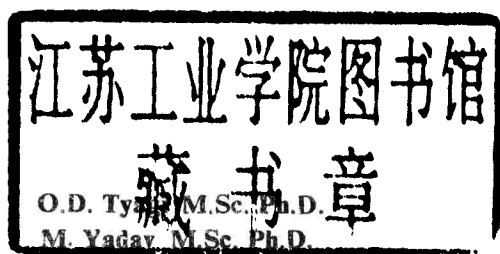


A
Text Book of
SYNTHETIC DYES

(For B.Sc. (Hons.) and M.Sc. students)



ANMOL PUBLICATIONS

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A Text Book of SYNTHETIC DYES

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Introduction and Development of Dyes

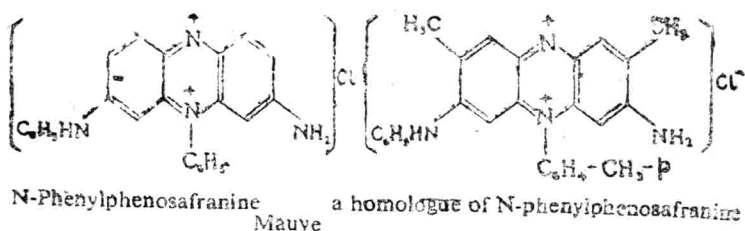
Dyes or dyestuffs are essentially coloured substances capable of imparting their characteristic colours, fast to light, water, soap etc to the fibres. *A dye may be defined as a coloured substance which when applied to the fabrics imparts a permanent colour and the colour is not removed by washing with water, soap or an exposure to sunlight.* All coloured substances are not necessarily dyes. For example though both picric acid and trinitrotoluene have yellow colour but only picric acid can fix to a cloth and in a dye where as trinitro toluene does not fix to a cloth and so is not a dye.

In old days when there was no industry on synthetic dyes the fibres were generally dyed by colouring matters obtained from plants and animals, until the middle of nineteenth century dyes were obtained from vegetables or in case of cochineal from insects. The following table lists some such sources.

(Colour) dyestuff	Source
(yellow) Saffron	dried flowers of colour thistle
(blue) Indigo	Indigo leaves
Madder or Turkey red or alizarin	Roots of madder plant
(red) cochineal	Female insect <i>Coccus cacti</i>
(red) Tyrian purple	Snail <i>Murex brandarín</i>

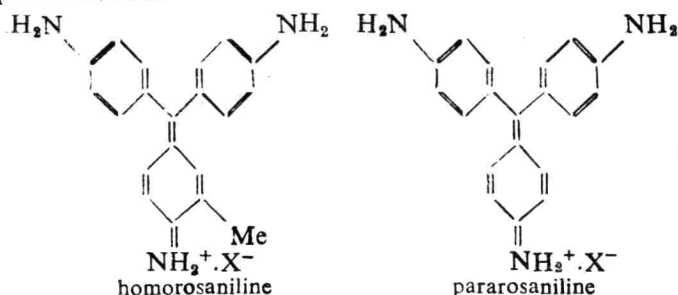
At present practically all dyes are synthetic products made by organic chemists. The revolution began in 1856 when W.H. Perkin, at the age of eighteen, discovered dye, aniline purple, in the

Mauveine was found to contain mainly N-phenyl phenosafranine and its homologue.



Perkin left the Royal College of Chemistry in London and founded a dye-works. At the age of thirty six he was able to retire from commercial life, a rich man, and retained active interest in organic chemistry for the rest of his life. He was a man who did not trouble about the distinction between pure chemistry and applied chemistry.

Verguin in 1859 discovered (*Magenta* or *Fuchsine*) while he was studying the reaction between crude aniline and Tin (iv) chloride (an oxidising agent), Magenta is a mixture of homorosaniline and pararosaniline.

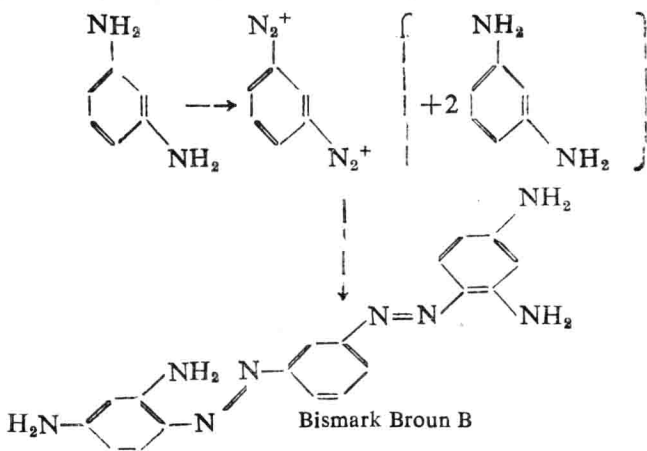


In this way Verguin discovered a new class of dyes, the *triphenylmethanes*

Another important class of dyestuffs, discovered in 1863, was the *aniline blacks*. These are large complex structures formed directly in the fibre by the oxidation of aniline. The aniline salt is impregnated into the fibre and then oxidised. The dyestuff formed precipitates within the fibre and is characterised by its high wet fastness. Aniline blacks are still widely used today as dyes for cotton.

The most important reaction carried out in synthetic dyestuff industry is the diazotisation reaction discovered by Peter Griess at Royal College, London. About half of the dyestuffs in use at present are obtained by diazotisation and are known as azo dyes. The first commercially successful azo dye, *Bismark Brown*, was discovered by

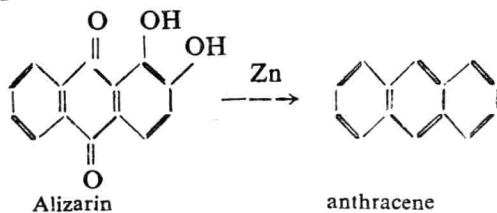
Martius in 1863. Bismark Broun is a mixture of dyestuffs produced from diazotisation of *m*-phenylenediamine. Bismark Broun B can be prepared by tetrazotisation of *m*-phenylenediamine to produce a bis diazonium salt which is then coupled with two moles of the parent diamine to give the disazo dyestuff.



The solution of structure of benzene by Kekule made an enormous impact on both organic chemistry and the dyestuff industry. This newly acquired information was put to use in synthesis of two natural dyestuff, Alizarin and Indigo. These two synthesis not only illustrate the ingenuity of the early organic chemists but also bear witness to the rapid advances in organic chemistry during the last century.

Alizarin

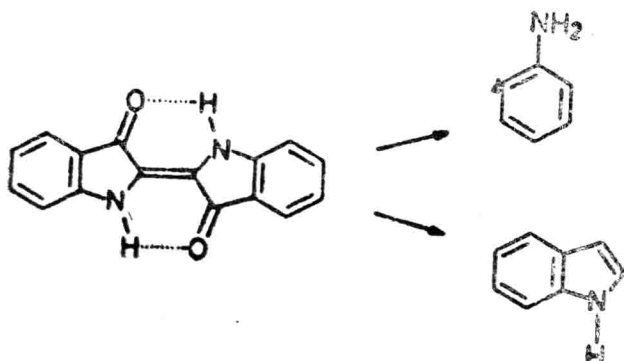
Alizarin obtained from Madder plant on distillation with zinc dust gave anthracene.



1, 2-dihydroxy-anthraquinone

This confirmed the presence of a tricyclic aromatic system in Alizarin Indigo.

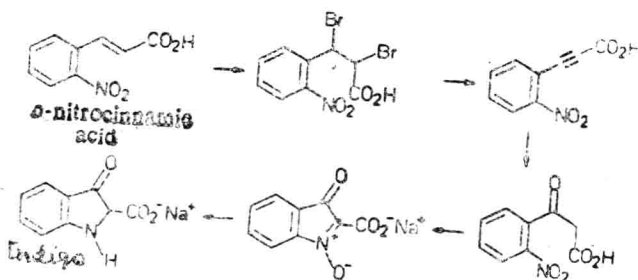
Von Baeyer was the principal figure in the researches on Indigo. In 1926 he obtained Indole from the reduction of Indigo.



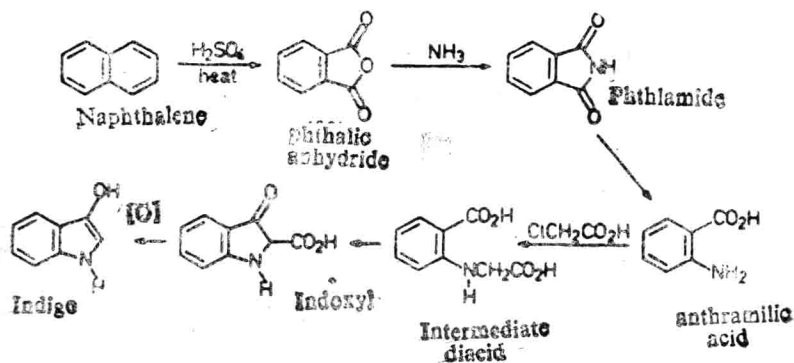
Indigo

Indole

Later on he gave a method of synthesis of Indigo from *o*-nitrocinnamic acid.



Commercially viable method for preparing Indigo was discovered by K. Heumann in 1897. It involves the conversion of naphthalene to phthalic anhydride, anthranilic acid, indoxyl and then Indigo.

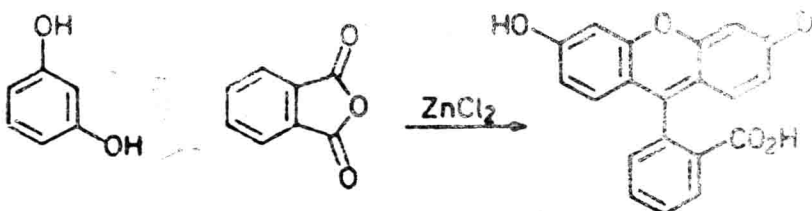


Despite its long reaction sequence, synthetic Indigo was cheaper and of superior quality to natural Indigo. The natural Indigo had impurities which resulted in its colour on fabric differing from that of the synthetic material but the advantages of using a relatively pure dye having predictable and reproducible shade made the use of synthetic Indigo very popular.

Some other Classes of Dyes

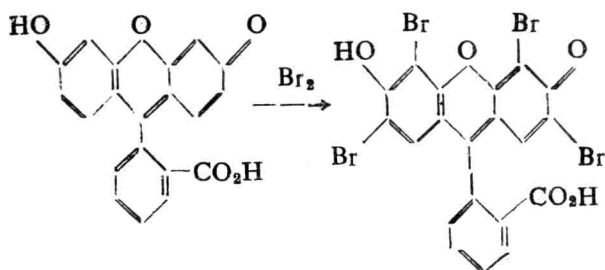
Some dyes having no natural counter parts were developed. New classes of dyes discovered included xanthenes, phenothiazines, sulphur dyes etc.

Von Baeyer discovered the first x-anthene dye. He obtained it when he condensed resorcinol and phthalic anhydride to give Fluorescein.



Resorcinol Fluorescein
Phthalic anhydride

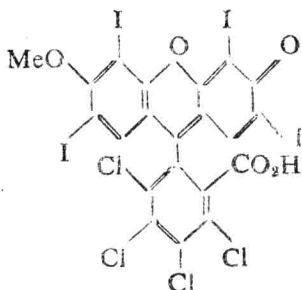
Caro brominated Fluorescein and obtained another useful dye Eosine.



Fluorescein

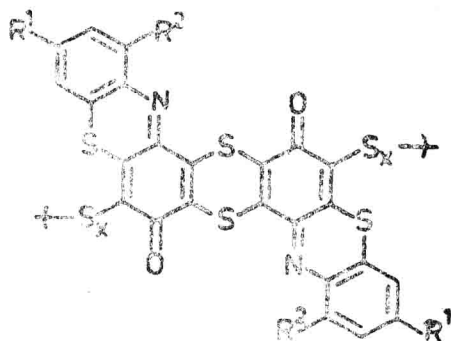
Eosine

Rose Bengal which is still used as a photosensitizer also belongs to this class.



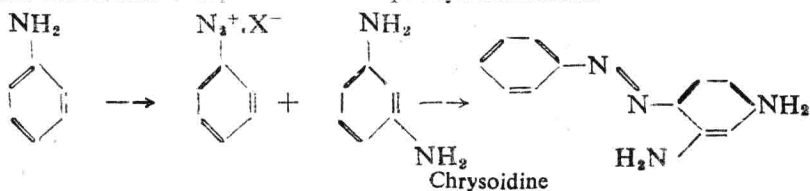
Rose Bengal

The first sulphur dye was discovered in 1873 by Croissant and Bretonniere. Sulphur dyes differ from other dyes in that they have complex macromolecular structures that are generated within the fibre. They are generally prepared by heating sulphur with aromatic amines, phenols or aminophenols. These dyes are water insoluble but get reduced in the dye-bath to give water soluble *leuco* derivatives which impregnate the fibre. Due to atmospheric oxidation the sulphur dye within the fibre gets oxidised to give dyeings fast to washing. The most important sulphur dye used today is *Sulphur Black*. It is prepared by boiling 2, 4-dinitrophenol with sodium poly sulphide. It is considered to be a phenothiazonethio anthrone type.



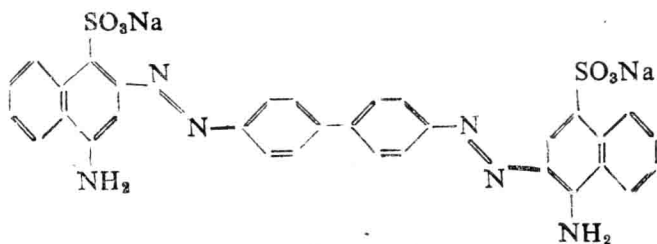
Sulphur Black

Chrysoidine, an azo dye, which is still used was discovered in 1875 by Caro. He obtained it by diazotising aniline and coupling the diazonium compound with *m*-phenylenediamine.



This was the first azo dye for wool.

Congo Red, which is now used as pH indicator was made in 1884 by tetrazotising benzidine and coupling the bis-diazonium salt with two molecules of 4-sulpho-1-naphthylamine. It was the first dye that could be directly dyed on cellulose.

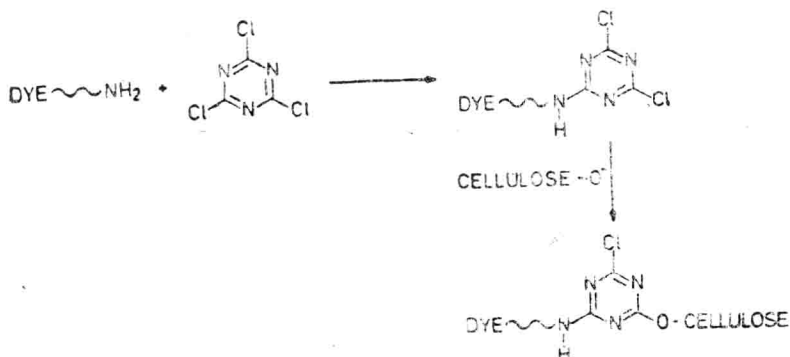


Congo Red

Many new classes of dyestuffs have been introduced in the second half of nineteenth century. Only a few new chromogens have been added to available dyestuffs since then. A high level of research has been maintained but the emphasis has been on optimisation and improvement of the available chromogens rather than the discovery of new types.

In 1954 Rattee and Stephen of ICI discovered a means by which dyes containing dichlorotriazinyl group could be made to react with cellulose under basic conditions.

The dye was bound to cellulose by a covalent bond and thus provided dye of high wet fastness for cotton.

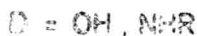
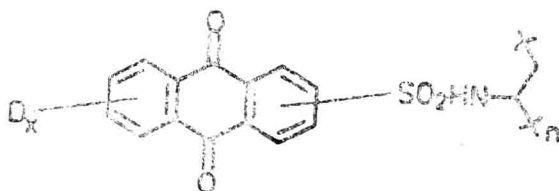


The major challenge to the dyestuffs manufacturers came with introduction of man-made fibres such as nylon, polyester and polyacrylonitrile. Soon the acid (anionic) dyes were discovered for nylon, Neutral, low molecular weight dyes (disperse dyes) were found suitable for polyester. Cationic or basic dyes were found suitable for polyacrylonitrile. All these were merely modifications of the dyes which were already available.

Future Trends

In the modern competitive world the dye manufacturers are devoting more effort into developing cheaper routes to existing dyes. Dyes are also finding new outlets. For example dyes are being evaluated in liquid crystal displays, lasers and solar cells.

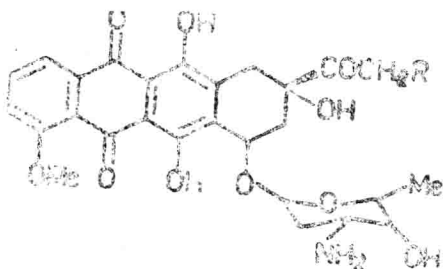
The polymeric dyes for food are polymeric anthraquinone dyes and have the general structure as shown below.



These dyes are completely harmless and also adhere to stringent health and safety laws. They have a bright future.

Some members of oldest class of dyes, the anthraquinone dyes, are found to possess properties to act as anti-cancer drugs. Examples of such drugs are Adriamycin and daunomycin. In this field also they have great potential to expand in future.

Adriamycin, $R=OH$
Daunomycin, $R=H$



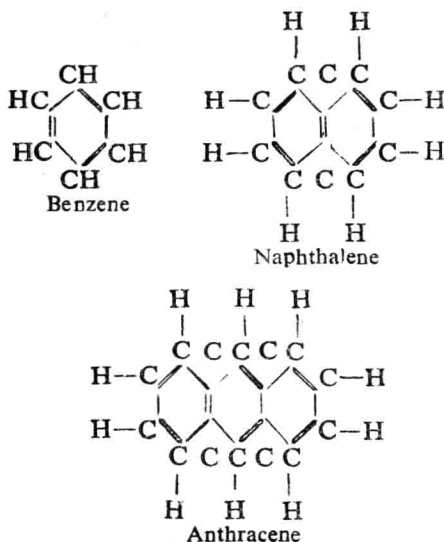
Because of close relationship between the advancement of organic chemistry and dyestuffs industry we find major dyestuff companies have successful pharmaceutical, agrochemical and other such organic chemistry intensive divisions.

Thus, just as Perkin is considered the Father of dyestuffs industry so the dyestuffs industry itself could be called the mother of the modern organic chemical industry.

Dye Intermediates and Their Synthesis

Introduction

The raw materials for the manufacture of dyes are mostly obtained from coal-tar. When coal is distilled it is separated into coal gas, a mixture of liquids and tarry products called coal-tar and coke. Coal-tar is rich in aromatic molecules with rings of carbon atoms like benzene, naphthalene and anthracene, and most dyes also contain ring structures.



Previously the dyes were called the 'coal-tar dyes' because of the fact that the raw materials commonly known as *primaries* were obtained exclusively from the distillation of coal-tar. These days some primaries particularly benzene and toluene are obtained mainly from petroleum and natural gas so the use of the term 'coal tar dyes' is no more considered correct.

Majority of dyes are obtained from intermediates which have been previously synthesised. In the final step for synthesis of a dye a chromogen is assembled as in case of diazotisation and coupling of aromatic animal to give azo dyes. Anthroquinone dyes are an exception. In their case the anthroquinone skelton is generally assembled first and the required substituent introduced afterwards.

For synthesis of dyes various unit processes like sulphonation, nitration, helogenation, reduction, oxidation condensation etc. are used.

Synthesis of Aromatic Carbocycles

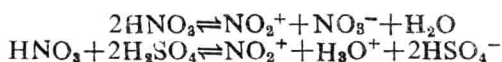
Benzene and naphthalene are the two most important aromatic carbocycles used in the dyestuffs industry. Both benzene and naphthalene can be obtained either from petroleum or coal tar by fractional distillation. The various intermediates can be prepared from these parent compounds by introducing a variety of substituents such as NO_2 , $\text{NR}'\text{R}''$, Cl , SO_3H , CN , SO_2R etc. Generally these substituents are introduced in the benzene ring either by electrophilic substitution or by nucleophilic substitution. Electrophilic substitution is easier but nucleophilic substitution can be brought about under forcing conditions. The presence of some powerful electron withdrawing group in the aromatic ring facilitates the nucleophilic attack because of reduced electron density at ring carbon atom.

An attempt will now be made to present the methods of introduction of some important groups encountered in dyestuffs industry.

1. Introduction of nitro groups or Nitration

Nitration is one of the most important processes encountered in the dyestuffs industry. In addition to itself being an important chromophore nitro group also provides an easy access to the amino group by reduction.

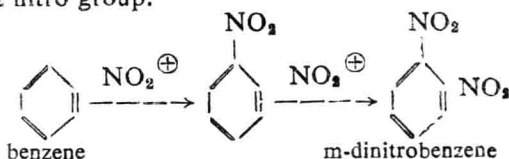
Generally for introducing nitro group in an aromatic ring either concentrated nitric acid or a mixture of concentrated nitric acid and concentrated sulphuric acid is used. Such a mixture is known as nitrating mixture and the active nitrating species is NO^+ (nitronium ion) which is formed as under.



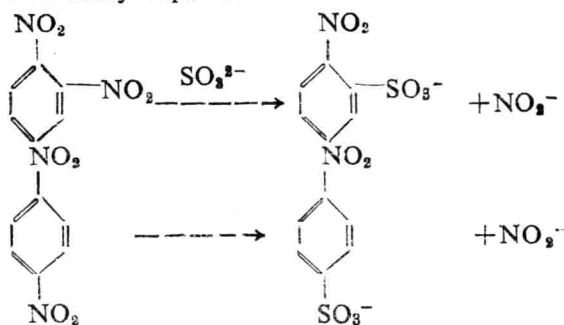
Preparations of some important nitro compounds used in dyestuffs industry are given below.

(i) *m*-Dinitrobenzene. Mono-nitration of benzene is quite easy and can be accomplished at about 50°C using a nitrating mixture. The introduction of second nitro group to prepare *m*-dinitrobenzene

requires a higher temperature. It may be attributed to the deactivating effect of first nitro group.



The formation of *m*-dinitrobenzene is accompanied by small quantities of *ortho*- and *para*-isomers. To remove these impurities, on the industrial scale, the dinitrated benzenes are treated with sodium sulphite. Sulphite reacts with *ortho*- and *para*-dinitrobenzenes and forms corresponding nitrosulphonates which are soluble in water where as *m*-dinitrobenzene remains insoluble in water and so can be easily separated *m*-dinitrobenzene is used for



making *m*-nitroaniline and *m*-phenylene diamine which are used as dyestuff intermediates.

(ii) *p*-Nitrotoluene. It is obtained when toluene is reacted with a nitrating mixture. It is used in the preparation of dinitrostilbene disulphonic acid.

