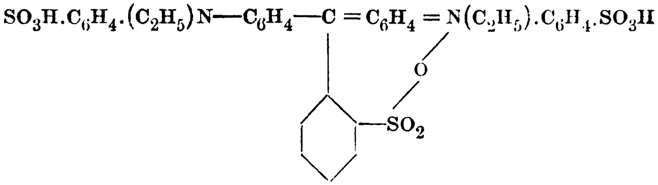


(I.)

(II.)

Compound (I.) is diazotised, boiled with alcohol to eliminate the amido-group, and then oxidised to give the dyestuff (II.), which is the *o*-sulphonic acid of Malachite green. This dyestuff differs in shade from Malachite green, being more bluish, and in its great fastness towards alkalies.

Sandmeyer condensed benzaldehyde *o*-sulphonic acid (obtained by heating *o*-chlorbenzaldehyde with sodium sulphite under pressure) with dimethylaniline, and after oxidation obtained the dyestuff (II.). This process was patented by the firm of Geigy (Basle), and is used in the preparation of *Erioglaucine* by condensing benzaldehyde *o*-sulphonic acid with ethylbenzylaniline or its sulphonic acids. This dyestuff has the formula:



More recent researches have shown that the sulphonic group in the *ortho*-position may be replaced by other acid or negative groups, such as Cl, Br, NO_2, CN, $COOCH_3$, etc. The dyestuffs *Eriochlorine*, *Setoglaucine*, *Setocyanine* and *Eriocyanine* [Geigy], apparently belong to this series.

Amongst the other substituted derivatives of Malachite green may be mentioned *Glacier blue* (*D.R.P.* 71,370 (1892)) and *Victoria green* 3*B* (*D.R.P.* 25,827), which are derivatives of dichlorobenzaldehyde.

The influence of substitution in the Malachite green series has been studied systematically by Nölting and Gerlinger (*Ber.*, 1906, **39**, 2041).

Attempts to condense tetramethyldiamidobenzhydrol with naphthalene disulphonic acid have been successful, giving the *Naphthalene greens* [M. L. B.] which are fast to alkali.

Triamido-derivatives of Triphenylmethane.

Historical. To this class belongs Magenta, the first synthetic dyestuff known, the study of whose properties and chemical composition has largely contributed to the rapid development of the aniline colour industry.

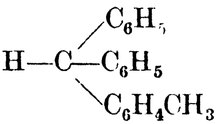
In 1856 Nathanson noticed that on heating crude aniline with ethylene chloride at 200° C., a red dyestuff was formed; in 1858 Hoffmann also obtained a red dyestuff by treating aniline with carbon tetrachloride. It was, however, the French chemist, Verguin, of Lyons, who, in 1859, discovered the process, employed commercially for some time, of heating commercial aniline with stannous chloride. This discovery was patented on 8th April, 1859, by Renard Bros. & Franc, of Lyons, and the dyestuff was sold under the name of "Fuchsiasine" or "Fuchsine." Shortly afterwards the manufacture of this substance became the property of the Fuchsine Company with a capital of four million francs. At first the profits made were enormous; about the year 1860, Magenta (Fuchsine) was sold at 1,500 francs per kilogram, an amount which is at present worth five to six francs. About the same time Durand and Gerber-Keller obtained a red dyestuff called *Azalein* by heating aniline with mercury nitrate; their French patent was annulled and their works taken into Switzerland. The Verguin process gave a very small yield (only 15·5 per cent.). In January, 1860, the use of syrupy arsenic acid for oxidising was patented about the same time by Medlock (*E.P.* 18th Jan., 1860) and Nicholson (*E.P.* 26th Jan., 1860) in England, and by Girard and de Laire (*B.F.* 26th Jan., 1860) in France. This arsenic acid process was gradually abandoned because the *Magenta* so obtained frequently contained arsenic acid, which rendered it poisonous. It was replaced by the nitrobenzene process discovered by Coupier in his works at Creil, where pure nitrobenzene and nitrotoluene were manufactured. He noticed that by heating a mixture of toluidine and nitrotoluene with iron and hydrochloric acid, there was produced a red dyestuff similar to or identical with Magenta. When the Fuchsine Company instituted proceedings against Coupier, Rosenstiehl succeeded in showing that Coupier's pure toluidine contained two isomers, *ortho*- and *para*-toluidine, and that the red obtained was different from Verguin's Magenta. Coupier's nitrobenzene process is the one generally used at the present time; homologues of Magenta are, however, obtained by the synthetic formaldehyde process.

Constitution of Magenta.

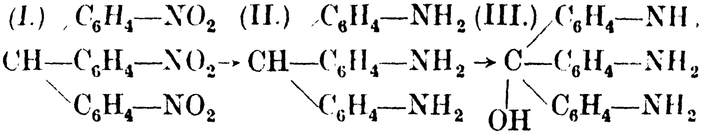
The detailed study of the Magenta obtained by oxidising commercial aniline, containing toluidines, was undertaken by Hofmann in 1862, and it was found by him to consist of the hydrochloride of a base $C_{20}H_{19}N_3H_2O$ which he called *rosaniline*. Pure aniline did not yield this red dyestuff on oxidation, and, in order to obtain the dyestuff, it was necessary to mix it with toluidine. The only toluidine known at that time was the solid *para*-toluidine, but, like pure aniline, this by itself did not give a red dyestuff on oxidation. Hofmann concluded that Magenta is formed by the oxidation of a mixture of two molecules of *p*-toluidine and one molecule of aniline:

$$C_6H_5NH_2 + 2C_7H_7NH_2 + 3O = 2H_2O + C_{20}H_{21}N_3O.$$

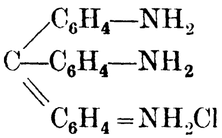
This equation proved to be insufficient when Coupier succeeded in preparing a red dyestuff by oxidising toluidine free from aniline, which he had obtained from pure toluene. Coupier's discovery appeared to contradict Hofmann's statement that pure toluidine does not give a red on oxidation. Rosenstiehl repeated Coupier's experiments, and confirmed his results, but found that the pure toluidine obtained by reduction of pure nitrotoluene was a mixture of the solid *p*-toluidine previously known, and an isomeric liquid *o*-toluidine. Coupier's red was hence obtained by oxidising a mixture of *o*- and *p*-toluidine, whereas that of Hofmann was produced by oxidising a mixture of *p*-toluidine and aniline, and hence they could not be identical. The constitution of these red dyestuffs still remained unknown. Hofmann, Paraf and Dale, Caro and Wanklyn, acted on rosaniline with nitrous acid, and obtained a true diazo-compound which on boiling with water evolved nitrogen and gave a product similar to rosolic acid. In the course of a notable research E. and O. Fischer (*Ann.*, 1878, **194**, 242) established the constitution of Magenta in the following manner: The dyestuff obtained by oxidising a mixture of *p*-toluidine and aniline, $C_{19}H_{17}N_3HCl$, was treated with alkali, and gave the base $C_{19}H_{17}N_3H_2O$ or $C_{19}H_{19}N_3O$, called *pararosaniline*, which loses its oxygen on reduction to give a leuco-base, $C_{19}H_{19}N_3$, *paraleucaniline*. Paraleucaniline is a triamine, $C_{19}H_{13}(NH_2)_3$, as on diazotising and boiling with alcohol, the NH_2 groups are replaced by three atoms of hydrogen giving a hydrocarbon, $C_{19}H_{16}$, which is really triphenylmethane $CH(C_6H_5)_3$. In the same manner, the Magenta formed by oxidising one molecule of *p*-toluidine, one molecule of *o*-toluidine and one molecule of aniline, having the composition $C_{20}H_{19}N_3HCl$, gives a base *rosaniline*, $C_{20}H_{21}N_3O$, which on reduction yields *leucaniline*, $C_{20}H_{21}N_3$. After diazotisation this compound yields on boiling with alcohol the hydrocarbon $C_{20}H_{18}$, which is diphenyltolyl methane:



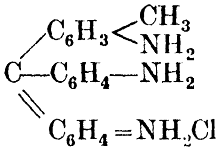
Having determined the constitution of the original hydrocarbons by this degradation process, they completed their research by conducting the synthesis of the dyestuffs. On treatment with nitric acid, triphenylmethane (I.) gives a trinitrotriphenylmethane which is converted by reduction into triamidotriphenylmethane, *(II.), and this is identical with paraleucaniline* :



On oxidation this gives the carbinol pararosaniline (III.), the hydrochloride of which has the following formula :

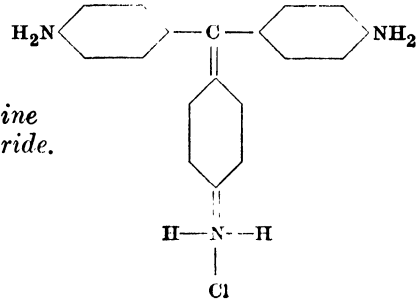


Pararosaniline hydrochloride.

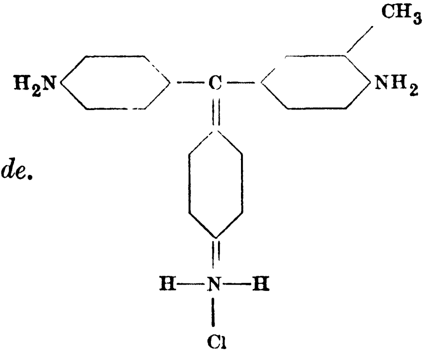


Rosaniline hydrochloride.

Hofmann's commercial Magenta, containing C_{20}, was hence the higher homologue of pararosaniline, *viz.* rosaniline, and Coupier's Magenta was the next higher homologue. This idea of homologues of the rosanilines was developed by the researches of Rosenstiehl and Gerber (*Ann. de chem. et phys.* (5) **8**, 176) and of Nölting. These homologues possess almost identical shades and very similar properties. To definitely establish the constitution of the rosanilines, it only remains to determine the position of the amido-groups in the phenyl rings. In the preparation of the rosanilines, *p*-toluidine is essential, as it is its methyl-group which yields the carbon atom of the methane residue. Hence, it follows that in rosaniline at least one NH_2 group should be in *p*-position to the methane carbon atom. The numerous syntheses of the rosanilines and their derivatives have shown that in these dyestuffs all three amido-groups are in *p*-position to the central carbon atom. The formulae of pararosaniline and rosaniline are as follows, being, according to Baeyer's nomenclature, diamidofuchsonimonium chloride and diamidomethylfuchsonimonium chloride.



Pararosaniline hydrochloride.



Rosaniline hydrochloride.

Manufacture of Magenta.

Magenta is manufactured by three processes :

(1) Oxidation of a mixture of aniline and toluidine by means of arsenic acid.

(2) Oxidation of the same mixture by nitrobenzene.

(3) The synthetic formaldehyde process.

(1) *Arsenic Acid Process.* (See Ch. Lauth, *Dict. de Würtz*, and Mulhäuser, *Dingler*, 1887, **266**, 455, 503, 547.) The mixture of aniline and toluidines used for the manufacture of Magenta is called "aniline oil for red." It is obtained by mixing one part of aniline with two parts of toluidine containing 36 per cent. of *para-* and 64 per cent. of *ortho*-toluidine. The average

composition of aniline oil for red is: aniline 33 per cent., *p*-toluidine 23 per cent., *o*-toluidine 44 per cent. The theoretical proportions necessary are those of an equimolecular mixture, containing aniline 30 per cent., *o*-toluidine 35 per cent., *p*-toluidine 35 per cent., but an excess of *o*-toluidine increases the yield.

570 kilograms of syrupy arsenic acid (SP. GR. 2·05) and 340 kilograms of aniline oil for red are placed in a cast-iron vessel fitted in the lower portion with a large inclined pipe for emptying. The vessel is closed by a cover carrying several openings (Fig. 5) for the axis of the stirrer, a tube for the thermometer, an inclined pipe leading to a condenser, and an opening for taking samples. The apparatus is heated by direct fire or in an oil bath first to 120° and then with constant stirring to 180-190° in seven hours. Water distils off, carrying oil with it, and this is called *Magenta échappés*. When half of the oil has distilled off, and a sample solidifies on cooling, the product is run off into wooden tanks.

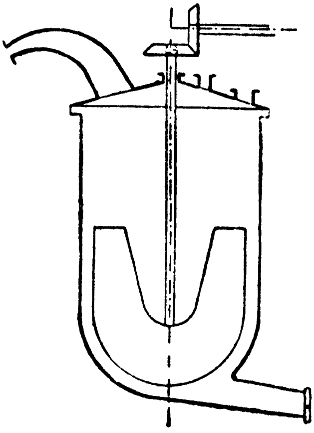


FIG. 5.

The Magenta *échappés* are separated from the water, and are used for the manufacture of azo-compounds and of Safranine : they contain very little *p*-toluidine and can no longer be used for the manufacture of Magenta. Their composition is : about 70 per cent. *o*-toluidine, 29 per cent. aniline, and a small amount of *p*-toluidine.

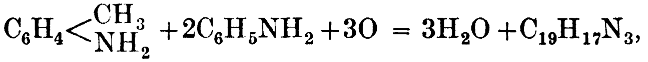
The mass resulting from the oxidation contains, in addition to Magenta, other soluble and insoluble products. It is crushed and placed in an extractor consisting of a horizontal cylinder fitted with a stirrer and covered with a round lid. 2500 litres of water are introduced into the extractor containing the crushed mass, the stirrer set in motion and the vessel sealed ; steam under pressure is then passed in to raise the temperature to 120-130°. After some time, the passage of steam is stopped, and the liquid allowed to stand until the pressure in the apparatus has fallen to one-third that of the atmosphere. The liquid is then passed through filter presses, which retain insoluble products, and the filtered liquid is placed in tanks ; it contains the arsenate and arsenite of rosaniline in addition to other soluble dyestuffs, such as *Chrysaniline*. Twelve kilograms of hydrochloric acid are added to keep the Chrysaniline in solution, fifty kilograms of common salt added to convert the arsenate and arsenite into the chloride, and the liquid allowed to cool. Magenta is deposited in crystalline cakes, and this crude product must be purified. The mother liquors are heated to 40° and neutralised with sodium carbonate, which precipitates a dyestuff, *Cerise*, as a resinous mass, which is separated, and the liquid which contains *échappés* in solution is made alkaline with lime and the bases separated by steam distillation. The crude Magenta is dissolved in 2500 litres of water, and the solution heated to the boiling point in the course of half an hour. Ten kilograms of calcined sodium carbonate are added in small portions to precipitate the Mauveines, which are deposited in the form of resins and may be separated. The solution will now only contain Magenta and Chrysaniline, and is heated for one hour, decanted, filtered, and then eighteen kilograms of hydrochloric acid and twenty-five kilograms common salt added, the whole being transferred to the crystallising tanks. On the surface of these are placed wooden sticks, on which the Magenta is deposited in large crystals; after standing for two days and three nights, the mother liquor is run off and the crystals sorted and dried. The largest crystals form *Diamond Magenta* or *Magenta OO*. The yield of Magenta crystals is not more than 35 per cent. of the weight of aniline oil for red used.

(2) *Nitrobenzene Process*. The apparatus used is similar to that of the preceding process, except that the vertical portion of the pipe leading to the condenser is somewhat longer, in order to allow the condensed liquid to flow back into the heating vessel. Two-thirds of the amount of aniline oil for red to be used are first neutralised with hydrochloric acid, the salt dried, and heated to 130-140°. The remaining third of the aniline oil for red is added and then an amount of nitrobenzene equal to one-half the total amount of aniline oil for red used. The liquid is gradually heated to 190° with addition of a quantity of iron filings amounting to 5 per cent. of the weight of the aniline oil. Water and *échappés*, consisting of nitrobenzene and a mixture of aniline and *o*-toluidine, distil from the end of the condenser. The progress of the reaction is followed by taking samples, and when it is finished, a current of steam is passed in through the axis of the stirrer to separate the remainder of the oils. The pasty mass is allowed to run into boiling water, to which has been added hydrochloric acid and salt, when the bases in the product dissolve as hydrochlorides, but the Magenta remains insoluble. The liquid is decanted, neutralised with lime, distilled. The Magenta is obtained as an mass with bronze reflex, which is purified as

[illegible]ifies on
tanks.

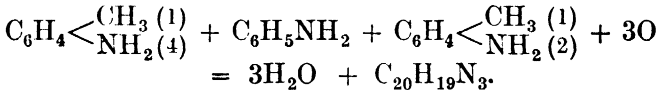
in the arsenic acid process. It is naturally free from arsenic, and the yield is somewhat higher, being about 42 per cent. In the commercial process, nitrotoluene is used, larger yields being obtained.

In the two processes outlined above, a mixture of pararosaniline and rosaniline is obtained, the former by oxidation of one molecule of *p*-toluidine and two molecules of aniline,



$$C_6H_4{<}\begin{smallmatrix}CH_3\\NH_2\end{smallmatrix} + 2C_6H_5NH_2 + 3O = 3H_2O + C_{19}H_{17}N_3,$$

and the latter from one molecule of *p*-toluidine, one molecule of aniline, and one molecule of *o*-toluidine.



$$C_6H_4{<}\begin{smallmatrix}CH_3\,(1)\\NH_2\,(4)\end{smallmatrix} + C_6H_5NH_2 + C_6H_4{<}\begin{smallmatrix}CH_3\,(1)\\NH_2\,(2)\end{smallmatrix} + 3O$$
$$= 3H_2O + C_{20}H_{19}N_3.$$

The necessary oxygen is obtained either by the conversion of the arsenic acid into arsenious acid, or from the nitrobenzene. In the latter case, the reaction is more complex, as the iron salts act as oxygen carriers, the ferrous chloride formed being oxidised by the nitrobenzene to give ferric chloride, which is the active agent in the oxidation of aniline oil for red. It would appear that the aniline formed from the nitrobenzene does not itself enter into the composition of the Magenta produced, for if the nitrobenzene is replaced by chloronitrobenzene or a sulphonated derivative, chlorinated or sulphonated rosanilines are not obtained.

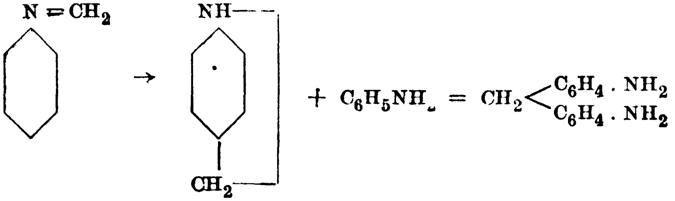
Rosenstiehl and Nölting have found that all the higher homologues of *p*-toluidine yield rosanilines on oxidation in presence of primary amines in which the *meta*- and *para*-positions are free.

3. *Formaldehyde Process.* By this process any of the rosanilines may be prepared in the pure state, and further, it is easy to obtain the rosaniline derived from tritolylmethane, *New Magenta*, containing C_{22}.

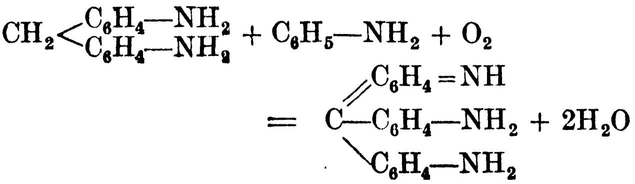
By the action of an aqueous solution of formaldehyde on a primary base such as aniline or toluidine there is first formed a methylene derivative. Thus in the case of aniline the following reaction occurs :

$$C_6H_5 . NH_2 + OCH_2 = C_6H_5—N : CH_2 + H_2O,$$

dehydro-formaldehyde aniline or methylene aniline being produced. On heating with an excess of aniline and its hydrochloride, these methylene derivatives first form the isomeric dehydro-amido-benzyl alcohols, which then combine with a further molecule of aniline to give diamidodiphenylmethane or its homologues (*D.R.P.* 53,937, 54,848, 55,565, 87,934 (Höchst), 96,762 (Kalle)).



Homolka in 1882 and Walter in 1887 obtained Magenta by oxidising a mixture of *p*-diamidodiphenylmethane and aniline. In the Höchst Farbwerke (*D.R.P.* 61,146) this oxidation is carried out by means of nitrobenzene and iron. The dehydro-bases may also be converted into dyestuffs directly by heating with an excess of aniline or another base or their hydrochloride, nitrobenzene and ferric chloride, the oxidation being represented by the following equation :



$$CH_2<\begin{matrix}C_6H_4—NH_2\\C_6H_4—NH_2\end{matrix} + C_6H_5—NH_2 + O_2 = C\begin{matrix}=C_6H_4=NH\\—C_6H_4—NH_2\\—C_6H_4—NH_2\end{matrix} + 2H_2O$$

By entirely or partly replacing the aniline by *o*-toluidine, homologous Magentas containing C_{20}, C_{21}, C_{22}, etc., may be obtained.

Other Synthetic Methods. Leuco-bases of the Magenta series may be obtained by condensing *p*-nitrobenzaldehyde with aniline or *o*-toluidine in presence of zinc chloride, the nitro-compound produced being then reduced. Another method is to act on aniline with *p*-nitrobenzylchloride, *p*-nitrobenzotrichloride, or *p*-nitrobenzyl alcohol.

General Properties of the Rosaniline Series.

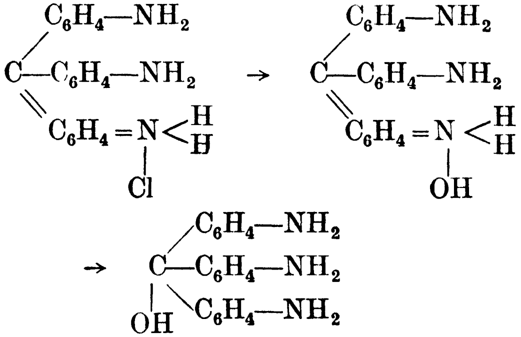
Most of the reactions of the Magenta series are common to all the amido- and alkylamido-triphenylmethane dyestuffs.

Action of Reducing Agents. Reduction converts the dyestuffs into the colourless leuco-bases, but these yield the dyestuff again on oxidation; the action of the air is not sufficient to cause the reappearance of the original colour.

Action of Oxidising Agents. The triphenylmethane dyestuffs are destroyed by oxidising agents. According to Georgievics, pararosaniline yields diamido-benzophenone. It is for that reason that it is essential not to use more than the theoretical amount of lead dioxide in oxidising leuco-bases.

Action of Acids. The colour bases (carbinols) give the mono-acid salts with acids, these forming the dyestuffs, whereas excess of acid gives yellow salts. Warm dilute acids bring about the hydrolysis of the dyestuffs. Concentrated sulphuric acid acts as a sulphonating agent, but this process occurs best with the leuco-bases. On treatment with nitrous acid the rosanilines give diazo-compounds, and these on boiling with water give rosolic acids.

Action of Alkalies. The dyestuffs derived from triamidodiphenylmethane are decolourised by alkalies owing to the formation of the carbinol bases. This conversion is not instantaneous, and has be hown to agree with the quinonoid theory, a coloured quinonoid ammonium base being first produced, which is slowly converted into the colourless carbinol :



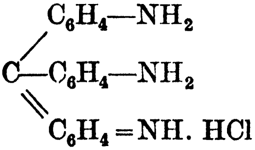
This has been found by Homolka, and proved more exactly by a study of the conductivity of the salts in presence of caustic alkali by Hantzsch and Osswald (*Ber.*, 1900, **33**, 278, 753).

Action of Ammonia. This has been shown by Villiger and Kopetschni (*Ber.*, 1912, **45**, 2910) to yield, not carbinols, as was previously considered, but amines of the type $R_3{\equiv}C.NH_2$, which are not much different from the carbinols, being stable to alkalies, but yielding ammonia on treatment with alcohols, thus :

$$R_3{\equiv}C{-}NH_2 + C_2H_5OH = R_3{\equiv}C{-}OC_2H_5 + NH_3.$$

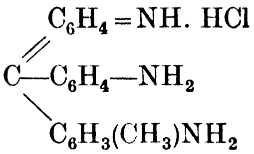
Action of Light. The triphenylmethane dyestuffs are not very resistant to the action of light, and hence the shades obtained are not fast.

Pararosaniline hydrochloride has the formula :

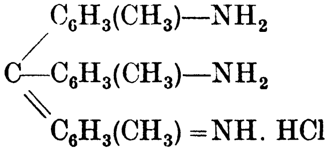


It is slightly soluble in water, from which it forms crystals with a metallic reflex, which contain $4H_2O$ (Schultz, *Die Chemie des Steinkohlenteers*, 3rd edition, vol. ii., p. 165). It is present in ordinary Magenta.

Magenta. The hydrochloride crystallises in large octahedra with a metallic reflex



New Magenta is the hydrochloride of triamidotritolylcarbinol, and is obtained by the formaldehyde process (*D.R.P.* 59,775).

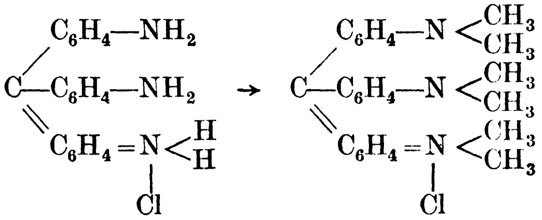


It is a crystalline powder which differs from the preceding dyestuffs in its greater solubility in water.

The Rosanilines are red basic dyestuffs which dye wool and silk direct, and also dye cotton mordanted with tannin. The sulphonic acids obtained by sulphonating Magenta, or, better, rosaniline, are acid dyestuffs which dye wool and silk from an acid bath. The sodium and ammonium salts have the names *Magenta S*, *Acid Magenta*, etc.

Alkylated Derivatives of the Rosanilines.

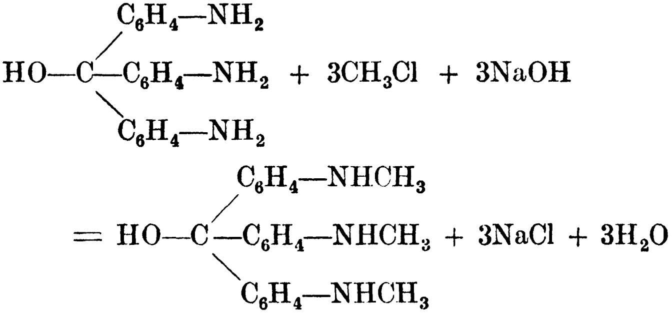
The substitution of a methyl group for one or more hydrogen atoms of the rings yields higher homologues of pararosaniline without changing the shade of the product. This is not the case, however, if one or more alkyl radicles are substituted for the hydrogen atoms of the amido-group; the shade is considerably modified and it becomes more violet the greater the number of hydrogen atoms replaced. Thus hexamethylpararosaniline hydrochloride, *Crystal violet*, gives pure violet shades.



Pararosaniline. Crystal violet.

General Methods of Preparation. The alkylated derivatives are obtained by methods which can be applied generally:

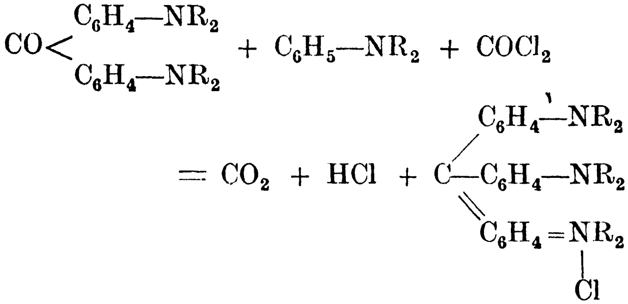
(1) The oldest method, used by A. W. Hofmann for first preparing the *Aniline violets*, consists of heating the rosaniline with alkylogens, for example:



Using methyl iodide or bromide, the substitution may be carried as far as the hexamethyl-derivative, and with ethyl esters, tri- or tetra-alkylated derivatives may be obtained.

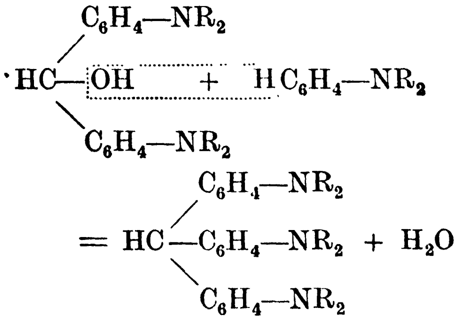
(2) Tetraalkyldiamidobenzophenones are condensed with tertiary amines in presence of phosphorus oxy-

chloride or carbonyl chloride. In the latter case, the carbonyl chloride may be allowed to act directly on a tertiary base.



$$CO<\begin{matrix}C_6H_4-NR_2\\ C_6H_4-NR_2\end{matrix} + C_6H_5-NR_2 + COCl_2 = CO_2 + HCl + C\begin{matrix}/C_6H_4-NR_2\\ -C_6H_4-NR_2\\ \backslash\backslash C_6H_4=NR_2\\ \quad\quad\quad\; | \\ \quad\quad\quad\; Cl\end{matrix}$$

(3) Tetraalkyldiamidobenzhydrols are condensed with tertiary bases, the leuco-bases so obtained being oxidised :



$$HC\begin{matrix}/C_6H_4-NR_2\\ -OH\\ \backslash C_6H_4-NR_2\end{matrix} + HC_6H_4-NR_2 = HC\begin{matrix}/C_6H_4-NR_2\\ -C_6H_4-NR_2\\ \backslash C_6H_4-NR_2\end{matrix} + H_2O$$

This process may be modified by oxidising a mixture of a tertiary base and a tetraalkyldiamidodiphenylmethane.

(4) A dialkyl-*p*-amidobenzaldehyde is condensed with two molecules of a tertiary amine and the leuco-base oxidised.

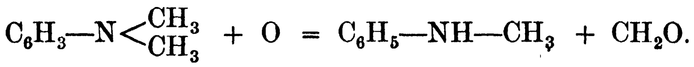
(5) Ethyl oxalate is condensed with secondary or tertiary amines in presence of aluminium chloride (A. Guyot, *Bull. Soc. chim.*, 1907, **1**, 937).

Methyl violet.

The formation of violet dyestuffs by alkylation of rosaniline was observed by Kopp in 1861, and studied in 1864 by A. W. Hofmann, who obtained *Iodine violet* or *Hofmann's violet* by the action of ethyl iodide on rosaniline. As the rosaniline which he used contained pararosaniline, the dyestuff obtained was a mixture of triethyl-rosaniline and triethyl-pararosaniline. This process was soon afterwards replaced by the one discovered by Lauth in 1866 and carried out by the firm of Poirrier at Saint-Denis, which consisted of oxidising dimethylaniline in presence of copper salts. In this manner the use of the very expensive iodine is avoided, and it is not necessary to first prepare rosaniline.

A mixture is made consisting of a copper salt (nitrate, sulphate or chloride), common salt, sand, dimethylaniline, and an acid, and heated to about 40-60°, when the formation of the dyestuff commences immediately and the mass assumes a metallic lustre. When the reaction is finished, the mass is extracted with water and the dyestuff precipitated by addition of salt. The yield obtained is from 70 to 75 per cent. of the weight of dimethylaniline used.

Fischer has shown that, during the oxidation of the dimethylaniline, formaldehyde and formic acid are also produced (E. and O. Fischer, *Ber.*, 1878, **11**, 2098; 1883, **16**, 2909), and hence the formation of the violet dyestuff may be explained by one of the methyl groups of the dimethylaniline yielding formaldehyde, whilst monomethylaniline remains :

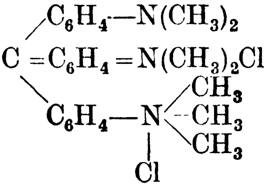


$$C_6H_3—N<\begin{matrix}CH_3\\CH_3\end{matrix} + O = C_6H_5—NH—CH_3 + CH_2O.$$

The formaldehyde then condenses with the dimethylaniline and the monomethylaniline, giving derivatives of diphenylmethane, and these are oxidised in presence of an excess of base, forming mixtures of tri-, tetra-, penta-, and hexa-methyl-pararosaniline. According to the proportions of the various products, a more or less violet dyestuff is obtained.

Crystal violet (hexamethyldiamidofuchsonimonium chloride). This dyestuff is prepared by one of the general methods. It forms brilliant green crystals containing $9H_2O$, and on reduction it gives hexamethyl paraleucaniline, which forms white plates of M.P. 173°.

By the action of methyl chloride on an alcoholic solution of *Methyl violet*, the liquid being kept neutral, the methyl chloride compound of hexamethyl-pararosaniline is obtained. It is a green dyestuff, which was discovered by Hofmann, and manufactured by Lauth and Baubigny in 1871. It is called *Methyl green*, and has the following constitution :



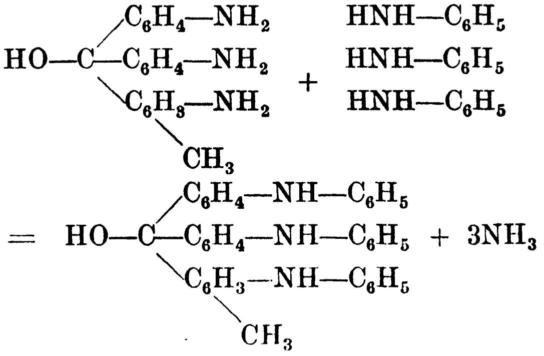
Benzylated Derivatives. By the action of benzyl chloride on *Methyl violet*, Lauth, in 1868, obtained *Benzyl violet.*

The dyestuffs containing benzyl groups are easily sulphonated, and to the class of substances so obtained belong *Acid violet* 6*B*, 10*B*, etc., and the *Formyl violets*, one of which is prepared by condensing formaldehyde with ethylbenzylaniline sulphonic acid and oxidising in presence of diethylaniline.

Phenylated Derivatives of the Rosanilines.

In 1861 Ch. Girard and de Laire prepared the first phenylated derivatives of Magenta by heating the salts of rosaniline with aniline to 160°, when violet and blue dyestuffs were obtained which they patented in France and in England (*B.F.* 2nd January, 1861). Their manufacture was undertaken by the Fuchsine Company at

Lyons, and by Simpson, Maule, and Nicholson in London. The process was slightly modified by the addition of various condensing agents, such as acetic acid, benzoic acid, etc. Later in 1867, Girard and de Laire succeeded in converting diphenylamine directly into *Aniline blue* by heating with oxalic acid at 110-120°. It was, however, Hofmann who established the constitution of these dyestuffs by showing that the formation of these violet and blue compounds from rosaniline is due to the substitution of one, two, or three phenyl groups for the hydrogen atoms of the amido-groups. Whereas the monophenyl-derivative is violet, the diphenyl-derivative is bluish violet, and the triphenyl-derivative is a slightly greenish blue dyestuff. As the rosaniline used for its preparation is mixed with pararosaniline, the blue dyestuff obtained is really a mixture of the phenyl derivatives of the two bases. The action of aniline on rosaniline may be represented by the equation:



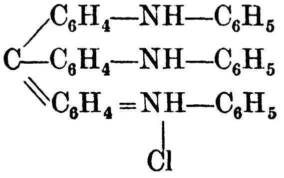
The shade of blue obtained is much purer than that of the original dyestuffs. It is essential to use aniline free from toluidines, as the dyestuffs obtained from the toluidines have a redder shade, and it is for this reason that pure aniline is sometimes still termed at the present time "aniline oil for blue" to distinguish it from "aniline oil for red."

Up to the present, it has not been found possible to introduce more than three phenyl groups into rosaniline. The salts of the bases so obtained are blue dyestuffs which are insoluble in water but soluble in alcohol. In order to make these dyestuffs soluble it is necessary to sulphonate them ; the free sulphonic acids are coloured and are insoluble in water but soluble in alkalies, giving colourless solutions of the alkali salts of the sulphonic acids of the carbinols. These are coloured in contact with acids, and constitute the *Alkali blues* of commerce.

Derivatives of Pararosaniline.

The monophenyl- and monotolyl-derivatives occur together with the diphenyl- and ditolyl-derivatives in the dyestuffs known as *Phenyl violet*, *Imperial violet*, *Regina violet*, *Lyons blue*, etc., being also mixed with the corresponding derivatives of rosaniline. They are obtained by heating rosaniline prepared by the arsenic acid method with the Magenta *échappés* formed at the same time, at 120° in presence of acetic acid.

Diphenylamine blue, triphenylpararosaniline hydrochloride:



is considered to be present, together with its higher homologue, in *Aniline blue*. It is obtained by heating aniline with pararosaniline and a condensing agent (an organic acid), by heating diphenylamine with perchlorethane (C_2Cl_6) or by heating diphenylamine with oxalic acid at 120°. In the last reaction, the oxalic acid yields the carbon atom for the methane residue by a process which is still unknown ; the yield is very small, being about 10 per cent. Baeyer and Villiger (*Ber.*, 1904, **37**, 2870) have been able to detect the presence of triphenylpararosaniline in *Diphenylamine blue*.

Diphenylamine blue is also known under the name of *Spirit Sky blue* or *Bavarian blue.* It is insoluble in water, and only slightly soluble in alcohol. Its sulphonic acids were prepared by Nicholson in 1862, and were the first sulphonic acid dyestuffs known. The trisulphonic acid is called *Soluble Sky blue*, *Cotton blue*, or *Helvetia blue*, and was prepared by Sandmeyer by condensing diphenylamine sulphonic acid with formaldehyde, and oxidising the diphenylmethane derivative produced in presence of a further molecule of the sulphonic acid (*D.R.P.* 73,092, 73,178, 76,072, 77,318).

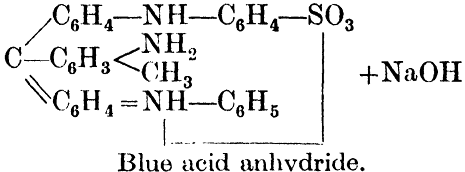
Whereas *Alkali blue XG*, the monosulphonic acid of β-naphthyl-pararosaniline, was not of great importance, *Soluble blue XG*, the trisulphonic acid, is valuable owing to the brilliancy and purity of its shade, and is commercial as the *Titan Comos* [H.], *Isamine blue* [C.], *Benzo Brilliant blue* [By.], etc. Unfortunately, as is the case with all the Triphenylmethanes and Phthaleïns, this dyestuff is not very fast to light.

Derivatives of Rosaniline.

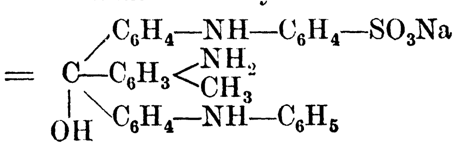
The most important dyestuffs of this group are *Aniline blue*, also known as *Spirit blue*, *Gentian blue*, *Opal blue*, or *Light blue*, and its sulphonic acids. It is prepared by heating 250 kilograms of aniline, 25 kilograms of rosaniline, and 3 kilograms of benzoic acid in a cast-iron vessel fitted with a stirrer and heated in an oil-bath or by direct fire. The aniline, rosaniline and five-sixths of the benzoic acid are first introduced and heated to 180°, and then the remainder of the benzoic acid added. An energetic reaction occurs, ammonia is liberated and aniline distils off. When samples taken show that the reaction is complete, the mass is run into dilute hydrochloric acid, which dissolves the excess of aniline and rosaniline, the *Aniline blue* remaining insoluble, and this is filtered off, washed, and dried. A small amount remains in the mother liquors, which are treated with lime and distilled to obtain the aniline. (See Schultz, *Chem. des Steinkohlenteers.*) Thirty-four to thirty-five kilograms of Aniline blue (theoretical 44·3) are obtained from twenty-five kilograms of rosaniline. In this reaction the exact part played by the benzoic acid is not known.

In the pure state, Aniline blue forms green crystals which are soluble in alcohol to a blue solution. This dyestuff was supposed to be triphenylrosaniline hydrochloride, but Baeyer and Villiger (*Ber.*, 1904, **37**, 2870) have shown that the Aniline blue of commerce consists of almost pure diphenylrosaniline, and that triphenylrosaniline cannot be prepared by the action of aniline on rosaniline; this has been confirmed by Knecht (*J. Soc. Dyers and Col.*, 1907, 119).

Aniline blue is easily sulphonated even by ordinary sulphuric acid, and as rosaniline can only be sulphonated with difficulty, the sulphonic groups are supposed to enter the substituted phenyl radicles. The sulphonation was first carried out by Nicholson, and the sodium salt of the monosulphonic acid is known as *Alkali blue* or *Nicholson's blue*. The free acid is blue and insoluble in water, whereas the alkali salts are colourless, probably being carbinols:



Blue acid anhydride.



Colourless sodium salt.

The alkali salt dyes wool from a bath containing sodium borate or phosphate, but the fibre so treated is only of a slightly bluish grey colour, and must be developed by passing through a bath of a dilute mineral acid, to convert the carbinol into the free acid, or, better, into its coloured anhydride.

More energetic sulphonation gives the disulphonic acid, or *Soluble Silk blue,* and then trisulphonic or tetrasulphonic acids, the *Soluble Cotton blues,* which are soluble in water and are used for dyeing wool and silk from an acid bath, and for dyeing cotton mordanted with tannin or alumina.

Triamido-derivatives of Diphenylnaphthylmethane.

The general methods used for the preparation of the alkylated derivatives of triphenylmethane may be extended to those of diphenylnaphthylmethane. To this group belong the following dyestuffs :

Victoria blue, obtained by condensing tetramethyldiamidobenzophenone chloride with phenyl-α-naphthylamine.

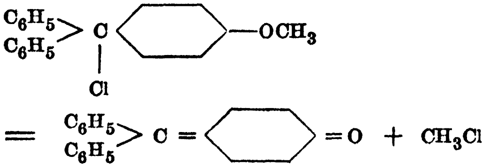
Night blue. Ketone base is condensed with p-tolyl-α-naphthylamine.

Both these basic dyestuffs dye wool and tanned cotton a pure blue (Kern and Caro, *D.R.P.* 29,060 ; Nathansohn and Müller, *Ber.*, 1889, **22**, 1891).

New Victoria blue is produced by the condensation of Michler's hydrol with ethyl-α-naphthylamine.

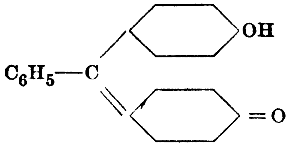
HYDROXY-DERIVATIVES OF TRIPHENYLMETHANE.

Just as fuchsonimine is the chromogen of amidotriphenylmethane dyestuffs, *fuchsone* is the chromogen of the hydroxy-derivatives. It is readily prepared by heating p-methoxytriphenylmethane to 180-200°, when methyl chloride is split off :



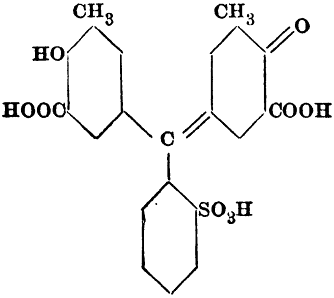
Bistrzycki and Herbst, who first isolated this product, called it diphenylquinomethane (*Ber.*, 1903, **36**, 2333). Baeyer, Villiger and Hallensleben (*Ber.*, 1903, **36**, 2791) prepared it by heating *p*-hydroxytriphenylcarbinol in a current of hydrogen, when it loses a molecule of water. Baeyer has suggested the name *fuchsone* for this compound. It forms brown crystals of M.P. 167-168°.

The hydroxy-dyestuffs are derived from fuchsone by the introduction of further hydroxy-groups in *para*-position. The simplest is *Benzaurine* or hydroxyfuchsone, discovered by Döbner (*Ber.*, 1879, **12**, 1462; 1880, **13**, 610) by heating benzotrichloride with phenol. It has the following constitution:



Benzaurine dissolves in alkalies, forming an intense red solution.

A new series of dyestuffs which are very fast to alkali, due to the presence of a substituted group in *ortho*-position to the methane carbon atom, has been prepared by A. Conzetti, by the condensation of *ortho*-substituted benzaldehydes with salicylic or cresotinic acid by means of sulphuric acid, and then oxidation by means of nitrosyl sulphate. From benzaldehyde *o*-sulphonic acid and *o*-cresotinic acid, there is produced *Erio Chrome cyanine R*:



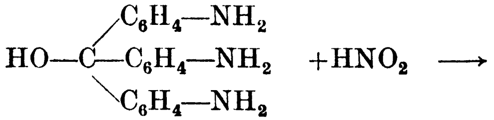
which gives a brick-red shade on wool, which turns to a violet-blue on after-chroming.

Erio Chrome Azurol B is prepared from *o*-chlorobenzaldehyde, and *Chromazurol S* from *o*-chlorobenzaldehyde sulphonic acid. The *Chromoxan* colours are similar dyestuffs derived from aldehydes of the naphthalene series.

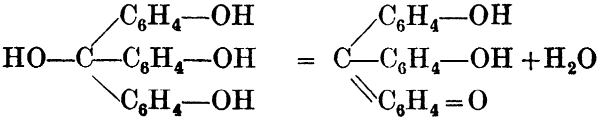
The most important compounds are the :

Trihydroxy-derivatives.

Historical. In 1834 Runge obtained a red dyestuff, by oxidising crude phenol, to which he gave the name *rosolic acid.* Later Kolbe and Schmidt, in 1859, prepared a similar red dyestuff by treating phenol with oxalic acid in presence of warm sulphuric acid ; they considered this product to be different to rosolic acid and called it *Aurine.* In 1866, Caro and Wanklyn showed the relationship of these dyestuffs to Magenta. By decomposing diazo-rosaniline with water, they obtained a red dyestuff which they believed to be identical with Runge's rosolic acid, and hence different from Aurine. In 1887, however, Dale and Schorlemmer succeeded in converting Aurine into rosaniline, which seemed to show that rosolic acid was identical with Aurine. It was only when the researches of Fischer had established the constitution of rosaniline, and the idea of homologues of rosaniline had been suggested by Rosenstiehl, that the difference between Aurine and rosolic acid was recognised. This difference is the same as that which exists between pararosaniline and rosaniline, rosolic acid being the higher homologue of Aurine. Diazotisation of pararosaniline gives Aurine, and diazotisation of rosaniline gives rosolic acid. The trihydroxy-carbinols are not known, as they immediately lose a molecule of water to give the dyestuffs :



Pararosaniline.



Aurine.

Aurine, pararosolic acid, or Yellow corallin is formed together with rosolic acid and many other products by heating phenol with a mixture of sulphuric and oxalic acids for twenty-four hours at 120-130°. As has been described, it is also obtained by decomposing diazo-pararosaniline with water. It forms red crystals which are soluble in alcohol and acetic acid to a yellowish-red, and in alkalies to a magenta coloured solution. Reducing agents convert it into leuco-Aurine or trioxytriphenylmethane.

By heating crude Aurine under pressure with ammonia, Guinon, Marnas, and Bonnet of Lyons obtained a red dyestuff, *Paeonine* or Red corallin ; by heating Aurine with aniline, a blue dyestuff, *Azuline*, is produced.

Rosolic acid is obtained by oxidising a mixture of cresol and phenol in presence of sulphuric acid by means of arsenic acid. A simpler method is to diazotise rosaniline and boil the diazo-compound with water. Rosolic acid crystallises in red prisms, which are soluble in alkalies to an intense red solution. All these compounds are now almost entirely used in the form of lakes in printing wall-papers.

Phenolphthaleïn * is a hydroxy-carboxylic acid dyestuff which may be compared with Aurine. Baeyer has

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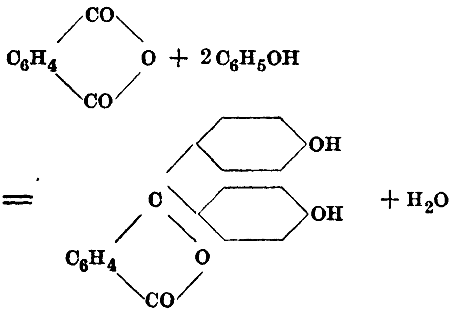
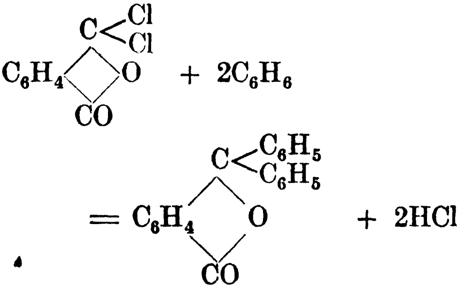
*Most authors place phenolphthaleïn among the phthaleïns, derived from fluorane; it is convenient to consider it immediately after the hydroxy-derivatives of triphenylmethane.

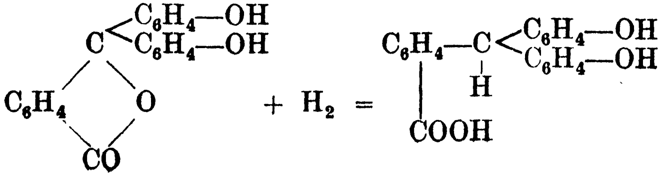
given the name "phthaleïns" to the compounds which are formed when phthalic anhydride is condensed with phenols. In the case of phenol the reaction is :



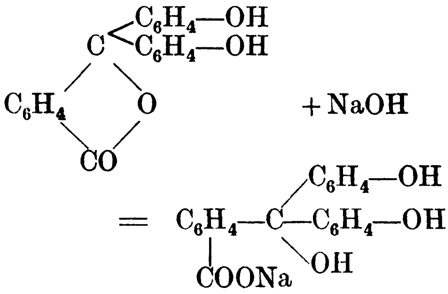
Phenolphthaleïn is the hydroxy-derivative of *phthalophenone*, which is obtained by condensing phthalyl chloride with benzene in presence of aluminium chloride.



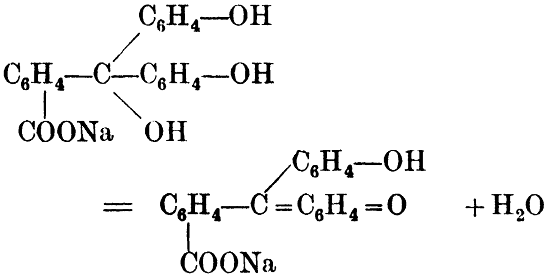
Phenolphthaleïn and most of the phthaleïns derived from it are colourless; on reduction they yield *phthalines*, which are hydroxy-carboxylic acids derived from triphenylmethane :



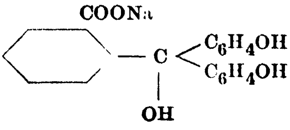
The phthaleïns dissolve in alkalies to form very intense reddish-violet solutions, which are decolorised even by very weak acids, such as carbonic acid. The salts formed contain two atoms of a monovalent metal, and their colour has been explained by the quinonoid theory. The alkali first breaks the lactone ring, then giving a salt of the carbinol, as follows :



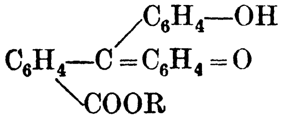
In the same manner that trihydroxytriphenylcarbinol loses water to form Aurine, this *o*-carboxylic acid of the carbinol loses water, thus :



and at the same time the remaining hydroxy-group is converted into the salt. Kober and Marshall (*Journ. Amer. C.S.*, 1912, 1424) have recently prepared the monosodium salt of phenolphthaleïn :



Phenolphthaleïn should have a different constitution in the free state than in the form of a salt, and this tautomerism has been made the subject of a number of researches which can only be mentioned. They include the work of Haller and Guyot (*Compt. rend.*, 1893, **116**, 479; 1895, **120**, 297), and of Friedländer, Meyer, etc. The recent researches of Green and King (*Ber.*, 1906, **39**, 2365; 1907, **40**, 3724), K. Meyer and Hantzsch (*Ber.*, 1907, **40**, 3484), R. Meyer and Marx (*Ber.*, 1907, **40**, 3603; 1908, **41**, 2446), have advanced very good arguments in favour of the quinonoid theory. Green and King have been able to show that the phthaleïns give coloured esters, in which the carboxyl group is esterified, and which should hence have a quinonoid structure, similar to that of the coloured salts; thus:



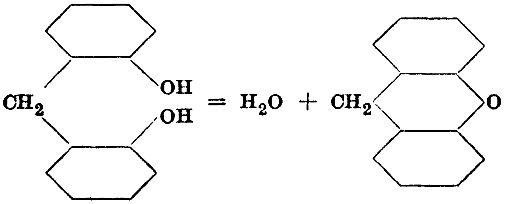
$$\begin{array}{l} \qquad\qquad \diagup C_6H_4-OH \\ C_6H_4-C=C_6H_4=O \\ \qquad \diagdown COOR \end{array}$$

Colourless esters of the lactone form have been known for a long time. In addition a coloured ethyl ether of tetrabromophenolphthaleïn is known which has a quinonoid structure.

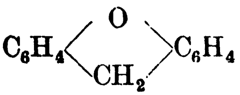
CHAPTER XVII.

XANTHENE DYESTUFFS.

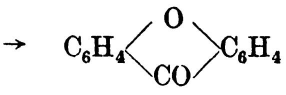
The name xanthene has been given to the internal anhydride of *o*-dihydroxydiphenylmethane :



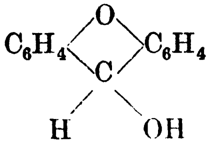
The *o*-dihydroxy-derivatives of di- and of tri-phenylmethane easily lose a molecule of water, being converted into xanthene derivatives. On oxidation xanthene yields a ketone, xanthone, which is converted into xanthhydrol by reducing agents. Xanthhydrol gives salts with acids, and according to present ideas of the basic properties of oxygen the halogen is considered to be attached to the oxygen, which becomes tetravalent.



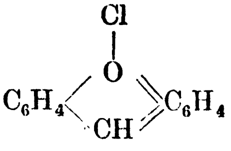
Xanthene.



Xanthone.



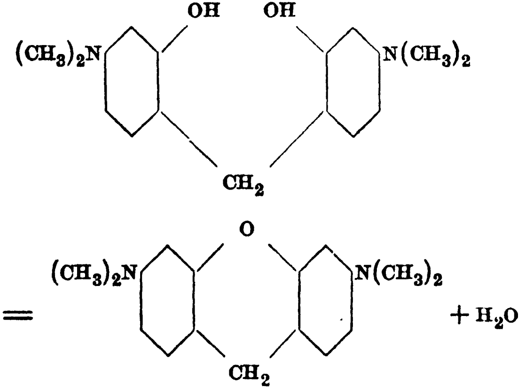
Xanthhydrol.



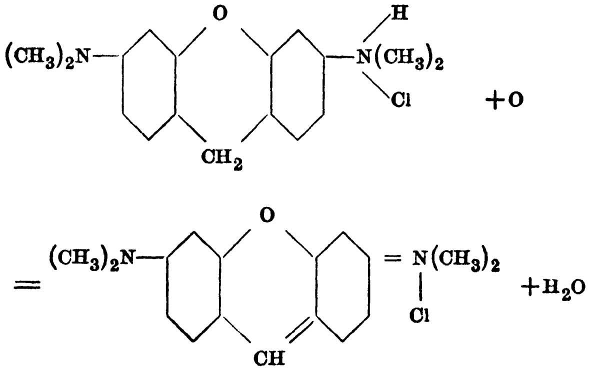
Xanthonium salt.

This last compound is called xanthonium chloride, and the formula given, which is in accordance with the "oxonium theory," represents the oxygen atom as basic and tetravalent. From the following it will be seen that numerous analogies exist to the Thiazines, in which the sulphur atom is tetravalent, and the compounds are called *thiazonium* or *azthionium* derivatives. These ideas were first suggested by A. G. Green (*J.C.S. Proc.*, 1892 and 1895) and have been developed by the researches of Kehrmann (*Ann.*, 1902, **322**, 1; 1910, **372**, 287), Fosse, etc.

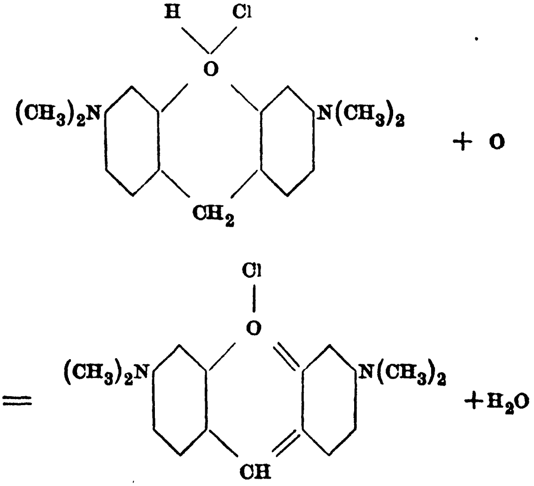
To obtain dyestuffs it is only necessary, as in the case of di- or tri-phenylmethane, to introduce auxochromes in *p*-position to the carbon atom of the methane residue in xanthene, and to oxidise the leuco bases so obtained. The general method for preparing these dyestuffs is to first obtain a *p*-disubstituted *o*-dihydroxy-derivative of di- or tri-phenylmethane, dehydrate this product, and oxidise the resulting compound; thus tetramethyl-*p*-diamido-*o*-dihydroxydiphenylmethane first gives a xanthene derivative:



which on oxidising in acid solution gives the dyestuff. Two constitutional formulae may be assigned to this dyestuff, one, the *para*-quinonoid formula, similar to that of the triphenylmethane dyestuff:

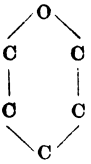


and the other, in which oxygen has become tetravalent, giving an *ortho*-quinonoid formula :



The formula according to the oxonium theory appears to be the one most favoured.

Whichever formula may be adopted, there is present a particular structure of carbon and oxygen atoms known as the *pyrone* ring :

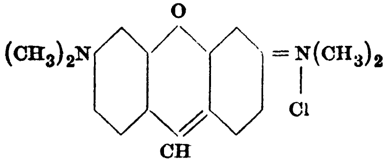


hence these dyestuffs are often called *Pyronines*. The Pyronines form fluorescent solutions.

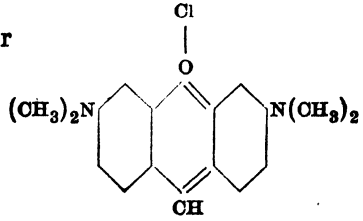
Derivatives of Xanthene.

These compounds are of little importance. They are obtained by condensing formaldehyde with two molecules of a dialkyl-*m*-amidophenol, and dehydrating the product by heating with concentrated sulphuric acid: the diluted solution is then oxidised by means of ferric chloride or nitrous acid (Biehringer, *Journ. f. prakt. Chem.*, 1896, **54**, 217). Another method is to condense formaldehyde with two molecules of an asymmetrical dialkyl-*m*-phenylenediamine, diazotise, boil with water, and convert the *o*-dihydroxy-derivative into a xanthene compound and into a dyestuff as previously described.

Pyronine G. [L.] was discovered by Bender in 1889 (*D.R.P.* 58,955 and 59,003) by condensing dimethyl-*m*-amidophenol with formaldehyde, dehydrating, and then oxidising. Its constitution is as follows:



or

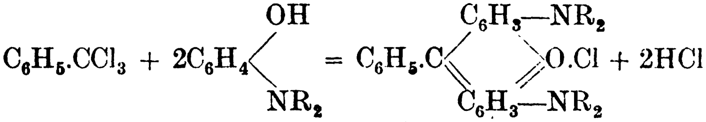


It is a crystalline powder which is soluble in alcohol and water to form a red solution with a yellowish fluorescence. It dyes silk and tanned cotton pink. On oxidising with permanganate it yields a new dyestuff called *Acridine red B*, of which the constitution is unknown.

Pyronine B is obtained by condensing formaldehyde with diethyl-*m*-amidophenol.

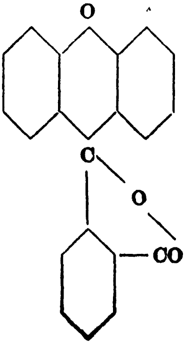
Derivatives of Phenylxanthene.

In the preparation of the Pyronines, if the formaldehyde is replaced by an aromatic aldehyde, benzaldehyde or its substitution derivatives, similar dyestuffs are obtained, which are derivatives of phenylxanthene (Farb. Bayer, *D.R.P.* 62,574). These dyestuffs were discovered by Heumann and Rey (*Ber.*, 1889, 22, 3001) by heating benzotrichloride with dialkyl-*m*-amidophenol:

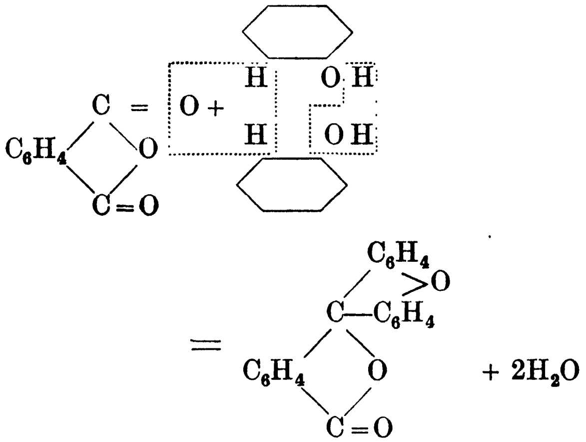


$$C_6H_5.CCl_3 + 2C_6H_4{<}\begin{matrix}OH\\ NR_2\end{matrix} = C_6H_5.C{<}\begin{matrix}C_6H_3-NR_2\\ C_6H_3-NR_2\end{matrix}{>}O.Cl + 2HCl$$

These compounds are called *Rosamines*; they are basic dyestuffs which are more bluish than the Pyronines, but are not of practical importance. The most important dyestuffs are those which are related to both xanthene and phthalophenone, that is to say, to the compound:



This compound has been called *fluorane*, and is formed to a small extent together with phenolphthaleïn on condensing phenol with phthalic anhydride. Its formation is explained by condensation in the *ortho*-position due to dehydration, thus :



Fluorane is a colourless crystalline substance of M.P. 180°. Its solution in sulphuric acid has a green fluorescence.

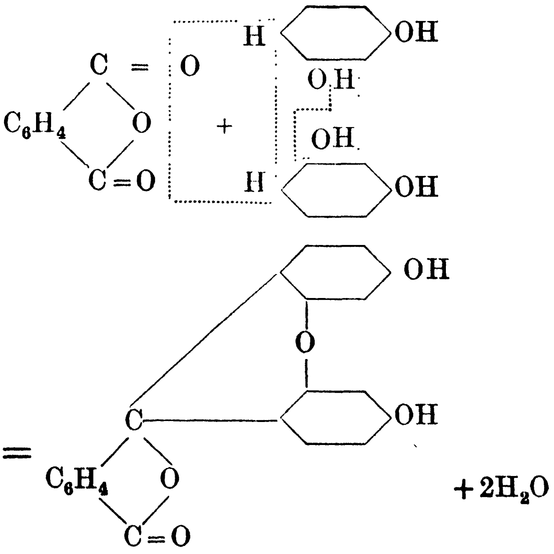
Dyestuffs are obtained by introducing auxochromes into the fluorane nucleus in the *para*-position. They may be divided into hydroxy-derivatives or *Phthaleïns*, and amido- or alkylamido-derivatives, known as *Rhodamines.*

Phthaleïns.

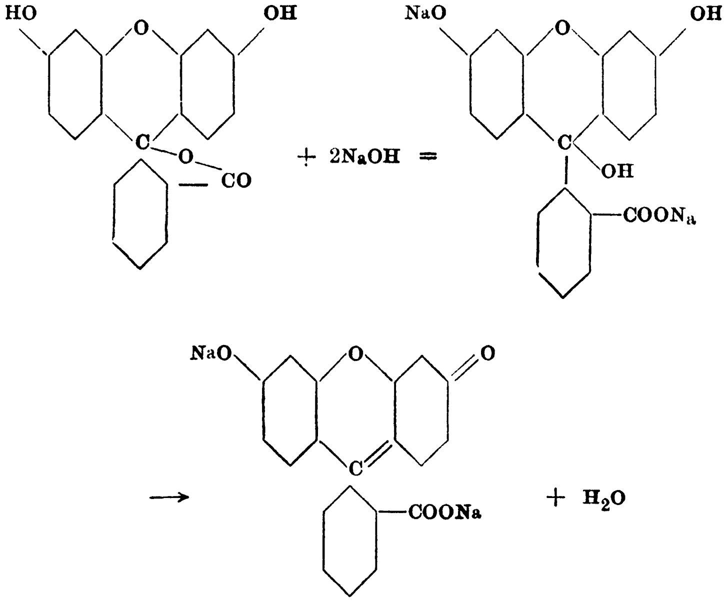
These are obtained by condensing phthalic anhydride with phenols. Whereas phenol yields phenolphthaleïn, which is a triphenylmethane derivative, *m*-dihydroxybenzenes give dyestuffs which are related to phenylxanthene, fluorane, and triphenylmethane.

Fluoresceïn was discovered by Baeyer in 1871 by heating phthalic anhydride with resorcinol to 200°. For its commercial preparation, a mixture of resorcinol and phthalic anhydride is heated in a cast-iron vessel to 180° and powdered zinc chloride added, when an energetic reaction takes place; the heating is continued for ten hours at 190-200°. The mass is dissolved in caustic soda, and the dyestuff precipitated by means of mineral acid. Fluoresceïn forms an orange powder which decomposes at about 300°, and dissolves in alkalies, giving a solution with a strong green fluorescence; its sodium salt is called *Uranine* [B.A.S.F.]. Reducing agents convert fluoresceïn into the colourless fluorescine.

The constitution of fluoresceïn is given by its mode of formation:



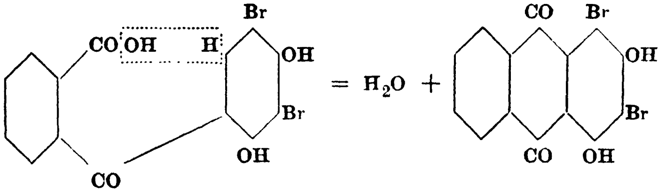
As in the case of phenolphthaleïn, its salts have a quinonoid constitution; alkalies cause the hydrolysis of the lactone ring, and the carbinol loses water as follows:



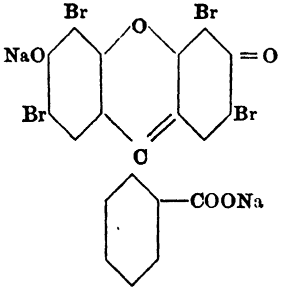
Nietzki and Schrötter (*Ber.*, 1895, **28**, 44) have been able to show that both the isomeric esters exist, one series being coloured and corresponding to the quinonoid formula ; the others colourless, and related to the lactone structure.

Uranine dyes wool yellow from an acid bath, and it is used for printing wool.

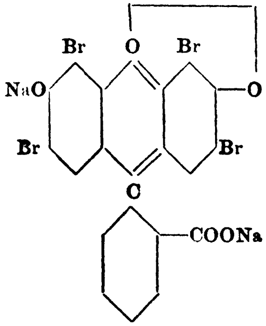
Eosine is the tetrabromo-derivative of fluoresceïn, and was discovered by Caro in 1874 at the Badische Anilin und Sodafabrik, the process being kept secret. Its constitution was established by Gnehm and Hofmann, and confirmed by Baeyer (*Ann.*, 1876, **183**, 1). It is obtained by treating an alcoholic solution of fluoresceïn with bromine, when the tetrabromo-derivative is precipitated in a crystalline form, or by adding an alkaline solution of bromine to an alkaline solution of fluoresceïn and sodium chlorate. Eosine is commercial in the form of its sodium and potassium salts as *Soluble Eosines.* Their constitution has been established by the following reactions: on heating with caustic soda, Eosine gives dibromoresorcinol and dibromodihydroxybenzoylbenzoic acid, which has the following constitution:



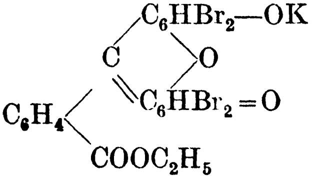
as on dehydrating it yields dibromoxanthopurpurin. On the other hand, this dibromodioxybenzoylbenzoic acid is converted by heating into Eosine and phthalic anhydride. Hence in the form of its salts, Eosine has the constitution:



or



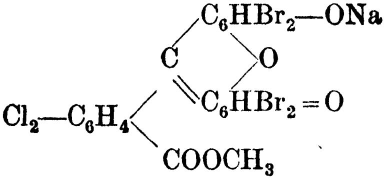
Eosine contains a carboxyl group which can be esterified, the dyestuffs so obtained being of a purer and more bluish shade, but their alkali salts are insoluble in water. These are the *Spirit Eosines* or *Erythrines.* The ethyl ester is prepared by brominating fluoresceïn in alcoholic solution and heating under pressure. The potassium salt is *Spirit Primrose* :



It is a red dyestuff used for dyeing silk.

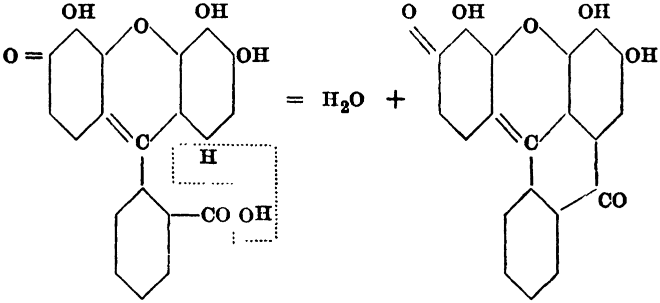
Erythrosines. These are iodo-derivatives of fluoresceïn, and were discovered by Nölting in 1875 by treating an alkaline solution of fluoresceïn with an alkaline solution of iodine. Di-iodo-fluoresceïn is called *Dianthine* or *Orient yellow*; the alkali salts of tetra-iodo-fluoresceïn form *Soluble Primrose*, *Erythrosine B*, etc.

By replacing the phthalic anhydride used in the preparation of fluoresceïn by its halogen derivatives di- or tetra-chlorphthalic anhydrides, di- or tetra-chlor-fluoresceïn is obtained. On treatment with bromine or iodine, these compounds yield the corresponding Erythrines or Erythrosines: thus di-chlor-fluoresceïn yields on bromination *Phloxine,* of which the methyl ester is *Cyanosine* :



Treatment with iodine yields *Rose Bengal.* Tetra-chlor-fluoresceïn gives similar dyestuffs.

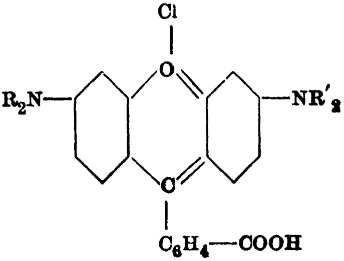
Galleïne is obtained by condensing phthalic anhydride with gallic acid or pyrogallol; thus it is a dioxy-fluoresceïn. It is a crystalline powder which dissolves in alkalies to form a red solution, due to the proximity of the two hydroxy-groups. Galleïne dyes on metallic mordants, giving a beautiful violet on chrome mordant. It is used in the form of a paste for calico-printing. If Galleïne is heated with concentrated sulphuric acid at 200° it is converted into a new dyestuff, *Cœruleïne*, the salts of which are green; this is also a mordant dyestuff used in the printing of calico. Cœruleïne is a derivative of anthracene, being formed as follows:



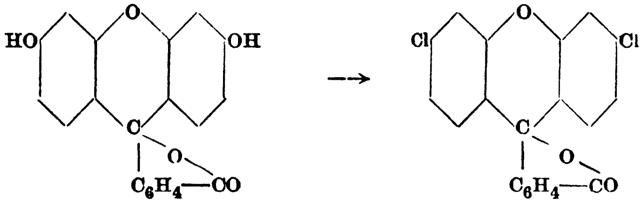
Cœruleïne S. is the bisulphite compound.

Rhodamines.

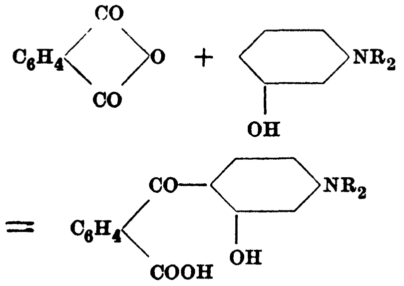
The name *Rhodamines* has been given to the alkyl-amido-derivatives of fluorane. Symmetrical and asymmetrical Rhodamines are known; in the latter the alkyl groups R and R′ are different in the two benzene nuclei, thus:



The symmetrical Rhodamines were obtained by Ceresole in 1887 by condensing phthalic anhydride with dialkyl-*m*-amidophenols. They can also be prepared by converting fluoresceïn into the dichloro-derivative by the action of phosphorus pentachloride, and acting on this compound with dialkylamines.



The asymmetrical Rhodamines are produced by first condensing a molecule of phthalic anhydride with a molecule of a dialkyl-*m*-amidophenol, when a dialkylamidohydroxybenzoylbenzoic acid is obtained :



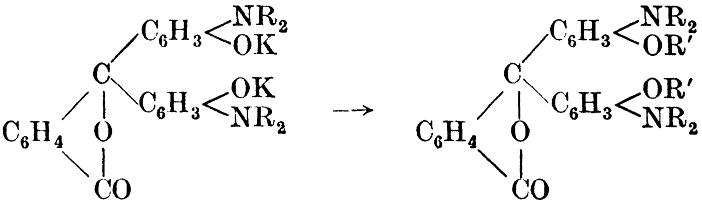
These acids may then be condensed with a further molecule of a dialkyl-*m*-amidophenol different from the first one used.

The Rhodamines are basic red dyestuffs of a remarkably pure shade, and with a strong fluorescence. They dye wool and silk, and cotton mordanted with tannin.

Rhodamine B is obtained by condensing phthalic anhydride with diethyl-*m*-amidophenol It dyes wool and silk a fluorescent bluish red, and dyes tanned cotton red.

Violamines B, R, 2R, G are the hydrochlorides of the phenyl- or tolyl-diamidofluoranes, obtained by the action of aromatic amines, such as aniline, toluidine, phenetidine, etc., on fluoresceïn chloride. Certain of these dyestuffs are the sulphonic acids of such products.

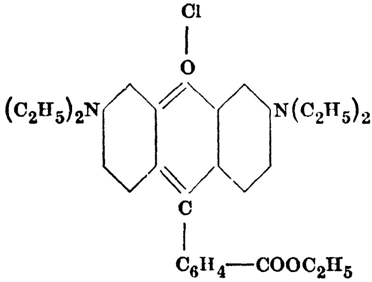
Anisolines. The Anisolines are the esters of the Rhodamines, just as the Erythrines are the esters of the Eosines. In 1891, Monnet of Lyons (*Bull. Soc. chim.*, 1892, 523) obtained new dyestuffs, to which he gave the name Anisolines, by treating the Rhodamine bases with alkylogens. This nomenclature led to an erroneous conception of the reaction, as it would appear that on treating Rhodamines with alcoholic potash the pyrone ring would be broken and the potassium salt of a dihydroxy-compound formed, which would be converted by the alkylogen into a phenolic ester ; hence the name *Anisoline* (from anisole) given to these compounds.



Bernthsen (*Chem.-Ztg.*, 1892, 1956), of the Badische Anilin und Sodafabrik, showed that Anisolines could be obtained by heating Rhodamines with alcohol and a mineral acid, and that the dyestuffs so obtained are esters of the Rhodamines. There resulted the famous lawsuit in London, in 1898 (*Mon. sci.*, 1897, 1898 and 1899) between the Société chimique des usines du Rhône and the Badische Anilin und Sodafabrik, which ended in the annulling of the two patents. That of Monnet, of the Société, was annulled because it claimed the alkylation of a phenol which did not exist ; that of the B.A.S.F. was annulled, due to the insufficient description of the process, as experts found that the esterification of the Rhodamine only proceeds satisfactorily in an iron autoclave, being incomplete if the vessel is enamelled or silvered.

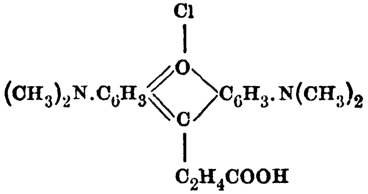
The Anisolines are dyestuffs which are more basic than the Rhodamines, and have the property of dyeing cotton direct, but give much better results on tannin mordanted cotton.

Rhodamine 3B or *Anisoline* is the ethyl ester of Rhodamine B:



Rhodamine 6G is the most important of the Anisolines, being the ethyl ester of the symmetrical diethyl Rhodamine which results from the condensation of phthalic anhydride with mono-ethyl-*m*-amidophenol. It dyes wool and silk a fluorescent red shade, and dyes cotton direct, but better if mordanted with tannin.

Succineïns. These dyestuffs are obtained by condensing succinic anhydride with dialkyl-*m*-amidophenols. *Rhodamine S* is the succineïn of dimethyl-*m*-amido-phenol:

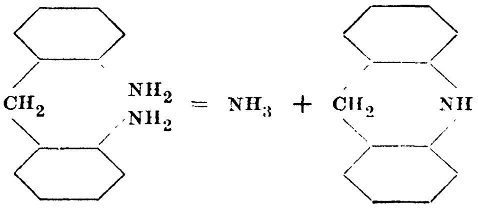


In the same way *saccharin* (*o*-benzoic sulphinide) yields *Sacchareïns* (Kötschet).

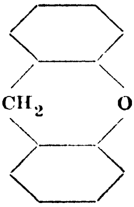
CHAPTER XVIII.

ACRIDINE DYESTUFFS.

The name hydroacridine has been given to the compound obtained by the loss of a molecule of ammonia from a molecule of *o*-diamidodiphenylmethane by the action of heat (I.):

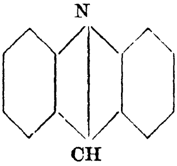


(I.)

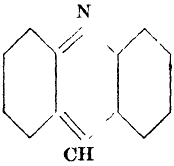


(II.)

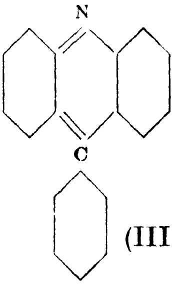
Hydroacridine (I.) and xanthene (II.) are very similar, the oxygen atom in xanthene being replaced by the divalent NH group to give hydroacridine, which on oxidation yields acridine, a basic yellow substance which forms fluorescent solutions; its constitution has been expressed by the formulae (I.) and (II.):



(I.)



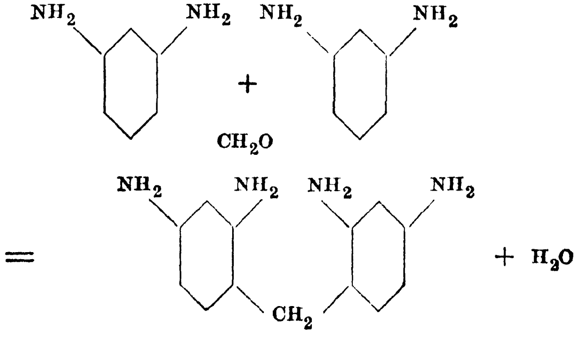
(II.)



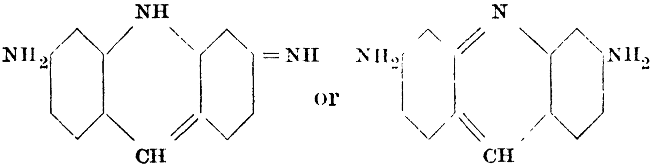
(III.)

Formula (II.), the *ortho*-quinonoid structure, is the one which agrees best with the present ideas of the constitution of coloured substances. Acridine may be considered as being derived from diphenylmethane; but there is also a phenylacridine (III.) which is related to triphenylmethane. To obtain dyestuffs, auxochromes must be introduced into the molecule in *para*-position to the carbon atom of the methane residue; the only dyestuffs of interest are those which contain amido- or alkylamido-groups.

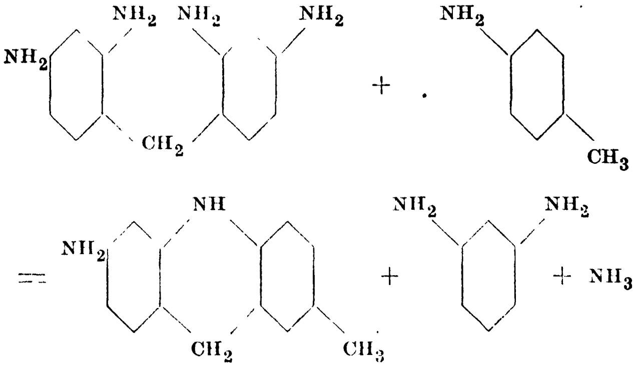
Preparation. The Acridine dyestuffs were discovered by Benda in 1889. They are obtained by methods similar to those used for xanthene derivatives. Formaldehyde is condensed with two molecules of a *m*-diamine or of an asymmetrical dialkyl-*m*-diamine; to obtain triphenylmethane derivatives, the formaldehyde is replaced by benzaldehyde.



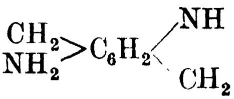
On heating the *o*-diamido derivative of diphenylmethane with an acid, it loses ammonia, yielding a hydroacridine which on oxidation gives the dyestuff. There are two methods of writing the formulae of these dyestuffs, according to whether they are considered as *para*- or *ortho*-quinonoid compounds :



The similarity between the properties of the bases of the dyestuffs and of acridine itself makes the *ortho*-quinonoid formula the more probable. The commercial products are the hydrochlorides of these bases. Asymmetrical acridines may be obtained by heating symmetrical tetramido-derivatives of diphenylmethane with bases, such as *p*-toluidine, or phenols, such as *β*-naphthol, a molecule of a *m*-diamine being eliminated :



This method may be modified by first acting on a molecule of a *m*-diamine with a molecule of aldehyde, when an intermediate compound is formed, which in the case of *m*-toluylenediamine appears to be ·



$$\begin{matrix}CH_2\\NH_2\end{matrix}>C_6H_2<\begin{matrix}NH\\CH_2\end{matrix}$$

On heating with amines or diamines, these intermediate products give symmetrical or asymmetrical Acridines.

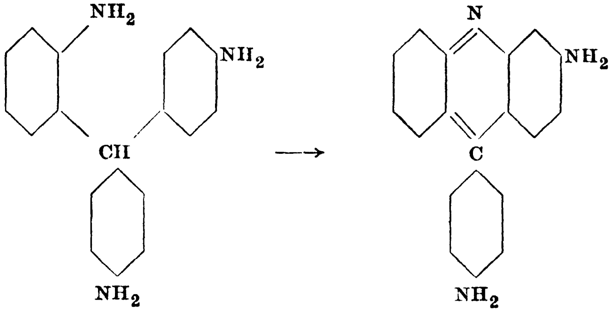
Finally, Michler's ketone condenses with *m*-diamines to give *Auramines*, which on heating are converted into *Acridines*.

Acridine yellow is the hydrochloride of diamidodimethylacridine, and is obtained by condensing formaldehyde with *m*-toluylenediamine and oxidising with ferric chloride the leuco-compound produced. It dyes tanned cotton yellow.

Acridine orange, the hydrochloride of tetramethyldiamidoacridine, is obtained by condensing formaldehyde with dimethyl-*m*-phenylenediamine.

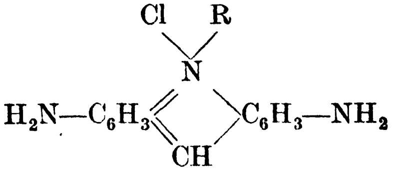
Benzoflavine, the hydrochloride of diamidodimethylphenylacridine, is obtained by condensing benzaldehyde with two molecules of *m*-toluylenediamine, and oxidising the leuco-derivative obtained. It gives yellow shades on wool, silk, and tanned cotton.

Chrysaniline. This is an asymmetrical isomeride of *Benzoflavine*, and was discovered by Nicholson in 1863 among the secondary products from the manufacture of Magenta by the arsenic acid method. Hofmann determined its composition and formula as $C_{20}H_{17}N_3$, and later Fischer and Körner (*Ber.*, 1884, **17**, 203) isolated a second base, the lower homologue, $C_{19}H_{15}N_3$, the constitution of which was established by condensing *o*-nitrobenzaldehyde with aniline, reducing the product, and oxidising the *p*-diamido-*o*-amidotriphenylmethane obtained.



Its formation in the manufacture of Magenta may be explained by supposing that on oxidation of a mixture of *p*-toluidine and aniline, the methyl group of the *p*-toluidine condenses with two molecules of aniline, combination occurring in the *para*-position with one and in the *ortho*-position with the other molecule. As the yield is greater in presence of *o*-toluidine, the higher homologue containing C_{20}, which was the one analysed by Hofmann, may be formed. The commercial product is actually a mixture of the two dyestuffs, which, in the form of their nitrates or hydrochlorides, form *Phosphine*, which is used for dyeing leather and for printing cotton.

The Acridines give alkylated derivatives of the type :

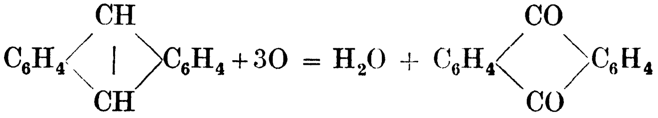


These substances have been studied by Ullmann and Naef (*Ber.*, 1900, **33**, 2470), and are strongly basic dyestuffs which have been called " acridinium " compounds.

CHAPTER XIX.

ANTHRACENE DYESTUFFS.

Anthracene is a colourless hydrocarbon which yields a diketone, anthraquinone, on oxidising with chromic acid :



$$C_6H_4\left\langle \begin{matrix} CH \\ | \\ CH \end{matrix} \right\rangle C_6H_4 + 3O = H_2O + C_6H_4\left\langle \begin{matrix} CO \\ \\ CO \end{matrix} \right\rangle C_6H_4$$

Anthraquinone is of a pale yellow colour, and is one of the most important chromogens. To obtain dyestuffs, it is only necessary to introduce OH, NH_2, NR_2, etc., groups in suitable positions.

Buntrock (*Ber.*, 1901, **34**, 2344) has proposed that the Anthraquinone dyestuffs should be divided into three classes :

(1) Those which only contain OH auxochromes, which only have pronounced tinctorial properties if they contain the two OH groups in *ortho*-position ; these dyestuffs only dye on mordants.

(2) Those containing both OH and NH_2, or NR_2, groups, which dye both on mordanted and unmordanted animal fibres, and in which the OH group need not be in *ortho*-position.

(3) Those which only contain NH_2 or NR_2 auxochromes and do not dye on mordants.

The dyestuffs derived from anthracene will here be discussed in the following order :

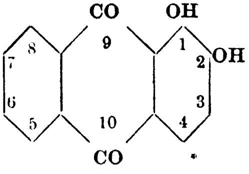
I. The hydroxy-dyestuffs, or *oxyanthraquinones.*

II. The amido-dyestuffs, or *amidoanthraquinones*, and their derivatives.

III. The dyestuffs which contain a further chromogen other than anthraquinone.

I. Oxyanthraquinones.

The hydroxy-derivatives of anthraquinone dissolve in alkalies to form violet or blue solutions. Their use in dyeing depends on their property of forming insoluble lakes with metallic hydroxides. This property is not, however, common to all the oxyanthraquinones. Of the two isomeric mono-oxyanthraquinones, the one in which the OH group is near to the chromophore (CO) has to some extent the property of dyeing on metallic mordants. The introduction of a second OH group in *ortho*-position to the first one increases the affinity for mordants, this affinity being greatest when, the two OH groups being in *ortho*-position to one another, one of them is near to the chromophore (CO). This is the case in *Alizarin*, 1 : 2-dioxyanthraquinone (the carbon atoms of anthracene are numbered from 1 to 10 as shown) :



At one time it was considered possible to generalise by stating that, for a polyoxyanthraquinone to be a useful mordant dyestuff, it must contain at least two OH groups in *ortho*-position, of which one should be adjacent to the CO group, this being known as the rule of Liebermann and Kostanecki. It has since been recognised that this is somewhat too general, as anthraquinone derivatives are now known which are mordant dyestuffs, but do not fulfil these conditions. Thus by introducing a hydroxyl group and a carboxyl, nitroso, quinone, or oxime group, or two oxime groups, in *ortho*-position into a chromogen, the resulting compound is a pronounced mordant dyestuff. Nölting has also shown (*Chem.-Ztg.*, 1910, 977) that the introduction of a hydroxy- and an amido-group in *ortho-* or *para*-position has the same effect (see p. 218); this is pronounced in the case of the Anthraquinone series, but is not so evident in the other series.

The rule of Liebermann and Kostanecki shows that, of the tri-, tetra-, or poly-oxyanthraquinones, the only ones of practical interest are the oxyalizarins, the mono-oxyanthraquinones being of no interest in dyeing.

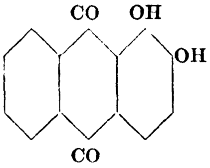
Dioxyanthraquinones.

All the ten dioxyanthraquinones predicted by theory have been prepared; they have the following names:

1 : 2	dioxyanthraquinone	Alizarin.
1 : 3	,, ,,	Purpuroxanthin.
1 : 4	,, ,,	Quinizarin.
1 : 5	,, ,,	Anthrarufin.
1 : 6	,, ,,	Recently prepared by Frobenius and Hepp (*Ber.*, 1907, **40**, 1048).
1 : 7	,, ,,	*m*-Dioxyanthraquinone.
1 : 8	,, ,,	Chrysazin.
2 : 3	,, ,,	Histazarin.
2 : 6	,, ,,	Anthraflavic acid.
2 : 7	,, ,,	Isoanthraflavic acid.

Of these, the most important are: *Alizarin*, which is itself a dyestuff, and the three dioxyanthraquinones which have the OH groups near to the chromophore: Quinizarin, Anthrarufin, and Chrysazin, which are used for the preparation of other dyestuffs.

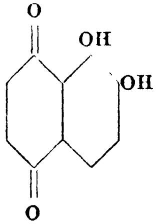
Alizarin.



Alizarin is a dyestuff which is present in the roots of plants of the madder-family, mainly in the *rubia tinctorum L* or madder, in which it occurs as the glucoside, ruberythric acid, together with the trioxyanthraquinone *Purpurin.*

According to Pliny, madder was used in the ancient civilisations. During the reign of Charlemagne, the cultivation of the madder was much encouraged, but it disappeared completely in the following years. It was taken up again in the sixteenth century in Holland and in Saxony about the year 1507, and again in France in 1729, where it was mainly carried on in Alsace, and then under Louis XVI. in Provence. With the Revolution and the Empire, the use of madder gradually decreased until the time of Louis-Philippe, when its culture was increased in consequence of its use for dyeing military materials. This prosperity continued until the synthetic manufacture of Alizarin completely replaced the cultivation of the madder plant. Although it is still used for dyeing military materials, synthetic Alizarin has almost entirely replaced the natural product.

Constitution of Alizarin. Alizarin and Purpurin were first extracted from madder-root by Robiquet and Colin in 1826. The constitution and even the exact composition of these products remained unknown for a very long time. This was partly due to the difficulty of obtaining them in the pure state, and partly to the inexact atomic weights which were then known. It was for these reasons that Robiquet, who published exact analyses of Alizarin in 1835, having found : C, 70·09 per cent., H, 3·73 per cent. ; (theoretical for $C_{14}H_8O_4$: C, 70·00 per cent., H, 3·33 per cent.), deduced an incorrect formula, $C_{37}H_{24}O_{10}$, which corresponds to $C_{37}H_{48}O_{10}$ with the present atomic weights. Other formulae proposed were : $C_{20}H_{18}O_9$ (Schiel), $C_{30}H_{20}O_9$ (Debus), $C_{14}H_{10}O_4$ (Schunck in 1848). From this time confusion was caused by the fact that Schunck obtained by the oxidation of Alizarin an acid which he called alizaric acid, and which Gerhardt in 1849 considered to be identical with phthalic acid, which Laurent had obtained by oxidising naphthalene. This view was confirmed by Wolff and Strecker in 1850, and from that time Alizarin was considered to be a derivative of naphthalene, the formula $C_{10}H_6O_3$ being assigned to it until 1868. These ideas led Roussin to the discovery of Naphthazarin, in 1861, by heating 1 : 5 and 1 : 8 dinitronaphthalene with sulphuric acid and zinc, the mechanism of the reaction being explained later by Zincke and Schmidt (*Ann.*, 1895, **286**, 27). This substance is a 1 : 2 dioxynaphthaquinone of the following formula :

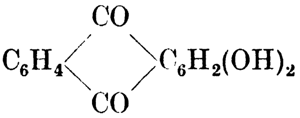


At about the same time that Roussin discovered Naphthazarin, Graebe and Liebermann were studying the quinones and their hydroxy-derivatives ; they found a great similarity between these compounds and Alizarin and Purpurin. By applying to the latter compounds the method of distilling with zinc powder, which gives the hydrocarbon, a method which Baeyer had just used with success in other cases, Graebe and Liebermann (*Ber.*, 1868, **1**, 49) obtained anthracene.

Alizarin and Purpurin were hence derivatives of anthracene, probably being dioxy- and trioxy-anthraquinones :

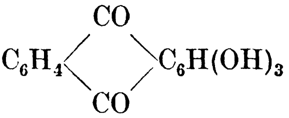
$$C_{14}H_6(OH)_2\left\{\begin{matrix}O\\O\end{matrix}\right.\!> \quad \text{and} \quad C_{14}H_5(OH)_3\left\{\begin{matrix}O\\O\end{matrix}\right.\!>$$

This deduction received a striking confirmation by the synthesis of Alizarin, carried out by Graebe and Liebermann on January 11th, 1869, by heating dibromoanthraquinone with caustic potash. This was the first synthesis of a naturally occurring dyestuff. De Lalande having shown that the oxidation of Alizarin gives Purpurin and then phthalic acid, it followed that the hydroxyl groups must be present in only one of the rings of anthraquinone, which according to Zincke and Fittig has a symmetrical constitution, and their constitutions become :



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_2(OH)_2$$

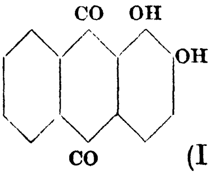
and



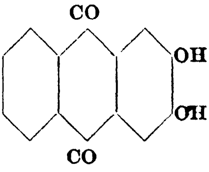
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H(OH)_3$$

Alizarin. Purpurin.

The positions of the OH groups were determined by Baeyer and Caro (1874-5), as follows : the condensation of phthalic anhydride with pyrocatechol in presence of sulphuric acid yields Alizarin, and hence the two hydroxyl groups are in *ortho*-position to one another. Two formulae are then possible :

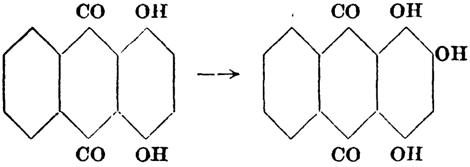


(I.)



(II.)

On the other hand, if hydroquinone is condensed with phthalic anhydride under the same conditions, an isomer of Alizarin is obtained, Quinizarin, in which the hydroxyl groups must be in *para*-position to one another :



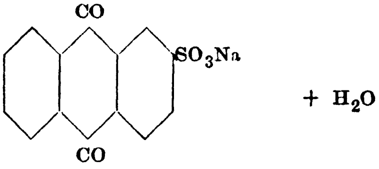
Quinizarin. Purpurin.

Careful oxidation of Quinizarin gives Purpurin, which must therefore be 1 : 2 : 4 trioxyanthraquinone. As Alizarin also gives Purpurin on oxidation, it must have in it two OH groups in 1 : 2 positions and not 2 : 3. Hence Alizarin is 1 : 2 dioxyanthraquinone and has formula (I.) on p. 205.

Manufacture of Alizarin. The commercial application of Graebe and Liebermann's synthesis encountered great practical difficulties ; at that time anthracene was still a rare product, and its conversion into dibromoanthraquinone was expensive. Caro, at the Badische Anilin und Sodafabrik (who used the method), found that anthraquinone may be converted under certain conditions into the sulphonic acid and this latter into Alizarin. This discovery was patented in England on the 25th of June, 1869. On the following day, Perkin applied for a provisional patent for an identical process which he had discovered independently. The two investigators then collaborated with the B.A.S.F.

The commercial manufacture includes three processes : oxidation of the anthracene to anthraquinone, sulphonation of this product, and then alkaline fusion of the sulphonic acid. The anthraquinone is prepared by oxidising anthracene with potassium or sodium dichromate and sulphuric acid. After being purified as already described (p. 17), the anthracene must be sublimed. This is carried out by heating in a horizontal vessel connected with a condensing apparatus, the anthracene vapours being carried forward by a current of superheated steam at 220-240°. The condensation is effected in an apparatus in which is a spray of water which precipitates the anthracene in small crystals. These are dried and then sieved to separate the fused particles which are rich in phenanthrene. The anthracene content of this product is determined and the amount of oxidising agent necessary is calculated. The dilute solution of sodium or potassium dichromate (100 to 150 kilograms in 1,500 litres of water) is placed in a lead-lined wooden vat fitted with a stirrer, and brought to the boil by passing in steam. 100 kilograms of the finely divided anthracene is then added, and the corresponding amount of dilute sulphuric acid (52° Tw.) then run in slowly over a period of nine to ten hours. The heat evolved by the reaction keeps the mass at the boil, and when all the acid has been added it is kept boiling for a short time and then allowed to cool. The crude anthraquinone which is precipitated, is separated by a filter press, washed, and then purified. For this purpose it is dried, two to three parts of sulphuric acid (168° Tw.) added, and the whole heated in a cast-iron vessel to 80° until the anthraquinone is completely dissolved. The liquid is then heated to 110° until a sample poured into water gives a pure white precipitate. All the impurities will then have been converted into sulphonic acids, the anthraquinone being unchanged. The liquid is allowed to cool, and then poured into twenty times its weight of water, the resulting liquid boiled and the anthraquinone separated and dried. It will then contain about 90 per cent. of anthraquinone, and may be further purified to a 98 per cent. content by boiling with a solution of sodium carbonate, and subliming. The yield is 96-98 per cent. of the theoretical.

Sulphonation of Anthraquinone. On heating anthraquinone to a high temperature (250-260°) with concentrated sulphuric acid, a mixture of the mono- and di-sulphonic acids is produced. Since the commencement of the manufacture of artificial Alizarin in 1871, it has been noticed that in order to obtain a bluish shade of Alizarin it is necessary to commence with the mono-sulphonic acid, whereas the use of anthraquinone di-sulphonic acid yields a yellowish Alizarin, which contains trioxyanthraquinone, and is of less value. Sulphonation with ordinary acid was then replaced by sulphonation with fuming sulphuric acid, which permits of the process being carried out at a lower temperature. The following conditions are those which obtain in practice: one part of 95 per cent. anthraquinone is heated with one part of fuming sulphuric acid (containing 45 per cent. of SO_3) for one hour at 160-170°, and then the mass is allowed to run in a thin stream into boiling water. Under these conditions about 20-25 per cent. of the anthraquinone remains unchanged, and, as it is insoluble, may be separated by filtration, leaving a solution containing a mixture of the mono- and di-sulphonic acids. The solution is neutralised by means of caustic soda, and, on cooling, the hydrated sodium salt of anthraquinone β-monosulphonic acid is precipitated in glistening plates known as "silver salt."



On concentration the mother liquors yield a further amount of a less pure sample of the salt, but if the concentration is carried further sodium sulphate separates; finally, by evaporating to dryness the solution freed from this salt, a mixture of the sodium salts of the α- and β-disulphonic acids is obtained. These disulphonic acids are obtained free from the mono-acid by sulphonating anthraquinone with two or three parts of the fuming acid until all the anthraquinone has been converted.

Alkaline Fusion of "Silver Salt." The sodium salt of anthraquinone monosulphonic acid yields Alizarin on fusing with caustic potash or caustic soda. In the same way the anthraquinone disulphonic acids yield trioxyanthraquinones (Purpurin, etc.). The number of hydroxy-groups which may be introduced in this manner is equal to the number of sulphonic acid groups *plus* 1, whereas in the case of the benzene and naphthalene sulphonic acids, alkaline fusion replaces the sulphonic acid groups by an *equal* number of hydroxy-groups. This further hydroxy-group is produced by oxidation:

$$\underset{\text{“Silver salt.”}}{C_{14}H_7O_2SO_3Na} + 3NaOH + O_2$$

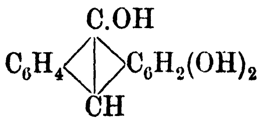
$$= \underset{\text{Sodium salt of Alizarin.}}{C_{14}H_6O_2(ONa)_2} + Na_2SO_4 + 2H_2O.$$

This fusion was originally carried out in shallow cast-iron vessels with a large surface, fitted with a mechanical stirrer, and heated to 200-280°. Under these conditions an oxidation occurs partly by the oxygen of the air and partly at the expense of the organic material itself. To avoid the latter, which results in a smaller yield, Koch has recommended the addition of sodium chlorate to the melt. The process is very long, lasting several days, and only gives a yield of 30-40 per cent. of the theoretical. This process has hence been modified: the mixture of "silver salt" and alkali is first melted in iron vessels and the mass spread out in a thin layer on iron plates heated in oil stoves. The air passing over the plates oxidises the mass completely, and the yield is raised to 80 per cent. of the theoretical. Since the year 1873, the "silver salt" has been heated under pressure with caustic soda solution; as the reaction takes place in a closed vessel, potassium chlorate is added to yield the necessary oxygen. The operation is carried out in wrought-iron vessels furnished with stirrers, and capable of withstanding great pressure. The temperature attained is 160°, and the reaction lasts for twenty hours (for details, see *Dict. de Würtz*, Suppl., p. 100, and A. G. Perkin (*Mon. sci.*, 1897, 498)). The mass is poured into water and the boiling liquid neutralised by hydrochloric acid or dilute sulphuric acid. Alizarin is precipitated, and is separated and washed. It comes into the market in the form of a 20 per cent. paste, or for export in 40 to 60 per cent. pastes to reduce the cost of transport.

Properties. Alizarin is almost insoluble in cold water; it crystallises from dilute alcohol in yellow plates of M.P. 289-290°. It is used in dyeing and printing to obtain shades which are fast to washing and to light. When used on mordanted material, it gives the following shades: With aluminium hydroxide, bluish red; with chromium hydroxide, reddish brown; with ferric hydroxide, deep violet; and with stannic hydroxide, violet. Liechti and Suida, Liebermann, Guggiari (*Ber.*, 1912, **45**, 2442) and others, have shown that the composition of these lakes approaches those of the normal salts. On the other hand, Biltz, Haller (*Färb.-Ztg.*, 1912, 489, 523) and others, are of the opinion that lake-formation is a phenomenon of a colloidal character.

According to the purity of the Alizarin, the red obtained with alumina is more or less yellow; the production of blue shades of Alizarin is due to the use of pure Alizarin or admixture with a little Purpurin; yellowish shades of Alizarin consist mainly of Isopurpurin and Flavopurpurin.

The leuco-compounds of Alizarin and of its derivatives which only contain one oxygen atom in the nucleus, for example:

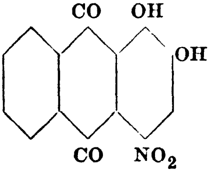


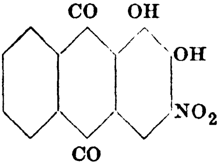
$$C_6H_4\left\langle \begin{array}{c} C.OH \\ | \\ CH \end{array} \right\rangle C_6H_2(OH)_2$$

are mordant dyestuffs, which give fast shades with wool and cotton on chrome mordant, and on wool by the after-chrome method (Bayer Co., *E.P.* 27,028 (1909)).

On treatment with fuming sulphuric acid at 140°, Alizarin gives a sulphonic acid, the sodium salt of which forms *Alizarin S*, used for dyeing wool on alumina or chrome mordant.

There should exist 6 nitroalizarins, of which three are known; the most important are *a*- and *β*-nitroalizarin :





a-Nitroalizarin is obtained by nitrating diacetylalizarin or benzoylalizarin, or by nitrating Alizarin itself in sulphuric acid solution. It crystallises in needles of M.P. 194-196°.

β-Nitroalizarin is the most important. It is prepared by treating solid Alizarin with nitrous fumes, or by passing these fumes into a solution of Alizarin in nitrobenzene, petroleum ether, ether, etc. Alizarin may also be nitrated in glacial acetic acid solution (Rosenstiehl, *Compt. rend.*, 1876, **82**, 1455; **83**, 73; Schunck and Römer, *Ber.*, 1879, **12**, 581). *β*-Nitroalizarin forms orange needles of M.P. 244°. It comes on the market in the form of a 20 per cent. paste under the name of *Alizarin orange*, and is used on alumina or chrome mordant, with which it gives orange and brown shades respectively. It is also used for the manufacture of *Alizarin blue.*

Isomers of Alizarin.

Quinizarin, or 1 : 4 dioxyanthraquinone, is obtained by condensing phthalic anhydride with hydroquinone by means of sulphuric acid, or by heating anthraquinone with concentrated sulphuric acid in presence of boric acid or sodium nitrite. It crystallises from alcohol in red needles.

Anthrarufin, or 1 : 5 dioxyanthraquinone, is obtained by condensing two molecules of *m*-oxybenzoic acid in sulphuric acid solution, or by treating anthraquinone or erythroanthraquinone with fuming sulphuric acid, containing 75-95 per cent. SO_3, in presence of boric acid. Finally, it may be obtained by heating anthraquinone 1 : 5-disulphonic acid with milk of lime under pressure (Höchst Farbwerke, *D.R.P.* 106,505).

Chrysazin, or 1 : 8-dioxyanthraquinone, is prepared by heating the corresponding 1 : 8-disulphonic acid under pressure with lime.

Trioxyanthraquinones.

The most important trioxyanthraquinones are those which have two hydroxyl-groups in *ortho*-position to one another, one being adjacent to the CO, that is to say, the oxyalizarins, of which there are six :

Anthragallol,	1 : 2 : 3-	trioxy	anthraquinone.
Purpurin,	1 : 2 : 4-	,,	,,
Oxyanthrarufin,	1 : 2 : 5-	,,	,,
Flavopurpurin,	1 : 2 : 6-	,,	,,
Isopurpurin,	1 : 2 : 7-	,,	,,
Oxychrysazin,	1 : 2 : 8-	,,	,,

Anthragallol is obtained by condensing benzoic acid and gallic acid in molecular proportions in sulphuric acid solution. Anthragallol is present together with rufigallic acid in *Anthracene brown*, which gives brown shades on alumina or chrome mordant.

Purpurin was found to be present with Alizarin in the madder-root in 1826. Lalande prepared it synthetically by oxidising Alizarin with arsenic acid, or with manganese dioxide and sulphuric acid. It forms orange needles of M.P. 253°. Purpurin dissolves in a boiling solution of alum, forming a yellowish red fluorescent liquid. By this reaction, natural Alizarin extracted from madder, which contains Purpurin, may be distinguished from synthetic Alizarin. Purpurin gives scarlet shades on alumina mordant.

Oxyanthrarufin is obtained by the action of fuming sulphuric acid on Alizarin in presence of boric acid.

Flavopurpurin is prepared by the alkaline fusion of anthraquinone disulphonic acid in a closed vessel in presence of potassium chlorate. It is commercial in the form of a 20 per cent. paste, and gives a yellowish red shade on alumina mordant and a violet red on iron mordant; it is called *Alizarin GI*, *RG*, *SDG*, *X*, etc.

Isopurpurin is obtained by the alkaline fusion of anthraquinone-2 : 7-disulphonic acid. It is also called *Anthrapurpurin*, or oxyisoanthraflavic acid, and gives scarlet shades on alumina mordant.

Polyoxyanthraquinones.

The polyoxyanthraquinones are obtained by oxidising the di- or tri-oxyanthraquinones. This oxidation may be carried out by means of manganese dioxide in sulphuric acid solution, or by sulphuric anhydride. The latter process has become of considerable importance, tetra- and penta-oxyanthraquinones, etc., being readily obtained by its use. The oxidising action of SO_3 had already been employed by Bohn (*Ber.*, 1890, **23**, 3739) in the case of Alizarin blue, and was extended by Graebe and Phillips (*Ann.*, 1893, **276**, 21), and Gattermann and Schmidt (*J. prakt. Chem.*, 1891, **43**. 237, 246; 1892, **44**, 103) to the hydroxy-derivatives. This oxidation with fuming sulphuric acid commences even at 50°, whereas ordinary sulphuric acid requires higher temperatures (200°), at which secondary reactions occur. By this process two hydroxyl groups can generally be introduced in *para*-position to one another. The oxidising action of sulphuric anhydride may be represented by the following equation :

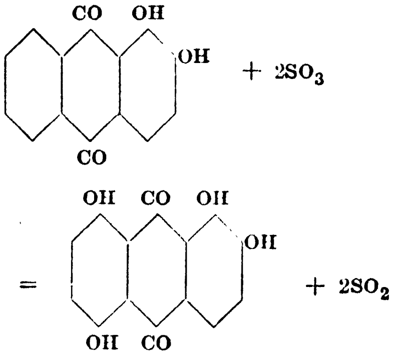
$$R<{}^{H}_{H}+2SO_3 = R<{}^{OH}_{OH}+2SO_2$$

but actually the reaction is more complicated ; neutral sulphuric esters are formed which are converted by the action of alkalies and acids into acid esters and then into diphenols :

$$R<{}^{O}_{O}>SO_2 \longrightarrow R<{}^{OSO_3H}_{OH} \longrightarrow R<{}^{OH}_{OH}$$

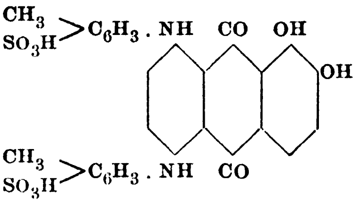
It has further been found that the presence of boric acid aids this reaction considerably, and it may then be effected even by means of concentrated sulphuric acid. By this last process, anthraquinone may be converted directly into *Quinizarin.*

Alizarin bordeaux, or 1 : 2 : 5 : 8-tetraoxyanthraquinone, is obtained by heating Alizarin with fuming sulphuric acid containing 70 per cent. of SO_3, and then saponifying the sulphuric ester formed :



It dyes wool mordanted with alumina a claret shade, and gives dark violet shades on chrome mordanted wool.

Alizarin Viridine DG or *FF* [By.] is obtained by heating Alizarin bordeaux with *p*-toluidine and sulphonating the product ; it has the following constitution :



In presence of a large excess of chromium acetate, green shades are obtained which are exceedingly fast to washing (Hannay, *Journ. Soc. Dyers and Col.*, 1913, 36).

Alizarin Cyanine, 1 : 2 : 4 : 5 : 8-pentaoxyanthraquinone, is related to *Alizarin bordeaux* in the same manner that *Purpurin* is related to *Alizarin.* It is obtained by oxidising this dyestuff with manganese dioxide and sulphuric acid. It dyes wool mordanted with alumina a blue shade.

The other pentaoxyanthraquinones are prepared by oxidising trioxyanthraquinones with SO_3.

Rufigallic acid, 1 : 2 ; 3 : 5 : 6 : 7-hexaoxyanthraquinone, was obtained by Robiquet in 1836 by heating gallic acid with sulphuric acid. It gives brown shades on chrome mordanted material.

Anthracene blue, 1 : 3 : 4 : 5 : 7 : 8-hexaoxyanthraquinone, is obtained by heating 1 : 5-dinitroanthraquinone with fuming sulphuric acid, containing 40 per cent. of SO_3, with or without a reducing agent. Sulphuric esters are first formed and are then hydrolysed. It is commercial in the form of a paste, and dyes chrome mordanted material blue. Its sulphonic acids form the *Alizarin Acid blues BB* and *GR* [M.L.B.].

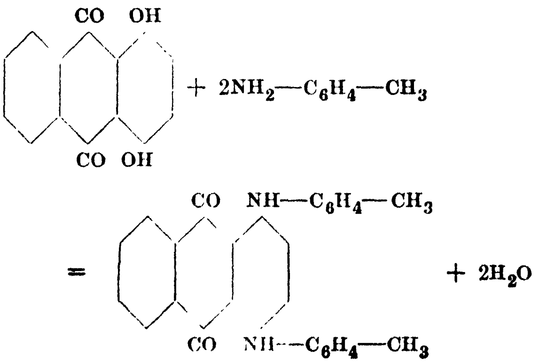
Octaoxyanthraquinone has recently been prepared by Georgievics (*Monatsh. f. Chem.*, 1911, **32**, 347) by oxidising Rufigallol with sulphuric acid in presence of boric acid and mercury.

II. Amido- and Hydroxyamido-Dyestuffs.

If polyoxyanthraquinones are heated with ammonia under pressure, new dyestuffs are obtained in which a certain number of the NH_2 groups are substituted for hydroxyl groups. The amido- and alkyl- or aryl-amido-derivatives of anthraquinone are very valuable dyestuffs, being used in the form of their sulphonic acids. These dyestuffs generally have the amido-groups in *α*-position, that is, adjacent to the ketonic group. Their sulphonic acids are acid dyestuffs for wool which dye from an acid bath ; they yield very bright shades, similar to those of the triphenylmethane dyestuffs, but differing from these in their great fastness to light, a property which is characteristic of the anthracene derivatives.

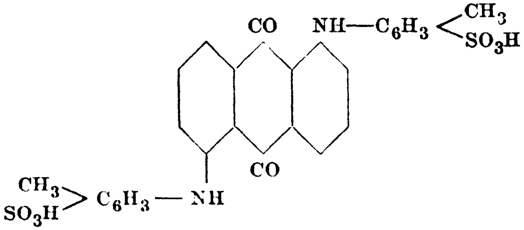
Amidoanthraquinone and its Derivatives.

The most important of these dyestuffs are those which contain one or two NHR groups, where R represents a sulphonated aromatic nucleus. They are obtained by heating disubstituted derivatives of anthraquinone with aromatic amines ; these derivatives may be dibrom-, dichlor-, dinitro- or dihydroxy-anthraquinones, or anthraquinone disulphonic acids, or their reduction products, or mixed derivatives such as the bromonitro-, hydroxynitro-, etc., compounds. Thus on boiling Quinizarin or leuco-Quinizarin with *p*-toluidine, with or without the addition of boric acid, the following reaction occurs :

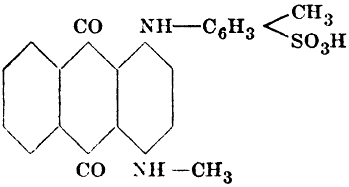


In order to render this product soluble, it is sulphonated, when the sulphonic acid groups enter the toluidine nucleus, giving *Alizarin Cyanine green.*

By using a 1 : 5-disubstituted anthraquinone, the isomer, *Anthraquinone violet*, is produced :



The reaction may also be made to take place in such a manner as to introduce two different amine residues in turn ; thus one may be aromatic, the other aliphatic, as in *Alizarin Astrol* :

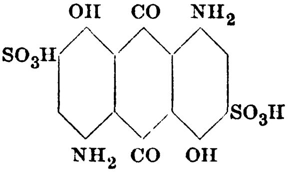


The constitution of these dyestuffs has been established by Friedländer and Schick (*Zeitsch. Farben- u. Textil-Chemie*, 1902, **2**, 429 ; 1903, **3**, 218).

Hydroxyamidoanthraquinones and their Derivatives.

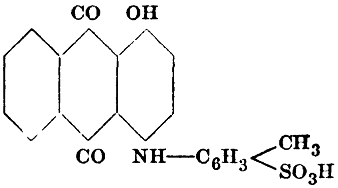
These compounds may be obtained in several ways : by heating hydroxyanthraquinones with ammonia under pressure ; by partial reduction of the nitro-derivatives ; or by carefully heating aromatic amines with α-hydroxy-derivatives of anthraquinone. Again in this case the sulphonic acids are used as acid dyestuffs for wool.

The oldest dyestuff known of this series is *Alizarin Saphirol*, which may be obtained either from Anthrarufin, by sulphonating, nitrating, and then reducing, or from 1 : 5-dinitroanthraquinone, by reducing carefully in alkaline solution, acidifying, and sulphonating the product. It has the following constitution :

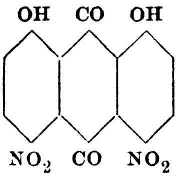


By the action of formaldehyde, *Alizarin Celestol* is obtained.

If, in the preparation of Alizarin Cyanine green, only one group is replaced by *p*-toluidine, there is obtained the arylamido-hydroxy-dyestuff, *Alizarin Irisol* :



Certain of these *p*-hydroxyamido-dyestuffs also dye on metallic mordants (Nölting, *Mon. sci.*, 1911, 540 ; *Färb.-Ztg.*, 1911, 22, 174). Thus the Bayer Co. discovered that dinitrochrysazin :



gives blue shades on chrome mordanted wool, and it has since been shown that it also dyes on mordanted cotton ; diamidochrysazin possesses the same properties.

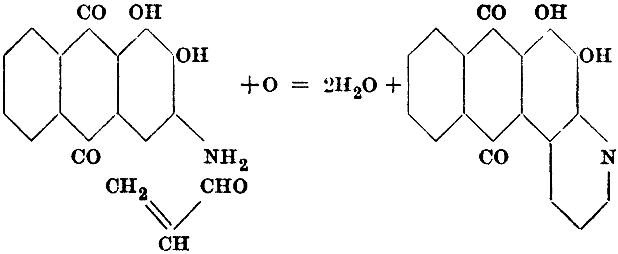
The hydroxyamido-derivatives give full shades on copper mordant (Nölting, *Chem.-Ztg.*, 1910, 977).

III. Anthraquinone Derivatives containing a Further Grouping.

By treating β-nitroalizarin with glycerol and sulphuric acid, Prudhomme (*Bull. Soc. ind. de Mulhouse*, 1877, **28**, 62) obtained a substance which crystallised in blue needles, dyed chrome mordanted wool, and which he called *Alizarin blue.* Graebe (*Ber.*, 1878, **11**, 522, 1646; 1879, **12**, 1416; and 1882, **15**, 1783) determined its constitution, and showed that it is formed according to the following equation:

$$C_{14}H_7(NO_2)O_4 + C_3H_8O_3 = C_{17}H_9NO_4 + 3H_2O + O_2.$$

The oxygen liberated causes the formation of brown secondary products. *Alizarin blue* is also obtained by heating β-amidoalizarin with glycerine, sulphuric acid, and nitrobenzene. In these reactions the glycerine yields acroleïn, which condenses with the Alizarin derivative, giving a dioxyanthraquinolinequinone:

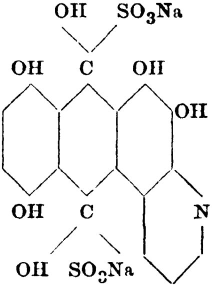


This is identical with the reaction which is used for the synthesis of quinoline from aniline, glycerine, and sulphuric acid (Skraup's reaction).

Alizarin blue is more often found in commerce in combination with sodium bisulphite as *Alizarin blue S*, which is used for printing chrome mordanted cotton.

If the β-nitroalizarin is replaced by its α-isomer, a green dyestuff is obtained, *Alizarin green S* [M.L.B.], which is used on nickel mordant.

In 1890 R. Bohn found that on treating *Alizarin blue* with fuming sulphuric acid containing 70 per cent. of anhydride, there were formed successively several products. *Alizarin blue-green,* which is the sulphonic acid of a trioxyanthraquinolinequinone, is first produced, and then this compound is converted by treatment with concentrated sulphuric acid at 120° into tetraoxyanthraquinolinequinone, the bisulphite compound of which is *Alizarin green S* [B.A.S.F.] :

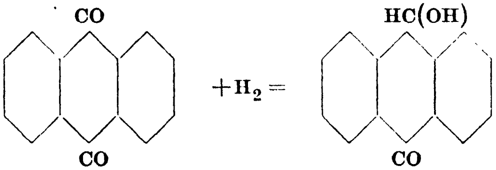


By raising the temperature to 200°, another hydroxyl group is introduced, giving *Alizarin indigo blue.*

Vat Dyestuffs derived from Anthracene.

The name " vat-dyestuffs " has been given to those dyestuffs which are insoluble in water, but give soluble products on reduction, which may be coloured or otherwise, and which have a distinct affinity for textile fibres. For dyeing it is sufficient to allow the material to remain in the vat, remove it, and expose to air ; the original insoluble substance is again formed inside the cells of the fibre, on which it is thus fixed. Indigo is a typical vat-dyestuff, and for a long time the vat-dyestuffs were limited to Indigo, its derivatives, and the Indophenols. Some twelve years ago it was found that certain compounds derived from anthracene also had the property of dyeing vegetable fibres from a vat. The number and variety of these new dyestuffs has increased in a remarkable manner since 1901, and their commercial importance is now very considerable.

Anthraquinone itself dissolves in alkaline reducing agents to give oxanthranol,



which is soluble in alkalies, forming blood-red solutions which oxidise even on exposure to air, regenerating anthraquinone. The tinctorial properties of anthraquinone and its simple derivatives are not, as a rule, sufficiently pronounced to allow of their use as vat dyestuffs. For these it is generally necessary to obtain more complex compounds of much higher molecular weight, containing, in addition to the ketone groups of anthraquinone, nitrogen, sulphur, etc., groups. These products may be divided into several classes. Thus Bohn divides them into Indanthrene, Flavanthrene, Benzanthrone, anthraquinoneimides and acylamidoanthraquinones.

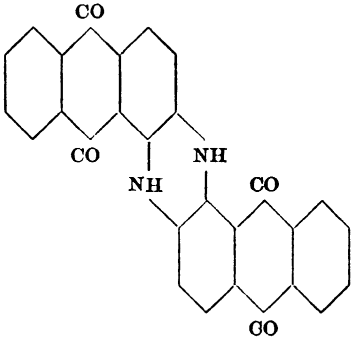
Indanthrene.

This was the first of the anthracene vat dyestuffs known. It was discovered by R. Bohn at the Badische Anilin und Sodafabrik in 1901 by heating β-amidoanthraquinone with caustic potash at 200-300° (B.A.S.F., *D.R.P.* 129,845 to 129,848 (1901)). The mass is dissolved in boiling water, and deposits the dyestuff in the crystalline form if the liquid is agitated by a current of air. The reaction has been studied by R. Scholl (*Ber.*, 1903, **36**, 3410, 3710), Scholl and Berblinger (*Ibid.*, 3427), Scholl, Berblinger and Mansfeld (*Ber.*, 1907, **40**, 320,326), Scholl, Steinkopf and Kabaczník (*Ibid.*, 390), Scholl and Berblinger (*Ibid.*, 395), Scholl and Stegmüller (*Ibid.*, 924), and Scholl (*Ber.*, 1907, **40**, 933 ; 1908, **41**, 2320), and has been found to result from the condensation of amidoanthraquinone with liberation of hydrogen :

$$2C_{14}H_9O_2N = C_{28}H_{14}O_4N_2 + 2H_2.$$

It has been stated that Alizarin is obtained as a bye-product.

Scholl has shown that *Indanthrene blue RS* is 1 : 2 : 1′ : 2′-anthraquinoneazine :



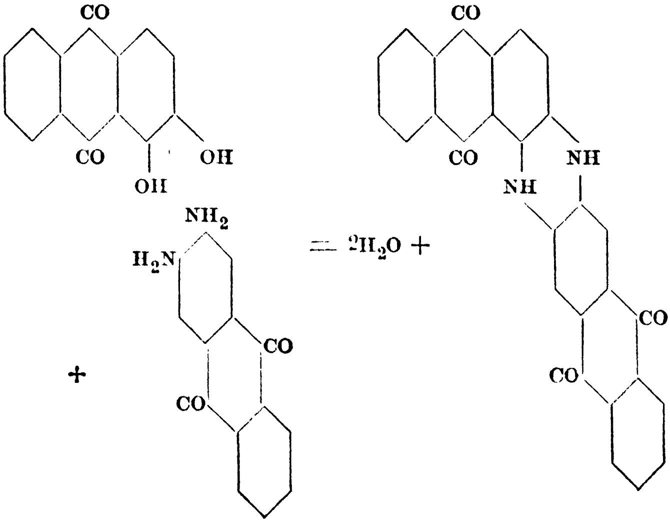
The B.A.S.F. have now adopted "Indanthrene" as a trade description of all their anthraquinone vat colours.

The action of alkaline reducing agents on Indanthrene gives a blue substance, which dyes vegetable fibres blue shades which are extremely fast to light and washing, but are not resistant to chlorine, such compounds being obtained by introducing halogens into the dyestuff ; for example, the monobromo-derivative *Indanthrene blue RC*, and the dibromo-derivative *Indanthrene blue GC* (*E.P.*, 4035 (1912)), and the chloro-derivatives *Indanthrene blue GCD* (dichloro-indanthrene, *E.P.* 23,179 (1903)), and *CE* (*D.R.P.* 168,042), and *Algol blue CF*.

Algol blue 3G is a dihydroxy-indanthrene, and gives bright greenish blue shades (*D.R.P.* 193,121). *Indanthrene blue* 3*G* and 2*GS* (*D.R.P.* 227,790) are probably hydroxy-indanthrenes, the former giving bright greenish blus shades, and the latter ultramarine shades. *Algol blue K* is N-dimethyl-indanthrene (*D.R.P.* 158,287), and is fairly fast. *Algol green B* is dibromodiamido-indanthrene (*D.R.P.* 193,121); it is fast except to bleaching.

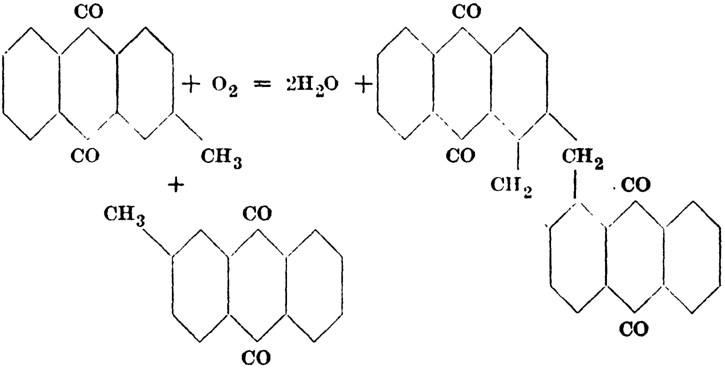
Indanthrene grey B (*E.P.* 712 (1904)) is obtained by the alkaline fusion of 1 : 5-diamidoanthraquinone, and is exceedingly fast to light and washing. By alkaline fusion of the formaldehyde compound of the above diamine, there is produced *Indanthrene maroon*, which yields brown shades, fast to light and washing.

When the azine constitution of Indanthrene had been established, the various methods for the synthesis of the azines (see p. 258) were applied to the anthracene series. Thus the Bayer Co. (*D.R.P.* 178,130) have obtained a compound isomeric with Indanthrene by condensing Alizarin with *o*-diamidoanthraquinone.



The reaction which occurs on the alkaline fusion of β-amidoanthraquinone being one of oxidation, attempts were made to carry out the oxidation in aqueous solution. β-Amidoanthraquinone actually gives a mixture of Indanthrene and Flavanthrene (see later) on oxidising with chromic acid, lead dioxide or nitric acid.

If instead of oxidising an amido-derivative, a methylanthraquinone, such as 2-methylanthraquinone, is oxidised in acid solution by means of lead dioxide, a dyestuff is obtained which, in place of the two NH groups of Indanthrene, contains methylene groups:



This compound is known as *Anthraflavone*, and is a yellow dyestuff which is not very fast to light.

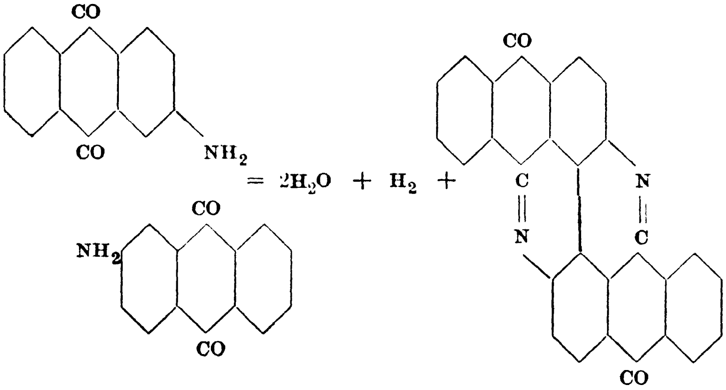
Flavanthrene.

Flavanthrene is formed together with Indanthrene by the alkaline fusion of β-amidoanthraquinone on raising the temperature to 300°. With hydrosulphite this dyestuff gives a blue compound, which oxidises in air to give Flavanthrene, which is yellow; the product obtained by the action of zinc powder and an alkali is brown. The blue compound is dihydroflavanthrene, whereas the brown compound is the tetrahydro-derivative. Both yield Flavanthrene on oxidation.

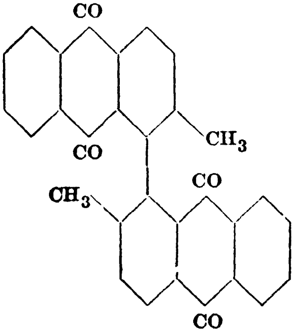
The constitution of Flavanthrene has been established by R. Scholl, the reaction which occurs on alkaline fusion resulting in the elimination of water, as follows :

$$2C_{14}H_9O_2N = C_{28}H_{12}O_2N_2 + 2H_2O + H_2.$$

It would appear probable that this is due to the condensation of amido-groups with ketonic groups :

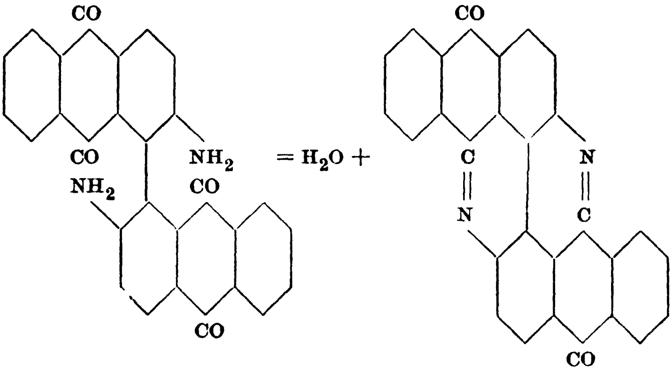


In order to prove this formula, Scholl has synthesised Flavanthrene as follows : β-methylanthracene is converted by oxidation into β-methylanthraquinone, which is nitrated, the product being reduced, the amido-compound diazotised, and the diazo-compound decomposed by means of cuprous chloride. The chloro-derivative so obtained is treated with powdered copper, when it loses its chlorine and gives 2 : 2′-dimethyldianthraquinonyl ·



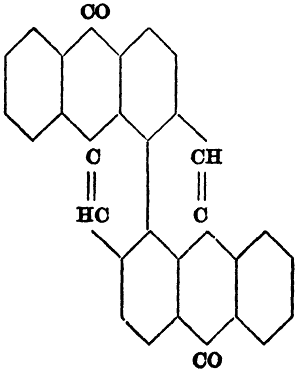
(I.)

On oxidising, the methyl groups of this compound are converted into carboxyl groups, and the product so obtained, on treatment with phosphorus pentachloride, ammonia, and then sodium hypobromite, yields diamidodianthraquinonyl, which is easily converted into Flavanthrene by dehydrating agents :



Flavanthrene is commercial under the name *Indanthrene yellow* (*E.P.* 24,354 (1901)).

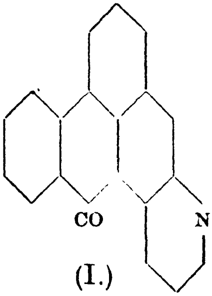
In the course of this research, Scholl found that dimethyldianthraquinonyl (I.) can itself be dehydrated, giving a new product, *pyranthrone*, which has the constitution :



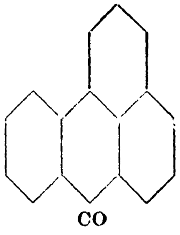
it dyes vegetable fibres from a vat yellowish orange shades (Scholl, *Ber.*, 1911, **44**, 1448), and comes into commerce as *Indanthrene golden orange G.* It is very fast to light and bleaching. Its halogenated derivatives are known as *Indanthrene golden orange R* and *Indanthrene scarlet G*, the latter being probably a dibromo-derivative, produced by bromination in the presence of nitrobenzene.

Benzanthrone.

In a research on Prudhomme's reaction, Bally (*Ber.*, 1905, **38**, 194) noticed that on heating β-amidoanthraquinone with glycerine and sulphuric acid, it is converted into *benzanthrone quinoline* (I.), and under the same conditions anthraquinone and oxanthranol react to give *benzanthrone* (II.) :



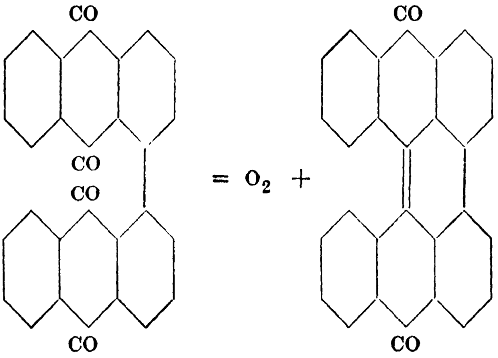
(I.)



(II.)

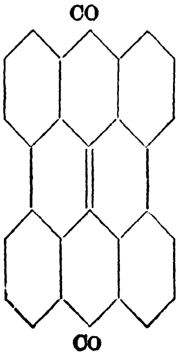
When benzanthrone quinoline is fused with a caustic alkali, a vat blue is obtained, *Cyanthrene*, whilst under the same conditions two molecules of benzanthrone condense to give a violet dyestuff, *Violanthrene BS*, or *Indanthrene dark blue BO* (*E.P.* 16,538 (1904), 22,519 (1905)). This dyestuff gives reddish violet shades on cotton, which are turned blue by washing. *Indanthrene violet RT* is a halogen derivative, and is an extremely fast dyestuff. *Indanthrene green* is a nitro-derivative.

Scholl and Mansfeld (*Ber.*, 1910, **43**, 1734) have recently described the *mesobenzdianthrone* which is formed by the reduction of dianthraquinonyl by means of copper and sulphuric acid :



Dianthraquinonyl itself is obtained by treating anthraquinone α-sulphonic acid with ammonia, converting the amidoanthraquinone produced into an iodo-derivative by diazotising and the Sandmeyer reaction, and treating this product with powdered copper.

On heating mesobenzdianthrone with aluminium chloride, it loses hydrogen and gives *mesonaphthodianthrone :*



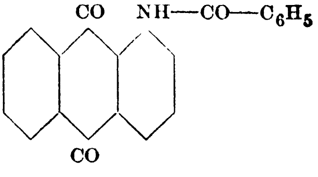
Anthraquinoneimides.

The dyestuffs of this class were shown by F. Ullmann to be formed by the linking up of several molecules of anthraquinone by means of NH groups, and are obtained by condensing amidoanthraquinones with halogen derivatives of anthraquinone in presence of small amounts of copper salts, generally with the addition of anhydrous sodium acetate. To this class belong *Indanthrene red G*, obtained by condensing one molecule of 2 : 6-dichlor-anthraquinone with two molecules of α-amidoanthraquinone (*E.P.* 4235 (1907)), *Indanthrene bordeaux B* (B.A.S.F., *E.P.* 10,324 (1907)), and *Algol orange R* (*E.P.* 24,810 (1908)), *red B* (*E.P.* 13,686 (1907)), and *bordeaux 3B* (*E.P.* 9219 (1909)) of the Bayer Co.

Algol grey B (*E.P.* 5382 (1909)) is obtained by nitrating the trianthramide obtained from 1 : 5-diamidoanthraquinone and two molecules of α-chloranthraquinone, and reducing the product with an alkali sulphide.

Acylamidoanthraquinones.

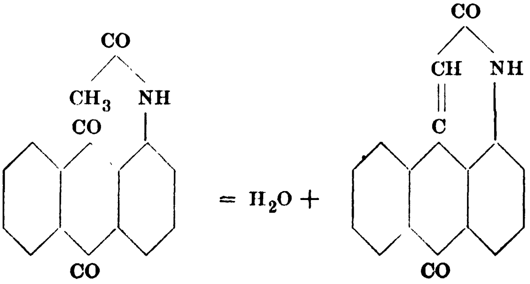
Benzoyl-1-amidoanthraquinone :



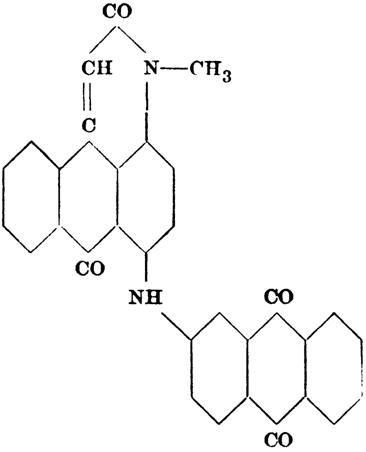
is a vat dyestuff, which dyes cotton rich yellow shades (Bayer, *B.F.*, 400,663). It is remarkable that such a simple compound should have the same properties as the much more complex compounds of the above classes. It is not, however, an isolated case, as the dibenzoyl-derivatives of the diamidoanthraquinones, and of the oxydiamidoanthraquinones, and also their succinyl-derivatives, and, generally, the acylated derivatives of these amines, form vat dyestuffs. The following table of these acylamido vat dyestuffs is of a representative character:

Algol yellow WG.		Benzoyl-1-amidoanthraquinone.
,, ,, *3G.*	*E.P.* 27,078 (1908).	Succinyl-(1-amidoanthraquinone)$_2$.
,, ,, *R.*	*E.P.* 3055 (1909).	Dibenzoyl-1 : 5-diamidoanthraquinone.
Algol red 5G.	*D.R.P.* 223,232.	Dibenzoyl-1 : 4-diamidoanthraquinone.
,, *R extra.*	*E.P.* 5786 (1909).	Dibenzoyl-1 : 5-diamido-8-hydroxyanthraquinone.
Algol pink R.	*D.R.P.* 225,232.	Benzoyl-4-amido-1-hydroxyanthraquinone.
Algol scarlet G.	Do.	Benzoyl-1-amido-4-methoxyanthraquinone.
Algol blue 3R.		Dibenzoyldiamidoanthrarufin.
Algol Brilliant violet 2B	*D.R.P.* 225,232.	Do.
Algol Brilliant orange FR.	Do.	Benzoyl-1 : 2 : 4-triamidoanthraquinone.
Algol Brilliant red 2B	Do.	1 : 5-Dibenzoyldiamido-4-hydroxyanthraquinone.
Algol Brilliant violet R.		Succinyldiamidoanthraquinone.
Algol olive R.	*D.R.P.* 225,232, 228,992.	Chlorsulphonic acid on dibenzoyldiamidoanthraquinone.
Algol violet B.	*D.R.P.* 225,232.	Benzoylamido-4 : 5 : 8-trihydroxyanthraquinone.
Helindone yellow 3GN.	*D.R.P.* 232,739.	Urea derivative of two molecules of β-amidoanthraquinone.

Certain of these acylated derivatives, such as the acetyl derivatives of the α-amidoanthraquinones, may again be dehydrated to give a new ring, *pyridone* :



This pyridone grouping may also be present in more complex molecules, for example, *Algol red B* is an anthraquinone-imide which contains the pyridone ring :



Although anthraquinone is a cheap raw material, a fact which has led to great activity in the preparation of vat dyestuffs derived from it, its use is limited on account of the relatively small proportion of the new products which have a marked affinity for the fibre. The complex character and high molecular weight of certain of these dyestuffs, together with the absence of nitrogen, are interesting features ; thus the empirical formula of *Indanthrene violet R*, $C_{31}H_{16}O_2$, approaches that of a hydrocarbon. That such a substance should form a soluble leuco-compound is remarkable, and it has been suggested that the leuco-compound is in colloidal solution.

The Anthraquinone vat dyestuffs generally require a more strongly alkaline vat than the Indigoid dyestuffs, and have hence, with few exceptions, been applied exclusively to the dyeing of cotton. Kann (*Färb.-Ztg.*, 1914, **25,** 73) points out that these vat dyestuffs may be used for dyeing wool which has been treated with formaldehyde to render it stable to alkalies.

New vat dyestuffs of the Anthraquinone series have been obtained by the action of diazo-anthraquinone on certain aromatic amines which are not suitable for combining to form normal Azo-dyestuffs, or by the action of aromatic diazo-compounds on amidoanthraquinones (Chem. Fabrik Griesheim-Elektron., *E.P.* 8422 (1912)). These new dyestuffs probably have the general formula $R_1—N=N—NR_2—R_3$, where R_1 and R_2 are aromatic radicles, of which one must be of the anthraquinone series, and R_3 may be H, CH_3, or a similar radicle.

CHAPTER XX.

QUINONE-IMIDE DYESTUFFS.

THE quinone-imide derivatives include certain dyestuffs related to quinones. When hydroquinone is oxidised, quinone is obtained, but for a long time it was not found possible to isolate similar products resulting from the oxidation of *p*-amidophenol or *p*-phenylenediamine. When this oxidation is carried out by means of hypochlorites, quinonechlorimide and quinonedichlor-di-imide are obtained respectively :

$$O = C_6H_4 = NCl \qquad ClN = C_6H_4 = NCl.$$

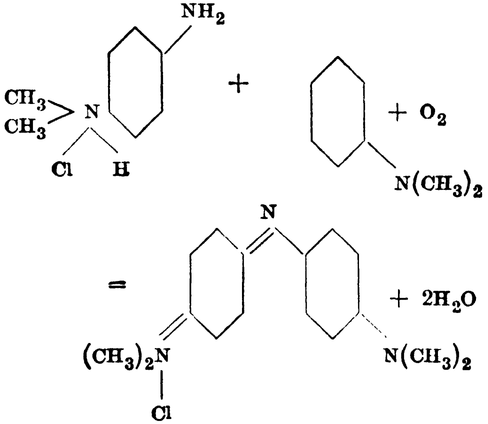
Willstätter (*Ber.*, 1904, **37**, 1494 and 4605) has succeeded in isolating quinoneimide and quinone-di-imide :

$$O = C_6H_4 = NH \qquad NH = C_6H_4 = NH.$$

Certain dyestuffs may be considered as derived from the *p*-quinoneimides, others as derivatives of the *o*-quinoneimides. The *Indamines* and the *Indophenols* are derived from *p*-quinone. The *Oxazines*, the *Thiazines*, and the *Azines* are *ortho*-quinonoid derivatives. This distinction is not generally recognised, certain authors considering all these dyestuffs to be *p*-quinonoid derivatives. (Compare Kehrmann, Havass, and Grandmougin, *Ber.*, 1913, **46**, 2131.)

(1) Indamines.

The Indamines were discovered in 1877 by Nietzki, who established their constitution. They are produced by oxidising an equimolecular mixture of a *p*-diamine and a monamine in cold dilute solution. The conditions which should be fulfilled by these amines are as follows : the *p*-diamine should have one free NH_2 group, the other may be substituted ; the monamine may be a primary, secondary, or tertiary amine, but the *para*-position to the amido-group must be free. For example, the oxidation of a mixture of *asym.*-dimethyl-*p*-phenylenediamine and dimethylaniline in acid solution gives an Indamine :

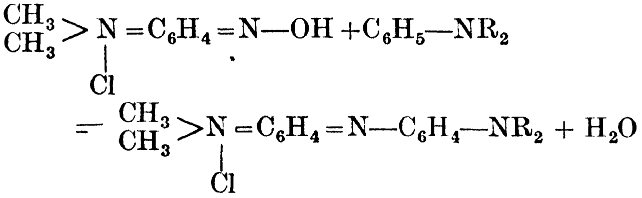


Oxidation eliminates the hydrogen atoms of the NH_2 group of the *p*-diamine, and also one hydrogen from the nucleus of the monamine from the *p*-position to the amido-group. This is established by the reduction of the Indamines, derivatives of *p*-diamidodiphenylamine being obtained :

$$
\begin{aligned}
Cl\,.\,R_2N = C_6H_4 = N—C_6H_4—NR_2 &+ H_2 \\
= R_2N—C_6H_4—NH—C_6H_4—NR_2 &+ HCl.
\end{aligned}
$$

These diphenylamines are leuco-derivatives of the Indamines, which are regenerated on oxidation. Finally, the fact that monamines in which the *para*-position is occupied do not give Indamines, proves that combination takes place in the *para*-position.

Indamines are also obtained by the action of nitroso-derivatives of tertiary amines on amines in which the *para*-position is free ; thus nitrosodimethylaniline hydrochloride condenses with amines in which the *para*-position is free :



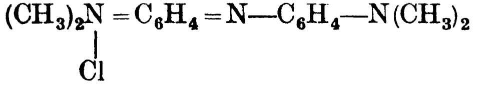
$$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\underset{\displaystyle |\atop Cl}{N} = C_6H_4 = N{-}OH + C_6H_5{-}NR_2$$

$$= \genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\underset{\displaystyle |\atop Cl}{N} = C_6H_4 = N{-}C_6H_4{-}NR_2 + H_2O$$

The Indamines are highly coloured compounds which form blue or green salts soluble in water. They are very sensitive to the action of acids, which hydrolyse them, giving quinone. It is for this reason that the Indamines are not used in dyeing, but are mainly used as raw materials for the manufacture of the *Oxazines*, the *Thiazines*, and the *Azines.*

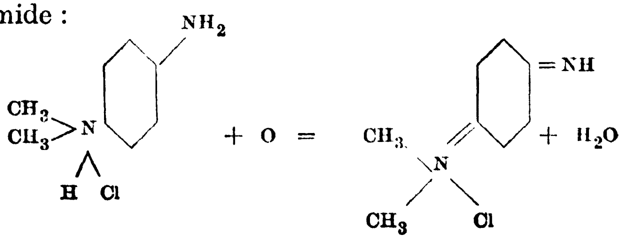
Phenylene blue is the simplest Indamine, being first obtained by Nietzki (*Ber.*, 1883, **16**, 464) by oxidising a solution of a mixture of *p*-phenylenediamine and aniline with potassium dichromate.

Bindschedler's green, or tetramethyl-indamine :



$$(CH_3)_2\underset{\displaystyle |\atop Cl}{N} = C_6H_4 = N{-}C_6H_4{-}N(CH_3)_2$$

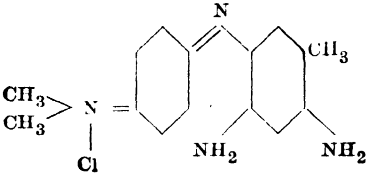
is obtained by oxidising an equimolecular mixture of dimethyl-*p*-phenylenediamine and dimethylaniline (Bindschedler, *Ber.*, 1883, **16**, 865), or by first oxidising the dimethyl-*p*-phenylenediamine and treating the intermediate red compound ("Wurster's red") obtained, with dimethylaniline. Wurster's red was at first considered to be the methyl chloride compound of methylquinone-di-imide :



but recent experiments (Willstätter and Piccard, *Ber.*, 1908, **41**, 1458) have shown that Wurster's red is a quinhydrone, that is, the compound of a molecule of the quinonoid salt with a molecule of the base. Compounds of this type are called "*meri*"-quinones by Willstätter, the quinonoid salts being called "*holo*"-quinones.

Witt has prepared tetramethyl-indamine by condensing nitrosodimethylaniline with dimethylaniline.

Toluylene Blue is formed by the oxidation of a mixture of a molecule of dimethyl-*p*-phenylenediamine and a molecule of *m*-toluylenediamine, or by the action of nitrosodimethylaniline hydrochloride on *m*-toluylenediamine; it has the following constitution:



Preparation of Bindschedler's Green.

A mixture of 13·6 parts of dimethyl-*p*-phenylenediamine and 12·1 parts of dimethylaniline is dissolved in 400 to 500 parts of water, to which have been added 20 parts of concentrated hydrochloric acid. This solution is cooled by immersion in ice, and is oxidised by a solution of 20 parts of potassium dichromate and 6 parts of acetic acid in 200 parts of water: The dyestuff is immediately formed, and is partly precipitated. Sufficient water is added to re-dissolve it, the solution is heated to 40-50° and zinc chloride added. On cooling, the zinc chloride compound of the dyestuff crystallises out.

(2) Indophenols.

The Indophenols are dyestuffs of which the properties and methods of preparation are very similar to those of the Indamines. The first Indophenol was discovered by Köchlin and Witt in 1881 by oxidising an equimolecular mixture of dimethyl-*p*-phenylenediamine and α-naphthol (*D.R.P.* 15,915; Köchlin, *Bull. Soc. ind. de Mulhouse*, 1882, 532; O. Witt, *J. Soc. Chem. Ind.*, 1882, 255).

The Indophenols are produced by oxidising a *p*-diamine in presence of a phenol or naphthol in which the *para*-position is free. As in the case of the Indamines, it is necessary that the diamine shall have one amido-group free, the other may be substituted. The oxidation is carried out in dilute acetic acid solution by means of potassium dichromate, or better in alkaline solution by means of hypochlorites, or merely by passing in air, in which case the addition of a trace of a copper salt aids the oxidation. There are two ways of explaining this reaction according to whether the quinonoid structure is formed in the amine nucleus, or in that of the phenol:

$$\text{(I.)}\quad NH_2—C_6H_4—NH_2 + C_6H_5OH + O_2$$
$$= 2H_2O + NH{=}C_6H_4{=}N—C_6H_4—OH.$$

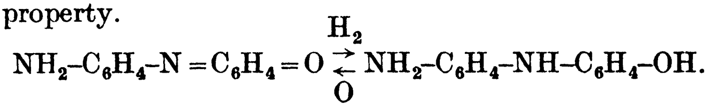
$$\text{(II.)}\quad NH_2—C_6H_4—NH_2 + C_6H_5OH + O_2$$
$$= 2H_2O + NH_2—C_6H_4—N{=}C_6H_4{=}O.$$

Hence, there are two possible constitutions. As the Indophenols have no acid properties, being insoluble in alkalies, but, on the other hand, have weak basic properties, they cannot be supposed to contain a phenol group, but must contain the basic NH_2 group. Thus the simplest Indophenol has the constitution:

$$NH_2—C_6H_4—N{=}C_6H_4{=}O.$$

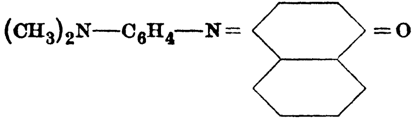
Indophenols are also formed by the action of nitrosodimethylaniline or quinonechlorimides on phenols or naphthols.

Properties. The Indophenols are very sensitive to the action of acids, by which they are decomposed, giving quinones. On reduction, the Indophenols are decolorised, giving leuco-Indophenols, which are soluble in alkali, and which regenerate the original substance on oxidation. The use of Indophenols in dyeing depends on this property.



$$NH_2{-}C_6H_4{-}N=C_6H_4=O \underset{O}{\overset{H_2}{\rightleftarrows}} NH_2{-}C_6H_4{-}NH{-}C_6H_4{-}OH.$$

Indophenol is the only important dyestuff of this class. It is obtained by oxidising an equimolecular mixture of α-naphthol and dimethyl-p-phenylene diamine, its constitution being :



It crystallises from benzene in bronze-coloured needles, and is hydrolysed by acids, giving α-naphthoquinone, which shows that the quinonoid structure is in the phenol nucleus.

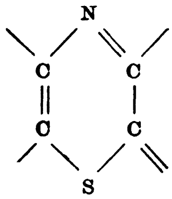
The Indophenols now find no application as dyestuffs, and are only used as raw materials for the preparation of Sulphur dyestuffs (p. 307).

Preparation of Indophenol.

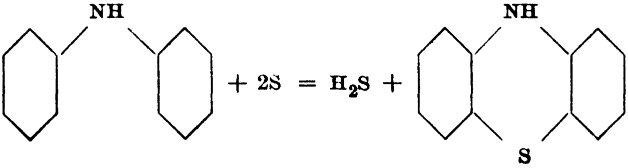
14·4 grm. of α-naphthol are dissolved in 250 ccs. of water containing 6 grm. of caustic soda, and a solution of 13·6 grm. of dimethyl-p-phenylenediamine in 250 ccs. of water added, the whole being then oxidised by means of sodium hypobromite, prepared by slowly pouring 32 grm. of bromine into a well-cooled solution of 20 grm. caustic soda in 150-200 ccs. water; the temperature should not rise above 5° C. Under these conditions the Indophenol is precipitated; it is allowed to settle, and is then separated, dried, and crystallised from benzene.

(3) Thiazines.

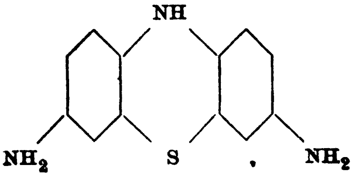
The Thiazines are dyestuffs which contain a characteristic ring containing nitrogen, carbon, and sulphur :



These dyestuffs are related to a sulphur base, thiodiphenylamine, in the same way that the Indamines and Indophenols are related to diphenylamine. By introducing auxochromes in *para*-position into diphenylamine leuco-Indamines or leuco-Indophenols are obtained, which are converted into dyestuffs by oxidation. On melting diphenylamine with sulphur, a new base is obtained, thiodiphenylamine :

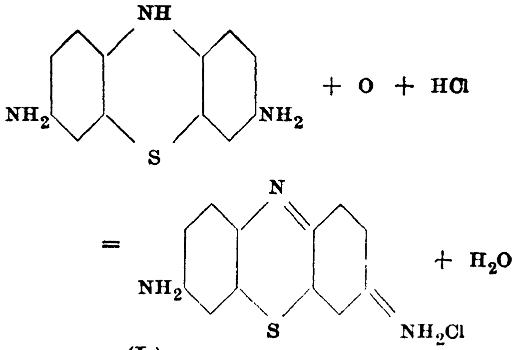


in which it is only necessary to introduce the auxochromes NH_2, NR_2, OH in *para*-position to the nitrogen to obtain leuco-derivatives of the Thiazines. Thus *p*-diamido-thiodiphenylamine :



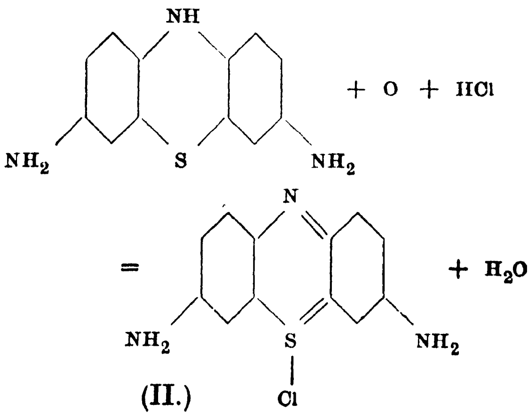
yields on oxidation in acid solution a violet dyestuff, *Lauth's violet*.

Before the quinonoid theory was generally accepted, the thiazine ring was considered to be a chromophore. Since that time these ideas have been modified, the chromophoric function being attributed to the quinonoid structure which is formed on oxidation of the leucothiazines. For a long time this chromophore was considered to be *para*-quinonoid (I.); at the present time this grouping is considered to have an *ortho*-quinonoid structure, the sulphur atom being basic and tetravalent, (II.):



(I.)

or



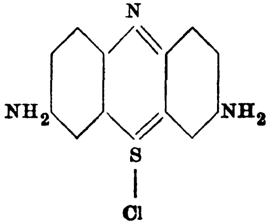
(II.)

This second method of formulation is supported by a number of experimental facts which are too long to detail in this book (see Kehrmann, *Ber.*, 1899, **32**, 2601; Green, *ibid.*, 3155), and has the advantage of representing by similar formulae the Azines, the Oxazines, and the Thiazines, which have very similar properties. To suggest the basicity of the sulphur in these molecules, the Thiazines have been called azthionium derivatives (Kehrmann, *Ann.*, 1902, **322**, 1; 1910, **372**, 287). By keeping the older method of writing (Formula I.) the Thiazines become Indamines or Indophenols in which the two benzene nuclei are also linked by a sulphur atom. This results in a greater stability of the molecule, which is no longer destroyed by acids. The Thiazines may be divided into two classes: the Thiazimes, corresponding to the Indamines; the *Thiazones*, corresponding to the Indophenols. The *Thiazimes* (*Amido-Thiazines*) are the most important.

Amido-Thiazines (Thiazimes).

Historical. The first Thiazine dyestuff was discovered by Lauth (*Compt. rend.*, **82**. 1441; *Bull. Soc. chim.*, 1876, 422) by a reaction which is named after him, and which consists in oxidising *p*-phenylenediamine in acid solution by means of ferric chloride in presence of sulphuretted hydrogen. The product is called *Lauth's violet* or *Thionine*, and is also formed by oxidising the product obtained by the action of sulphur on *p*-phenylenediamine. At about the same time, Caro (*Ber.*, 1878, **11**, 1705) prepared *Methylene blue* by applying Lauth's reaction to dimethyl-*p*-phenylenediamine. Koch (*Ber.*, 1879, **12**, 592) found that only the *para*-diamines gave Lauth's reaction, ammonia being eliminated. The detailed researches of Bernthsen (*Ann.*, 1885, **230**, 73; 1889, **251**, 1) definitely established the constitution of the Thiazines and led to the discovery of new processes for their preparation, which were of great theoretical and commercial interest. Lauth's reaction only gives small yields, whereas Bernthsen's method gives excellent yields.

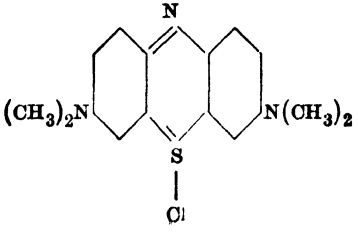
Lauth's violet, or diamidodiphenazthionium chloride,



Two methods of preparation have already been outlined: (1) oxidation of *p*-phenylenediamine with ferric chloride in presence of sulphuretted hydrogen; (2) fusion of *p*-phenylenediamine with sulphur, and oxidation. It is also obtained by oxidising a mixture of *p*-phenylenediamine and aniline in presence of sodium thiosulphate.

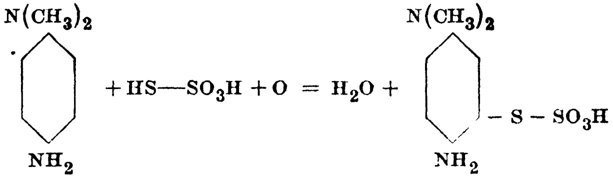
Bernthsen has proved its constitution as follows: thiodiphenylamine gives on treatment with nitric acid a *p*-dinitro derivative which on reduction yields diamidothiodiphenylamine, which is identical with leucothionine. The base forms a crystalline powder soluble in alcohol to a violet solution. Lauth's violet, its hydrochloride, crystallises in glistening needles.

Methylene blue, or tetramethyldiamidodiphenazthionium chloride:

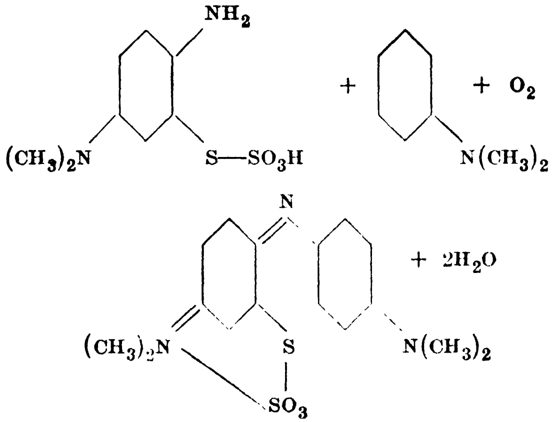


was first obtained by Caro by oxidising dimethyl-*p*-phenylenediamine with ferric chloride in presence of sulphuretted hydrogen. The process patented by the B.A.S.F. consists of converting dimethylaniline into its nitroso-compound, and then reducing this derivative with sulphuretted hydrogen. In this reaction there is formed the leuco-derivative of the dyestuff, together with dimethyl-*p*-phenylenediamine. On addition of ferric chloride, the dyestuff is produced, and may be precipitated by the addition of common salt and zinc chloride. The yield is small; moreover, two molecules of the diamine enter into the reaction, ammonia being eliminated. This process has been replaced by the thiosulphate process of Bernthsen (*D.R.P.* 38,573; 39,757; 45,839; 46,805), which in addition to giving a better yield, has the advantage of replacing one molecule of dimethyl-*p*-phenylenediamine by a molecule of the less expensive dimethylaniline. According to *D.R.P.* 46,805 the method is as follows: 6 kilograms of dimethylaniline are converted into the nitroso-compound, which is then reduced by zinc dust. The product is diluted to give about 250 litres of solution, which are neutralised with caustic soda until a permanent opalescence is obtained. Sixteen kilograms of aluminium sulphate are then added, and after stirring for half an hour, a solution of 13 kilograms of sodium thiosulphate is poured into the mixture, which is then oxidised by means of 4·8 kilograms potassium dichromate dissolved in 75 litres of water. After stirring for an hour, the liquid is diluted to 600 litres with water, and 6 kilograms of dimethylaniline added in the form of its hydrochloride. A saturated solution of 14 kilograms of potassium dichromate is added fairly quickly at a temperature not exceeding 10-12° C., and then a solution of 65 kilograms zinc chloride (142° Tw.) added, and the liquid boiled for half an hour. On cooling, Methylene blue crystallises out.

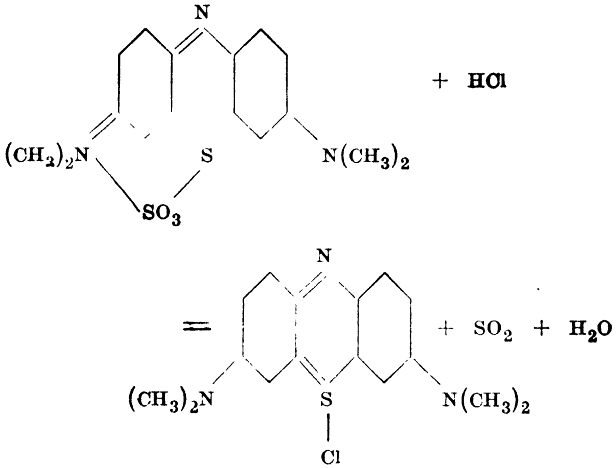
Theory of the Reaction. Bernthsen (*loc. cit.*) has shown that, on oxidising with potassium dichromate in the cold, *p*-diamines in presence of sodium thiosulphate, or better in presence of aluminium thiosulphate, form well defined crystalline thiosulphonic acids. Thus, in the above example, dimethyl-*p*-phenylenediamine in presence of thiosulphate and an oxidising agent gives :



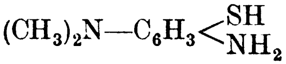
the aluminium thiosulphate, being hydrolysed, acts as free thiosulphuric acid and dimethyl-*p*-phenylenediamine thiosulphonic acid is obtained, the constitution of which was established by Bernthsen. By oxidising this acid in presence of a further molecule of dimethylaniline an Indamine thiosulphonic acid is formed :



On heating in dilute acid solution, this compound gives sulphurous acid, of which one portion is eliminated, whilst another portion of the acid converts the dyestuff into its leuco-derivative.



The thiosulphonic acids may be converted into mercaptans by reduction :



$$(CH_3)_2N—C_6H_3<\begin{matrix}SH\\NH_2\end{matrix}$$

and these compounds on oxidising in presence of amines first yield mercaptans of the Indamines and then dyestuffs.

Methylene blue is hence the tetramethyl-derivative of Lauth's violet, although it cannot be obtained by methylating this compound. Commercial Methylene blue is the zinc chloride compound :

$$2C_{16}H_{18}N_3SCl + ZnCl_2 + H_2O.$$

It is a basic dyestuff which is much used for dyeing cotton mordanted with tannin. The free base can only be obtained by treating the hydrochloride with silver hydroxide.

Owing to its high tinctorial power, Methylene blue has been used in analytical chemistry for the detection and estimation of many reducing and oxidising agents. (See Knecht and Hibbert, *New Reduction Methods in*

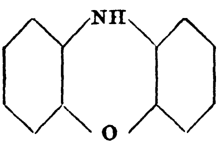
Volumetric Analysis; also Atack, *J. Soc. Dyers and Col.*, 1913, 9; *Analyst*, 1913, 99; *J.C.S.*, 1913, 1319.) It has also been recommended for use in place of starch for iodimetric titrations (Sinnatt, *Analyst*, 1910, **35**, 309; 1912, 252).

On nitration, Methylene blue gives *Methylene green*. On exposure to air, alkaline solutions of Methylene blue give a new dyestuff, *Methylene azure*, which differs from the original dyestuff by the loss of one of the methyl groups. This dyestuff has a greater intensity, and dyes redder shades than Methylene blue, and is prepared by the B.A.S.F. by oxidising this dyestuff with bichromate in sulphuric acid solution. The Basle *Société* has shown that oxidation with permanganate in alkaline solution gives a different result; in all probability a sulphone or sulphoxide is produced.

New Methylene blue is obtained from diethyl-*o*-toluidine and the *Thiocarmines* from ethylbenzylaniline sulphonic acid.

(4) Oxazines.

The Oxazines are very similar to the Thiazines, differing by the substitution of an oxygen atom for the characteristic sulphur atom. In the same manner that thiodiphenylamine is considered the parent substance of the Thiazines, so the Oxazines may be considered to be derived from *diphenoxazine*:



This base is obtained by condensing *o*-diamidophenol with pyrocatechol. If auxochromes are introduced in *para*-position to the nitrogen, leuco-Oxazines are obtained, which on oxidising yield dyestuffs. According to whether these auxochromes are amido- or alkylamido-groups, or hydroxy-groups, these dyestuffs are called *Oxazimes* or *Oxazones*.

The Oxazines are generally obtained from *o*-hydroxy-derivatives of the Indamines or Indophenols, which are readily converted into Oxazine dyestuffs, the preparation of which hence involves that of *o*-hydroxy-Indamines or Indophenols, which may be carried out in several ways :

(1) Nitroso-derivatives of tertiary amines or of phenols are condensed with phenols or naphthols in which the *para*-position is occupied ;

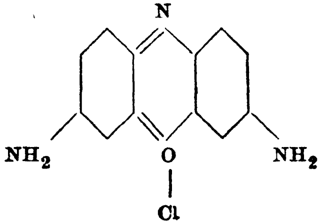
(2) In the above reaction the nitroso derivatives may be replaced by the corresponding quinonechlorimides ;

(3) Nitroso-derivatives of the *m*-amidophenols are condensed with amines.

In these reactions it is necessary to use an excess of the nitroso- or quinonoid compound, this being reduced by the hydrogen liberated during the reaction.

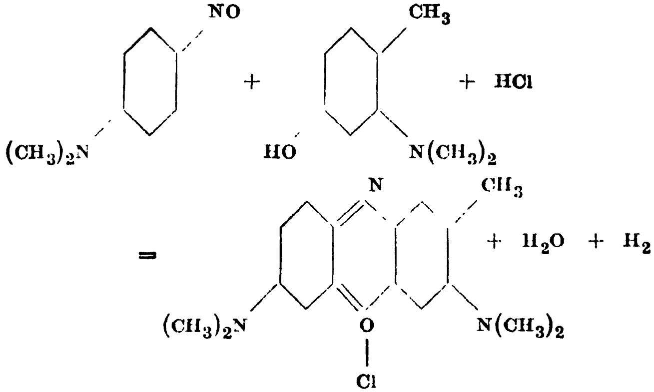
Amido-Oxazines (Oxazimes).

The simplest dyestuff of this series is the oxygen analogue of Lauth's violet :



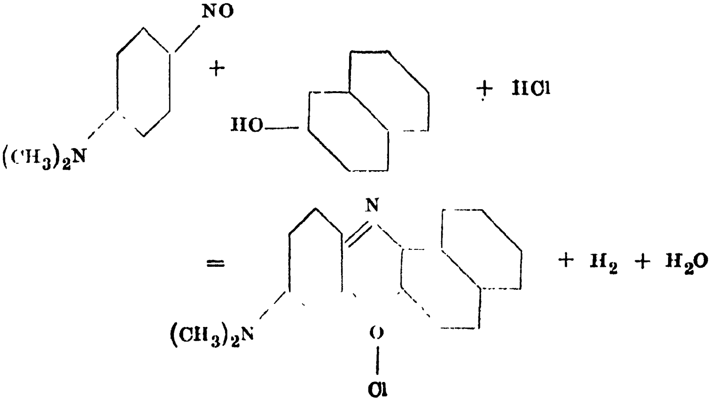
This compound is only of theoretical interest, being obtained by nitrating phenoxazine, reducing the nitro-derivative, and then oxidising the product formed.

Capri blue may be considered to be the higher homologue of the tetramethyl-derivative of the above compound. It was obtained by Bender in 1890 (Leonhardt & Co., *D.R.P.* 62,367) by condensing nitroso-dimethylaniline with dimethyl-*m*-amidocresol :



The methyl group of the cresol derivative causes condensation of the phenol group to take place in *ortho*-position. The hydrogen liberated reduces a molecule of the nitroso-compound to dimethyl-*p*-phenylenediamine. The commercial product is the zinc chloride compound of the dyestuff. It is a basic dyestuff, which dyes tanned cotton a greenish blue, and forms glittering reddish-brown crystals.

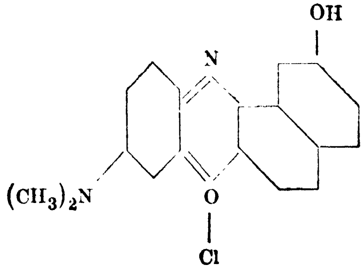
Naphthol blue or *Meldola's blue,* was discovered by R. Meldola (*Ber.*, 1879, **12**, 2065) by condensing nitroso-dimethylaniline hydrochloride with β-naphthol in alcoholic solution in presence of zinc chloride :



Preparation. 14 grams of β-naphthol are dissolved in the same weight of glacial acetic acid, and heated to 110°. 18·5 grams of nitrosodimethylaniline hydrochloride are then added in small portions, when a vigorous reaction occurs. When all the hydrochloride has been added, the mass is poured into water. A tarry black mass separates, which is dissolved in boiling alcohol; hydrochloric acid is added to the filtered solution, and, on cooling, reddish-brown needles of the hydrochloride of the dyestuff separate.

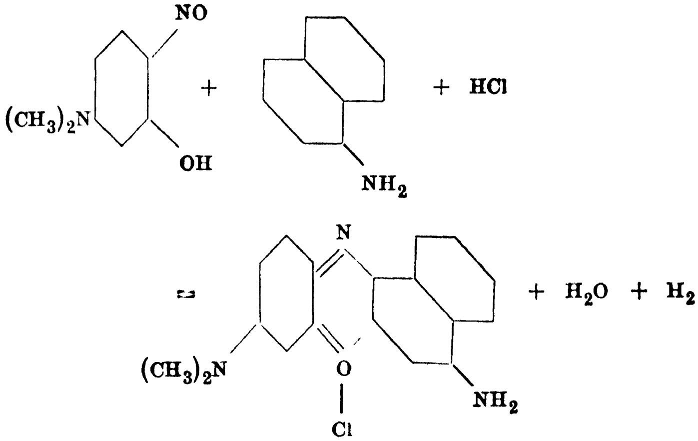
The commercial product is the zinc chloride compound, which crystallises in bronze coloured needles and is known as *New blue R*, *New Fast Cotton blue*, *Naphthylene blue*, *Cotton blue R*, *Fast Marine blue*, etc. It is used for dyeing cotton mordanted with tannin, which it dyes an indigo blue.

In the above preparation, if β-naphthol is replaced by 2 : 7-dihydroxynaphthalene, a very pure blue dyestuff known as *Muscarine* is obtained, the constitution of which is as follows:



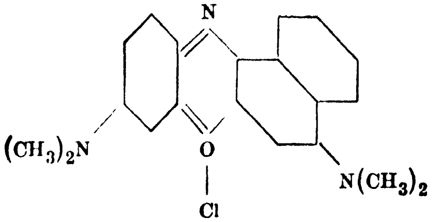
It forms crystals with a copper reflex. Its free base is soluble in caustic alkalies, but not in ammonia.

Nile blue is the amido-derivative of Meldola's blue, and was discovered by Reissig at the B.A.S.F. in 1888 (*D.R.P.* 45,268) by condensing nitrosodimethyl-*m*-amidophenol with α-naphthylamine:



Nile blue A is the corresponding diethyl-derivative. The dyestuff obtained from benzyl-*a*-naphthylamine is known as *Nile blue 2B*. They are all basic dyestuffs, dyeing tanned cotton very pure greenish blue shades.

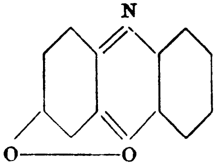
Witt has given the name *Cyanamines* to dyestuffs produced by the action of primary or secondary amines on Meldola's blue. Thus dimethylamine gives with this dyestuff a new product, *New Methylene blue N.G.G.* (Nietzki and Bossi, *Ber.*, 1892, **25**, 3002):



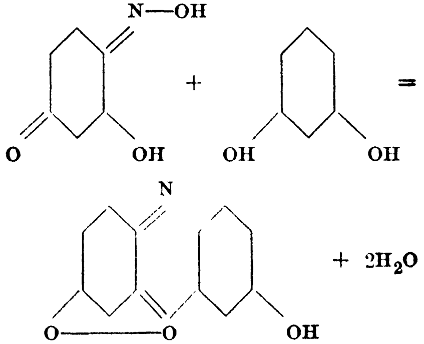
Aniline gives the corresponding phenyl derivative. In these reactions hydrogen is liberated, and this converts the dyestuff into its leuco-compound.

Oxazones.

The simplest Oxazone :



was obtained by Kehrmann by oxidising diphenoxazine. The most important compounds of this class are *Resorufine*, or hydroxydiphenoxazone, and *Resazurine*, both of which are produced by the action of nitric acid containing nitrous fumes on an ethereal solution of resorcinol. The formation of Resorufine is explained by the action of the nitrosoresorcinol on the excess of resorcinol :

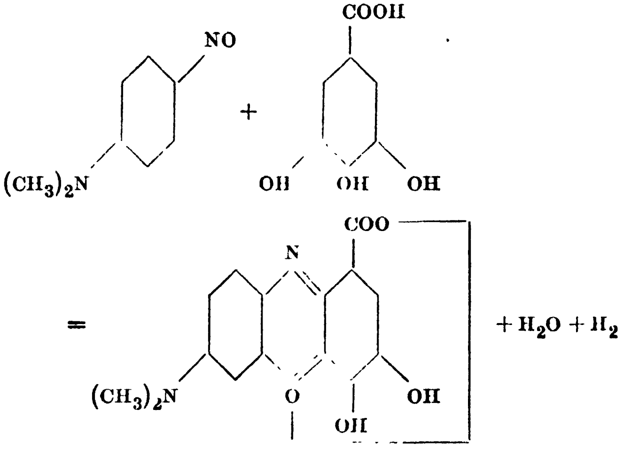


It forms small reddish-brown crystals. Its tetrabromderivative is *Fluorescent blue*, which dyes wool and silk blue with a red fluorescence. Resazurine is produced by the oxidation of Resorufine.

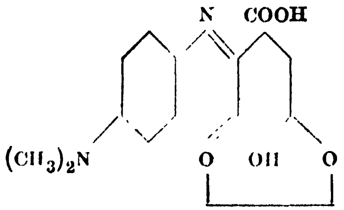
Oxazime-Oxazone Dyestuffs.

The simplest of these compounds is *Resorufamine*, which is formed by the action of quinonedichlordiimide on resorcinol. Its methyl derivative, *dimethylresorufamine*, is obtained by condensing nitrosodimethylaniline with resorcinol. It is a basic dyestuff which gives a very fast blue lake with tannin. This lake is produced directly on the fibre by printing with a thickened mixture of nitrosodimethylaniline, resorcinol, and tannin, drying, and steaming, when the lake formed remains fixed on the fibre.

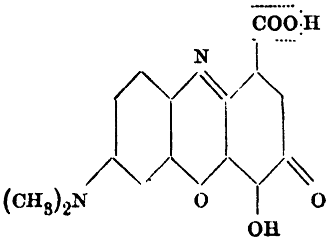
Gallocyanine was discovered by Köchlin in 1881 (*D.R.P.* 19,580) by heating nitrosodimethylaniline in alcoholic or acetic acid solution with gallic acid. The dyestuff crystallises in green needles ; the mother liquor contains dimethyl-*p*-phenylenediamine. *Gallocyanine* is produced as follows :



This formula was suggested because the methyl ester of Gallocyanine behaves as a dihydroxy-compound, but Kehrmann considers that the compound contains a carboxyl group, and gives it the following constitution

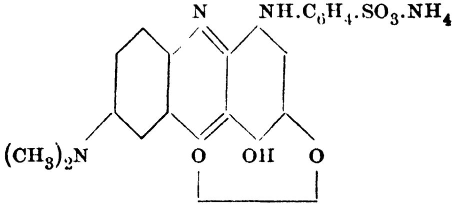


It dyes on metallic mordants; with chromium hydroxide it gives a violet lake much used in calico-printing. Owing to its insoluble character, Gallocyanine has not been satisfactory for printing, although largely used for dyeing wool. The leuco-compound is more soluble, and gives more intense and brighter shades in combination with chromium acetate. *Modern violet, blue* (1900), etc., are leuco-compounds of *Gallocyanine, Gallamine blue, Celestine blue*, etc. *Modern heliotrope PH* is obtained by condensing nitroso-monoethyl-*o*-toluidine with gallamide, and subsequently reducing to the leuco-compound. The *Ultra violet* dyestuffs [S.] are quinhydrones obtained by condensing a leuco-Gallocyanine with a Gallocyanine. On heating Gallocyanine base with water, the carboxyl-group is eliminated (Bayer Co.. *D.R.P.* 192,971):



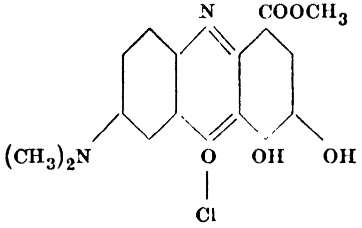
These Pyrogallocyanines are commercial as leuco-compounds, which are extremely soluble, such as *Gallo violet* [By.] and *Modern violet N* [D.H.], the chrome lakes of which are easily developed by steaming.

The condensation of Gallocyanines with aromatic alkylated diamines possessing a free amido-group, yields a new series of dyestuffs, such as the *Modern Cyanines, Anthracyanines, Chromeacetine blue*, and *Modern blue CVI*, which are easily fixed with chromium acetate, and have largely replaced the older brands of Phenocyanines. During the reaction, half of the Gallocyanine used is reduced, and can no longer react with amine. Hence the yield of *Delphine blue B* [S.]:



prepared by the action of aniline on Gallocyanine and subsequent sulphonation, is much improved by blowing air into the mixture to oxidise the leuco-Gallocyanine. *Chromazurine G* and *E* [D.H.] appear to be isomeric with Delphine blue. These dyestuffs give blue shades on chrome mordant.

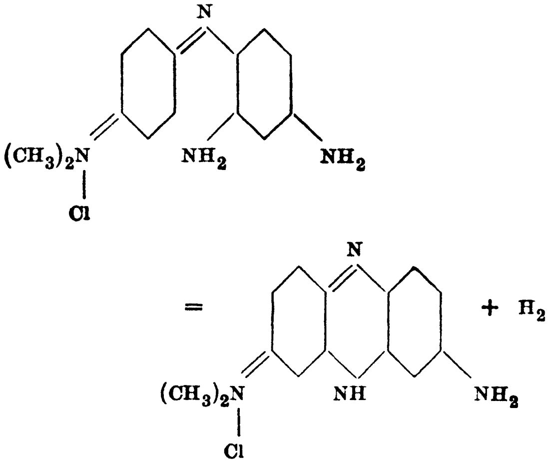
The dyestuff known as *Prune* is obtained by condensing nitrosodimethylaniline with methyl gallate; it is a basic dyestuff having the constitution:



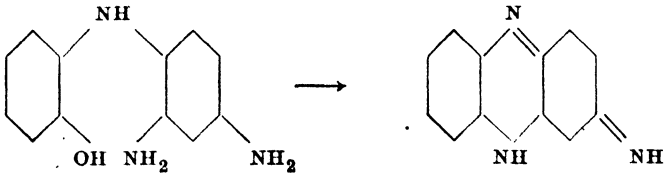
Nitrosodimethylaniline and gallamide yield *Gallamine blue*, which on heating with aniline gives *Gallanil blue*, of which the sulphonic acid is known as *Gallanil indigo*, and the nitro-derivative as *Gallanil green* (see Rittermann, *Färb.-Ztg.*, 1912, 282, 302).

(5) Azines.

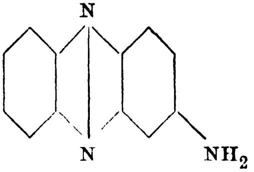
The *Azines* are closely related to the *Indamines* and the *Indophenols*. Thus, on heating an aqueous solution of an *o*-amido-Indamine it is converted into an Azine with liberation of hydrogen. For example, if a solution of *Toluylene blue* is heated, it gradually becomes red, owing to the formation of an Azine, Toluylene red :



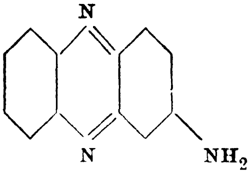
The hydrogen liberated reduces part of the dyestuff to its leuco-compound. This relation between the Azines and the Indamines seems to indicate a similarity in their constitution and the Azines have for a long time been considered as *para*-quinonoid compounds. Facts are, however, known which are against such a structure. Thus on oxidising *o*-hydroxydiamidodiphenylamine, there is obtained under certain conditions an Azine, *amidophenazine* :



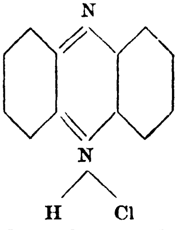
This compound, however, contains a free amido-group, which cannot be brought into agreement with a *para*-quinonoid constitution. This formula was hence replaced by the formula:



but this does not contain the chromophore, the quinonoid group, and was hence replaced by the following formula, which represents Azines as *ortho*-quinonoid compounds:



The nitrogen atoms of the azine ring have very decided basic properties, it is considered that in the formation of salts, the molecule of acid becomes attached to one of these atoms. The chromophore of the Azines should hence be:



Diphenazine hydrochloride, or phenazonium chloride.

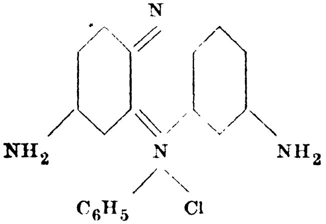
It will be seen that there is a very great analogy between the constitution of the Oxazines, the Thiazines, and the Azines, if the former are represented by formulae in which oxygen and sulphur are tetravalent.

The Azine dyestuffs may all be considered as phenazonium derivatives, and have various names:

The mono- and di-amidodiphenazines are called *Eurhodines*.

The mono- and di-hydroxydiphenazines are called *Eurhodoles.*

The *meso*-phenyl derivatives of the Eurhodines (diamido) are the *Safranines*:

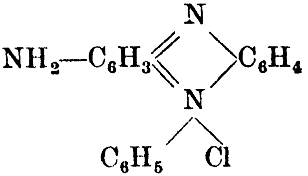


The *meso*-phenyl derivatives of the Eurhodoles are called *Safranoles.*

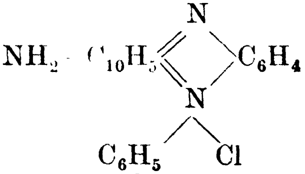
The *Mauveïnes* are Safranines in which the phenyl radicle is substituted for one hydrogen in the amido-group.

Finally, the phenylamido-derivatives of the Mauveïnes are called *Indulines.*

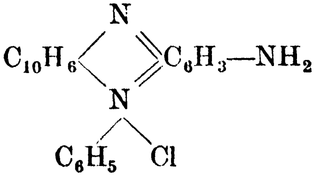
Safranines from which one of the amido-groups have been eliminated are known as *Aposafranines,* which have particular names if derived from naphthophenazine, according to the position of the amido-group; if this is present in the naphthalene nucleus, they are termed *Rosindulines,* if present in the other nucleus, *Isorosindulines*:



Aposafranine.



Rosinduline.



Isorosinduline.

Eurhodines.

These were discovered by Witt (*Ber.*, 1886, **19**, 441) by heating *o*-amidoazo-compounds with amines. They may also be obtained :

(*a*) By heating *o*-amido-Indamines in aqueous solution ;

(*b*) By oxidising certain *o*-diamines ; thus *o*-phenylenediamine gives *asym.*-diamidodiphenazine.

(*c*) By condensing nitroso-derivatives of tertiary amines or quinonedichlordiimides with amines in which the *para*-position is occupied ;

(*d*) By oxidising certain triamido-derivatives of diphenylamine, thus *o*-di-*p*-tri-amido-diphenylamine gives diamidodiphenazine ;

(*e*) By condensing *ortho*-quinones with amido-derivatives of *ortho*-diamines.

Properties. The Eurhodines are weak bases of which the monoacid salts are red and the diacid salts green ; these salts are hydrolysed by water.

The most important compound of this class is *Toluylene red*, which is derived from Toluylene blue, and is most easily prepared by oxidising a warm mixture of dimethyl-*p*-phenylenediamine and *m*-toluylenediamine. It is commercial as *Neutral red*, and gives red shades on tanned cotton.

Neutral violet is the lower homologue, obtained by using *m*-phenylenediamine (Witt, *Ber.*, 1879, **12**, 931 ; *D.R.P.* 15,272).

Eurhodoles.

These compounds are obtained by heating Eurhodines with concentrated hydrochloric acid at 180°, or by the alkaline fusion of the sulphonic acids of the Azines, or by condensing hydroxy-*ortho*-quinones with *ortho*-diamines.

Safranines.

Historical. Perkin was the first to manufacture a red dyestuff, *Mauveïne* being first prepared by him in 1861. It was patented by D. Price in England and by F. Duprey in France in 1869. These two processes consisted of oxidising aniline in acid solution by means of lead dioxide or barium peroxide. *Safranine* was manufactured at Basle in 1868, and in England by Caro in 1871. Later Nietzki obtained a better yield by heating amidoazotoluenes with dilute nitric acid.

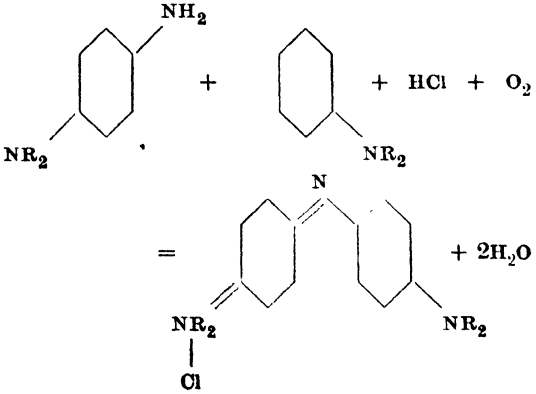
The researches of A. W. Hofmann, Witt, and Nietzki, have determined the constitution of the Safranines, by showing that they may be obtained :

(*a*) By heating Indamines with primary monamines ;

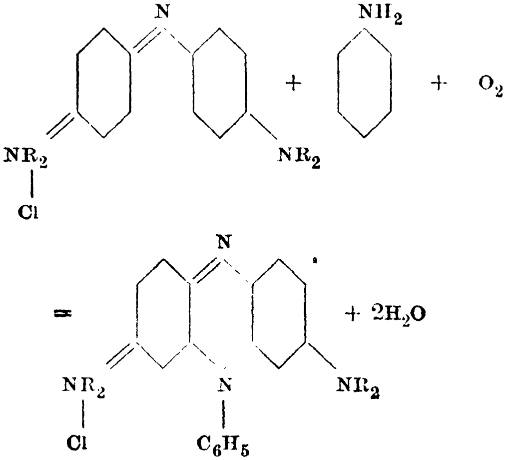
(*b*) By oxidising *p*-diamidodiphenylamines in presence of primary amines ;

(*c*) By oxidising a *para*-diamine in presence of *m*-amido-diphenylamine ;

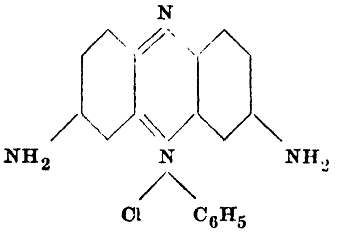
(*d*) By oxidising a mixture of one molecule of a *para*-diamine and two molecules of a monamine, this being the process used commercially. In this case the *para*-diamine should contain a free amido-group, and the monamine should be a primary amine, but two molecules of different monamines may be used, in which case one of them must be a primary amine. An Indamine is first formed :



On oxidising in presence of a primary amine, the Indamine yields a Safranine :



According to their method of formation, it would appear that the Safranines are *para*-quinonoid, but it has been proved that there are two free amido-groups in *Phenosafranine*, the simplest member of this class. Hence the Safranines should be represented by *ortho*-quinonoid formulae, thus :



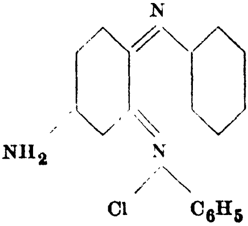
Properties. The Safranines are very basic dyestuffs which form three series of salts : the monoacid salts are red and are not hydrolysed by water, whereas the diacid and triacid salts, which are blue and green respectively, only exist in concentrated acid solution. The monoacid salts are well crystallised substances which dye wool, silk, and tanned cotton red shades ; to some extent they also dye cotton direct. Alkylation of the amido-groups gives a more violet shade.

Phenosafranine is prepared according to Witt by oxidising a mixture of one molecule of *p*-phenylenediamine and two molecules of aniline, or by oxidising an equimolecular mixture of *p*-diamidodiphenylamine and aniline. This mixture of the diamine and aniline is obtained by diazotising aniline in presence of an insufficient amount of acid, and converting the diazoamidobenzene formed into amidoazobenzene by heating with aniline hydrochloride. On reduction of amidoazobenzene, it gives one molecule of *p*-phenylenediamine and one molecule of aniline :

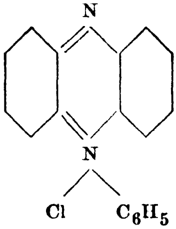
$$C_6H_5—N=N—C_6H_4—NH_2 + 4H$$
$$= C_6H_5—NH_2 + NH_2—C_6H_4—NH_2.$$

A further molecule of aniline hydrochloride is added to the solution, which is then oxidised with potassium dichromate. In this reaction Mauveïnes are formed which are less basic than Safranine, and these are precipitated by addition of chalk. The filtered liquid contains the Safranine, which is then isolated by salting out with common salt. The hydrochloride crystallises from dilute hydrochloric acid in green plates, which are soluble in water to a red solution. The alcoholic solution is fluorescent. The free base is obtained by decomposing the sulphate by means of barium hydrate, and crystallises in green plates.

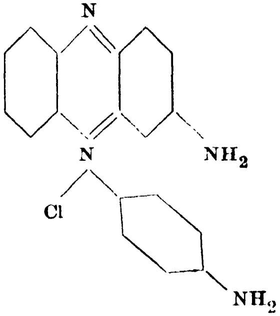
Safranine readily gives a diazo-compound, and in concentrated sulphuric acid solution will give a tetrazo-compound. On boiling with alcohol, the diazo-compound yields *Aposafranine* (Nietzki and Otto, *Ber.*, 1888, 21, 1736) :



the hydrochloride of which dissolves in water and alcohol, giving red solutions, the alcoholic solution being fluorescent. Under the same conditions, the tetrazo-compound gives phenylphenazonium chloride, the parent substance of the Safranines :



It is to be noted that in addition to symmetrical Safranine, an asymmetrical isomer can exist :



This compound has been prepared by Barbier and Sisley (*Bull. Soc. chim.*, 1905, **33**, 995, 1190, 1232 ; 1906, **35**, 1282) by oxidising a mixture of *o-p*-diamidodiphenylamine and aniline. They have further shown that this asymmetrical Safranine is formed together with ordinary Safranine by the oxidation of a *para*-diamine in presence of aniline, the two isomers being separated by fractional crystallisation. To differentiate between these two dyestuffs they called the symmetrical Safranines the *Indophenosafranines*, and their isomers the *Azophenosafranines*.

Dimethylphenosafranine is obtained by oxidising a mixture of one molecule of dimethyl-*p*-phenylenediamine and two molecules of aniline ; its zinc chloride compound is known as *Fuchsia* or *Methylene violet* ; a higher homologue, *Giroflée* or *Tannin heliotrope* is obtained by condensing nitrosodimethylaniline with xylidine.

Tetraethylphenosafranine is prepared by oxidising an equimolecular mixture of diethyl-*p*-phenylenediamine, diethylaniline, and aniline. It is a violet dyestuff known as *Amethyst violet.*

Safranine T is commercial Safranine or Tolusafranine, and is generally prepared from a mixture of bases containing a large amount of *o*-toluidine, such as Magenta échappés. Its appearance and shade do not differ appreciably from that of Phenosafranine, but the yield obtained is much higher than with the simpler substance.

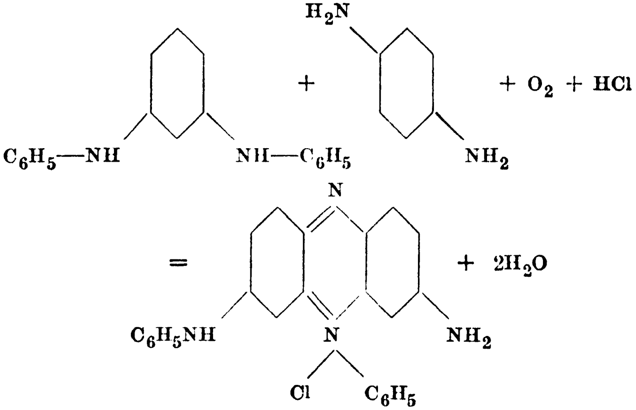
Magdala red is a Safranine of the naphthalene series, and was obtained by Schiendl in 1868 by heating the hydrochloride of α-amidoazonaphthalene with α-naphthylamine. It is a basic red dyestuff which is soluble in alcohol, forming a solution with a brilliant yellow fluorescence.

Naphthyl violet and *Naphthyl blue* are produced by heating nitroso-β-naphthylamine with the hydrochlorides of α-naphthylamine and aniline. The commercial products are the sulphonic acids, which give fluorescent shades on silk.

Basle blue is the basic dyestuff obtained by condensing nitrosodimethylaniline with diphenyl-2 : 7-naphthalenediamine. It may be dyed on tanned cotton.

Mauveïnes.

The Mauveïnes were the first synthetic dyestuffs used in dyeing. In 1856, Perkin obtained Mauveïne by oxidising impure aniline ; it is a violet dyestuff and was used at that time for dyeing silk. Perkin described two Mauveïnes, *Pseudo-Mauveïne*, $C_{24}H_{18}N_4$, prepared from pure aniline, and *Mauveïne* $C_{27}H_{24}N_4$, obtained by using a mixture of aniline and toluidine. As early as 1871 Hofmann and Geyger recognised the analogy which exists between the Mauveïnes and the Safranines. The constitution of *Pseudo*-Mauveïne was established synthetically by Nietzki by oxidising a mixture of *p*-phenylenediamine and diphenyl-*m*-phenylenediamine:



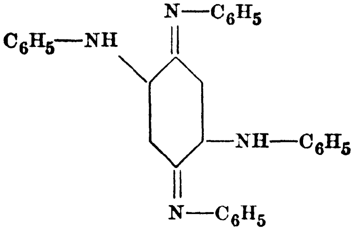
The Mauveïnes are hence phenyl-derivatives of the Safranines. They are less basic in character than the Safranines, and are only of historical interest. For many years one of these products was used for printing the English penny stamp.

Indulines.

These dyestuffs have been known since 1865, being obtained by heating amidoazobenzene under pressure with an aqueous solution of aniline hydrochloride. Indulines are produced by heating aniline hydrochloride with amidoazobenzene, azobenzene, azoxybenzene, etc., more or less complex mixtures being formed, according to the conditions of the reaction. The Indulines which are soluble in water are the alkaline salts of the sulphonic acids of the Indulines, which are themselves insoluble in water, but are soluble in alcohol.

The *Nigrosines* are grey dyestuffs obtained by heating aniline with nitrobenzene in presence of a little hydrochloric acid and iron at a temperature of 160° to 200°. Similar dyestuffs are obtained by heating aniline with nitrophenol and aniline hydrochloride at 180° to 200°.

Witt found that, by the action of aniline on amidoazobenzene at a low temperature, there is formed an intermediate product, *azophenine*, the constitution of which was established by Fischer and Hepp as diphenylamidoquinonedianilide :



By raising the temperature to 125° to 130°, *Induline 3B* is obtained, and, at 165° to 170°, *Induline 6B*.

The *Indulines* appear to be phenylamido-derivatives of the *Mauveïnes.* They are used in the printing of cotton in the form of a thickened mixture of the Induline, tannin, and a solvent such as acetin (glyceryl acetate).

CHAPTER XXI.

INDIGO AND INDIGOID DYESTUFFS.

Historical. Indigo is one of the oldest dyestuffs known, being found on the wrappings of Egyptian mummies. Originally it came from India; Pliny and Discorides mention unsuccessful attempts to acclimatise it to European countries. After being forgotten for many years, the Dutch imported the dyestuff from their colonies of Batavia and Java in 1631. Indigo is also found in a crucifera, the "dyer's woad" (*Isatis tinctoria*), which was cultivated in France and in Germany as early as the ninth century; this culture was prosperous in Thuringia in the sixteenth and seventeenth centuries. This was used under the name of *Persian blue*, and when Indigo came from the East it encountered serious difficulties. At first the use of Indigo for dyeing was forbidden, and at Nüremberg the dyers were obliged to take an oath not to use this "devil's colour" (*Teufelsfarbe*). It was only in 1737 that a royal edict in France allowed the use of Indigo from the Indies; from that time its use extended to other countries, and finally the culture of dyer's woad disappeared in spite of the aid given to it by Napoleon I. The purple which was of such great importance to the Romans, who extracted it from a certain species of mollusc found on the shores of Italy, has recently been shown by Friedländer to be a derivative of Indigo.

The commercial manufacture of Indigo by synthetic methods was commenced about fifteen years ago, and the artificial dyestuff has gradually replaced the natural Indigo. This industry is restricted almost entirely to Germany, where it is very prosperous, as shown by the following statistics, relating to the value of imports and exports of Indigo :

GERMANY.	IMPORTS.	EXPORTS.
1895	21·5 million marks	—
1898	8·3 ,, ,,	7·6 million marks
1904	—	21·7 ,, ,,
1906	0·8 ,, ,,	31·6 ,, ,,

Towards the end of the year 1905, the production of synthetic Indigo in Germany had reached three thousand tons. This struggle between natural Indigo and the synthetic product has caused a considerable decrease in the price, which had fallen from seven to nine shillings to three to four shillings a pound in 1908 (Nietzki, *Chemie der organische Farbstoffe*, 5th edition, p. 345). Whereas the amount of Indigo exported by Germany has increased rapidly, the culture of the plant in India has decreased considerably. Thus, in the four provinces which produce it, Bengal, Madras, Punjab and the United Provinces, the area used for its culture from 1902 to 1907 amounted to 487,000 acres, in 1908-9 its culture only occupied 283,900 acres (*J. Soc. Chem. Ind.*, 1910, 146), and for the year 1910-11 only 263,700 acres. It is estimated that at present the production of synthetic Indigo has reached a value of three and a half million sterling per annum, over 35,000 tons of 20 per cent. paste, sold at sixpence per pound, being produced per annum. Some 3,000 tons per annum are made in England.

Extraction of Indigo. Indigo does not occur in the state of Indigotine in the plant from which it is extracted, but is found as a compound which was first isolated by Schunck, who termed it *indican*, and gave its formula as $C_{26}H_{31}O_{17}N$. It was supposed (and this view is still to be found even in many recent text-books) that indican was a glucoside, resulting from the combination of Indigo with a certain sugar, indiglucine, this glucoside being decomposed by dilute acids or ferments as follows :

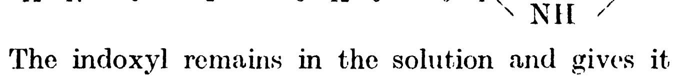
$$2C_{26}H_{31}NO_{17} + 4H_2O = C_{16}H_{10}N_2O_2 + 6C_6H_{10}O_6.$$

Indican. Indigotine. Indiglucine.

Marchlewski (*J. Soc. Chem. Ind.*, 1898, 430), however, suggested that indican is the product obtained by condensing a molecule of indoxyl with glucose (see below), according to which indican should decompose to give these two constituents. This has actually been found to occur by Hazewinkel, Beyerinck and van Romburg. Moreover, Hoogewerff and Ter Meulen (*Rec. trav. chim. P.-B.*, 1900, **19**, 106) have succeeded in isolating indican in the form of a crystalline hydrate of formula :

$$C_{14}H_{17}NO_6 + 2H_2O.$$

The extraction of the Indigo is carried out as follows : The plants are cut down some time before flowering and are placed in tanks or wooden vessels known as "steeping vats." These are then covered with boards or bamboos on which are laid stones, and water added ; a very vigorous fermentation occurs, lasting for twelve to fifteen hours, during which time the indican is decomposed according to the following equation :



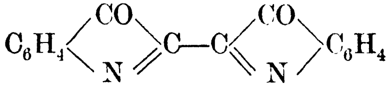
$$C_{14}H_{17}NO_6 + H_2O = C_6H_{12}O_6 + C_6H_4\left\langle\begin{matrix} C(OH) \\ NH \end{matrix}\right\rangle CH.$$

The indoxyl remains in the solution and gives it a greenish yellow fluorescence. This solution is drawn off into larger vats, in which it is exposed by some mechanical means to the action of air. The air oxidises the indoxyl, and then the leuco-Indigo gives *Indigotine*, which is precipitated in fluorescent blue particles. After standing for several hours, the supernatant liquid is decanted, the precipitate boiled with water to prevent destructive fermentation, and the dyestuff is filtered off. The mass obtained is compressed and broken into lumps which are then dried. The yield of Indigo is about 0·2 per cent. of the weight of the plants used, the average yield being 2,500 to 3,000 kilograms of the plant per acre of ground. The Indigo obtained is, however, often very impure, containing 20 to 90 per cent. of *Indigotine* in addition to a red dyestuff known as *Indirubine*, *Indigo yellow*, *Indigo brown*, Indigo gluten, mineral matter, etc. Occasionally it has to be purified to increase its value. Chemically pure Indigotine is very difficult to obtain; after repeated purification by chemical means it is often necessary to sublime it *in vacuo*.

Properties of Indigotine. This compound is obtained as an amorphous powder which has a copper reflex when it is compressed. It crystallises from acetic acid, phthalic anhydride, nitrobenzene, aniline, or phenol, and also sublimes, forming crystals with a brilliant metallic lustre. On heating it forms violet vapours, and at a high temperature decomposes. It dissolves in cold sulphuric acid to form a green solution, addition of water precipitating the dyestuff unchanged; on heating the sulphuric acid solution, it becomes blue and the substance remains in solution on diluting, owing to the formation of sulphonic acids. According to the conditions, mono-, di-, tri- or tetra-sulphonic acids are obtained; the sodium salt of the disulphonic acid is known as *Indigo carmine.* Oxidising agents destroy Indigotine, giving isatin.

The most interesting property is its conversion by alkaline reducing agents to leuco-Indigo (*Indigo white*), which dissolves, forming a yellow solution. This solution oxidises in contact with air, regenerating Indigotine. This property is applied in the dyeing of textile fabrics, a solution of the reduced Indigo, known as an "Indigo vat," being prepared, and the fibre immersed in it; after being squeezed the fibre is exposed to air to regenerate the dyestuff. The reducing agents in general use are: ferrous sulphate and lime; zinc and an alkali; glucose and caustic soda; and sodium hydrosulphite. The people of the East, who were able to dye with Indigo more than five thousand years ago, used vats obtained by fermentation as described above, these being still employed in certain countries. In these vats the reduction is effected by the fermentation of various organic substances, such as bran, glucose, fæces, etc. The reduction of Indigo is assisted by the presence of a small quantity of Induline scarlet (B.A.S.F., *E.P.* 29,918 (1910)).

Kalb (*Ber.*, 1909, **42**, 3642) suggests a new method in which *dehydroindigo*, obtained by oxidising Indigo with lead dioxide in non-aqueous suspension, is used:



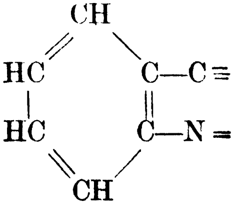
It forms stable, crystalline, bisulphite compounds, with which the fibre is padded, dried, and then passed into an acid or alkaline bath at 80-100° C. to regenerate Indigo.

Constitution of Indigotine. The percentage composition of Indigotine corresponds to the formula C_8H_5ON, but determination of its molecular weight gives the formula $C_{16}H_{10}O_2N_2$, and in certain solvents the cryoscopic method gives values corresponding to double this formula (Sommaragu, *Ann.*, 1879, **195**, 312; Vaubel, *Zeitsch. f. Farben- u. Textil-Chem.*, 1902, **1**, 39).

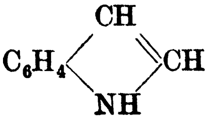
Oxidation with chromic acid decomposes Indigotine, giving two molecules of isatin:

$$C_{16}H_{10}O_2N_2 + O_2 = 2C_8H_5O_2N,$$

showing that the Indigotine molecule is symmetrical and formed from two C_8H_5ON groups linked together. Isatin is hence derived directly from the complex C_8H_5ON, and if the constitution of this group of atoms is determined, that of Indigotine may easily be deduced. On reduction, under different conditions, isatin yields three products (Baeyer and Knopp. *Ann.*, 1868, **140**, 295): dioxindol, $C_8H_7O_2N$; oxindol, C_8H_7ON; and indol, C_8H_7N. Indol may also be obtained directly by reduction of Indigotine, which it regenerates to some extent on oxidising with ozone (Nencki, *Ber.*, 1876, **9**, 299). This was one of the first syntheses of Indigo, Nencki having extracted indol from the products obtained by the pancreatic digestion of albumen (*Ber.*, 1874, **7**, 1593). Hence, indol may be regarded as the parent substance of isatin and of Indigotine, the manner in which the atoms are arranged being the same in these various compounds. The dry distillation of Indigotine gives aniline, whilst in the products obtained by the alkaline fusion of Indigotine or isatin is found *o*-amidobenzoic acid. Hence, these substances (Indigotine, isatin and indol) contain the same grouping, namely, a benzene nucleus in which one of the carbon atoms is bound to nitrogen; the formation of *o*-amidobenzoic acid shows that there is also a carbon atom attached to the nucleus in *ortho*-position to the nitrogen atom. Indol contains the grouping, C_7H_4N:

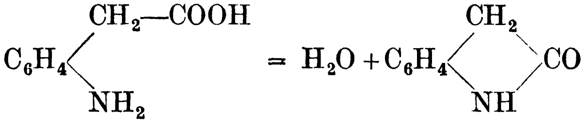


To this grouping CH_3 must be added to give indol. Indol is a weak base, but does not contain an amido-group. It gives a nitroso-compound and an acetyl compound. These properties would agree with those of a compound containing the imido-group, NH, and hence indicates the following constitution:

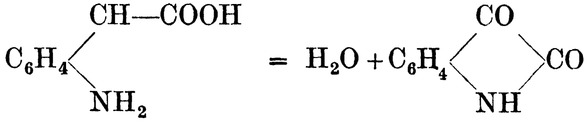


This has been proved by the synthesis of indol. Baeyer and Emmerling (*Ber.*, 1869, **2**, 680) obtained indol by fusing *o*-nitrocinnamic acid with caustic potash and iron filings. Baeyer and Caro (*Ber.*, 1877, **10**, 692, 1262) observed the formation of indol on passing the vapours of diethyl-*o*-toluidine through a red-hot tube.

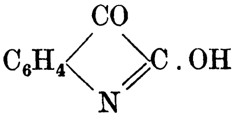
The constitutions of isatin and oxindol have been established by their synthesis. Oxindol is the internal anhydride of *o*-amidophenylacetic acid (Baeyer and Knopp, *loc. cit.*) :



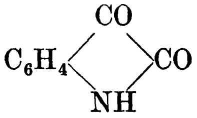
and isatin is the internal anhydride of *o*-amidophenylglyoxylic acid (Claisen and Shadwell, *Ber.*, 1879, **12**, 350) :



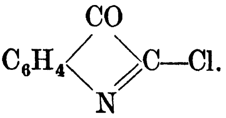
Isatin has the property of reacting in either of two tautomeric forms, either as a *lactam*, known as *pseudo*-isatin, or as the *lactim*, for which the name isatin is reserved ; these two forms have not been isolated in the free state, but Pummerer (*Ber.*, 1911, **44**, 338) has recently prepared certain of their derivatives.



Isatin.

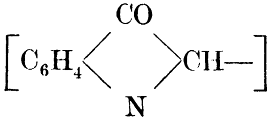


Pseudo-Isatin.



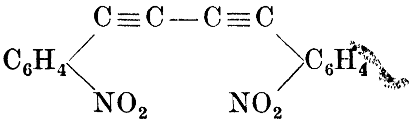
Isatin Chloride.

With phosphorus pentachloride, a chloride is obtained which is a derivative of isatin. Comparing the molecular formula of this chloride, C_8H_4ONCl, with that of Indigotine $(C_8H_5ON)_2$, it will be seen that they differ by the substitution of Cl for H. By eliminating the chlorine and replacing it by hydrogen, Indigotine should be obtained. Baeyer (*Ber.*, 1879, **12**, 456) has actually obtained Indigo by reducing isatin chloride with zinc, and hence Indigotine results from the combination of two groupings of the formula :



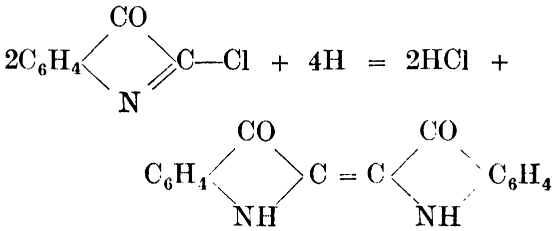
$$\left[C_6H_4\overset{CO}{\underset{N}{\langle\quad\rangle}}CH-\right]$$

It only remains to determine exactly how this combination occurs. On boiling *o*-nitrophenylpropiolic acid with water, it loses carbon dioxide, and gives *ortho*-nitrophenylacetylene. On oxidising with potassium ferricyanide two molecules combine, giving di-*o*-nitrophenyldiacetylene :



$$C_6H_4\overset{C\equiv C-C\equiv C}{\underset{NO_2\qquad NO_2}{\langle\qquad\qquad\rangle}}C_6H_4$$

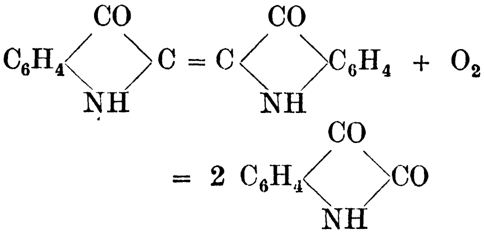
On treating this compound with sulphuric acid and reducing with ammonium sulphide, Indigotine is produced (Baeyer, *Ber.*, 1882, **15**, 50). This synthesis shows that the two benzene rings in Indigotine are linked together by a chain of four carbon atoms. Hence on reduction of isatin chloride, combination must occur by the linking of the carbon atoms adjacent to nitrogen, thus establishing the constitution of Indigotine, as follows :



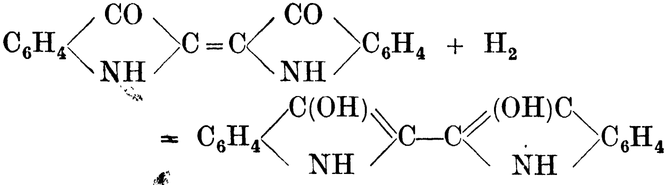
$$2C_6H_4\overset{CO}{\underset{N}{\langle\quad\rangle}}C-Cl + 4H = 2HCl +$$

$$C_6H_4\overset{CO}{\underset{NH}{\langle\quad\rangle}}C=C\overset{CO}{\underset{NH}{\langle\quad\rangle}}C_6H_4$$

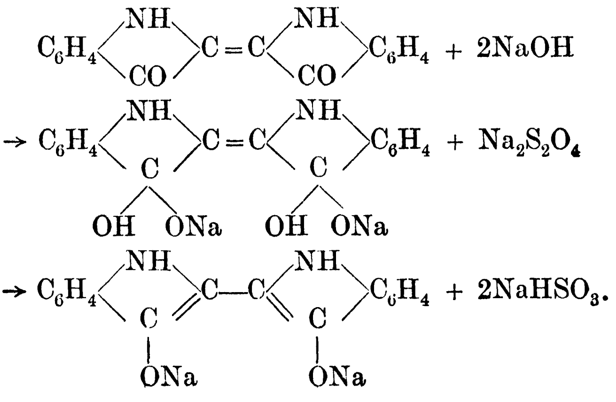
This formula also explains its properties. Thus oxidation yields two molecules of isatin :



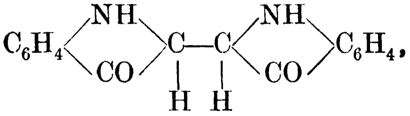
Reduction gives *leuco*-Indigo (Indigo white), which is soluble in alkalies, due to the presence of hydroxyl groups :



Binz and Walter (*Zeitschr. angew. Chem.*, 1906, **19**, 1415) showed that the formation of an Indigo vat, using caustic soda and sodium hydrosulphite, depends upon the sodium salt of Indigo first produced passing into solution owing to the loss of two hydroxyl groups. This is represented by the following equations :



On reoxidising, which only takes place in presence of moisture, caustic soda is produced, leaving Indigotine on the fibre. Other reactions accompany this oxidation (see Crowther, *J. Soc. Dyers and Col.*, 1911, **27**, 146; also Ehrhardt, *ibid.*, 1913, **29**, 121). Binz and Schädel (*Ber.*, 1912, **45**, 586) have obtained further evidence that the formation of the Indigo vat is due to removal of oxygen, and not to addition of hydrogen. Liebermann had previously found that on acetylation, Indigo white behaved as though it possessed the formula:

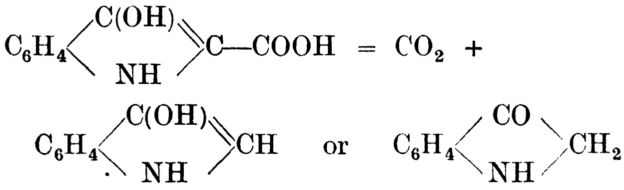


$$C_6H_4\left\langle\begin{matrix}NH\\CO\end{matrix}\right\rangle\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}\left\langle\begin{matrix}NH\\CO\end{matrix}\right\rangle C_6H_4,$$

and hence exists in two tautomeric forms.

The constitution of isatin accounts for its conversion into dioxindol and oxindol by reducing agents.

Indoxyl is an isomer of oxindol and is found in the urine of herbivorous animals in the form of its sulphuric ester (Baumann and Tiemann, *Ber.*, 1879, **12**, 1192; 1880, **13**, 415); it was synthesised by Baeyer (*Ber.*, 1881, **14**, 1741) by reducing *o*-nitrophenylpropiolic acid with ammonium sulphide, when the indoxylic acid first produced loses carbon dioxide, giving indoxyl:



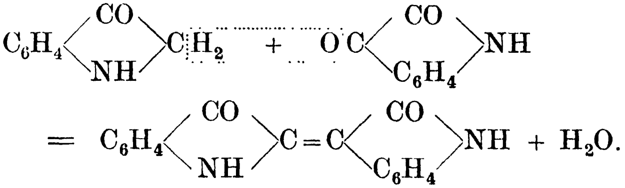
$$C_6H_4\left\langle\begin{matrix}C(OH)\\NH\end{matrix}\right\rangle C-COOH = CO_2 +$$

$$C_6H_4\left\langle\begin{matrix}C(OH)\\NH\end{matrix}\right\rangle CH \quad \text{or} \quad C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CH_2$$

(I.) (II.)

Indoxyl can also react in either of two tautomeric forms, which are called indoxyl (I.) and *pseudo*-indoxyl (II.). It has been obtained in the pure state by Vorländer (*Ber.*, 1902, **35**, 1701) in the form of yellow crystals. Indoxyl oxidises rapidly on exposure to air, giving

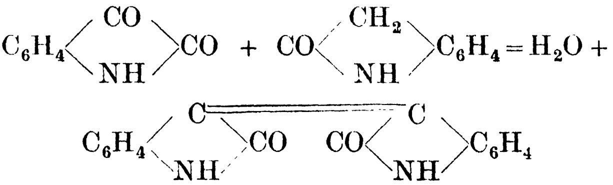
Indigotine. It condenses with aldehydes and with ketones to give the *indogenides* (Baeyer, *Ber.*, 1882, **16**, 2197; Nölting, *Bull. Soc. chim.*, 1902, **27**, 835); thus with isatin it yields the indogenide *Indirubine*, a red dyestuff which is an isomer of Indigotine, with which it occurs in natural Indigo, and which has the following constitution:



$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CH_2 + OC\left\langle\begin{matrix}CO\\C_6H_4\end{matrix}\right\rangle NH$$

$$= C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C=C\left\langle\begin{matrix}CO\\C_6H_4\end{matrix}\right\rangle NH + H_2O.$$

This constitution, which was established by Baeyer, has recently been further proved by Wahl and Bagard (*Bull. Soc. chim.*, 1909, **5**, 1041), who have synthesised Indirubine by condensing isatin chloride with oxindol. In addition to Baeyer's indogenides, Wahl and Bagard have prepared a series of the isomeric compounds, the *iso-indogenides*, from oxindol. The *iso*-indogenide of isatin is a further isomer of Indigotine:



$$C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle CO + CO\left\langle\begin{matrix}CH_2\\NH\end{matrix}\right\rangle C_6H_4 = H_2O +$$

$$C_6H_4\left\langle\begin{matrix}C\\NH\end{matrix}\right\rangle CO \quad CO\left\langle\begin{matrix}C\\NH\end{matrix}\right\rangle C_6H_4 \quad (C=C)$$

to which these authors have given the name *iso*-Indigotine; it crystallises in garnet coloured needles which are insoluble in alkaline reducing agents.

SYNTHESES OF INDIGOTINE.

In the preceding portion it has been seen that Indigotine may be synthesised by various methods: by the oxidation of indol by ozone (Nencki in 1875); the synthesis of oxindol and its conversion into isatin (Baeyer and Commstock, *Ber.*, 1883, **16**, 1704); the synthesis of isatin and isatin chloride, the reduction of which gives a mixture of Indigotine and Indirubine (1879). It was not, however, until the year 1882 that Baeyer and Drewsen's synthesis from *o*-nitrobenzaldehyde gave a process with some possibility of commercial application. Even this possibility was not quickly realised, as attempts to carry out the process on a large scale failed for a long time. In his address to the German Chemical Society (March, 1910), R. Bohn remarked that "The historian will not be able to pass over in silence the period of deep depression which was produced by difficulties encountered in all the various attempts made to apply the results of Baeyer's researches in commerce. New dyestuffs were then sought to replace Indigo."

With the synthesis of Heumann (*Ber.*, 1890, **23**, 3044, 3431; *D.R.P.* 54,626 and 56,273 (1890)), using phenylglycine and its carboxylic acid, a new method was available to investigators which finally solved the problem of the manufacture of Indigo, one of the most striking chemical syntheses.

The various synthetic processes will be described in the following order:

I. Syntheses from cinnamic acid.

II. Syntheses from *o*-nitrobenzaldehyde.

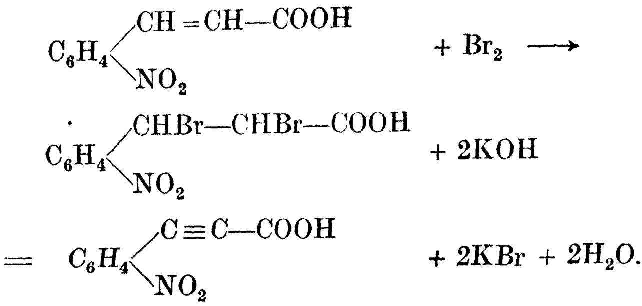
III. Syntheses from thiodiphenylurea and nitrosoethyldiphenylamidine (Sandmeyer's synthesis).

IV. Syntheses from phenylglycine.

V. Syntheses from anthranilic acid.

I. Syntheses from Cinnamic Acid.

The nitration of cinnamic acid or its esters yields a mixture of isomerides, of which only the *o*-nitrocinnamic acid can be converted into Indigotine, this being carried out in several ways. On treating with bromine and then with alcoholic potash, this compound gives *o*-nitrophenylpropiolic acid :

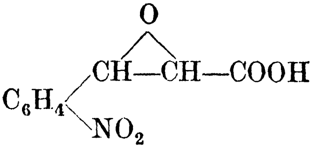


$$C_6H_4\begin{cases}CH{=}CH{-}COOH\\NO_2\end{cases} + Br_2 \longrightarrow$$

$$C_6H_4\begin{cases}CHBr{-}CHBr{-}COOH\\NO_2\end{cases} + 2KOH$$

$$= C_6H_4\begin{cases}C{\equiv}C{-}COOH\\NO_2\end{cases} + 2KBr + 2H_2O.$$

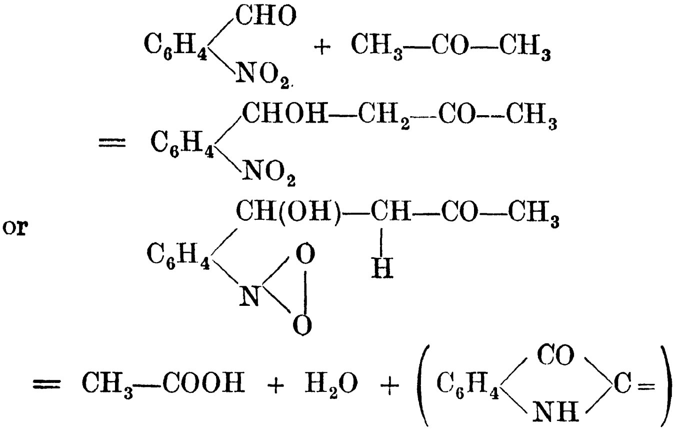
The action of reducing agents (glucose and caustic soda, or alkali xanthates) converts this acid into Indigotine ; the yield is about 70 per cent. and the process was used for some time in calico-printing (*D.R.P.* 15,516). It has already been shown that this acid may also be converted into nitrophenylacetylene. Finally, *o*-nitrocinnamic acid combines with a molecule of hypochlorous acid, giving *o*-nitrophenylchlorlactic acid, which on treatment with alkalies loses hydrochloric acid to give *o*-nitrophenyloxyacrylic acid :



This compound gives Indigotine on fusing or heating with acetic acid or phenol (*D.R.P.* 11,857 (1880)).

II. Syntheses from *o*-Nitrobenzaldehyde.

In 1882, Baeyer and Drewsen (*Ber.*, 1882, **15**, 2856) showed that an excellent yield of Indigotine was obtained by treating *o*-nitrobenzaldehyde dissolved in acetone with caustic soda. Aldol condensation first takes place, and then acetic acid and water are split off :

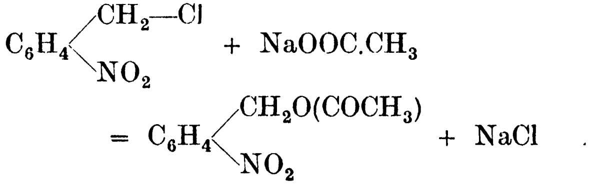


Two of the groupings so obtained then combine to give Indigotine.

The acetone may be replaced by acetaldehyde or by pyruvic acid (Baeyer and Drewsen, *Ber.*, 1883, **16**, 2205 ; *D.R.P.* 19,768) ; moreover, by using a substituted *o*-nitrobenzaldehyde, a substituted Indigo is readily obtained. Thus, *o*-nitro-*m*-toluic aldehyde (Höchst Farbwerke, *D.R.P.* 21,683), chlor- and brom-*o*-nitrobenzaldehyde (*D.R.P.* 30,339), and dichlor-*o*-nitrobenzaldehyde (*D.R.P.* 32,238) have been used.

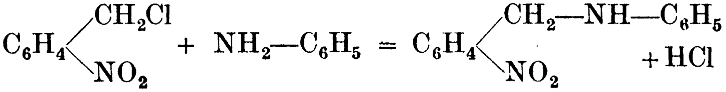
" Indigo salt," used to some extent in printing, is formed by combining the above alcohol (*o*-nitrophenyllactylketone) with sodium bisulphite ; it is a white substance which is stable in air, but yields Indigo with alkalies.

Syntheses by means of *o*-nitrobenzaldehyde are, however, dependent on the preparation of this compound, which is rather difficult. The nitration of benzaldehyde only gives a small amount of the *ortho*-compound, yielding 100 to 105 per cent. of its weight of the *p*-nitro-derivative and only 20 to 25 per cent. of the *ortho*-derivative. By treating *o*-nitrotoluene with chlorine under certain conditions, it is partly converted into *o*-nitrobenzyl chloride, and this compound may be converted into the aldehyde by several processes. Thus on heating with alkali salts, acetates, sulphites, or thiosulphates, it is converted into the corresponding esters of *o*-nitrobenzyl alcohol, which are then oxidised (*D.R.P.* 48,722, 104,360):

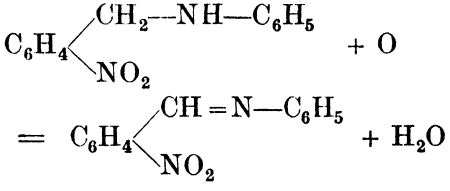


$$C_6H_4\left\langle\begin{matrix}CH_2{-}Cl\\NO_2\end{matrix}\right. + NaOOC.CH_3 = C_6H_4\left\langle\begin{matrix}CH_2O(COCH_3)\\NO_2\end{matrix}\right. + NaCl$$

or the product may be heated with aniline, the benzylaniline oxidised, and then the benzylidene aniline so obtained hydrolysed (Höchst Farbwerke, *D.R.P.* 91,503, 92,084, 93,539, 97,847, 97,948):

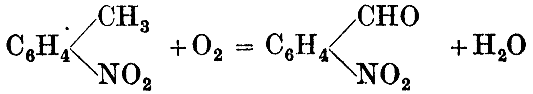


$$C_6H_4\left\langle\begin{matrix}CH_2Cl\\NO_2\end{matrix}\right. + NH_2{-}C_6H_5 = C_6H_4\left\langle\begin{matrix}CH_2{-}NH{-}C_6H_5\\NO_2\end{matrix}\right. + HCl$$



$$C_6H_4\left\langle\begin{matrix}CH_2{-}NH{-}C_6H_5\\NO_2\end{matrix}\right. + O = C_6H_4\left\langle\begin{matrix}CH{=}N{-}C_6H_5\\NO_2\end{matrix}\right. + H_2O$$

Finally, the side chain of hydrocarbons has been converted into the aldehyde group; thus, on oxidising *o*-nitrotoluene with manganese dioxide in presence of sulphuric acid:



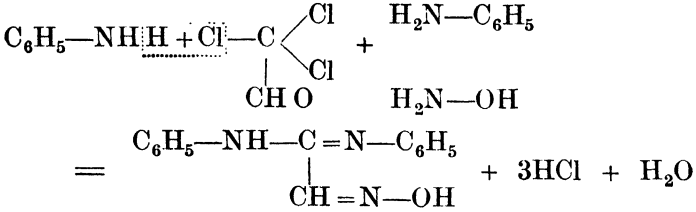
$$C_6H_4\left\langle\begin{matrix}CH_3\\NO_2\end{matrix}\right. + O_2 = C_6H_4\left\langle\begin{matrix}CHO\\NO_2\end{matrix}\right. + H_2O$$

Other methods are known, but they are of less importance.

III. Sandmeyer's Syntheses.

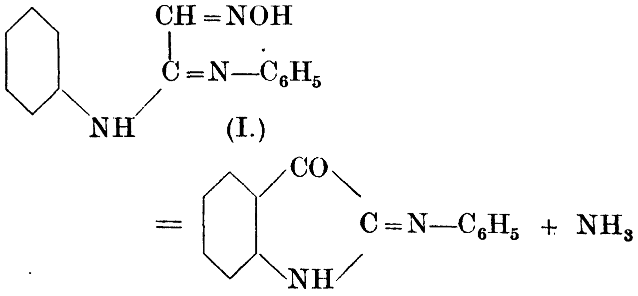
These were discovered by Sandmeyer at the works of Geigy and Co. in Basle in 1899. There are two processes :

(1) By the action of chloral on a mixture of aniline and hydroxylamine hydrochlorides, an isonitroso-derivative is obtained :



$$C_6H_5{-}NH\underline{H+Cl}{-}\underset{CHO}{\overset{}{C}}\begin{matrix}{/}Cl\\ {\backslash}Cl\end{matrix} + \begin{matrix}H_2N{-}C_6H_5\\ \\ H_2N{-}OH\end{matrix} = \begin{matrix}C_6H_5{-}NH{-}C{=}N{-}C_6H_5\\ |\\ CH{=}N{-}OH\end{matrix} + 3HCl + H_2O$$

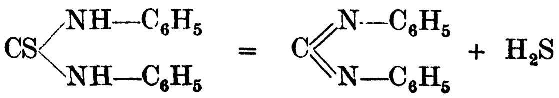
On heating with sulphuric acid, this compound loses ammonia, giving isatin α-anilide :



(I.)

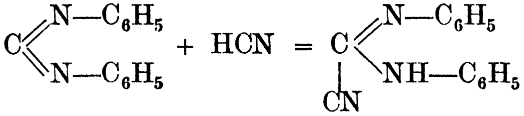
and this compound is readily and quantitatively converted by means of reducing agents, such as ammonium sulphide, into Indigotine.

(2) Carbon disulphide gives symmetrical diphenylthiourea with aniline, from which lead salts remove sulphuretted hydrogen :

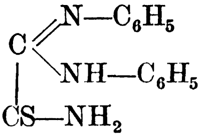


$$CS\begin{matrix}{/}NH{-}C_6H_5\\ {\backslash}NH{-}C_6H_5\end{matrix} = C\begin{matrix}{/\!/}N{-}C_6H_5\\ {\backslash\!\backslash}N{-}C_6H_5\end{matrix} + H_2S$$

On treating this compound with potassium cyanide, hydrocyanocarbodiphenylimide is produced :

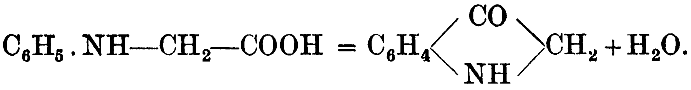


This product is also formed by dehydrating the above isonitroso-compound, and is readily converted into the anilide obtained in (I.) by treating with ammonium sulphide and then with concentrated sulphuric acid. The following thioamide is formed as an intermediate product:



IV. Syntheses from Phenylglycine.

In 1890 Heumann (*Ber.*, 1893, **26**, 225; *D.R.P.* 54,626 and 54,988) showed that the product obtained by the alkaline fusion of phenylglycine yielded a small amount of Indigotine on oxidation in air. It may be supposed to be formed from indoxyl according to the equation :



Phenylglycine is obtained by condensing aniline with monochloracetic acid :

$$C_6H_5NH_2 + ClCH_2COOH = HCl + C_6H_5NH\text{-}CH_2COOH$$

or by the action of a mixture of formaldehyde and potassium cyanide on aniline (Deutsche Gold- und Silberscheide Anstalt, *D.R.P.* 117,623, 137,955, 141,749) :

$$C_6H_5—NH_2 + CH_2O + HCN = C_6H_5—NH—CH_2—CN \longrightarrow C_6H_5—NH—CH_2—COOH.$$

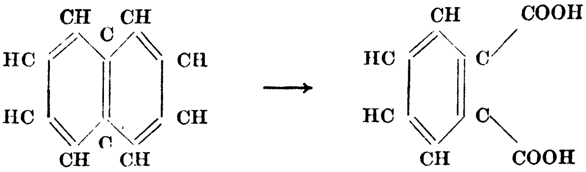
This preparation has been the subject of a number of patents (Bucherer, *D.R.P.* 157,710, 157,909, 157,910; B.A.S.F., *D.R.P.* 156,760, 157,617, 158,346, 158,090, 158,718, 181,723).

The alkaline fusion of phenylglycine only gives a very small yield of Indigotine, owing to decomposition occurring at the high temperature (300°) at which the reaction must be carried out. Hence an attempt has been made to replace caustic alkalies by mixtures, in order to lower the temperature of reaction to about 200°; thus, by mixing phenylglycine with a mixture of alkalies and sodium peroxide, sodium ethylate, lime, etc., greater yields are generally obtained. In 1900 it was found that sodamide was a very suitable reagent for converting phenylglycine into Indigotine (Deutsche Gold- u. Silberscheide Anstalt, *D.R.P.* 169,186). This process has been used by the Höchst Farbwerke, and gives good results (see p. 286).

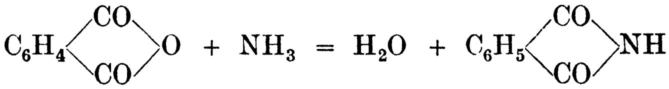
V. Syntheses from Anthranilic Acid.

Heumann noticed that Indigotine is also formed by the alkaline fusion of phenylglycine *o*-carboxylic acid. In this reaction the yield is considerably greater than that obtained with phenylglycine under the same conditions, and this method became the commercial process as soon as phenylglycine *o*-carboxylic acid could be satisfactorily obtained. The commercial preparation of this acid, and hence of Indigo, was first carried out by the B.A.S.F., who have devoted a large amount of capital to the installation of the necessary plant.

The raw material is naphthalene, which is first converted into phthalic acid by oxidation; the most suitable oxidising agent is fuming sulphuric acid, the action of which is made more energetic by the addition of mercury salts:

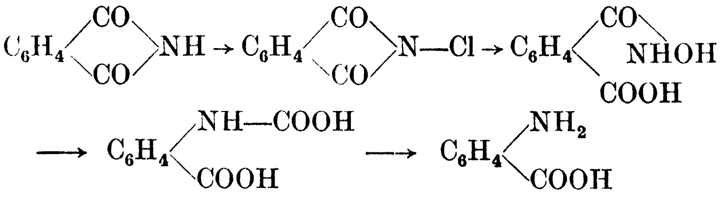


This reaction is carried out at about 280-300°. Phthalic acid, or better, its anhydride, is then converted into phthalimide by heating to 225° with ammonium carbonate, or by passing ammonia into fused phthalic anhydride :



$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>O + NH_3 = H_2O + C_6H_5\left<\begin{matrix}CO\\CO\end{matrix}\right>NH$$

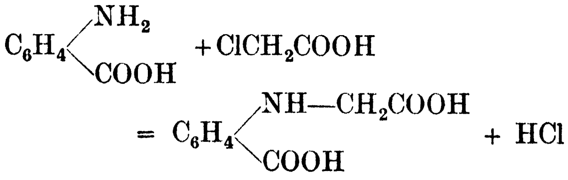
The phthalimide is then treated with alkaline hypochlorites (Hofmann's reaction), and gives anthranilic acid, intermediate compounds probably being produced as follows :



$$C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NH \rightarrow C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>N—Cl \rightarrow C_6H_4\left<\begin{matrix}CO\diagdown\\ \quad NHOH\\COOH\end{matrix}\right.$$

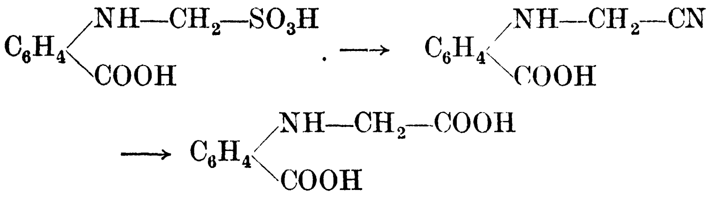
$$\longrightarrow C_6H_4\left<\begin{matrix}NH—COOH\\COOH\end{matrix}\right. \longrightarrow C_6H_4\left<\begin{matrix}NH_2\\COOH\end{matrix}\right.$$

The conversion of anthranilic acid into phenylglycine *o*-carboxylic acid can be carried out in several ways. Thus anthranilic acid may be treated with monochloracetic acid. The reaction must be carried out at a low temperature (40°), being then very slow ; at higher temperatures secondary products are obtained.



$$C_6H_4\left<\begin{matrix}NH_2\\COOH\end{matrix}\right. + ClCH_2COOH = C_6H_4\left<\begin{matrix}NH—CH_2COOH\\COOH\end{matrix}\right. + HCl$$

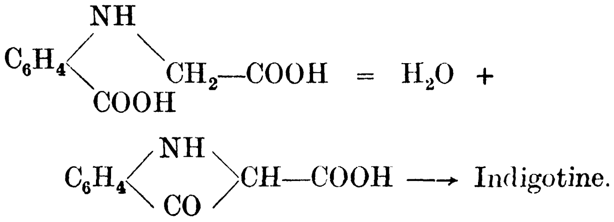
By the action of a mixture of formaldehyde, sodium bisulphite and potassium cyanide on anthranilic acid in aqueous solution, the following changes occur rapidly, giving an excellent yield :



$$C_6H_4\Big<\begin{matrix}NH-CH_2-SO_3H\\COOH\end{matrix} \longrightarrow C_6H_4\Big<\begin{matrix}NH-CH_2-CN\\COOH\end{matrix}$$

$$\longrightarrow C_6H_4\Big<\begin{matrix}NH-CH_2-COOH\\COOH\end{matrix}$$

This acid is then fused with an alkali, the resulting mass dissolved in water and oxidised by a current of air :



Synthetic Indigotine contains impurities which may be removed by various methods, such as boiling with pyridine. Indigo comes into commerce in the form of a paste or an impalpable powder.

Sandmeyer's syntheses have not yet received practical application, as the works at which this process was attempted (Geigy and Co., Basle) were destroyed by fire some years ago. This process has been perfected by Rahtjen, and a company has been formed at Hamburg, with a capital of a quarter of a million sterling, with a view to its exploitation (*Chem.-Ztg.*, 1910, 162).

Syntheses from *o*-nitrobenzaldehyde are dependent on toluene as the raw material, and the production of this substance is somewhat limited. It has been calculated that four tons of this hydrocarbon yield one ton of Indigo, and as the monthly consumption of Indigo is seven to eight thousand tons, this would require thirty thousand tons of toluene. Hence the production of toluene is not sufficient under present conditions, although the increasing use of bye-product coke-ovens will naturally lead to an increase in the production.

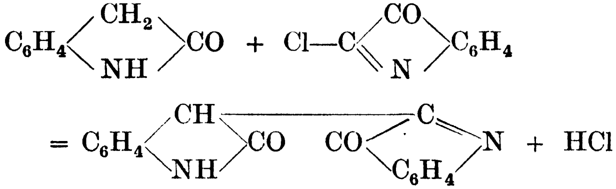
Syntheses from phenylglycine or its carboxylic acid require as raw materials aniline, naphthalene, and monochloracetic acid. The electrolytic soda industry yields the necessary amount of chlorine for the ready preparation of monochloracetic acid. Naphthalene is the commonest of the hydrocarbons ; according to Brunck, its production amounts to forty or fifty thousand tons per annum, and its price is about £4 per ton. Its conversion into phthalic anhydride can be carried out very economically, as the catalytic process yields fuming sulphuric acid at a very low price. The Badische Co. manufactures its *Indigo Pure B.A.S.F.* in a works which cost over a million sterling to erect.

Of the numerous syntheses of Indigotine which have been suggested or actually carried out on a large scale, the sodamide modification of Heumann's process is the chief one. This great improvement over the original caustic fusion was the invention of the Deutsche Gold und Silberscheide Anstalt, and was acquired by Meister, Lucius and Brüning. The yield of the alkaline fusion method was 13 per cent., whereas it is stated that the sodamide process gives over 75 per cent. of the theoretical amount. To avoid handling sodamide as such, it is probable that ammonia gas is passed over a mixture of phenylglycine, caustic alkali, and sodium, sodamide being thereby formed *in situ*.

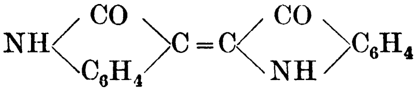
The leuco-compound, Indigo white, is now commercial, various patents having been taken out of methods used to increase its stability, and at the same time to facilitate its solution or the ease of obtaining a vat. (For details see Vlies, *J. Soc. Dyers and Col.*, 1914, 22.)

Indirubine.

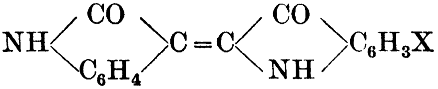
This compound is the isomer of Indigotine, together with which it occurs in almost all the natural products, particularly in Indigo from Java, which frequently contains 5 to 7 per cent. of Indirubine, from which Indigo from India is practically free (see A. G. Perkin, *J. Soc. Dyers and Col.*, 1911, 52). Its constitution was established by Baeyer (*Ber.*, 1881, **14**, 1745), who synthesised it from isatin and indoxyl. Another synthesis has recently been carried out by Wahl and Bagard (*Bull. Soc. chim.*, 1910, **7**, 1090; 1911, **9**, 56) by condensing isatin chloride with oxindol, thus:



which passes into the isomeric compound *Indirubine*:



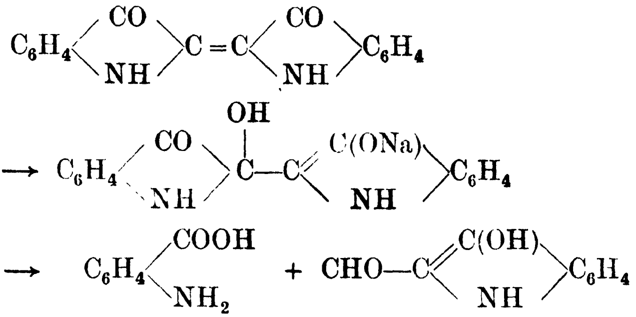
This reaction may be applied to substituted derivatives of isatin, which yield, on condensation with oxindol, substituted derivatives of Indirubine of the type:



The same derivatives may be obtained by condensing isatin with substituted derivatives of indoxyl, X being Br, Cl, NO_2, etc.

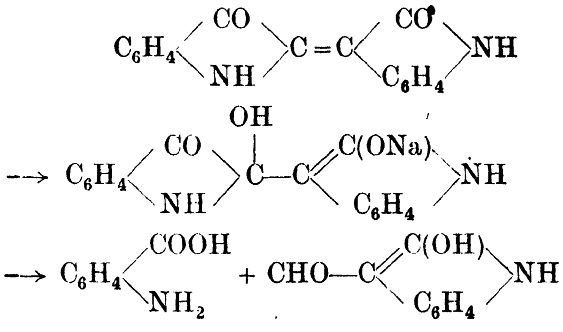
Action of Alkalies on Indigotine and on Indirubine.

Warm concentrated alkalies decompose Indigotine, giving an orange solution from which acids precipitate chrysanilic acid. Friedländer and Schwenk (*Ber.*, 1910, **43**, 1971) have shown that this acid is not the first product formed, indoxyl-2-aldehyde and anthranilic acid being first produced, thus:



Unless the indoxyl-2-aldehyde is removed by ether, these products condense on acidifying to give chrysanilic acid.

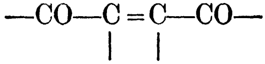
Under the same conditions, Indirubine yields an isomeric aldehyde, oxindol-3-aldehyde, as follows:



This reaction occurs with all the Indigoid dyestuffs, and also with derivatives of Thioindigo. Thus *Thioindigo scarlet R* yields chrysanilic acid and thiosalicylic acid.

INDIGOID DYESTUFFS.

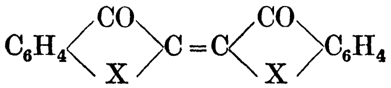
For a long time Indigo and Indirubine occupied an isolated position amongst the organic dyestuffs. Friedländer (for nomenclature of the Indigoid compounds see Friedländer, *Monatsh. f. Chem.*, 1898, **29**, 359) has shown that there exists a class of dyestuffs which he terms "Indigoid" dyestuffs, of which Indigo and Indirubine only constitute the first members. The Indigoid dyestuffs are characterised by the presence of the grouping:



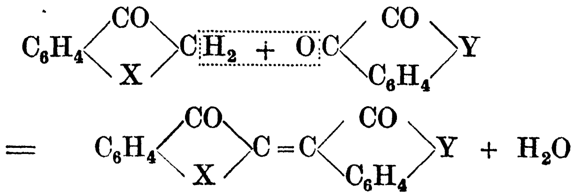
$$-CO-\underset{|}{C}=\underset{|}{C}-CO-$$

which occurs in Indigotine and its two isomers, Indirubine and *iso*-Indigotine. Indigoid dyestuffs may be symmetrical or asymmetrical according to whether the two parts of the molecule united by the double bond are identical and apparently similarly arranged, or whether they are different in structure or orientation.

The symmetrical dyestuffs are obtained by oxidising products similar to indoxyl, and have the constitution:



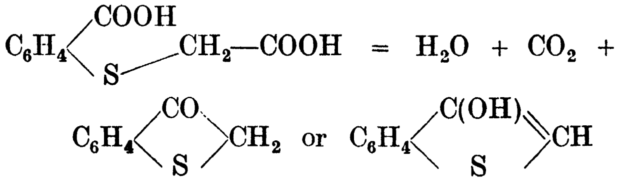
in which X represents a divalent atom or group, such as O, CO, S, NH, CO . NH, etc.; the group C_6H_4 may itself be replaced by another ring. The asymmetrical dyestuffs are prepared by condensing a compound similar to indoxyl with a cyclic ketone such as isatin, thus:



They are also obtained by condensing isatin chloride or isatin anilides with cyclic molecules containing a C(OH)=CH group, such as phenols, diphenols, naphthols, pyrazolones, isoxazolones, pyramidines, etc. (Friedländer, *Ber.*, 1908, **41**, 772 ; Friedländer, Bezdrik, and Königer, *ibid.*, 227). It will hence be seen that a large variety of Indigoid dyestuffs can be obtained, some of which have already met with great commercial success.

Thioindigo.

The preparation of this dyestuff is very similar to the synthesis of Indigotine from anthranilic acid (Kalle, *D.R.P.* 188,702, 192,075, 194,237, 194,254, 177,346 (1905). For further details see *J. Soc. Chem. Ind.*, 1909, **32**, 565). It consists in fusing phenylthioglycine-*o*-carboxylic acid with alkalies and oxidising the aqueous solution of the resulting product, by means of a current of air, or other oxidising agent, such as dichromate, ferric chloride, etc.



$$C_6H_4{<}^{COOH}_{S-CH_2-COOH} = H_2O + CO_2 + C_6H_4{<}^{CO}_{S}{>}CH_2 \text{ or } C_6H_4{<}^{C(OH)}_{S}{>}CH$$

There is produced a compound which differs from indoxyl by the replacement of the NH group by S, and is called thioindoxyl or 3-oxythionaphthen.* Like indoxyl, this is oxidised on exposure to air, giving the dyestuff.

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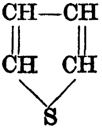
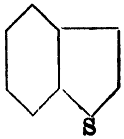
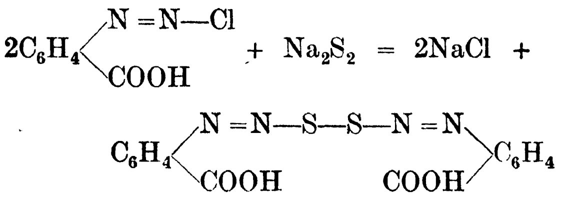
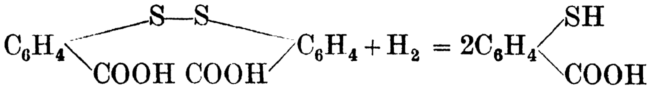
*Thiophen has the constitution:  and hence the name thionaphthen has been given to the compound: 

The raw material for this process, phenylthioglycine-*o*-carboxylic acid, may be obtained in several ways; thus, if anthranilic acid is diazotised and treated with a solution of sodium disulphide, obtained by dissolving sulphur in sodium sulphide, the following reaction occurs:



$$2C_6H_4\left\langle\begin{matrix}N=N-Cl\\ COOH\end{matrix}\right. + Na_2S_2 = 2NaCl + C_6H_4\left\langle\begin{matrix}N=N-S-S-N=N\\ COOH \qquad\qquad COOH\end{matrix}\right\rangle C_6H_4$$

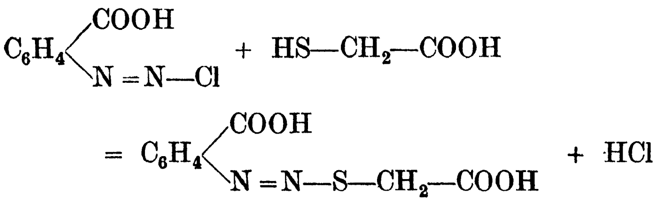
The diazodisulphide produced is very unstable, and loses its nitrogen, giving dithiosalicylic acid, which is converted by reducing agents into thiosalicylic acid:



$$C_6H_4\left\langle\begin{matrix}S-S\\ COOH \quad COOH\end{matrix}\right\rangle C_6H_4 + H_2 = 2C_6H_4\left\langle\begin{matrix}SH\\ COOH\end{matrix}\right.$$

Finally, by the action of monochloracetic acid on this acid, phenylthioglycine-*o*-carboxylic acid is obtained.

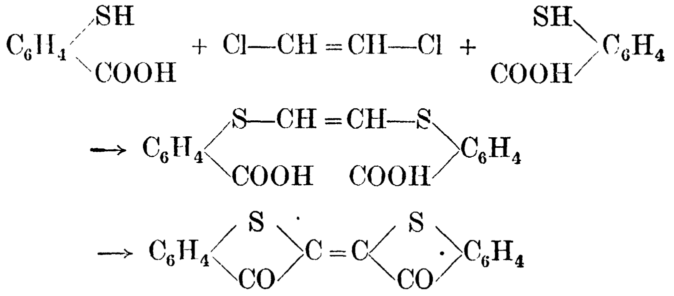
Diazoanthranilic acid may also be combined with thioglycine, obtained by treating monochloracetic acid with sodium sulphide:



$$C_6H_4\left\langle\begin{matrix}COOH\\ N=N-Cl\end{matrix}\right. + HS-CH_2-COOH$$
$$= C_6H_4\left\langle\begin{matrix}COOH\\ N=N-S-CH_2-COOH\end{matrix}\right. + HCl$$

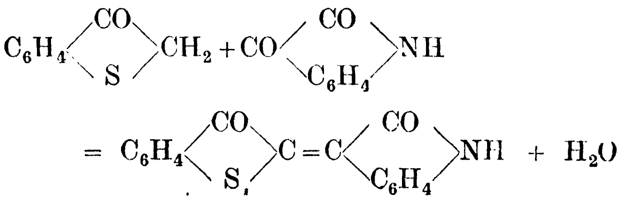
This diazosulphide also readily loses its nitrogen and yields the acid required.

Of the numerous processes for the preparation of Thioindigo which have been made the subject of patents may be mentioned the process which consists in condensing acetylene dichloride with thiosalicylic acid and dehydrating the compound formed (Münch, *Zeitsch. angew. Chem.*, 1908, **21**, 2059 ; *D.R.P.* 205,324) :



The commercial product *Thioindigo (red) B*, which is prepared by the firm of Kalle according to Friedländer's patents, dyes cotton from a vat, giving fairly fast violet red shades. (See Knecht, *J. Soc. Dyers and Col.*, 1906, 56.)

Thioindigo scarlet R (Kalle, *D.R.P.* 187,586, 190,292, 182,260, 193,150) is the dyestuff obtained by condensing isatin with oxythionaphthen :

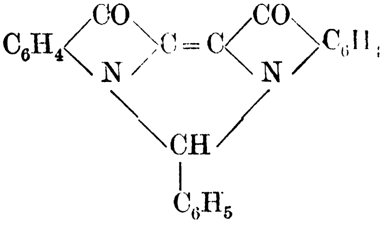


Its constitution is determined by its method of formation. It dyes cotton brilliant scarlet shades.

Substituted Indigoid Dyestuffs.

Ciba Dyestuffs (*Soc. pour l'ind. chim.*, Basle, *D.R.P.* 190,292, 192,682, 193,438). These dyestuffs are polyhalogenated derivatives of the Indigoid dyestuffs, Indigotine, Indirubine, Thioindigo, Thioindigo scarlet, etc., produced by halogenation at high temperatures in absence of water, using nitrobenzene, dichlorbenzene, glacial acetic acid, etc., as solvents (*E.P.* 5122, 6105, 9546, and 13,148 (1907); 19,563 (1908)). The original name is now used as a trade name for all the Indigo derivatives of this firm. Whereas the mono- and dihalogenated derivatives are only of slight importance, the tri- and tetra-halogenated derivatives have very pure shades which differ from those of the original substances. The position of the substituted atoms has a great influence on the shade produced. *Ciba blue B* and *2B* are tri- and tetra-brom-Indigotine.

On heating Indigo with an excess of benzoyl chloride, dibenzoyl-Indigo, a brown amorphous powder of M.P. 108°, is produced. In presence of condensing agents, such as copper, using nitrobenzene as solvent, an intense yellow dyestuff is produced (Engi and Fröhlich, U.S.A. Pat., 1026,574 (1912)), *Indigo yellow 3G Ciba*, which probably has the following composition:

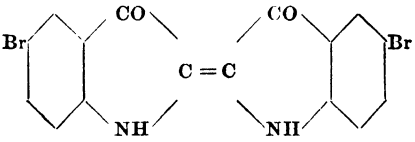


This dyestuff and the bromo-derivative *Ciba yellow G* (*D.R.P.* 246,837) were the first yellow vat dyestuffs for wool; they also dye cotton and silk from a vat. (Wuth, *J. Soc. Dyers and Col.*, 1911, 201; Engi, *Chem.-Ztg.*, 1914, 199.)

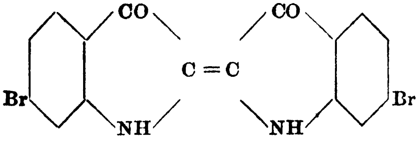
Although Indirubine itself is practically useless for dyeing purposes, its bromo-derivatives possess a much greater affinity for the fibre, and excel in purity of shade and general fastness. *Ciba heliotrope* (*E.P.* 6106 (1907)) is prepared by brominating Indirubine in presence of an excess of nitrobenzene at 130° C. The *Helindone* dyestuffs of the Höchst Farbwerke are also substituted derivatives of Indigoid compounds.

On condensation with isatin and subsequent bromination, methylindoxyl gives new violet dyestuffs, such as *Helindone violet D* (M.L.B., *E.P.* 24,886 (1910)).

Whereas the Anthraquinone derivatives are with very few exceptions (for example, *Helindone blue 3G*) unsuitable for wool dyeing, the Helindone dyestuffs of the Indigoid or Thioindigoid series are suitable for dyeing on wool (Kämmerer, *J. Soc. Dyers and Col.*, 1913, 68), for example, *Helindone blue 2B*, which is mainly 5 : 5′-dibrom-Indigo :

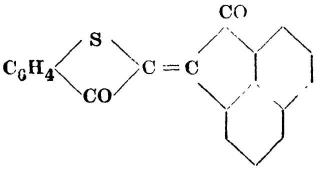


It is interesting to note that Friedländer (*Mon. sci.*, 1909, 570) has recently proved the identity of Tyrian purple with dibrom-Indigotine, which has the constitution :

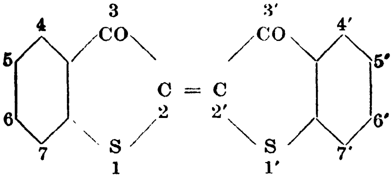


This dyestuff of the Romans was extracted from a species of mollusc found in the Mediterranean, known as the *murex brandaris.*

On condensing with acenaphthene quinone, oxythionaphthen gives an interesting dyestuff, for the preparation of which the acenaphthene extracted from coal-tar, which previously had no commercial application, may be used. This product is known as *Ciba scarlet G* (*Soc. pour l'ind. chim.*, Basle, *D.R.P.* 205,377), and has the following constitution :



The substitution derivatives of Thioindigo form a very important class ; whereas the derivatives of Indigo do not differ greatly in colour, those of Thioindigo cover almost the whole range of the spectrum. Thioindigo can be substituted in seven different positions:

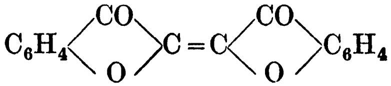


The remarkable influence of substituents on the colour is illustrated by the following examples (Friedländer, vol. ix, p. 502) : 6 : 6'-methoxy-thioindigo gives an orange-red shade, the 4 : 4' compound, blue-violet ; 6 : 6'-diamido-thioindigo gives an orange-brown shade, the 4 : 4' compound, green-black ; 6 : 6'-di-ethoxy-thioindigo is a bright orange dyestuff, the 5 : 5' compound, dark violet.

The following Helindone [M.L.B.], Thioindigo [K.], and Ciba [C.I.B.] dyestuffs are commercial, and are derivatives of Thioindigo :

DYESTUFF.	PATENT NO.	CONSTITUTION.
Thioindigo red BG.	*D.R.P.* 198,864	5 : 5′-Dichlorthioindigo.
Helindone red B.		
Ciba red B.	*E.P.* 6490 (1907)	6 : 6′-Dichlorthioindigo.
Thioindigo red 3B.	*D.R.P.* 241,910	5 : 5′-Dichlor-6 : 6′-dimethylthioindigo.
Helindone red 3B.		
Helindone Fast scarlet R.	*D.R.P.* 213,465	5 : 5′-Dichlor-6 : 6′-diethoxythioindigo.
Helindone grey BR.	*D.R.P.* 216,224	Dichlor-7 : 7′-diamido thioindigo.
Helindone violet 2B.	*D.R.P.* 241,910	Dichlor-dimethyl-dimethoxy-thioindigo.
Thioindigo violet 2B.		
Ciba bordeaux B.	*E.P.* 6490 (1907)	5 : 5′-Dibrom-thioindigo.
Helindone pink BN.	*D.R.P.* 239,094	6 : 6′-Dibrom-dimethyl-thioindigo.
Thioindigo pink BN.		
Helindone orange D.	*D.R.P.* 198,644	Dibrom-6 : 6′-diamido-thioindigo.
Helindone orange R.	*E.P.* 1472 (1907)	6 : 6′-Diethoxy-thioindigo.
Thioindigo orange R.		
Thioindigo scarlet S.	*D.R.P.* 239,089	6 : 6′-Dithioxyl-thioindigo.
Helindone scarlet S.		
Helindone grey 2B.	*D.R.P.* 241,910	7:7′-Diamido-thioindigo.
Thioindigo grey 2B.		

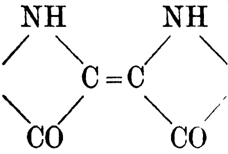
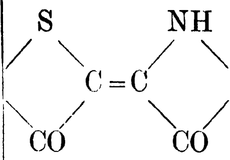
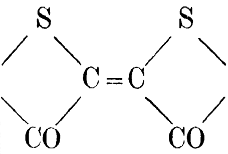
According to Bohn (*Ber.*, 1910, **43**, 987), the Indigoid dyestuffs may be divided into symmetrical and asymmetrical dyestuffs, and each of these groups may be divided into three classes, as shown in the following table. This classification does not include *Oxindigo*



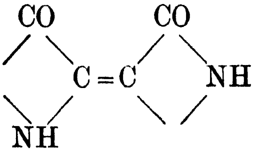
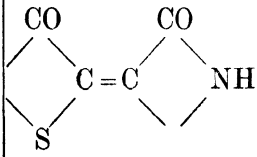
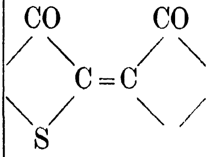
which has recently been obtained by Fries and Hasselbach (*Ber.*, 1911, **44**, 124) and by Störmer and Brachmann (*Ibid.*, 315). This substance is unstable, and is decomposed by caustic alkalies

Indigoid Dyestuffs.

I. SYMMETRICAL DYESTUFFS.

Class I.	Class II.	Class III.
Nitrogen compounds.	Sulphur-nitrogen compounds.	Sulphur compounds.
Chromogen : 	Chromogen : 	Chromogen : 
Indigo and derivatives.	*Ciba violet* and derivatives.	*Thioindigo B* and derivatives.

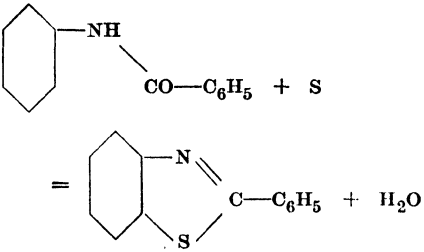
II. ASYMMETRICAL DYESTUFFS.

Class IV.	Class V.	Class VI.
Nitrogen compounds.	Sulphur-nitrogen compounds.	Sulphur compounds.
Chromogen : 	Chromogen : 	Chromogen : 
Indirubine and derivatives.	*Thioindigo scarlet* and derivatives.	*Ciba scarlet G* and derivatives.

CHAPTER XXII.

THIAZOL DYESTUFFS.

THE name *thiazol* has been given to a heterocyclic ring containing three carbon atoms, one nitrogen atom, and one sulphur atom. The first derivative of this group known, phenylbenzthiazol, was obtained by Hofmann by fusing benzanilide with sulphur:

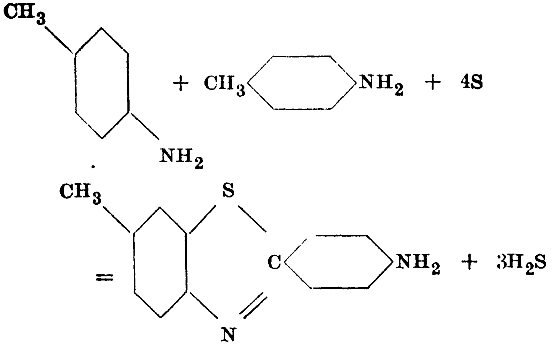


The simplest derivatives of thiazol are colourless. Phenylbenzthiazol is, however, a chromogen, as the introduction of basic groups in *para*-position to the carbon of the thiazol ring gives feebly yellow coloured substances.

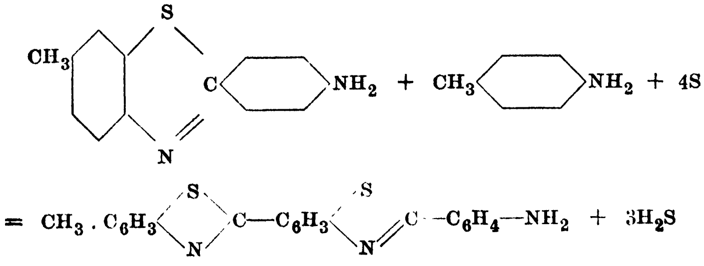
The thiazol derivatives used in the manufacture of dyestuffs are those obtained by fusing *p*-toluidine or its homologues with sulphur. This reaction was discovered by Green in 1887 (*Ber.*, 1889, **22**, 969) and led to the preparation of *Primuline*, the manufacture of which was immediately undertaken by Brooke, Simpson and Spiller, near London. The process was not patented, and the researches of Jacobson (*Ibid.*, 331), Gattermann (*Ibid.*, 424, 1064), Anschütz and Schultz (*Ibid.*, 581) soon gave the chemical constitution and method of preparation of this compound. Since that time the manufacture of Primuline has been the subject of a number of patents, mainly relating to the separation of the products formed in the reaction, Primuline and dehydrothiotoluidine.

Manufacture of Primuline.

When *p*-toluidine is fused with sulphur and the mass heated to 200°, sulphuretted hydrogen is liberated, and there are produced two products, dehydrothiotoluidine and Primuline, the relative amounts of which depend on the duration of the reaction, the temperature, and the amount of sulphur. Dehydrothiotoluidine, or *p*-amidophenyltoluthiazol, results from the action of four atoms of sulphur on two molecules of the base, thus :



When the reaction lasts for a longer period, or is carried out at a higher temperature, Primuline is produced by the action of sulphur on a molecule of dehydrothiotoluidine and a molecule of *p*-toluidine :



$$= CH_3 \cdot C_6H_3 \begin{smallmatrix} S \\ N \end{smallmatrix} C-C_6H_3 \begin{smallmatrix} S \\ N \end{smallmatrix} C-C_6H_4-NH_2 + 3H_2S$$

It is difficult to limit this reaction, and hence a mixture of the two products is obtained. On heating 100 parts of *p*-toluidine with 60 parts of sulphur for twenty-four hours, there is obtained a mixture containing 50 per cent. of dehydrothiotoluidine, 40 per cent. of Primuline, and 10 per cent. of unchanged *p*-toluidine. The two bases may be separated by their different solubilities in alcohol, Primuline being insoluble. In order to obtain soluble dyestuffs it is necessary to use the sulphonated derivatives of these bases, which can be separated fairly easily commercially.

The reaction between sulphur and *p*-toluidine is carried out in a directly heated cast-iron vessel, closed by a cover carrying one or two fairly large pipes surrounded by warm water, in order to condense the vapours of the *p*-toluidine without solidifying the base; the sulphuretted hydrogen which escapes is led by a pipe to the fire where it burns. When the reaction has commenced, the combustion of the sulphuretted hydrogen formed supplies the heat necessary to maintain the required temperature. When the liberation of gas diminishes the reaction is finished, and the contents of the vessel are forced into a sheet-iron tank and allowed to solidify; the yellowish brown mass obtained contains a mixture of dehydrothiotoluidine and Primuline.

In order to sulphonate this product, it is first finely powdered, and then added to four or five times its weight of fuming sulphuric acid, containing 23 per cent. of the anhydride, kept at 70°. The sulphonation is finished when the precipitate formed by pouring a drop of the sulphuric acid solution into water is completely soluble in caustic soda or sodium carbonate. The sulphuric acid solution is then poured into water and the precipitate separated; it consists of a mixture of the sulphonic acids of dehydrothio-*p*-toluidine and Primuline. For some preparations this mixture may be used direct, but for others the products must be separated. For this purpose the sulphonic acids are treated with concentrated ammonia solution, when the ammonium salt of the sulphonic acid of Primuline, being very soluble, dissolves, whilst that of dehydrothiotoluidine sulphonic acid is only slightly soluble and is precipitated in the form of a paste of fine yellow needles which is separated from the liquid. The solution obtained is then treated with caustic soda, which replaces the ammonia on heating, and by addition of salt there is obtained the sodium salt of Primuline sulphonic acid, which constitutes the Primuline of commerce.

Dehydrothio-*p*-toluidine is insoluble in water, and crystallises from alcohol in yellow needles of M.P. 191°, B.P. 434°. Its sulphonic acid crystallises in small yellow needles which are insoluble in water but soluble in alkalies ; in dilute alkaline solutions it has a violet fluorescence. The alkali salts have a very slight affinity for cotton.

Primuline base is insoluble in water, and in alcohol. Its sulphonic acid is an amorphous yellow powder which is insoluble in water but soluble in alkalies, forming a light yellow solution which has a violet fluorescence when dilute.

Application of Primuline.

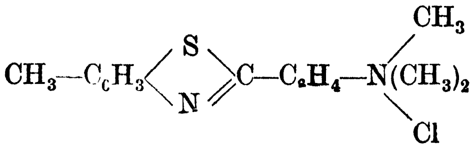
Primuline of commerce is the sodium salt of Primuline sulphonic acid, and has the property of dyeing cotton direct a greenish yellow shade, which of itself is not of much interest. Primuline, however, contains a free NH_2 group, which can be diazotised on the fibre and then combined with amines or phenols to give various shades. A. G. Green, who discovered this property, gave the names " Ingrain " dyestuffs to those which are obtained directly on the fibre, thus indicating that these dyestuffs are produced inside the cells of the fibres. The production of Ingrain dyestuffs includes three operations : dyeing, diazotising, and coupling or developing.

The dyeing of cotton with Primuline is carried out under the same conditions as with the direct cotton colours, that is, from a warm bath containing common salt. The diazotisation is effected by immersing the dyed fibre in a dilute solution of sodium nitrite acidified with hydrochloric acid, and is complete in a few minutes. After washing thoroughly, the dyestuff is developed by immersing the fibre in an alkaline solution of a phenol, a naphthol, or their derivatives, or in an acid solution of an amine. The development is almost instantaneous. The shades obtained are as follows : yellow with phenol, orange with resorcinol, red with β-naphthol, bordeaux with ethyl-β-naphthylamine, garnet with N.W. acid, brown with *m*-phenylenediamine.

The Ingrain dyestuffs are very fast to washing, but not to light. Green, Cross and Bevan (*E.P.* 7453 (1890)) have applied the instability of the diazo-compound of Primuline to light, in photography. The dyed material is diazotised, washed and dried ; on placing under a negative and exposing to the sun, the diazo-compound is destroyed in the exposed places, and on developing these portions remain yellow, whereas the remainder is altered. This process, though interesting, has not met with any commercial success.

Dyestuffs derived from Dehydrothiotoluidine.

Dehydrothiotoluidine has no affinity for cotton. On methylating the free base by heating to 170° with methyl alcohol and a mineral acid, a methyl chloride compound of dimethyldehydrothiotoluidine is obtained, which is soluble in water to a yellow solution :



This is a basic dyestuff, *Thioflavine T* (Green and Lawson, *J.C.S.*, 1889, **55**, 230), which dyes wool and tanned cotton greenish yellow shades.

When dehydrothiotoluidine sulphonic acid is oxidised with an alkali hypochlorite, a yellow dyestuff is obtained, which is known as *Chlorophenine* (Clayton Aniline Co.) or *Chloramine yellow*, and which gives yellow shades on cotton which are very fast to light. Oxidation of the mixture of the sulphonic acids of dehydrothiotoluidine and Primuline gives a product, *Oxyphenine*, the shade of which is not so pure.

Clayton yellow or *Thiazol yellow S.* (*D.R.P.* 53,935) is a direct yellow dyestuff, which is prepared by diazotising dehydrothiotoluidine sulphonic acid and combining the diazo-compound obtained with a further molecule of that substance. It is not a true azo-dyestuff, as it no longer contains the NH_2 group, but is very probably a diazoamido-compound.

The higher homologues of *p*-toluidine, such as *m*-xylidine and *pseudo*-cumidine, give similar compounds.

The Thiazol dyestuffs are not destroyed by reducing agents, and this property is used in printing for obtaining coloured discharges.

CHAPTER XXIII.

SULPHUR DYESTUFFS.

THE Sulphur or Sulphide colours are prepared by heating various organic substances with sulphur, alone or mixed with alkali sulphides. They are direct dyestuffs for vegetable fibres.

The first definite product was obtained by treating crude dinitronaphthalene with alkali sulphides, but the first commercial dyestuff of this class was discovered by Croissant and Bretonnière in 1873 by heating sawdust, bran, and similar substances with sulphur and alkali sulphides. This dyestuff was known as *Cachou de Laval*, and dyed cotton directly a greyish brown. Its preparation from almost any organic debris, coupled with its very weak tinctorial properties, did not encourage further research. The discovery remained at this stage until 1893, when R. Vidal extended this reaction in an unexpected manner. He found that on heating a mixture of quinone and phenols with sulphur and alkali sulphides in presence of ammonia, intensely coloured dyestuffs were produced. On replacing this mixture by *p*-phenylenediamine, *p*-amidophenol, etc., he found that the latter substance, for example, gave under these conditions a product which was soluble in alkali sulphides, forming a green solution which dyed cotton black; this was called *Vidal black*, and was manufactured by the firm of Poirrier at Saint-Denis.

The appearance of Vidal black was followed by that of an enormous number of dyestuffs, obtained by applying the above reaction to other organic substances. The various colour firms have given the Sulphur dyestuffs which they manufacture different names, as follows:

Sulphur colours	(Berlin Aktiengesellschaft).
Kryogen colours	(B.A.S.F.).
Katigen colours	(Bayer Co.).
Immedial colours	(Cassella).
Thioxin colours	(Griesheim Elektron).
Clayton colours	(Clayton Aniline Co.).
Pyrogen colours	(Basle Société).
Rexoll colours	(Claus & Co.).
Eclipse colours	(Geigy & Co., Basle).
Amidazol or *Sulpho* colours *Cross dyes*	(Read Holliday).
Thiophor colours	(Jäger).
Thion colours	(Kalle Co.).
Pyrol colours	(Leonhardt).
Thionol colours	(Levinstein).
Thiogen *Melanogen* colours	(Höchst Farbwerke).
Thional colours	(Sandoz).
Auronal colours	(Weiler-Ter Meer).

The Sulphur dyestuffs have a certain number of properties in common; they are almost all coloured, amorphous powders, insoluble in water, acids, and the usual solvents. They dissolve in cold alkalies in the presence of reducing agents, such as sodium sulphide or glucose, and the solutions so obtained are decolorised by stronger reducing agents such as hydrosulphites. On immersion in these coloured solutions, vegetable fibres absorb the dyestuff, which is partly fixed, and the fixation is completed by passing through a warm, dilute dichromate or copper sulphate bath, or in many cases by mere exposure to air.

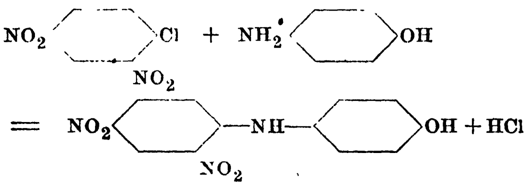
The Sulphur colours may also be precipitated from solutions and fixed on the fibre by means of animal colloids, such as glue, albumen, casein, etc. (Cassella, *D.R.P.* 225, 314).

By evaporating a solution of a Sulphur dyestuff to dryness with a caustic alkali and a reducing agent other than sodium sulphide, such as glucose, a solid, stable leuco-preparation of the dyestuff is obtained as an alkali salt (Meister, Lucius and Brüning, *E.P.* 4510 (1912)). These products are useful on account of their solubility, and can be used in the so-called lime-fermentation vat, or the lime-glucose vat.

Manufacture of Sulphur Dyestuffs.

The methods used for manufacture have been further improved since the discovery of Vidal black. These improvements are to a large extent due to better knowledge, even yet incomplete however, of the chemical reaction which gives these dyestuffs. Vidal was the first to attempt an explanation; he supposed that on heating *p*-diamines and *p*-amidophenols with sulphur and alkali sulphides, there is first produced a derivative of diphenylamine, which seems very probable, as ammonia is liberated. The dyestuff is then formed by the action of sulphur and alkali sulphides on the substituted derivative of diphenylamine so produced. Vidal's view was subsequently confirmed, as a short time afterwards the firm of Cassella obtained *Immedial black* by fusing hydroxydinitrodiphenylamine with sulphur and alkali sulphides. This discovery gave a new impetus to the manufacture of Sulphur colours by a different method to that previously employed. Various derivatives of diphenylamine, such as the hydroxy-, amido-, alkylamido-, and chloro-compounds, and sulphonic and carboxylic acid derivatives, were fused with sulphur and alkali sulphides. Hence, methods for preparing these substances had to be found, as most of them were then unknown, and they became raw materials of very great importance.

Two methods are available by which these substances can readily be prepared. The first is to treat substituted aromatic amines with chlordinitrobenzene. Whereas the chlorine atom of monochlorbenzene is only eliminated with very great difficulty, the presence of the nitro-groups in chlordinitrobenzene makes the chlorine easy to remove. Thus, on heating in dilute alcoholic solution with *p*-amidophenol in presence of an alkali salt, chlordinitrobenzene yields hydroxydinitrodiphenylamine, the raw material used in the manufacture of Immedial black, thus:

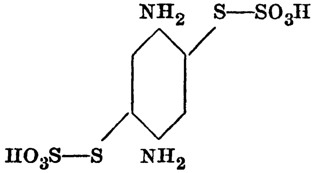


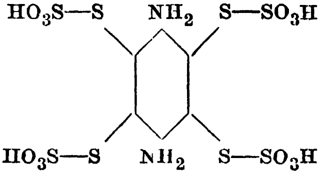
The second method is to reduce Indophenols or Indamines; but this reduction need not actually be carried out, as the sodium sulphide reduces the Indophenol or Indamine, and the sulphur then converts the derivative of diphenylamine so obtained into a dyestuff. An attempt has also been made to replace the fusion method, which is a rather destructive process, by the use of alkali sulphides in the presence of a solvent such as alcohol, glycerine, or even water. Finally, it has been found that the presence of copper, manganese, zinc, etc., salts considerably modifies the shade of the dyestuff formed in these reactions.

Constitution of Sulphur Dyestuffs.

The constitution of most of the Sulphur dyestuffs has not been definitely established; indeed, the study of these products is met with several difficulties. First of all, they are generally amorphous substances which are insoluble in the usual solvents, and are hence very difficult to isolate in the state of purity essential for examination. Moreover, in these reactions there are often formed mixtures of several dyestuffs, which it is difficult, if not impossible, to separate. Vidal supposed that the sulphur contained in the products was combined to form a certain number of thiazine rings. This view has recently been confirmed by the discovery of a new process for manufacturing Sulphur dyestuffs (A. G. Green, Meyenberg, and the Clayton Aniline Co., *D.R.P.*

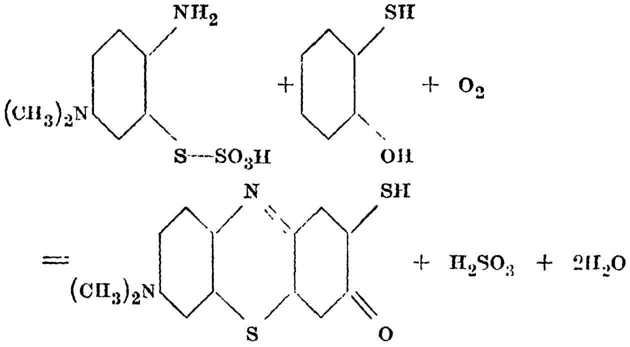
120,560, 127,856, 128,916, 130,440), which is in some respects similar to that used for Methylene blue. On oxidising with cold potassium dichromate in presence of a large excess of sodium thiosulphate, a *p*-diamine or a *p*-amidophenol does not give Bernthsen's monothiosulphonic acid, but yields di- or tetra-thiosulphonic acids, according to the experimental conditions. Thus, *p*-phenylenediamine yields the two acids :



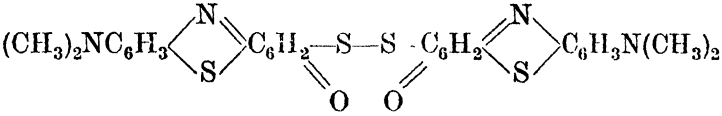


On oxidising with dichromate in presence of amines, amidophenols, etc., these two acids yield, as intermediate products, Indamine thiosulphonic acids, which lose sulphur dioxide on boiling with dilute mineral acids, giving insoluble dyestuffs which have all the properties of the Sulphur colours. This process makes it very probable that thiazine rings are present in dyestuffs of this group. All the sulphur is not, however, present in this form. It is known that on heating with sulphur a large number of organic substances yield organic disulphides, which are generally only slightly soluble. These disulphides are converted by reducing agents into mercaptans, which are soluble in alkalies, and are easily oxidised, regenerating the original insoluble sulphur compounds.

The Clayton Aniline Co. (*D.R.P.* 140,964) have obtained a process for preparing a blue dyestuff which has made this view extremely probable. When a mixture of dimethyl-*p*-phenylenediamine thiosulphonic acid and *o*-hydroxythiophenol is oxidised in alkaline solution, an insoluble dyestuff very similar to, or identical with, the *Immedial Pure blue* of Cassella is obtained. The reaction should therefore be represented by the following equation :



the mercaptan so formed then oxidising to give a disulphide, which is the dyestuff :

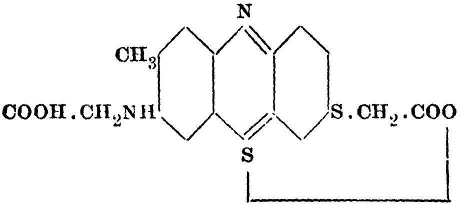


$$(CH_3)_2NC_6H_3\left\langle{}^{N}_{S}\right\rangle C_6H_2(=O)—S—S—C_6H_2(=O)\left\langle{}^{N}_{S}\right\rangle C_6H_3N(CH_3)_2$$

That such a compound is soluble in alkaline reducing agents (sulphides, or glucose and caustic soda) is explained by the disulphide being converted on reduction into two molecules of the mercaptan.

The thiazine constitution of *Immedial Pure blue* has also been confirmed by its conversion into tetrabrom-Methylene violet (Gnehm and Kaufler, *Ber.*, 1904, **37**, 2617, 3032).

Immedial Indone has been found by Frank (*J.C.S.*, 1910, 97, 218) to give a dicarboxylic derivative $C_{17}H_{14}O_4N_2S_2$, which requires two atoms of hydrogen for its reduction to the leuco-compound. The constitution suggested for this derivative is :



There is another class of Sulphur dyestuffs known which are obtained by fusing methyl ring-substituted derivatives of *m*-diamines with sulphur and alkali sulphides. They are yellow, orange, or brown dyestuffs, which appear to be somewhat similar to the Thiazol derivatives, dehydrothiotoluidine and Primuline.

According to Nietzki (*Chemie der organischen Farbstoffe*), the Sulphur dyestuffs may be divided provisionally into the following six clasess :

(1) *Immedial Yellow* class. This includes dyestuffs similar to those from thiazol, obtained from *m*-diamines, particularly from *m*-toluylenediamine and its formyl, acetyl, etc., derivatives. These compounds are fused with sulphur, and the products so obtained are heated with a concentrated solution of sodium sulphide, in which they dissolve; the dyestuff is then precipitated by addition of an acid.

(2) *Vidal Black* class. Of the substances stated by R. Vidal to give Sulphur colours on fusing with alkali polysulphides, only *p*-amidophenol and dinitrophenol give products of practical importance.

(3) *Immedial Black* class. These dyestuffs are obtained by treating the derivatives of diphenylamine with alkali polysulphides. The first of these products was *Immedial black*, which rapidly replaced *Vidal black*.

(4) *Immedial Pure Blue* class. The Basle Société pour l'industrie chimique has prepared blue dyestuffs by treating Indophenols, for example the one formed by the oxidation of a mixture of dimethyl-*p*-phenylenediamine and *p*-amidophenol, with alkali polysulphides. In the same way, the firm of Cassella have obtained *Immedial pure blue* dyestuffs by the action of polysulphides on derivatives of diphenylamine at a low temperature.

(5) This class includes the violet and red dyestuffs obtained by treating with sulphur the dyestuffs derived from phenazine, such as amidooxyphenazine, Safranoles, Rosindones, etc.

(6) This group contains the products obtained by

treating 1 : 5- and 1 : 8-dinitronaphthalene, and the intermediate products obtained in the manufacture of naphthazarin, with alkali sulphides. The most important dyestuff of this group is *Fast black* (B.A.S.F.), obtained by heating dinitronaphthalene with an aqueous solution of sodium sulphide.

The following table gives the principal Sulphur dyestuffs (Nietzki, *Chemie der organischen Farbstoffe*, 5th edition) :

DYESTUFF.	PATENT NO.	PREPARATION.
Vidal black [P.]	*D.R.P.* 82,748 84,632, 85,330, 88,392, 91,719, 94,501	Fusion of *p*-amidophenol and *p*-diamines with alkali polysulphides.
Fast black [B.A.S.F.]	*D.R.P.* 139,099	Dinitronaphthalene is treated with alkali sulphides in aqueous solution.
Immedial black V. [C.]	*D.R.P.* 103,861	Fusion of hydroxydinitrodiphenylamine with alkali polysulphides.
Sulphur black T. [A.]	*D.R.P.* 127,835	Dinitrophenol is treated with an aqueous solution of polysulphides.
Auronal black [W.]	*D.R.P.* 144,119	*p*-Amidodinitrodiphenylamine is treated with sulphides in presence of glycerol.
Katigen black 2B. [By.]	*E.P.* 15,625.	From chlordinitrophenol.
Immedial blue [C.]	*D.R.P.* 103,861, 104,283	Hydroxydinitrodiphenylamine is treated with polysulphides at a low temperature.
Pyrogen direct blue, *Pyrogen blue R.* [C.I.B.]	*D.R.P.* 132,424	Hydroxydinitrodiphenylamine is treated with polysulphides in alcoholic solution.
Immedial Pure blue [C.]	*D.R.P.* 134,947	*p*-Dimethylamidohydroxydiphenylamine is treated with sulphur.
Pyrogen yellow M. *Pyrogen olive* [C.I.B.]	*D.R.P.* 135,335	Fusion of oxybenzylidene compounds with polysulphides.

DYESTUFF.	PATENT NO.	PREPARATION.
Eclipse yellow G and *3G* [G.].	*D.R.P.* 138,839	Fusion of mono- or diformyl-*m*-toluylene diamine, alone or mixed with benzidine, with sulphur at 240° C.
Immedial yellow D [C.]	*D.R.P.* 139,430	Fusion of *m*-toluylene diamine with sulphur at 190° C.
Immedial orange C [C.]	*D.R.P.* 152,595	Fusion of *m*-toluylene diamine with sulphur at 250° C.
Verde Italiano.	Lepetit, Dollfuss & Co. (1896).	Fusion of *p*-amidophenol or its substituted derivatives with polysulphides in presence of copper salts at 180° C.
Pyrogen green	*D.R.P.* 148,024	
Immedial bordeaux [C.] *Immedial maroon* [C.]	*D.R.P.* 126,175	Fusion of azines with sulphur and alkali sulphides.

The proportions of sulphur and sodium sulphide, and of the polysulphide to the raw material used, the temperature at which the reaction is carried out, and the methods used for the separation of the dyestuffs, all play an important part in determining the product which will be obtained. In many cases the best conditions lie between very small limits. The field being so extensive, in fact almost every class of organic compound appears to have been submitted to the action of sodium polysulphide, it is not surprising to find that products have been obtained which have subsequently been found to be mixtures of dyestuffs and their intermediate products. Taking into account the complexity of these dyestuffs, the chemical constitution of which is generally unknown, it is remarkable that there should not have been more cases of the patents of different firms clashing. Many of Vidal's patents were incomplete; thus *E.P.* 16,449 (1896) is an example of how to produce a Sulphur black from dinitrophenol under the worst possible conditions.

The compounds, and in some cases the methods, used for obtaining some of the recent yellow and brown dyestuffs are given in the following table. (See Vlies, *J. Soc. Dyers and Col.*, 1913, 316.)

Kryogen yellow R.	*m*-Toluylenediamine thiourea.
Thion yellow G.	*m*-Toluylenediamine.
Immedial yellow GG.	Dehydrothiotoluidine mixed with benzidine.
Kryogen yellow G.	Thiourea derivatives of *m*-toluylenediamine mixed with benzidine.
Thion brown.	Aniline-azo-*m*-toluylenediamine.
Eclipse brown colours.	Mixtures of *m*-toluylenediamine with several bases and acids, such as oxal-*m*-toluylenediamine, nitrotoluidines, phthalic acid, thio-diglycollic acid, etc.
Thio Katigen colours.	Fusion of acetyl-*p*-phenylenediamine with sulphur and solution in sodium sulphide ; *or* Action of sodium polysulphide on nitro-acetanilide, etc.
Immedial brown.	Action of caustic soda on hydroxydinitrodiphenylamine, which may be followed by fusion of the product with sodium polysulphide.
Immedial bronze.	Fusion of dinitrocresol with polysulphide.
Thiophor bronze 5G.	Fusion of a mixture of *p*-phenylenediamine and *p*-amidoacetanilide with sulphur.
„ „ *G.*	As above, but with addition of benzidine.
Kryogen brown.	Reduction of 1 : 8-dinitronaphthalene with sulphide or sulphite and subsequent treatment with polysulphide.
Thional brown G, etc. *Thional bronze.*	Fusion of β-oxynaphthaquinone anilides with sodium polysulphide.

The enormous number of Sulphur dyestuffs produced during the ten years which followed Vidal's discovery has left behind a host of prematurely extinct patents, and has been followed by a period of inactivity which is remarkable. During the last two years the production of new Sulphur dyestuffs has been so small that one might reasonably conclude that this group of colouring matters is not capable of any great extension. The original Vidal black from *p*-amidophenol appears to be no longer manufactured. Cheaper colours of higher tinctorial powers, such as the *Rexoll blacks* (Claus and Co.), have taken its place.

The Sulphurised Vat Dyestuffs.

The new " Hydron " dyestuffs of Cassella and similar products must not be confused with the Sulphur colours. Although produced by the action of polysulphides on certain organic compounds, they are vat dyestuffs, and are insoluble in sodium sulphide. The chemical constitution of these dyestuffs is quite unknown ; they may be divided into :

(1) Sulphurised anthracene derivatives.
(2) Sulphurised vat dyestuffs of Indophenols and allied compounds.

Sulphurised anthracene derivatives.

These compounds are prepared by melting anthracene and several of its more or less complicated derivatives with sulphur at high temperatures. The simplest representative is *Indanthrene olive G* (*D.R.P.* 186,990), which is obtained by melting anthracene with sulphur at 250° C., and gives olive shades fast to light and washing from a dark violet coloured vat. *Hydron olive G* [C.] is probably a similar dyestuff prepared by the action of sulphur chloride on anthracene (*D.R.P.* 247,416) at a high temperature.

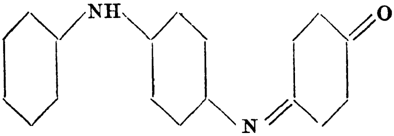
Cibanone blue 3*G* and *black B* (*E.P.* 20,094 (1908)), and probably the later brands, *Cibanone green B* and *black* 2*B*, are produced by treatment of 2-methylbenzanthrone with sulphur. 2-Methylanthraquinone, and also this compound halogenated in the methyl group, on fusion with sulphur, gives rise to compounds which possess dull and worthless shades, but on oxidising with hypochlorites are transformed into bright orange dyestuffs. *Cibanone yellow R* (*E.P.* 7583 (1908)) from ω-monochlor-methyl-anthraquinone, and *Cibanone orange R*, from the dichloro-derivatives, are so obtained.

Amido- and diamido-2-methylanthraquinone melted with sulphur give yellow to violet brown dyes. *Cibanone brown* (*E.P.* 13,057 (1908)) is probably prepared from the mono-amido compound.

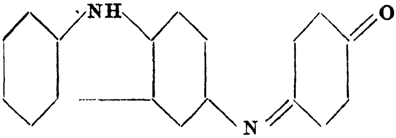
Sulphurised Vat Dyestuffs from Indophenol.

The colouring matters obtained by heating many organic compounds with sodium polysulphide, chiefly the tetrasulphide, are known as Sulphur dyestuffs. If, however, a poly-sulphide approaching the hypothetical Na_2S_7 and Na_2S_8 acts upon certain Indophenols, new dyestuffs are obtained which no longer dissolve in sodium sulphide, but form soluble leuco-compounds with hydrosulphite, and behave like true vat dyes.

L. Haas (*E.P.* 2918 (1909)) found that carbazol condenses with nitrosophenol in sulphuric acid solution, producing an Indophenol, analogous to the Indophenol of diphenylamine prepared in the same way, thus :



Indophenol of diphenylamine.



Indophenol of carbazol.

On heating with the usual proportion of sodium sulphide and sulphur, Indophenol-carbazol gives a blue Sulphur colour. The addition of copper sulphate to the mixture gives a product which dyes black shades, and is commercial as *Indocarbon S* [C.].

More intensive sulphurisation of Indophenol-carbazol or of its substitution products, alkyl or acyl derivatives, or of the condensation product of dinitrochlorbenzene with leuco-Indophenol-carbazol leads to the production of entirely different dyestuffs, which appear in commerce as *Hydron blue R, G, B* (*D.R.P.* 224,590-1 ; *E.P.* 956,348, Hertz and Cassella) and *Hydron blue-black.*

The trade name " Hydron " of Cassella does not only include carbazol dyestuffs, but also embraces vat dyestuffs belonging to other groups ; for example, *Hydron yellow G* is not a Sulphur vat dyestuff, and may be one of the colours obtained by condensing a diphthaloyl carbazol by means of sulphuric acid or other dehydrating agent (*E.P.* 28,874 (1911)). Grandmougin states that *Hydron violet B* resembles the Indigoid dyestuffs. All Hydron colours can be dyed in combination with one another. *Hydron blue G* and *R* approach Indigo in shade, being somewhat greener and redder respectively : Erban (*Färb.-Ztg.*, 1911) states that they are faster to washing, boiling, and bleaching than Indigo.

CHAPTER XXIV.

ANILINE BLACK.

Aniline black is an insoluble dyestuff which is produced on treating aniline with acid oxidising agents. Its formation was noticed by Runge as early as 1834. Aniline black is not used in the solid form for printing cotton, but is always prepared directly on the fibre by special dyeing or printing processes.

The first application of Aniline black in dyeing was made in England by Calvert, Clift and Lowe in 1862. The fibre was immersed in a solution containing aniline hydrochloride, potassium chlorate and an iron salt; it acquired a green shade, which was converted into black by subsequent passing through warm dilute bichromate ("chroming"). In the following year, Lightfoot improved the method, having observed that the presence of traces of a copper salt accelerated the formation of the black, the copper salt acting as an oxygen carrier. The black so obtained developed at a relatively low temperature (40-50°) in moist air. Lightfoot's method is still used at the present time, but has undergone certain modifications. Thus the presence of soluble copper salts has the disadvantage that they attack the steel doctors of the machines used in calico printing. In 1864 this difficulty was overcome by Lauth (*Mon. sci.*, 1865, 58) by adding to the mixture an insoluble copper salt, such as the sulphide, which is, however, oxidised on exposure to moist air and then becomes soluble. In 1876, Guyard and Witz discovered that vanadium salts exert a much more energetic catalytic action than copper salts; thus one part of vanadium is sufficient to promote the oxidation of 270,000 parts of aniline salt mixed with potassium chlorate. In order to prevent the tendering of the cotton fibre, which always takes place on dyeing with Aniline black, the copper or vanadium salts are replaced by ferrocyanides, which also neutralise the acidity due to the hydrochloric acid liberated from the aniline hydrochloride.

Ferrocyanide blacks are often called Steam blacks.

The three methods available for the production of Aniline black may be summarised as follows:

1. *Single Bath black.* This method is used chiefly for yarn dyeing. The fibre is sometimes bottomed with a Sulphur black, on which the Aniline black is then produced by immersing the cotton in a solution containing aniline salt, potassium dichromate and hydrochloric acid, in which it is worked in the cold, or better, slowly brought to the boil. The dyestuff is produced in the bath, a portion remaining on the fibre. If the black has been obtained in the cold the process must be finished by steaming.

2. *Aged black.* This is very much used for dyeing of pieces, but may also be used with certain precautions for hank dyeing. The method consists in padding the fibre with a solution containing aniline salt (which has been made basic by the addition of a small quantity of aniline), sodium chlorate, and copper sulphate. After the fibre has been wrung out, it is passed into an oxidation chamber in which the air is heated to 40-50° C., and kept sufficiently moist by means of steam. After leaving this chamber the fibre has a dark green colour due to the presence of emeraldine; the oxidation is finished by passing through warm dichromate solution, which converts the emeraldine into Aniline black. (See also N. Evans, *J. Soc. Dyers and Col.*, 1910, **26**, 117.)

A. G. Green has found that oxidation with chlorate may be replaced by oxidation with air alone, by adding to the mixture of aniline salt and the copper salt a trace of *p*-phenylenediamine or *p*-amidophenol (*E.P.* 16,189 (1907)), these substances acting as catalysts. Derivatives of *p*-phenylenediamine, and certain nitroso-compounds may also be used (Zeidler and Wengraf, *D.R.P.* 223,404, 224,384). This process has a great future, as it does not damage the fibre.

3. *Steam blacks.* These are used for dyeing pieces, and mainly for producing resists in printing. After padding in a bath containing aniline salt, sodium chlorate, and potassium ferrocyanide, the material is wrung out and steamed for two or three minutes in a rapid ager. The formation of the black is almost complete, the oxidation being finished by passing through bichromate. If the material has been printed with an alkaline substance before steaming, the black does not develop in the printed parts, and white resists are obtained (Prudhomme).

At the present time, Aniline black is one of the most important of all colouring matters in cotton dyeing and calico printing.

Constitution of Aniline Black.

Three stages may be distinguished in the oxidation of aniline: a green substance (emeraldine) is first produced, which is converted into a black, and this eventually becomes green (nigraniline), and by more complete oxidation becomes an ungreenable black. In spite of a considerable number of researches, the constitution and even the composition of the black remained undetermined for a considerable period, although some light was thrown on the subject by the researches of Caro, and more recently by those of Willstätter (Willstätter and Moore, *Ber.*, 1907, **40**, 2665; Willstätter and Dorogi, *ibid.*, 1909, **42**, 2148, 4118; Willstätter and Cramer, *ibid.*, 1910, **43**, 2976; 1911, **44**, 2162. See also Nover, *Ber.*, 1907, **40**, 288, and A. G. Green, *J. Soc. Dyers and Col.*, 1909, 189). According to Kayser, the composition of the black corresponded to $C_{12}H_{10}N_2$; according to Nietzki it was $C_{18}H_{15}N_3$, according to Goppelsröder, $C_{24}H_{20}N_4$; later analyses of Nietzki lead to the formula $C_{30}H_{25}N_5$, and finally Willstätter and Moore gave the minimum formula as $C_{48}H_{36}N_8$.

Caro has shown that on oxidation of aniline by potassium permanganate in cold aqueous solution, a yellow solution is obtained, from which an amorphous yellow substance may be extracted with ether which gives emeraldine on treatment with acids. This yellow substance has been isolated in a crystalline state by Willstätter and Moore, who have established its constitution as that of phenylquinonediimide :

$$C_6H_5—N = C_6H_4 = NH.$$

In contact with acids it is converted entirely into emeraldine, the base of which has been obtained in a crystalline condition, its molecular weight corresponding to $C_{24}H_{20}N_4$. It is hence a polymer of the above yellow substance. Oxidation of this base in benzene solution yields a red compound, $C_{24}H_{18}N_4$, which on polymerisation finally gives ungreenable Aniline black.

As emeraldine was formed by the condensation of phenylquinonediimide, the following formula was incorrectly assigned to it by Willstätter and Moore, the bonds being in *para*-position :

$$C_6H_5—N = C_6H_4 = N—C_6H_4—NH—C_6H_4—NH_2$$

The red base obtained by oxidation contains two atoms less of hydrogen ; its constitution may be represented by :

$$C_6H_5—N = C_6H_4 = N—C_6H_4—N = C_6H_4 = NH$$

This base polymerises even on heating with water in a sealed tube, giving an amorphous powder which is the Aniline black called "polymerisation black." The formula should therefore be $(C_{24}H_{18}N_4)_x$, and for the minimum value $x = 2$, the formula becomes $C_{48}H_{36}N_8$, which is the simplest possible formula for Aniline black.

The constitution of Aniline black has now been elucidated by A. G. Green and S. Wolff (*Ber.*, 1913, **46**, 33; *J. Soc. Dyers and Col.*, 1913, 105). It has been shown that the products obtained by earlier investigators, including those of Willstätter, consist of impure emeraldine or nigraniline (Green and Woodhead, *J.C.S.*, 1910, **97**, 2388; and Green and Wolff, *Ber.*, 1911, **44**, 2570; *J.C.S.*, 1912, **101**, 1117). Green states that these products are merely mixtures of emeraldine and nigraniline with a variable amount of polymerisation—or decomposition—compounds, produced by the action of the mineral acid employed for "purification," as none of these substances exhibit the characteristic behaviour of an ungreenable Aniline black formed on the fibre, which alone can be regarded as a true Aniline black. The oxidation of aniline to Aniline black has been shown by Green and Wolff to proceed by a series of quinonoid additions according to the scheme shown on next page.

In a later paper, Green and Johnson (*J. Soc. Dyers and Col.*, 1913, 338) give the results of investigations which further confirm the above formula for the hydrochloride.

On oxidation with lead dioxide suspended in dilute sulphuric acid, and allowing 5 per cent. for loss by overoxidation, the yield of quinone obtained from the Aniline black of Green and Wolff was 52·5 per cent., corresponding very closely to that theoretically indicated by the phenylazonium formula.

The above authors have also investigated the variety of Aniline black known as "Single Bath black" or "Bichromate black." The samples obtained by various practical methods had in general the same properties, differing only in the amount of impurities present. It is to be noted that the name "Aniline black" cannot properly be applied to any of the products prepared by Willstätter and his pupils, as Green and Wolff have shown them to be mixtures of emeraldine and nigrani-

$C_6H_5 . N : C_6H_4 : NH$ (Caro's Yellow Imide).

$$\downarrow$$

$C_6H_5 . N : C_6H_4 : N . C_6H_4 . NH . C_6H_4 . NH_2$ (Willstätter's Blue Imide) $\xrightarrow{+O}$ $C_6H_5 . N : C_6H_4 : N . C_6H_4 . N : C_6H_4 : NH.$ (Willstätter's Red Imide).

$$\underbrace{\qquad\qquad\qquad\qquad}\downarrow$$

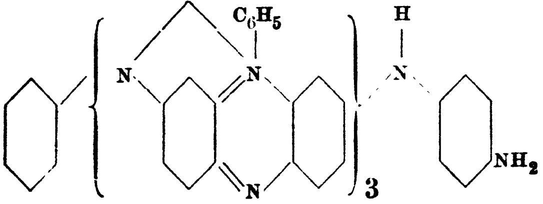
$C_6H_5 . N : C_6H_4 : N . C_6H_4N : C_6H_4 : N . C_6H_4 . NH . C_6H_4 . NH . C_6H_4 . NH . C_6H_4NH_2$ (Emeraldine).

$$\Big\downarrow{+O}$$

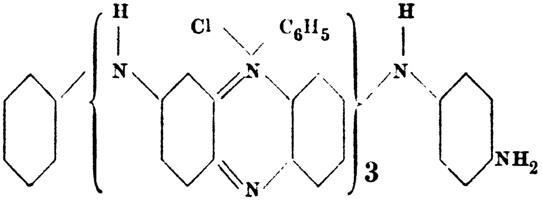
$C_6H_5 . N : C_6H_4 : N . C_6H_4 . N : C_6H_4 . N . C_6H_4 . N : C_6H_4 : N . C_6H_4 . NH . C_6H_4 . NH_2.$ (Nigraniline).

$$\Big\downarrow{+C_6H_5NH_2}$$

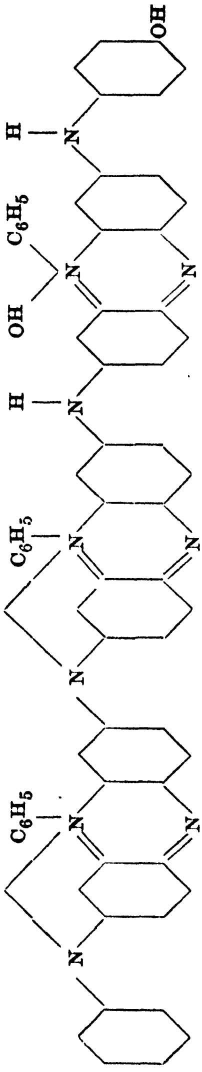
Aniline Black base.
(" Aged " or Chlorate black.)



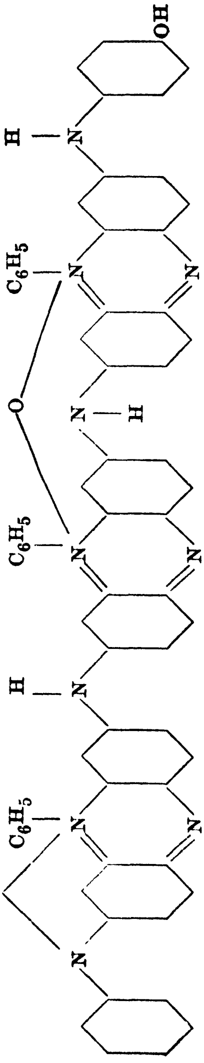
and the
hydrochloride



line. The results show that Bichromate black is an analogue of the Chlorate black, being a phenylazonium hydroxide :



or more probably a phenylazonium oxide :



as the presence of an OH group explains the difficulty experienced in removing the chromium, and the smaller solubility of the base in acetic acid. Further Bichromate black differs from the other quinonoid bases of the series in having a maximum combining capacity of two molecules of hydrochloric acid in place of three; as usual in this series, the dihydrochloride is not hydrolysed by water.

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Note.—For details of the character and contents of recently published books, readers should refer to the reviews in the *Journal of the Society of Dyers and Colourists*, which also contains abstracts of many of the important papers to which reference has been made.

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