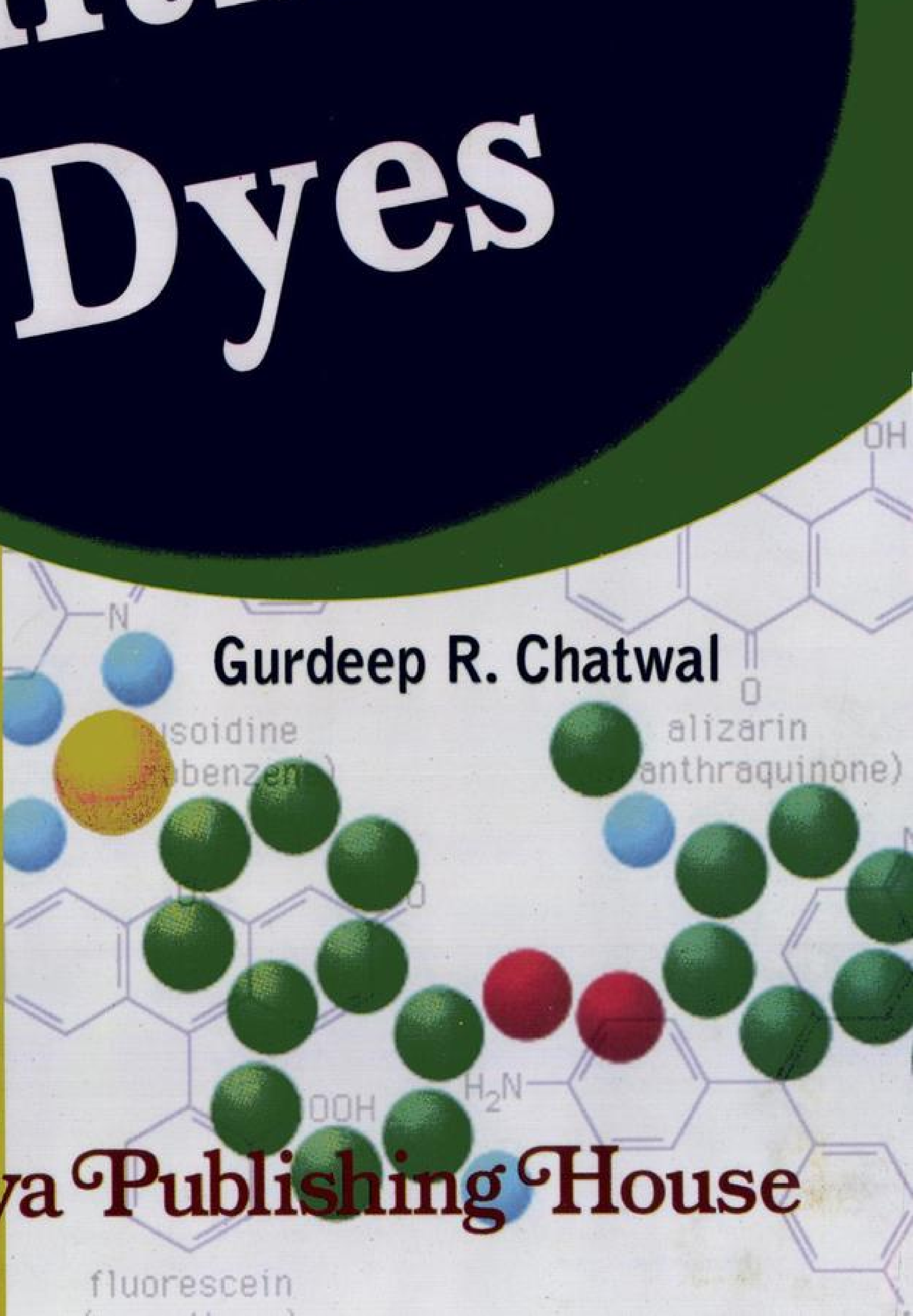
Synthetic Dyes

- ☐ Nitro Dyes
- ☐ Nitroso Dyes
- ☐ Azo Dyes
- ☐ Diphenylmethane Dyes
- ☐ Triphenylmethane Dyes



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Himalaya Publishing House

SYNTHETIC DYES

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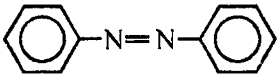
CHAPTER

INTRODUCTION TO DYES

1.1. Definitions

Dye or Dyestuff : A *dye or a dyestuff is usually a coloured organic compound or mixture that may be used for imparting colour to a substrate such as cloth, paper, plastic or leather in a reasonably permanent fashion.* In other words, a dyed substrate should be resistant to a normal laundry or cleansing procedures (*wash fast*) and stable to light (*light fast*). All the dyes may not necessarily be coloured substances. Therefore, optical brighteners or whiteners which may be called **white dyes** may be included in the term dye.

A dye is a coloured substance but all coloured substances are not dyes. Thus a dye should fix itself on the substrate to give it a permanent coloured appearance. Thus, azobenzene is not a dye even though it has red colour, as it cannot be attached to substrate. However, congo red is a dye as it can be applied on cotton and retained by it. Thus, the dyes should have certain groups which help the attachment to the fibre.



Azobenzene (Red coloured but not a dye)

White Dye : Some colourless compounds are used as the optical brighteners. They may also be called as the *white dyes.* They have the special property of absorbing ultraviolet light and re-emitting the visible light so that the fabric appears bright.

Pigment : The coloured substance which is insoluble in water or other solvents is called a pigment. Thus the application of dye and pigment will be different. A dye is applied in the form of a solution, whereas the pigment is applied in the form of a paste in a drying oil, in which it is insoluble.

Requisites of a True Dye : All coloured substances are not dyes. However, the requisites of a true dye are as follows :

(*i*) *It must have a stable colour.*

(*ii*) *It must have an attractive colour i.e., it should not undergo structural changes readily.*

(*iii*) *It must be able to attach itself to material from solution or to be capable to fixed on it.* For example, azobenzene is coloured but cannot fix itself to a fabric. Therefore, azobenzene is not a dye. Further, a dye may not be able to dye all types of substrates. For example, picric acid is able to dye silk or wool a permanent yellow but not cotton. Thus, a dye either forms a chemical union with the substrate being dyed or it may get associated with it an intimate physical union.

(*iv*) *It must be soluble in water or must form a stable and good dispersion in water.* Alternatively, *it must be soluble in the medium other than water. However, it is to be remembered that the pick up of the dye from the medium should be good.*

(*v*) *The substrate to be dyed must have a natural affinity for an appropriate dye and must be able to absorb it from solution or aqueous dispersion. If necessary, in the presence of auxiliary substances under suitable conditions of concentration, temperature and pH.*

(*vi*) *When a dye is fixed to a substrate, it must be fast to washing, dry cleaning, perspiration, light, heat and other agencies.* It must be resistant to the action of water, acids or alkalis, particularly the latter due to the alkaline nature of washing soda and washing soap.

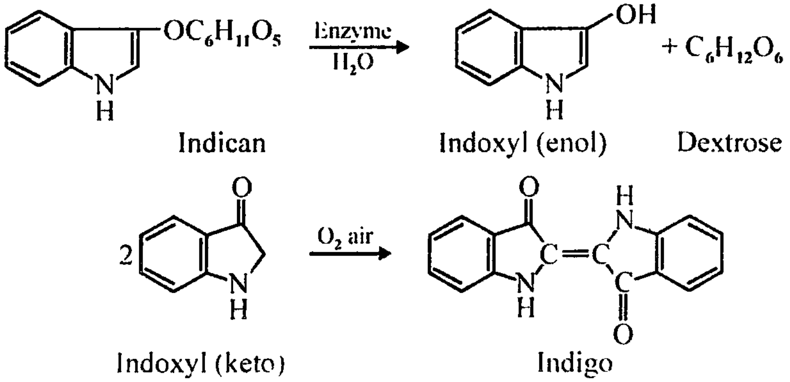
There is probably no dye which can be guaranteed not to alter shade under all conditions.

(*vii*) The shade and fastness of a given dye may vary depending on the substrate due to different interactions of the molecular orbitals of the dye with the substrate, and the ease with which the dye may dissipate its absorbed energy to its environment without itself decomposing.

1.2. Historical Development from Natural to Synthetic Dyes

Era of Natural Dyes : These have been used since ancient times for colouring and printing fabrics. Until the middle of last century most of the dyes were derived from plants or animal sources by long and elaborate processes. Ancient Egyptian hieroglyphs contain a thorough description of the extraction of natural dyes and their application in dyeing. Further developments extending over many thousands of years led to rather complicated dyeing processes and high-quality dyeings. Among these the following deserve special mention :

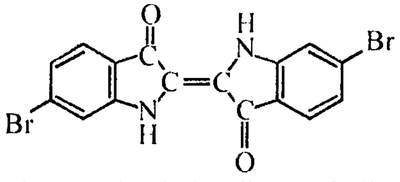
(*i*) *Indigo :* It is one of the earliest natural dyes and it originated in India. The art of dyeing with this bluish indigo dye was practised in this country, using primitive fermentation methods. Then the use of this dye spread to Egypt. Indigo occurs in the *indigo-ferae* species of plants as a glucoside called indican. This is extracted with water, when it gets hydrolysed by the enzyme into indoxyl and dextrose. In alkaline medium indoxyl gets oxidized into indigo, which is precipitated.



Ancient Britons obtained a dye called woad from the plant called *isatis tinctoria*. The active compound is called indigotin from which indigo was prepared. Indigotin is insoluble and hence it was reduced by fermentation and then applied.

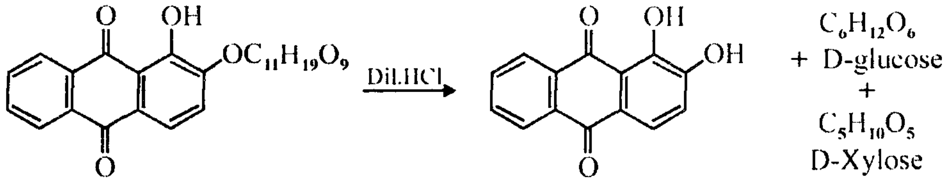
(*ii*) *Tyrian Purple* : It is a natural dye which originated in the ancient city of Tyre in Phoenicia. This dye was extracted from certain kinds of shell-fish. However, at that time the dye was so expensive that it was called *Royal purple*.

Later, Friedlander showed that it was a derivative of indigo.



Tyrian purple (6, 6′-Dibromo indigo)

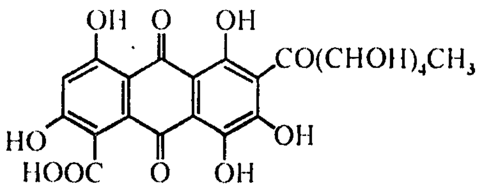
(*iii*) *Alizarin* : It is extracted from the roots of madder plant. It occurs as a glycoside called ruberythric acid. On hydrolysis with dilute acid it gives dextrose, rhamnose and alizarin which is 1,2-dihydroxy anthraquinone. The extract also contains a dye called purpurine (1, 2, 4-trihydroxy anthraquinone). Alizarin is a natural mordant dye and it produces various colours using different compounds of the metals Al, Cr, Cu, etc.



Ruberythric acid

Alizarin

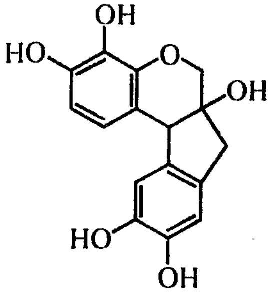
(*iv*) *Cohineal* : It was extracted from the insect *coccus Cacti* which is found mainly in South America and Mexico. The active dye is called carminic acid which is a derivative of antraquinone. It is also a natural mordant dye and gives different shades of purple by using compounds of Cr, Al, Fe, etc. It is used for dyeing of wool and silk and also as non-poisonous food colourant.



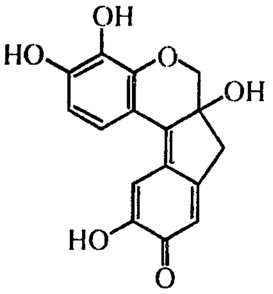
Carminic acid

(*v*) **Logwood :** It is the only natural dye which is still isolated on a large scale from the wood of the tree *Haematoxylon campechianum*. It is cultivated and also grows wild in the central America. The fermentation of the wood of this tree contains a glucoside of haematoxylin which on oxidation yields a colouring matter called haematin.

Haematin is an active dye which when mordanted with chromium compounds gives blue and black shades. It is still used for dyeing silk, viscose and acetate fibres, nylon, etc. It also gives cheap black shade of good fastness properties.



Haematoxylin



Haematin

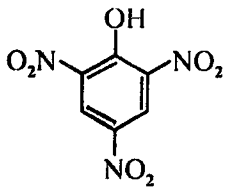
Although the isolation of natural dyes has been abandoned, they still retain the interest of chemists and a great ideal of work is being still performed for the determination of their structures.

Limitations of Natural Dyes

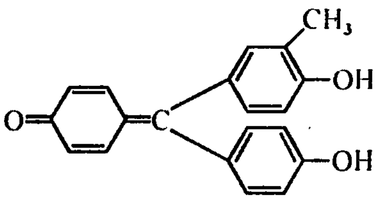
A large number of natural dyes were thus extensively used earlier. However, the preparation of dyes by extraction has number of limitations. The extractions are unsuitable for large scale preparation as they are labourious and time consuming. Only a small amount of the dye can be obtained by processing a large amount of the animal or vegetable matter. Hence they were invariably expensive. The natural dyes are not pure and lack uniformity of quality. Further their fastness properties were not good and they fades in light. Thus only a handful of natural dyes are still extracted and used. Some of them like indigo and alizarin are now prepared by synthetic methods. Otherwise the natural dyes are largely replaced by synthetic dyes.

Era of Synthetic Dyes

The era of synthetic dyestuffs started with development of synthetic organic chemistry. The earliest artificial dyes to be prepared were picric acid by Woulfe and aurine (rosolic acid) by Runge. However, they were not prepared commercially at that time due to high cost of raw materials.

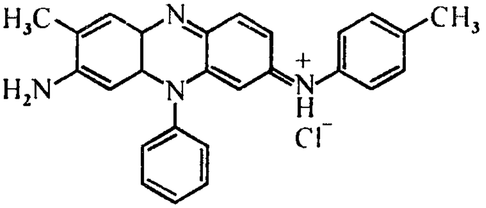


Picric acid



Rosolic acid

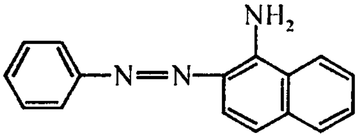
William H. Perkin is considered as the founder of synthetic dyestuffs. In 1865, he prepared the first synthetic dye called Perkins Mauve or Mauveine. He oxidized crude aniline with potassium dichromate and concentrated sulphuric acid and extracted the resulting black resinous mass with alcohol to get a violet compound which was the dye. He was already having a factory for manufacture of aniline. Later he set up facilities to manufacture the dye mauveine.



Mauveine

Later he prepared another dye called safranine by oxidation of mauve by lead peroxide. This dye was found suitable for wool and silk. However, only pale shades were obtained with cotton. Then Perkin developed the use of tannin and sodium stannite as mordants in dyeing to get bright shades.

Almost during the same period (1858) Griess discovered the diazotization reaction and reactions of diazotised base. He prepared the first azodye by coupling diazotised aniline with α-naphthyl amine.



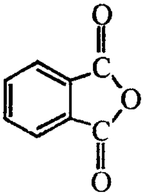
This was followed by preparation of other azodyes like Bismark Brown (1865) and aniline yellow (1869) and congo red (1884). Thus azo dyes gave direct colours for cotton.

The mordant dye called alizarin was prepared from anthraquinone by Graebe and Libermann in 1868. Later in 1880 von Baeyer established the structure of indigo, followed by the synthesis of this vat dye.

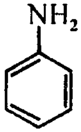
In 1901, Bohn prepared indanthrene blue by alkali-fusion of 2-amino-anthraquinone. Then a series of indanthrene vat dyes were prepared between 1901-1911. Around this period many unit processes were discovered, *i.e.*, sulphonation, nitration, alkali fusion, thionation etc. They were used in preparation of several important intermediates like β-naphthol, H-and J-acids, anthraquinone derivatives.

An important dye intermediate, phthalic anhydride, was prepared by air oxidation of naphthalene using V_2O_5 as catalyst by Gibbs in 1917.

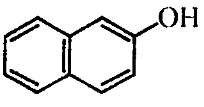
Important Dyestuff Intermediates



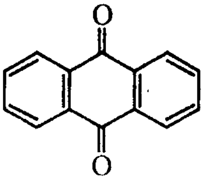
Phthalic anhydride



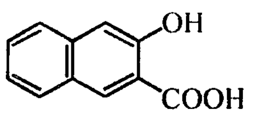
Aniline



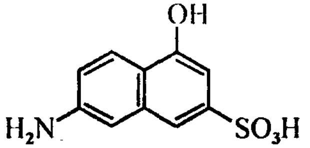
β-Naphthol



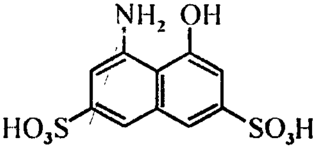
Anthraquinone



BON acid



J-acid



H-acid

Raymond Vidal discovered sulphur dyes in 1893, by heating *p*-nitro phenol or *p*-amino phenol with sodium polysulphide.

The effect of these discoveries was that cost of dyestuff production was reduced.

During 1914-1918 the developments in the dyestuff chemistry were slowed down due to World War I. After this period cellulose acetate fibres were discovered (1918) but they could not be dyed by any of the earlier dyes. Certain basic dyes derived from gallocyanine were used but they had limited range of colours. Then Green and Saunders introduced the ionamines (1922). Later it was found that acetate fibres could be dyed by using dispersion of anthraquinone dyes and this led to the discovery of the dispersed dyes.

In 1928 the metal complexes of phthalocyanines were prepared but due to its insolubility it could be used as pigment. In 1935 ICI started manufacture of copper-phthalocyanine which is called monastral fast blue B. Later a German firm called Baeyer founded a method of impregnating Cu of Ni phthalocyanines in the fibre.

In 1929 Krais found that a compound called aesculin (6, 7-dihydroxy coumarin) shows fluorescene when applied on bleached fibres. This was the foundation for the development of fluorescent brighteners. In 1934, ICI patented the use of amino stilbene disulphonic acid as brightening agents. Later British industrial solvents Ltd., introduced β-methyl umbelliferone as substitute for bleaching agent. The dyestuff industry was again disturbed by World War II (1939-45). The first firm to manufacture dyestuffs was Arlabs in 1940. It should be noted that in the post war period the further development in the field of dyestuff chemistry was made more by companies and institutions rather than individuals. With the discovery of the synthetic fibres like polyester and polyamide again posed a problem as they were hydrophobic. This lead to the discovery fo the new class of dyes called dispersed dyes.

In 1956 an entirely new class of dyes were discovered by ICI which were called procion dyes. The speciality of these dyes was that they could be directly attached to fibres by chemical linkage. Hence this new class of dyes were called reactive dyes. The compounds prepared were procion brilliant red 2B and procion blue 3G.

Further advances resulted in newer and modified dyes at lower cost. However, the extensive manufacture of dyes lead to pollution problems and hence pollution control measures became necessary.

Most of the dyes made in the nineteenth century were derived from the aromatic intermediate chemicals isolated from the coal tar distillation and the synthetic dyes are, therefore, known as coal-tar dyes. Several hundred varieties of dyes are produced on a large scale in our country today. Some of these dyes are being exported to other countries. The export market possibilities in the recent years has also increased the horizon of many ambitious dye-stuff firms to enter in the world wide competition in the dyestuffs and intermediates.

1.3. Nomenclature of Dyes Intermediates

A large number of variety of intermediates involved in dyestuff production cannot always be named by their chemical names because chemical nomenclatures may lead to confusion. For example, H-acid may be named chemically as 1-amino-8-hydroxy-naphthalene-3, 6-disulphonic acid or 1-hydroxy-8-amino-naphthalene-3, 5 disulphonic acid, the chemical names are different but the compounds are identical.

The usual practice is to name dyes intermediates by commercial names such as H-acid, Y-acid, naphthol AS, Fast blue B base, Fast scarlet G base, etc. These commercial names as compared to the nomenclature are short, symbolic and simple even for a layman in trade.

1.4. Nomenclature of Dyes

Hundreds of dyes are being synthesised in the laboratory. Of these about 3600 are used commercially. Various systems of nomenclature are known. Two of these are as follows :

1. **Commercial Naming of Dyes :** In the earlier times, the commercial names of dyes are coined by individual manufacturers and these usually consist of three or four parts. The trade-mark name of the class comes first and is followed by words, letters or numbers. These describe the shade and other characteristics, strength, physical form, etc. The alphabetical letters following the trade names may refer to the shade of the dye, *e.g.*,

Y or G = Yellow (gelb)

R = Red (rot)

B = Blue

O = Orange, etc.

Similarly, other letters indicate the type of dye, fastness property, temperature of dyeing etc.

D = Direct dye for cotton

S = Acid dye (German, *Sauer* = acid)

F = Fastness to specific agencies

L = Light fastness

C = Cold brand reactive dye

H = Hot brand reactive dye

I = Vat dye

I_k, I_n = Dyeing in cold (*kalt*) and normal temperature.

Thus, 'G' stands for (German word *gelb* = yellow) 'R' for (German word *rot* = red) and 'B' for (German word *blau* = blue) yellowish, reddish and bluish tones respectively. For example, Astrazon Yellow 3G is a basic dye having considerable yellowish tone, Chrysophenine G is a direct dye with a yellowish tone. Similarly, Acridine Orange R and Astrazon Orange R both are basic dyes and Rhodamine B (basic dye) and Remazol Red B (reactive dye) with bluish tone. Similarly, in Vat Pink R, 'R' indicates the red tone of the pink.

The repetition of the above letters indicates the greater intensity of the tone. For example, methyl violet 6B is a very deep purple (close of bluish) tone, similarly Alkali Fast Green 3B is a green acid dye having considerable bluish tone.

Sometimes the letters are used to represent the class of the dye. For example, in Alizarin Blue D, the letter 'D' indicates that dye is a direct cotton colour. In Fuchsines, the letter 'S' indicates that the dye is an acid (saver).

Sometimes the letters are also used to represent the property of a dye. For example, the letter 'F' is used to indicate that the dye is fast to certain agencies such as light, washing, etc. The letter 'L' appears in the name of the dye, indicating that this dye produces a shade on a fibre and is fast to light. Examples having this letter are Basacryl Yellow 5 GL, Basacryl Yellow 5 RL and Basacryl Violet RL, disperse dyes for polyester fibres such as Foron Grey S-4 GL and Foron Scarlet E-2 GFL; direct dyes such as Kiton Fast Yellow 2 GL, Chlorantine Fast Blue 10 GL and Benzo Fast REd 8 BL.

In the case of reactive dyes, belonging to the chlorotriazine class, reactivity has been found to depend upon the number of chlorine atoms present in the molecule. If the molecule of a dye has two chlorine atoms, they are highly reactive and can be used in the cold condition. Hence they are termed as *cold brand* (cold dying) *reactive dyes*. Thus, their names have the letter 'C' *e.g.*, Premactive C and Goldazol C.

There are also dyes which have only one chlorine atom. These dyes are less reactive and, therefore, the dye solutions have to be heated for their greater reactivity. Thus, they are termed as *hot brand* (hot dyeing) *reactive dyes* and hence their names have the letter 'H', *e.g.*, Procion H and Premactive H.

The letter 'I' generally indicates that the dye belongs to a special class of vat dyes, the solubilised vat dyes. They are subdivided into various groups such as I_k, I_w, I_n depending on the condition of temperature used. For example, I_k group of vat dyes are employed in the cold condition, *i.e.*, at 20-30°C. Further, I_w and I_n group of vat dyes are employed under conditions of temperature 30-40°C and 50-60°C respectively,

The letters 'N' and 'K' indicate that it is vat dye which can be applied to cellulosic fibres by a particular method of dyeing involving normal and cold temperature conditions respectively *e.g.*, Indanthrene Golden Yellow GK, Indanthrene Brilliant Orange RK, Algol Yellow GCN, Caledon Jade Green BN.

Hence the intensity of the tone, tone of the colour and condition of temperature of dyeing are indicated as in Indanthrene Yellow GK, Indanthrene Yellow 4 GK, Indanthrene Yellow 5 GK and Indanthrene Yellow 7 GK (In this case, yellowish tone tends to increase).

Advantage : The commercial names as compared to the nomenclature are short, symbolic and simple even for a layman in trade. Chemical nomenclature may often lead to confusion.

Drawback : The main drawback of this system of nomenclature is that the same dye has been given various names by different manufacturers, *e.g.*, rose-red dye is named either by pararosaniline, magneta or fuchsine. In order to overcome this difficulty, a colour index has been compiled.

2. **Colour Index Naming of Dyes :** The best method for the nomenclature of dyes is that used in the Colour Index, a publication sponsored by the Society of Dyers and Colourists (England) and the American Association of Textile Chemists and Colourists. In this, each dye is given two reference numbers, one relating to its class with respect to dyeing method (*e.g.*, C.I. Vat Blue 4 for indanthrone) and the other to its chemical description in five digits (*e.g.*, C.I. 69800 for indanthrone). All the commercial names under which dye is sold (over 37 of indanthrone *e.g.*, Indanthrene Blue RS, Cibanone Blue RSN, Caledon XRN, Ponsol Blue GZ, etc.) are also listed in the colour Index.

2

CHAPTER

GENERAL INFORMATION ABOUT FIBRES AND DYEING METHODS

2.1. Introduction

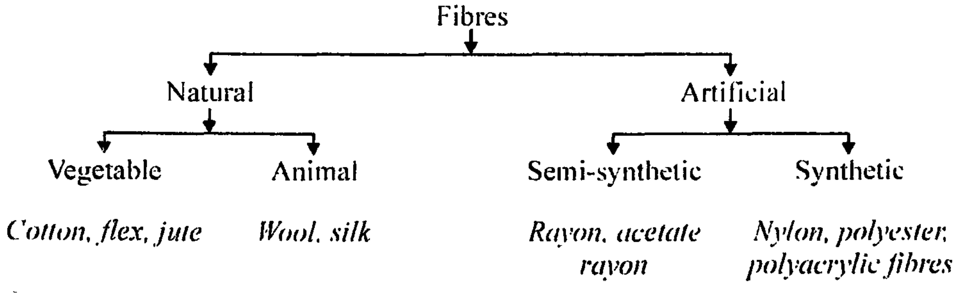
The application of dyes to textile fibres is one of the most important use of dyestuffs. Dyeing is the process of application of dyes to the fibres to make it permanently coloured. The exact method used for dyeing depends on two factors :

(*i*) The chemical structure as well as physical properties of the dyestuff.

(*ii*) The chemical nature and also physical characteristic of the fibres.

Textile Fibres

The fibres are high molecular weight organic polymers having linear structure. They may have different chemical structures. They should have chemical stability and tensile strength along the axis of the fibre. They should have sufficiently high softening point and low static electricity. However, cotton is affected by acids and wool and silk by alkali. The fibres are classified on the basis of their source :



The fibres are also classified as follows :

(*i*) **Hydrophilic Fibres :** They have affinity to water (wetted by water) *e.g.*, cotton, wool, silk. The presence of many hydroxyl groups make the fibres hydrophilic.

(*ii*) **Hydrophobic Fibres :** They have no affinity to water (not wetted by water), *e.g.*, synthetic fibres like nylon, polyester, acetate rayon, etc. These fibres should have sublimation fastness.

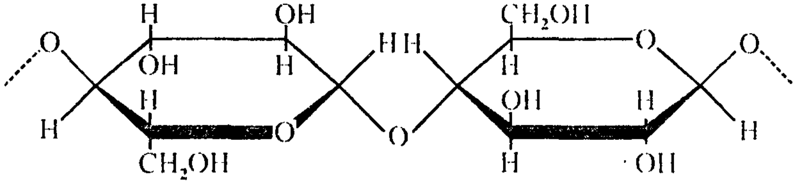
The physical and chemical nature of various fibres are discussed in the following section.

2.2. Textile Fibres or Types of Fibres

The broad classification of textile fibres may be done on the basis of origin of fibres such as natural, semisynthetic (also known as man made) and synthetic fibres. These different varieties of fibres have different structural features which are outlined as follows :

(*a*) ***Cotton :*** It is composed of cellulose units in quite pure form. Cellulose lacks significant acidic or basic properties but consists of a chain of linearly arranged biglucose units with ether bridge linkages. The side groups of these units are primary and secondary alcoholic hydroxy groups which make the fibre hydrophilic. This property of cotton fibre is responsible for its dyeing.

Dyeing of cotton fibres may take place by adsorption, occlusion or reaction which the hydroxyl groups. It is also possible to make cotton fibres receptive to a variety of dyes by pretreatment or mordanting with a material capable of binding the dyes.

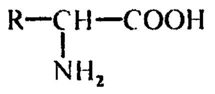


Biglucose units in cotton

Mercerisation : When cotton is swollen by concentrated alkali under tension, so that the fibres cannot shrink lengthwise, it produces a silk-like lustre. This process is called *mercerisation*. The affinity of mercerised cotton for dyes is greater than that of untreated.

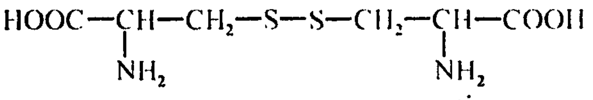
(*b*) ***Wool :*** It is the natural animal fibre. It is composed of protein substances which, in turn, are composed of polypeptide structures with amino and carboxylic acid end groupings and side chains (R) having disulphide groupings which keep the main polypeptide skeleton parallel to each other.

In the polypeptide structure of wool, twenty amino acids like cystine have been isolated by the hydrolysis of wool.



$$\mathrm{R{-}\underset{\underset{NH_2}{|}}{C}H{-}COOH}$$

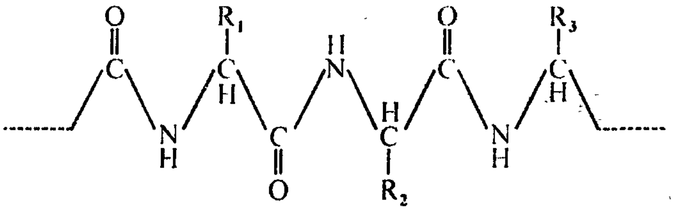
amino acid in wool fibre
(R) is variable



$$\mathrm{HOOC{-}\underset{\underset{NH_2}{|}}{C}H{-}CH_2{-}S{-}S{-}CH_2{-}\underset{\underset{NH_2}{|}}{C}H{-}COOH}$$

cystine

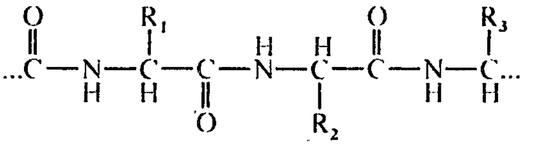
The structure of wool fibre is destroyed by strong alkali. Strong acid causes hydrolysis but the process may be controlled to permit dyeing from acidic solutions.



Structure of wool fibre (R_1 R_2 R_3..... are the side groupings)

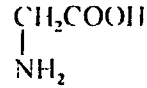
• Wool is dyed with either acidic or basic dyes through the formation of salt linkages with amino or carboxylic acid end groupings. Wool may also be dyed with reactive dyes with reactive dyes that form covalent bonds with available amino groups. In some cases, mordanting is used to alter the dye ability of wool.

(*c*) ***Silk :*** Like wool, it is also the natural animal fibre. It is also a protein fibre which is made up of linearly arranged (stretched) polypeptide structures called *fibroin* having much simpler side chains. When silk is hydrolysed, the main amino acids isolated are glycine, alanine, serine and tyrosine.



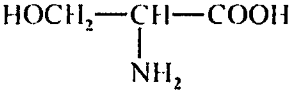
$$\cdots\overset{\overset{O}{\|}}{C}—\underset{H}{N}—\underset{H}{\overset{\overset{R_1}{|}}{C}}—\underset{\underset{O}{\|}}{C}—\overset{H}{N}—\overset{H}{\underset{\underset{R_2}{|}}{C}}—\overset{\overset{O}{\|}}{C}—\underset{H}{N}—\underset{H}{\overset{\overset{R_3}{|}}{C}}\cdots$$

Structure of silk fibre
(R are the side groupings)



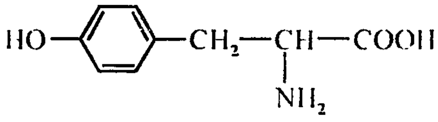
$$\underset{\underset{NH_2}{|}}{CH_2}COOH$$

glycine

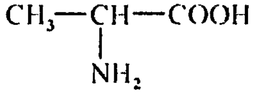


$$HOCH_2—\underset{\underset{NH_2}{|}}{CH}—COOH$$

serine



tyrosine



$$CH_3—\underset{\underset{NH_2}{|}}{CH}—COOH$$

alanine

Like wool, silk is wetted by water and dyed with either acid or basic dyes through the formation of salt linkages.

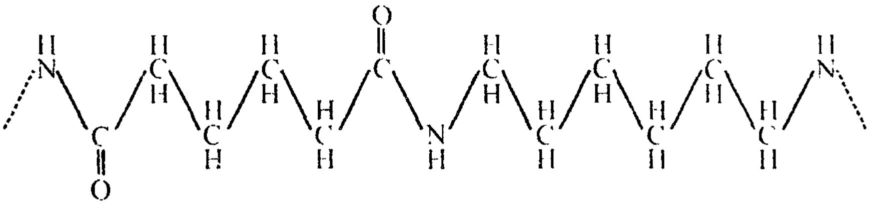
(*d*) ***Cellulose Acetate :*** It is a man-made fibre which is made by acetylation of alcoholic groups of cellulose fibre (cotton). The three hydroxyl groups present in the single glucose unit of cellulose can be replaced in succession depending upon the degree of acetylatin. The higher the degree of acetylation, the more unlike cotton the cellulose acetate becomes.

Acetylated cellulose differs from cellulose fibres in that they are more hydrophobic and lack large number of free hydroxyl groups. Cellulose triacetate fibre is the most hydrophobic and the most stable.

Dyeing of cellulose acetates is affected with dyes of low water solubility which become dissolved in the fibre or by occlusion of dyes formed in situ. Acid, basic and reactive dyes cannot be used because of the lack of sites for attachment.

The other less important semisynthetic fibres are nitro cellulose, cuprammonium and viscose which are obtained from cotton by nitration, by treatment with ammoniacal copper hydroxide and by treatment with carbon disulphide and alkali respectively.

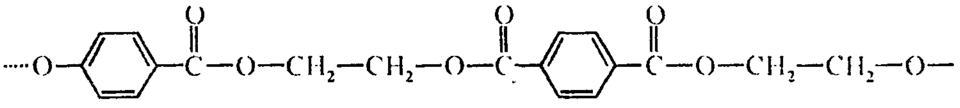
(*e*) ***Polyamide (nylon, Du pont) :*** These are synthetic fibres possessing properties somewhat like those of wool and silk. These synthetic fibres are made from condensing diamine with a diacid or by self-condensation of a lactam. For example, nylon 6 is made from caprolactam and nylon 66 is made from hexamethylene diamine and adipic acid. By changing the aliphatic residues, the carbon chains between the two amide linkages can be varied resulting in variable property of the amide fibres.



Structure of polyamide fibre

Polyamide fibres are dyeable near the boiling point of water with acid dyes that form salt linkages with basic sites. Dyeing by this means is limited by the availability of these sites.

(*f*) ***Polyester Fibres :*** These are synthetic fibres unlike any produced in nature. They are synthesised by condensing ethyl glycol (aliphatic dialcohol) with terephthalic acid (aryl-1. 4-dicarboxylic acid) to form a chain of easter linkages between phenylene and ethylene linkages



Structure of polyester fibres

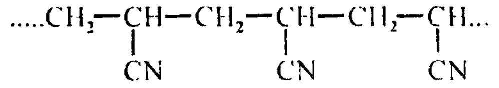
Polyster fibres are hydrophobic. Some polyester fibres do not have functional groups while others are provided with acidic groups or otherwise modified to make them hydrophilic.

Modified polyester fibres could be dyed by solution of dyes in the fibre or by occlusion of dyes formed in situ. Modified polyester fibres could be dyed in these ways or with the dyes selected according to the nature of the sites introduced by the modification.

(*g*) ***Polyacrylonitrile :*** This is the synthetic fibre which is obtained by the polymerisation of acrylonitrile. It contains a linear carbon chain with cyano groups attached to the alternate carbon atoms.

$CH_2{=}CH{-}CN$

acrylonitrile



$$\ldots CH_2{-}\underset{CN}{\underset{|}{CH}}{-}CH_2{-}\underset{CN}{\underset{|}{CH}}{-}CH_2{-}\underset{CN}{\underset{|}{CH}}\ldots$$

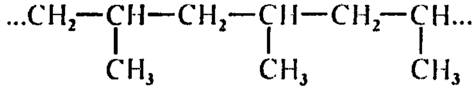
polyacrylonitrile fibre structure

In polyacrylonitrile, the cyano groups are the dye sites. However, the dyeing character of polyacrylonitrile can be improved by making available better dye sites through its modification with other copolymers.

(*h*) ***Polyolefin Fibres*** : These are obtained from the products of polymerisation of unsaturated compounds of carbon and hydrogen. For example, polypropylene is obtained by the polymerisation of propylene. In polypropylene, the methyl side groups are attached to alternate carbon atoms of the main skeleton.

$CH_2{=}CH{-}CH_3$

propylene



$$...CH_2{-}\underset{CH_3}{\underset{|}{CH}}{-}CH_2{-}\underset{CH_3}{\underset{|}{CH}}{-}CH_2{-}\underset{CH_3}{\underset{|}{CH}}...$$

polypropylene

Polyolefin fibres do not absorb water and are chemically quite inert. They can be dyed with special disperse dyes by are coloured best by introducing a colorant into the polymer before the fibres are spun.

Hydrophobic and Hydrophilic Fibres : Most of the synthetic fibres do not attract water molecules and are called *hydrophobic fibres* (means water repelling). On the other hand, cotton, wool, silk and other natural fibres attract water molecules strongly and are referred to as *hydrophilic fibres*.

2.3. Dyeing

It is a process which is used to transfer the colour to the substances being dyed. The dyeing process even now is being extensively studied with the help of modern instruments. However, the dyeing of fibres involves one or more of the following four types of forces :

(*a*) **Ionic Interactions** : These arise from ionic sites of opposite charge in the fibre and the dye molecules. For example, the dyeing of wool with acid dyes of the levelling type (*i.e.*, those with fairly simple structures) is mainly due to the formation of salt-type chemical links between dye anions and cationic groups in that fibre. This is shown in Fig. 2.1.

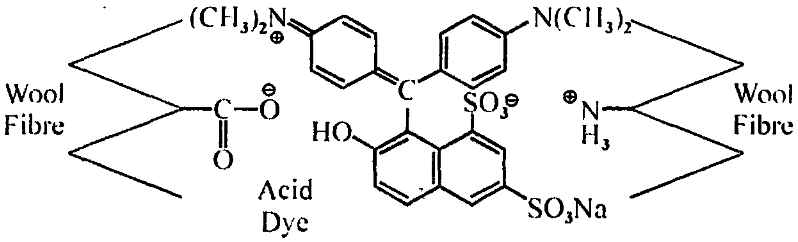


Fig. 2.1 : Dye-fibre attachment by ionic forces

As the salt-type chemical links between dye anions and cationic fibres are easily broken, the resulting dyeings have somewhat poor fastness to wet treatments.

Basic dyes are attached to wool, silk or acrylic fibres containing anionic sites by salt-type linkages. Fastness to washing on wool and silk is in most cases rather poor but usually reaches a high standard grade on polyacrylonitrile fibres. This has been attributed partly to difference in the strength of salt bonds and partly to the hydrophobic nature of the synthetic fibre.

(*b*) **Hydrogen Bonds** : These interactions are weak and are formed by sharing a lone pair of electrons on nitrogen, oxygen or fluorine in a molecule with covalently bonded hydrogen atom. The hydrogen bonds are involved in dyeing of wool, silk and man-made fibres. Several hydrogen bonds forming between the dye molecule and the fibre structure at a time may be sufficiently strong to hold the dye molecule to the fibre structure. This is shown in Fig. 2.2. However, the dyeing of cellulose is not explained through hydrogen bonding because water has more affinity for cellulose than dye molecules.

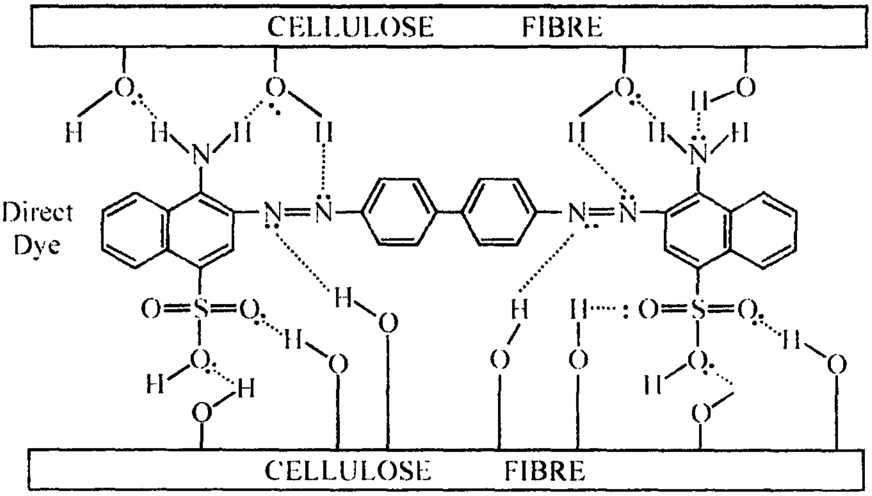


Fig. 2.2 : Dye-fibre attachment by hydrogen bonding.

(*c*) **van der Waal's Interactions** : These interactions are weak and mainly arise due to interactions between molecules close to one another. In dyeing, these interactions arise due to the interaction between π orbitals of dye and fibre molecule in linear fashion. van der Waal's interactions become stronger between similar groups, *e.g.*, alkyl aryl in polyester dyes. When the total effect of such interactions become greater than a critical requirement, the dye will attach to the fibre. This is shown in Fig. 2.3.

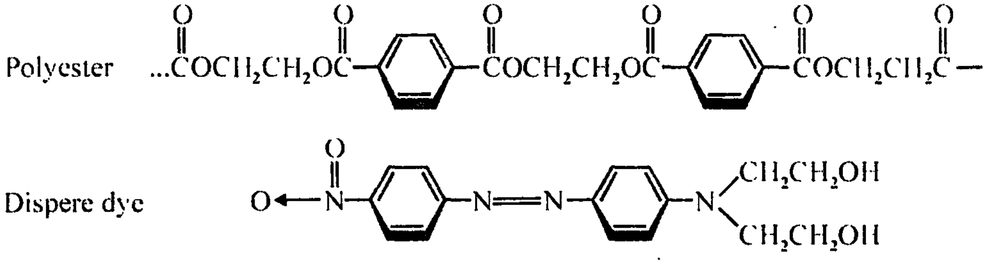


Fig. 2.3

It appears that van der Waal's forces are effective only when the dye and fibre are brought into proximity by some means as a salt-type link.

(*d*) **Covalent Bonds** : These bonds are formed between dye and fibre molecules due to the reaction between a reactive dye and a group such as –OH. Such reactive dyes were first introduced by ICI in 1956 under the name *procion dyes*. They were soon followed by Cibacron dyes by CIBA. These dyes are fast to washing.

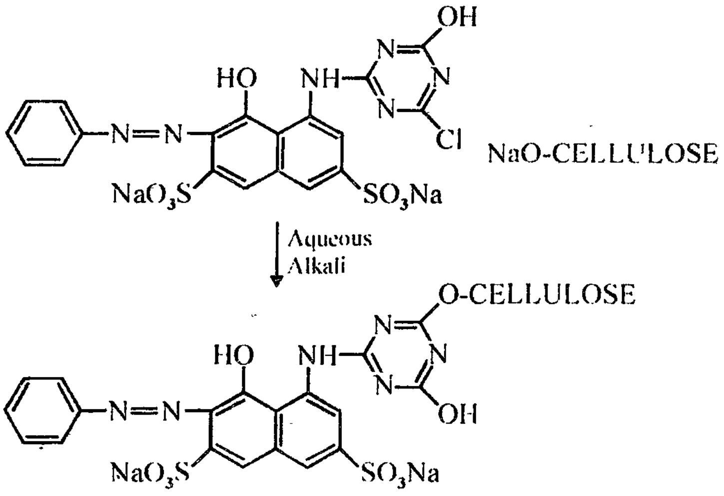


Fig. 2.4 : Dye-fibre attachment by covalent bonding.

When a reactive dye having, dichloroazine reactive system undergoes reaction with the cellulose structure having alcoholic hydroxy groups, one of the chlorine atoms undergoes reaction with the hydroxy group of the fibre yielding a dye-fibre attachment. This is shown in Fig. 2.4.

When the dyeing is carried out in aqueous medium, one chlorine atom gets replaced by the oxygen of the hydroxy groups originally present in the cellulose while the other chlorine atom gets replaced by hydroxy group by the reaction with water.

On the basis of various types of interactions between fibre and dye, it becomes possible to know that which fibre should be dyed with particular dye (or dyes) or not. The various conclusions are summarised as follows :

(*i*) Cotton may be dyed or printed by direct dyes, vat dyes, solubilised vat dyes, sulphur dyes, ingrain dyes, azoics, reactive dyes and pigment emulsions.

(*ii*) Wool may be dyed with acid dyes, acid-mordant dyes, basic dyes and reactive dyes.

(*iii*) Silk may be dyed with direct dyes, acid dyes, mordant dyes and basic dyes.

(*iv*) Polyamide fibres may be dyed with acid dyes, disperse dyes and disperse reactive dyes.

(*v*) Polyester fibres may be only dyed with disperse dyes.

(*vi*) Modified polyprolene fibres may be dyed with only specially selected disperse dyes.

(*vii*) Polyacrylonitrile fibres may be dyed most suitably by cationic dyes. However, disperse dyes can be employed but with certain limitations.

Cross Dyeing : The polymer chemist is now successful in increasing the versatility of the new fibres by incorporating dye sites of a varying nature as required to achieve dyeability with a predetermined class of dyes. It has now become possible to have polyesters, acrylics and polyamide fibres which may be dyed with positive (basic, cationic), negative (acid, anionic) or neutral (disperse) dyes. These developments have made possible for fabric designer to produce materials (textiles, carpets) fabricated in patterns which can be dyed for three different colours from one dye bath having three types of dyes. This concept is known as *cross dyeing*. This has now become popular as a low cost method of colouration.

Basic Operations in the Dyeing Process : The basic operation of the dyeing process involves the following steps :

(*a*) Preparation of the fibre,

(*b*) Preparation of the dye bath,

(*c*) Application of the dye, and

(*d*) Finishing

We shall discuss these steps one by one.

(*a*) **Preparation of the Fibre :** In order for the dyeing to be successful, it is essential that the preceding operations must be performed carefully. The raw fibres get associated with foreign substances like oils, waxes, lubricants used while spinning. These also get associated with sizing material and dirt processing. Hence the fibres are scoured with soap and other detergents before these are dyed. This step helps the dye liquor to penetrate through the fibrous material and thus produces level dyeing. This treatment has been found to depend upon various factors like the nature of the fibre, the depth of the shade and the processing material to which the dyed material is submitted.

(*b*) **Preparation of the Dye Bath :** The dye bath is prepared by adding necessary chemicals to the solution of water soluble acidic, basic and direct dyes. If there are insoluble vat dyes in the dyeing bath, they are reduced with alkaline hydrosulphite to render them water soluble leuco compounds. After dyeing, the fibres are subjected to air oxidation when the original colour on the fibres is generated.

Beside dye, some other substances like wetting agents salts, carriers, retarders and other assistants are also added to the dye bath. The function of the carriers is to improve the dyeing rate of hydrophobic fibres (*e.g.*, polyester) because they act as swelling agents. The function of retarders, which are colourless compounds, is to slow down the dyeing process to the desired level by competing with the dye for the reactive sites on the fibre. For example, acetic acid is used as retarder when dyeing of wool is done with acid dyes.

(*c*) **Application of the Dye :** In order to dye the fibre, it is immersed in the dye for a specified time at optimum temperature. For getting level dyeing, stirring arrangement is used. Level dyeing indicates the uniformity of the dye on the fabric. This depends on the nature of the dye, the absorptive power of the fibre and the conditions of the dyeing.

Dyeing can be achieved by a hand operation or on a machine. In *hand operation* the fibrous material is moved in an open vat containing the dye colour. In *continuous dyeing process*, two types of dyeing machinery are used. In *one type*, the dyeing bath is kept stationary while the yarn or cloth is moved in it. This agitates the liquor kept in the dyeing bath. The excess dye is squeezed out by passing the yarn or cloth through a pair of rollers. This also assures penetration of the dye. In *second type*, the fibrous material is properly supported while the dye liquor is passed through it under pressure in one direction. At intervals, the direction of flow of the dye liquor is reversed.

As the dyeing process is continued, there occurs the gradual decrease of the concentration of the dye in the dyeing bath but there occurs the gradual increase of the concentration of the dye on the fibre. At last a stage is reached when the dyeing bath contains practically no dye and it is then said to be exhausted.

(*d*) **Finishing :** Various finishing processes are applied to dyed fibres or cloth. These processes are essential to produce lustre resistance to shrinkage and creasing the other desirable qualities of feel and appearance.

Dyeing processes are generally carried out using water as the medium. Hence purity of water is very important. It is necessary to soften water if not pure.

The above operations may not be carried out in stated sequence. For example, in the dyeing of wool, first of all finishing treatments are carried out and then the dyeing operations are carried out. On the other hand, in the dyeing of cotton, the dyeing process may be carried out in between the two preparatory treatments.

Various Methods of Dyeing : These are as follows :

(*a*) **Direct Dyeing :** The method of dyeing depends on the absorptive power of the fibre, the nature of the dye and the conditions of dyeing. However, it is necessary that the dye applied is fast to light, washing, bleaching and other treatments and possesses an intensity comparable to the standard sample.

As wool and silk are amphoteric proteins, they can be dyed directly either by acidic or basic dyes. However, mordant dyeing is used to get faster and brighter shades. The dye bath is prepared by dissolving the dye in cold water and to this small quantities of sodium sulphate and sulphuric acid or acetic acid are added. The material to be dyed is now introduced into the dyeing bath. Then, the temperature of the bath is gradually raised to about 60°C. At this juncture, exhausting agent like common salt or Glauber's salt is added and the temperature is raised to boiling. The material is rinsed cold and dried after dyeing is complete. The washing fastness is improved by after treatments of the dyed fibre in a separate bath. The various treatments are as follows :

(*i*) Development with diazonium salts,

(*ii*) Diazotisation and development,

(*iii*) Treatment with chromium fluoride or sulphate and sulphate.

(*iv*) Treatment with formaldehyde, and

(*v*) Treatment with copper salts.

Treatments (*i*) and (*ii*) are quite useful in modifying the shade of the dyed fibre.

The cotton, linen and rayons do not show affinity for many dyes which are sued for dyeing wool and silk. However, they can be dyed with substantive dyes by direct dyeing method. The dye is dissolved in hot water. To this dye bath 5-20% sodium sulphate and 0.5-2% sodium carbonane are added. Now the fibres are introduced in the dyeing bath which is first maintained at 50-60°C and then raised in half an hour to 85-95°C. The dyeing is completed in about 1 hour.

As the synthetic fibres are hydrophobic, they are resistant to the usually cotton dyes. However, they can be best dyed from an aqueous dispersion of a water-insoluble anthraquinone or azo dye in the presence of a dispersing agent such as soap. In this process of dyeing, the dye enters the fibres in the form of a solid solution.

(*b*) **Vat Dyeing :** The ability of a colouring substance to function as a vat dye has been found to depend upon (*i*) the property of the insoluble dye to form a soluble alkali salt by reducing with alkaline reducing agent such as sodium hydrosulphite and (*ii*) the affinity of the leuco salt for textile fibres especially the cellulose fibres. If fibre is immersed in the alkaline solution of a reduced dye (called vat) and exposed to atmospheric oxygen or oxidising agent the insoluble dye is regenerated by oxidation which remains fixed to the fibre.

The dye bath for vat dyeing is prepared by adding the dye (in the form of paste with water) and a dispersing agent to water containing caustic soda and hydrosulphite. Vat dyeing is carried out partly by a continuous process in which the cotton cloth is impregnated with vat liquor. Then, it is steamed so that there occurs proper fixation of the leuco compound to the fabric. Further, it is allowed to pass through a bath which contains oxidising agent such as chromate and acetic acid or perchlorate. This generates the colour. Finally, it is soaped, rinsed and dried.

When sulphur dyes are applied by vatting, sodium sulphide is used as a reducing agent. Vatting method cannot be used to dye wool and silk because the alkali used damages the fibre.

The best example of vat dye is Indigo. Its two carbonyl groups are reduced to hydoxyls. The sodium salts of these hydroxyl groups are substantive to cotton. The two of the four carbonyl groups of Indanthrene Blue RNS are reduced to hydroxyl groups.

Vat dyes are quite expensive and must be applied with care. They offer excellent fastness when properly selected. They are the dyes most often used on cotton fabrics.

(*c*) **Mordant Dyeing :** Whenever mordant dyes are applied, a pretreatment of the fibre with a mordant material designed to bind the dye is essential. The mordant becomes attached to the fibre and then combines with the dye to form an insoluble complex called a lake. An example of mordant is aluminium hydroxide which is precipitated in cotton fibre. This mordant binds such dyes as Alizarin by formation of an aluminium lake.

When the mordant dyes are applied to wool, there occurs the combination of a metal with the wool fibre and the lacking of the dye with combined metal gives the fibre very good fastness to washing. The metal used for wool is commonly chromium which can be applied before, during or after dyeing. The colour can be changed using various metals.

The dyeing bath for mordant dyeing is made by adding 2-5% acetic acid (40% solution) and 10% sodium sulphate solution to the dye solution. The temperature of the bath is initially maintained at 50-60%. When the fibre is introduced in the dyeing bath, the temperature of the bath is gradually raised to boil till level dyeing is obtained. The temperature is allowed to drop and sodium dichromate, equal to half the weight of the dye is added. Finally the material is rinsed.

Mordant dyes have declined in importance mainly because equal or superior results can be obtained with other classes of dyes at less expense in time and labour.

(*d*) **Disperse Dyeing :** This method is now used for dyeing polyester fibres although it was originally developed for cellulose acetate and polyamide fibres.

In disperse dyeing, the dye is pasted to the fibre with water at about 40°C. Now a suitable dispersing agent and carrier (trichlorobenzene, biphenyl or *o*-phenyl phenol) are added to the dye bath for maintaining a fine dispersion and the dyeing is carried out at 80°C. Alternatively, disperse dyes may be applied by a dry heat (Thermosol) process to polyester fibres. In this case the dye achieves molecular form by sublimation (vaporisation) from the solid dye to the fibre surface. Extremely small particle size is also important for this process.

(*e*) **Formation of Dye on the Fibre :** Azoic dyes are produced inside textile fibres by zao coupling. In the usual procedure, the fibre is first impregnated with an alkaline solution of the coupling component and then treated with a solution of the diazonium compound. Finally, the dyed goods are soaped and raised.

Special techniques have been devised for forming azoic dyes on synthetic fibres. It is sometimes possible to apply both the diazo component and the coupling component simultaneously from aqueous dispersion and then to treat the goods with nitrous acid to produce the colour.

(*f*) **Dyeing of the Wool with Acid Dyes :** The dyeing bath is prepared by dissolving the dye in cold water. To this small quantities of sodium sulphate and sulphuric or acetic acid are added. Now the fibre to be dyed is introduced into the dye bath. Then the temperature of the dye bath is gradually raised. The dyeing is completed at the boiling temperature in one and half hours. The fibre is then rinsed and finally dried.

This process of dyeing is simple and cheap. It gives the brightness of the shades.

(*g*) **Dyeing with the Reactive Dyes :** Two methods are used for dyeing fibres with the reactive dyes. These methods are as follows :

(*i*) Impregnation by padding and

(*ii*) Dyeing in the dye bath.

In the first process (*i*), the dye is dissolved in one vessel. Wetting agent, sodium sulphate and sodium bicarbonate are dissolved in another vessel. The two solutions are mixed before use. The cotton fabric is first padded through it and then dyed above 100°C. The function of bicarbonate is to yield alkali which fixes the reactive dye on the fabric. The function of sodium sulphate is to prevent the movement of the dye during drying because if unlevel results are obtained, they are difficult to correct. The treatment is concluded with a light scour so as to remove unfixed colour.

In the second process (*ii*), the dyeing with certain reactive dyes may be carried out in cold, using 2-3% of the dye along with relatively high concentration of common salt.

2.4. Fastness Properties

These are the properties of the dyes which indicate the tolerance of the dyes on the fibres towards the action of various foreign agencies like light, washing, heat (sublimation), rubbing, perspiration, milling (rotating in wash wheel) etc. These fastness properties have been carefully standardised by various agencies. For a given dye to be a commercial dye, it should have at least the minimum rating number in each fastness concerned with the type of the dye. However, certain exceptions are known. For example, most of the triphenylmethane (TPM) basic dyes have low light fastness but they owe commercial value due to the brilliancy of shades obtained on the fibres.

The various fastness properties are as follows :

(*a*) **Colour Fastness :** This measures the resistance of the textiles when they are exposed to various agencies. The usual practice is to apply the dye on the fabric in specified strength and subjected to the various agencies. For this, a scale of 1–5 is employed. In this scale, 1 means poor fastness while 5 means excellent.

(*b*) **Light Fastness :** This measures the resistance of dyed fabric to light under standard conditions. For this a scale of 1–8 is employed. In this scale, 1 denotes poor light fastness while 8 denotes best fastness to light.

(*c*) **Sublimation Fastness :** A dyed piece is kept in contact with undyed piece and subjected to heat. Alteration in colour and degree are noted. This fastness is graded from 1–5: 1 denotes lowest rate in sublimation while 5 denotes highest rate in sublimation.

Sublimation fastness is useful for synthetic fibres.

(*d*) **Burnt Gas Fumes Fastness :** A dyed piece is exposed to oxides of nitrogen. Alternation in colour is assessed. This test is largely used for synthetic fibres.

Many other fastness properties, *e.g.*, bleaching, milling, hand washing, rubbing perspiration, etc. are also determined.

Note : The types of dyes used for various types of fibres are summarised in Table 2.1.

Table 2.1

No.	*Fibres*	*Chemical Nature*	*Physical Property*	*Types of Dyes Used*
1.	Cotton	Cellulose fibre (polymer of cellobiose)	Hydrophilic	Direct dyes, Reactive dyes Azoics, vat dyes, mordant dyes
2.	Wool	Protein fibre (Natural Polyamide)	Hydrophilic	Acidic and basic dyes
3.	Silk	Protein fibre (Natural Polyamide)	Hydrophilic	Direct dyes, Acidic, Basic dyes
4.	Cellulose acetate	Acetylated cellulose fibre	Hydrophilic	Disperse dyes, Solvent dyes, Vat dyes
5.	Nylon	Synthetic (Linear polyamide)	Hydrophilic	Acidic dyes, Disperse dyes
6.	Terylene	Linear polyester	Hydrophilic.	Disperse dyes
7.	Orlon Acrilan	Polyacrilo-nitrile	Hydrophilic	Basic dyes, Vat dyes, Disperse dyes

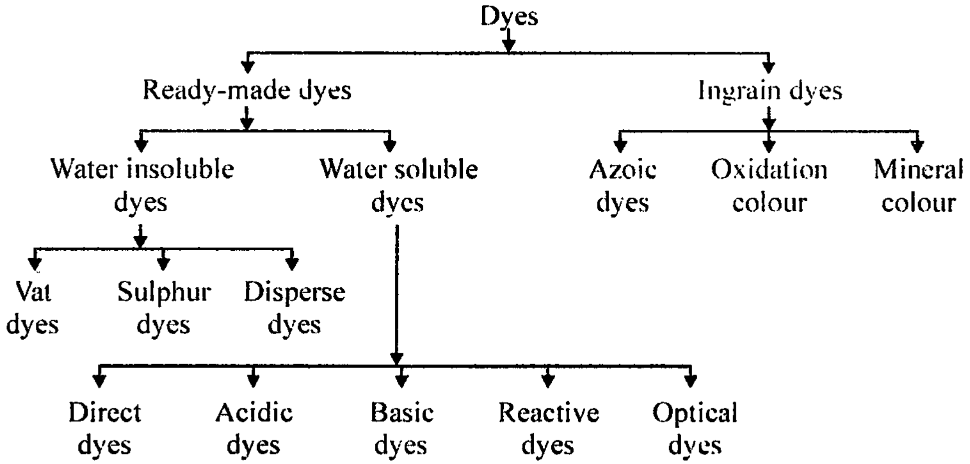
3

CHAPTER

CLASSIFICATION OF DYES ON THE BASIS OF MODE OF APPLICATION

Introduction

There are different methods by which dyes are applied on the fibres. This depends on the structure of the dye, nature of the fibre and physical properties such as solubility. Thus, a method used for one group of dyes may not be suitable for another group of dyes. Therefore, dyes can be classified on the basis of mode of application. When dyes are classified in this way, the dyes with similar structure will be placed in different groups. Some dyes are prepared in the final form and then applied on the fibres whereas some of them are prepared on the fibre itself (Ingrain dyes).



1. **Direct Dyes :** These are the dyes which can be directly applied in aqueous solution to cotton fibres. These dyes generally contain sulphonic acid groups and hence they are soluble in water. The dyeing is carried out in the presence of salts (Na_2SO_4) and hence they are called **salt dyes or substantive dyes.** They have affinity to celluosic fibres and are attached to them by H-bonding. The direct cotton dyes have poor light and washing fastness but they are extensively used due to their low cost and simplicity of dyeing process. *Examples :* Azo dyes (Congo red), stilbene, phthalocyanine dyes, etc.

2. **Acid Dyes :** These are water soluble dyes having acidic groups, like $-SO_3H$ or phenolic -OH. Hence they are used as their sodium salts (anionic dyes). They have affinity for the protein

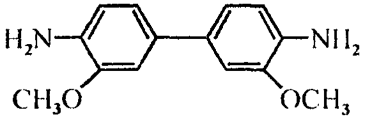
fibres like wool, silk (and even leather) but have no affinity to cotton. These are applied to fibres from an acidic bath containing dilute sulphuric or acetic acids. The dye is held on the fibre by ionic forces.

Examples : Nitro dyes (picric acid, naphthol yellow), azo dyes (Metanil Yellow, Orange II).

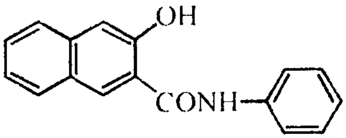
3. **Basic Dyes :** They contain basic groups ($-NH_2$, $-NR_2$) in the color base. When it is treated with acid the dye is formed (cationic dye). They can be directly applied to protein fibres like wool, and silk. However, they have poor affinity to celluosic fibres. Hence, cellulosic fibres are first treated with an intermediate compound called *mordant* such as tannic acid and then it is dyed. The basic dyes form brilliant shades but they do not have good fastness to light. They are used when these properties are not very much needed. These dyes are the earliest known synthetic dyes as Perkin's mauve was the first synthetic basic dye.

Examples : Triphenylmethane dyes (Crystal violet, Malachite green, Megenta), xanthene dyes (Rhodamine B), thiazine dyes (Methylene blue).

4. **Developed Dyes (Ingrain Dyes) :** These are not the readymade dyes but they are formed on the cellulosic material itself. As the dye is developed on the fibre they are called *developed* or *ingrain dyes*. The fibre is impregnated with the coupling component followed by treatment with the solution of diazonium salt. The azoic couplers are arylamides of 3-hydroxy-2 naphthoic acid (BON acid) which belong to naphthol AS series. The diazonium salt is derived from the fast bases. The coupling takes place on the fibres itself at low temperatures forming the insoluble azoic dye. Hence they are also called *ice colours*. They give brilliant shades with very good light and washing fastness. They are not suitable for protein fibres like wool and silk as they are sensitive to alkali which is used as the medium for coupling.



Fast Blue B Base
(Azoic base)



Naphthol AS
(Azoic Coupler)

There are also other examples of ingrain dyes. Aniline Black is an ingrain dye as it is produced by heating the fibre in a solution containing aniline salt and an oxidizing agent like $KClO_3$. These are called *Oxidation colours*.

5. **Mordant Dyes :** Mordant is an intermediate organic or inorganic compound which is used to fix a dye on the fibre. The mordant dyes have the groups capable of forming stable complexes with the metal atom. The type of the mordant used depends on the nature of the fibre and the structure of the dye molecule.

(*i*) *Basic Mordants* are hydroxides of Cr, Al, Fe, Sn, Co, etc., which are used for acidic dyes.

(*ii*) *Acidic Mordants* such as tannin or tannic acid which are used for basic dyes.

Mordants are used for dyes which have low affinity for the fibres *i.e.*, they are used to increase the dye-fibre affinity. The mordant dyes have good fastness property. The dye and mordant combine to form a "*lake*" (a coloured substance formed by combination of a dye with a mordant) which has brilliant colour. The fibres may be treated with the mordant before or after the application of the dye. Now-a-days the metal complex of the dye is prepared in advance and then applied to the fibre.

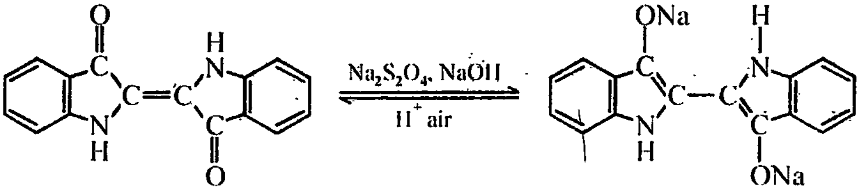
Examples : Anthraquinone dyes (alizarin), azo dyes (Eriochrome Black T). Alizarin is applied to cotton mordanted with $Al(OH)_3$.

Chrome dyes are a type of mordant dyes for which chromium is used as mordant for dyeing mainly for protein fibres like wool and leather. The dyed wool is treated with $Na_2Cr_2O_7$ in the presence of formic acid which reduces it to $Cr(OH)_3$. This forms a complex with wool and the process is called chroming. Chrome dyes have light and washing fastness but they are dull.

Examples : Eriochrome Black T, Eriochrome Red B.

6. **Vat Dyes :** These dyes are insoluble in water and hence cannot be directly applied to the cellulosic fibres. When such a dye is reduced by sodium hydrosulphite ($Na_2S_2O_4$) in an alkaline medium, colourless leuco compound is formed. This compound is soluble in alkali. This process of reduction and solubilising is known as *vatting*. The carbonyl group is reduced to phenolic hydroxyl group which is soluble in alkali. The fibres are immersed in the solution of the leuco compound which has affinity to cellulosic fibres. The original dye is then regenerated by air oxidation in the presence of mild acid. They are mainly used for cotton and cellulosic fibres. They are not suitable for wool and silk because the fibres are damaged in alkaline medium. They have low affinity for synthetic fibres.

Example : Indigoid dyes (Indigo), Anthraquinone dyes (Indanthrene Yellow GK). The anthraquinone vat dyes are found to have the highest fastness properties among the synthetic dyes.



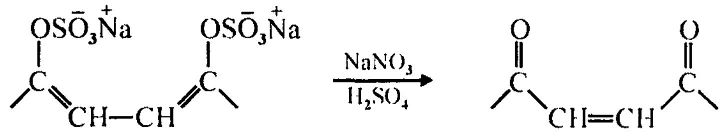
Indigo Dye
(Coloured, Insoluble)

Leuco Compound
(Colourless, Soluble)

Earlier indigo was fermented in the wooden vats with vegetable matter and released hydrocarbons acted as the reducing agent.

Solubilized Vat Dyes

These are an extension of the vat dyes. They are sodium salts of the sulphuric estes of leuco compounds. The fibre is impregnated with the vat solution and treated with an oxidixing agent ($NaNO_3$ solution) followed by an acid (dilute H_2SO_4). The dye is regenerated on the fibre by hydrolysis and oxidation. They have two advantages over vat dyes. They are stable and can be easily stored, whereas the sodium salts of leuco compounds are prone to air oxidation. Further, since no alkali is involved in the process, they can be applied to wool unlike vat dyes. These dyes are used more extensively for cotton than wool. These dyes belong to indigoid and anthraquinone class of dyes.



Solubilised Vat dye Dye

7. **Sulphur Dyes :** They are also insoluble dyes similar to vat dyes. They are reduced and solubilised by hot sodium sulphide in alkaline medium. The sulphur dyes have complex structures having disulphide linkages. On reduction they split into simpler molecules which are water soluble. The cellulosic fibres are impregnated with this solution for which they have affinity. Then the original dye is regenerated by atmospheric oxidation.

$$\underset{\text{Sulphur dye}}{R{-}S{-}S{-}R} \quad \underset{\text{air (O)}}{\overset{Na_2S.\ 2(H)}{\rightleftharpoons}} \quad \underset{\text{Solubilised dye}}{2R{-}SH}$$

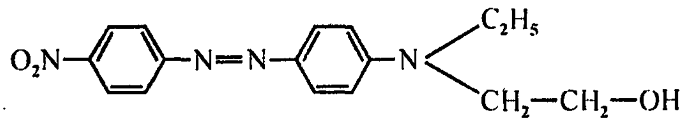
Sulphur dyes are cheap and give dark shades. They have very good fastness towards light and washing, but their drawback is that they are affected by chlorine. They cannot be applied to wool and silk as they are damaged by alkali and sodium sulphide.

Examples : Sulphur Black T for umbrella cloth.

Sulphurised vat dyes are obtained by sulphurisation (thionation) of antraquinone and indophenol derivatives. They are insoluble and hence made soluble by reduction with sodium hydrosulphite ($Na_2S_2O_4$). The solution is applied to fibres and dye is regenerated by oxidation. They are inexpensive and have better fastness properties than sulphur dyes.

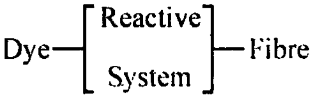
8. **Disperse Dyes :** The semi-synthetic and synthetic fibres like cellulose acetate, polyamides, etc., are hydrophobic fibres. Hence they cannot be dyed by aqueous solutions of dyes. These insoluble dyes are finely ground and dispersed in water using suitable dispersing agent. These microfine dispersions are applied to fibres either by using organic carriers or by using high temperature and pressure. The fine particles of the dye diffuse into the material of the fibre and are held by adsorption. The nitro, azo, and anthraquinone dyes are used as dispersed dyes. They are supplied as a mixture of insoluble dyes and dispersion agent in the powder form. These dyes must have low molecular weight and should have a group like that in ethanolamine ($-NH-CH_2 CH_2OH$), which helps in dispersion.

Example of disperse azo dye is Celliton Scarlet B.



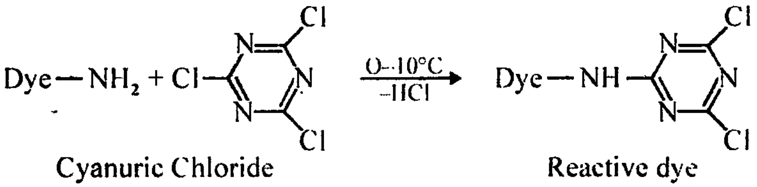
Celliton Scarlet B

9. **Reactive Dyes :** The reactive dye molecule consists of a dye (with chromophore) attached to a fibre reactive system. These are mainly used for cotton and cellulosic fibres. The reactive system is a heterocyclic compound containing groups which chemically react with hydroxyl groups of cellulose. Hence, the dye molecule gets attached to the fibre by means of covalent bonds.

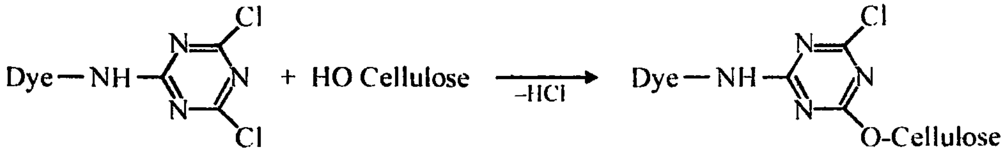


The reactive dyes can be derived from azo, antraquinone and phthalocyanine dyes. The most common fibre reactive system is cyanuric chloride (*s*-triazine trichloride) in which the chlorine atoms are reactive groups and can be replaced.

A reactive dye can be obtained by action of cyanuric chloride on a dye containing amino group at low temperature and in neutral medium. One of the chlorine atoms of the cyanuric chloride is substituted by amino group of the dye. This is called *cyanuration*.



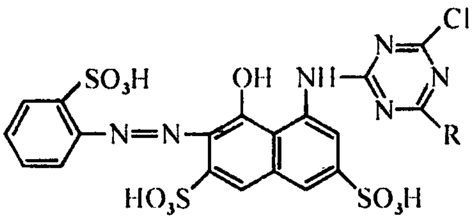
The reactive dyes are soluble in water due to the presence of sulphonic acid groups. Thus, the cotton fibres are impregnated with this solution and then heated under mild alkaline condition. The remaining chlorine atoms of reactive dye react with hydroxyl groups of cellulose forming covalent bonds. Thus, the dye and fibre are attached through an ether linkage. This is called the *fixation of the dye*. Finally, the fibres are washed with soap to remove the partially hydrolysed reactive dye molecules.



There are two types of reactive dyes based on cyanuric chloride.

(*i*) *Dichlorotriazine dyes* are more reactive and can be dyed at low temperatures (20-30°C) and they are called *cold brand reactive dyes, e.g.*, Procion Brilliant Red M-2B.

(*ii*) *Monochlorotriazine dyes* are less reactive and hence dyed at higher temperatures (80-90°C). Therefore they are called *hot brand dyes, e.g.*, Cibracron Brilliant Red B.



Procion Brilliant Red M-2B (R = Cl)

Cibracron Brilliant Red B (R = NH_2)

10. **Solvent Dyes :** These are insoluble in water but they are soluble in organic solvents such as alcohols, hydrocarbons, chlorinated hydrocarbons, esters, oils etc. They are used to dye oils, fats, waxes, printing inks, carbon paper and ribbons, soap, varnishes, etc. They are also used for bulk dyeing for plastics or synthetics by adding the dye in the molten polymer.

Examples : Azo, anthraquinone and triphenylmethane dyes.

In addition to these, there are many other dyes used in variety of applications such as food colours, photographic dyes, optical brightners etc., which are discussed in subsequent chapters.

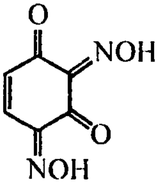
4
CHAPTER

CHEMICAL CLASSIFICATION OF DYES

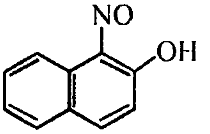
Introduction

The dyes have different chemical structures derived from aromatic and hetero-aromatic compounds. They mainly differ in chromophores and auxochromes. Hence, dyes can be classified on the basis of chemical structure, particularly considering the chromophoric system. However, it should be noted that the dyes of a particular chemical class may not have same properties or mode of application. Some of these classes may be further sub-classified.

1. Nitroso Dyes : They contain nitroso (–N = O) group as the chromophore. It may also be present as the oximino (= N – OH) group. They are derivatives of phenols and naphthols which are prepared by the action of nitrous acid. They are used as complexes with iron which gives green coloured lakes.

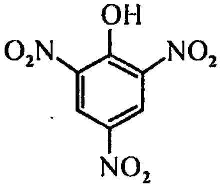


Fast Green O

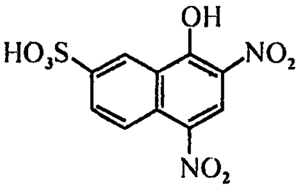


Naphthol Green G

2. Nitro Dyes : They contain nitro $\left(-N\begin{smallmatrix}=O\\ \rightarrow O\end{smallmatrix}\right)$ group as the chromophore and hydroxyl group as auxochrome. They are obtained by nitration of phenols. They are generally acidic dyes and have yellowish colours. However, their use is limited as they are not fast to light.



Picric acid

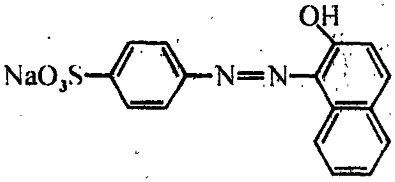


Naphthol Yellow S

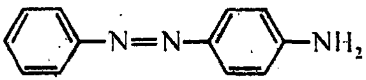
3. Azo Dyes : They contain an azo (–N = N–) group as a chromophore in between two aromatic rings. The azo dyes form the largest group among the synthetic dyes and give a wide variety of colours. They are further classified according to the number of azo groups, into monoazo, diazo dyes etc. The azo dyes are prepared by coupling a diazonium salt with an amine or phenol. They are also classified on the basis of the nature of the auxochrome.

(*a*) ***Basic azo dyes*** : Contain basic groups like $-NH_2$, $-NR_2$.

Mono Azo Dyes

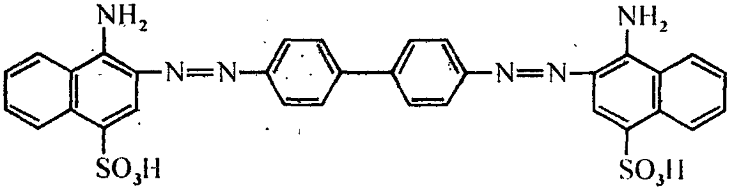


Orange II
(Acidic azo dye)



Aniline Yellow
(Basic azo dye)

Diazo Dyes



Congo Red

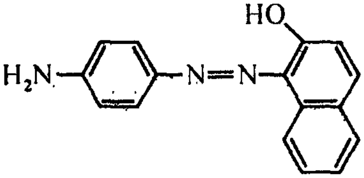
The azo dyes are also classified on the basis of mode of application as follows :

(*i*) Direction or Substantive Azo Dyes

These are the azo dyes which can be directly applied to cellulosic substrates such as cotton, linen, paper etc. They do not need the help of the intemediates called mordants for their application. The examples of direct azo dyes are, a disazo dye called cogo red and a tris azo dye called direct deep black.

(*ii*) Ingrain Azo Dyes

These are water insoluble azo dyes which are formed on the fibre itself. The fibre is dipped in the alkaline solution of a naphthol and then treated with a solution of the diazotised amine, which results in the formation of the azo dye on the fibre for example,



Para Red

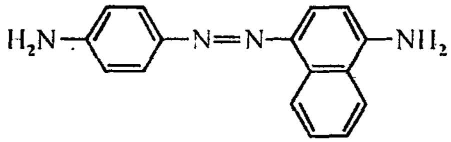
The aniline black is considered as a special case of ingrain dyes. The fabric is first dipped in a solution of aniline hydrochloride and then with solution of potassium dichromate solution in sulphuric acid. The aniline black is formed by oxidation on the fibre itself.

(*iii*) Mordant Azo Dyes

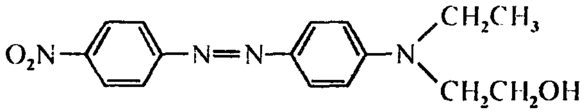
These are azo dyes which require a metal as a mordant. Chromium is commonly used as the salts sodium chromate, dichromate or chromium fluoride. The chromium salts can be applied to the fibre before dyeing (chrome-mordant method), along with the dye (metachrome method) or after dyeing (after chrome method). The application of mordant helps to increase the molecular surface, decrease in solubility, improve the brightness and fastness properties. Eriochrome black T and red B and diamond black F are examples of this type.

(*iv*) Synthetic Fibre Azo Dyes

There are several azo dyes used for dyeing synthetic fibres like rayon, nylon, terylene etc. They may be acidic, basic or disperse dyes.

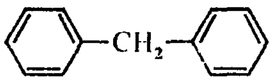


Orange Dye for rayon

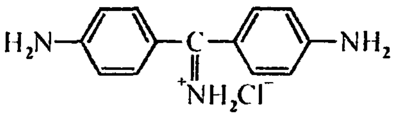


Celleton scarlet B (For cellulose acetate and nylon)

4. Diphenylmethane Dyes : They are derivatives of diphenylmethane. They are basic dyes used as salts.

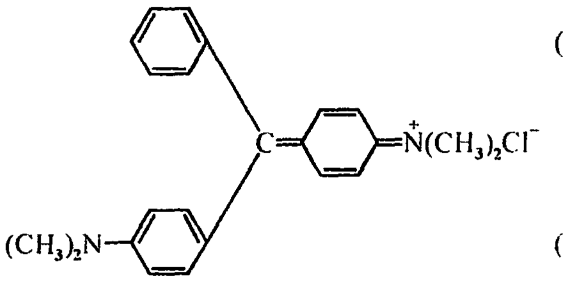


Diphenylmethane

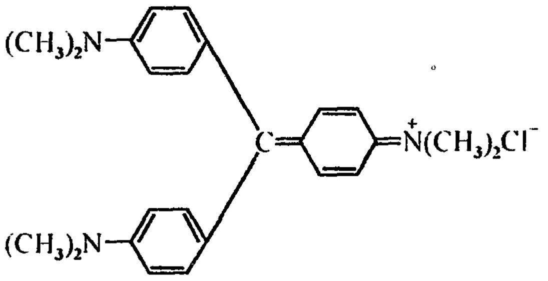


Auramine O

5. Triphenylmethane Dyes : They are derivatives of triphenylmethane containing $-NH_2$, $-NR_2$ or $-OH$ groups at para positions as auxochromes. They are however, colourless compounds called leuco bases. These compounds on oxidation give coloured bases which on treatment with acid give the salt. The dye contains the quinonoid group as the chromophore.

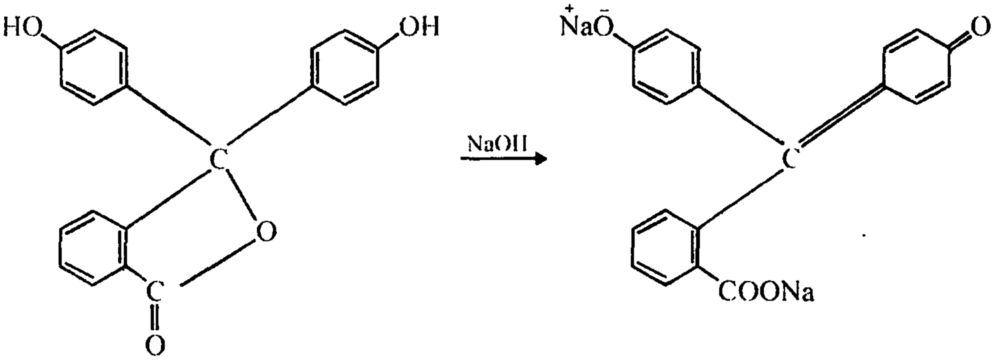


Malachite green



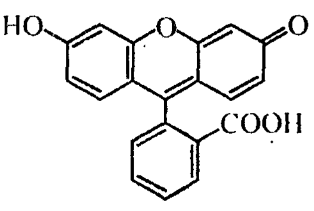
Crystal violet

6. Phthalein Dyes : They may also be considered as derivatives of triphenylmethane with hydroxy and carboxylic groups. They are prepared by condensation of phthalic anhydride with *m*-dihydroxyphenols or *m*-aminophenols in the presence of dehydrating agents. Phenolphthalein is a phthalein dye which is colourless in acidic medium and pink in alaline medium. It is mainly used as an indicator.

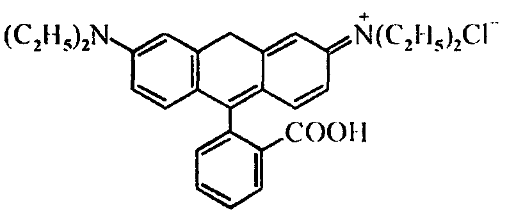


Phenolphthalein (colourless) Na-salt of phenolphthalein (coloured)

7. Xanthene Dyes : They are derivatives of xanthene (dibenzo-1, 4-pyran). They contain –OH, –NHR$_2$, –COOH groups as auxochromes. These dyes resemble phthalein dyes as they are also prepared by similar methods using phthalic anhydride. They also have quinonoid group as chromophore. These dyes give brilliant shades with fluorescence, but they lac light fastness. They also form bright coloured lies with metal salts.



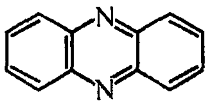
Fluorescein



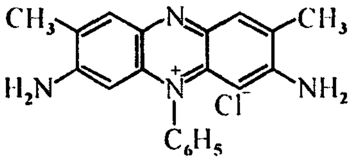
Rhodamine B

8. Heterocyclic Dyes : They are derivatives of heterocyclic rings with –NH$_2$ and –NR$_2$ groups as auxochromes. They contain the mixed heterocyclic rings of nitrogen, oxygen and sulphur atoms. They are all basic dyes and their salts are coloured. They are further classified on the basis of the type of heterocyclic rings present. The ring itself acts as the chromophore.

(*i*) ***Azine Dyes :*** They are derivatives of the heterocyclic ring called phenazine. They give variety of colours and are relatively inexpensive. These dyes are of historical importance because the first synthetic dye *i.e.*, Perkin's Mauve belongs to this group. They are used for dyeing of silk, wool and also cotton using mordants.

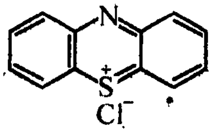


Phenazine

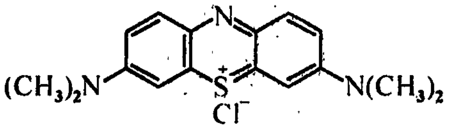


Safranine T

(*ii*) ***Thiazine Dyes :*** These are derivatives of the heteroxyclic ring phenothiazine with $-NH_2$, $-NR_2$ etc., groups as auxochromes. It is a basic dye used as a salt for paper and also for cotton and silk using mordants.

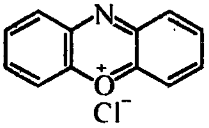


Phenathiazine

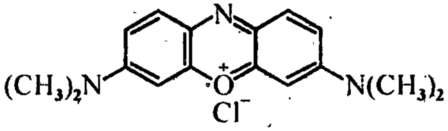


Methylene blue

(*iii*) ***Oxazine Dyes :*** They are derivatives of phenoxazine ring containing $-NR_2$, $-OH$ groups as auxochromes. The dye is in the form of an oxonium salt

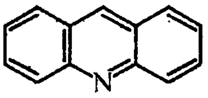


Phenoxazonium chloride

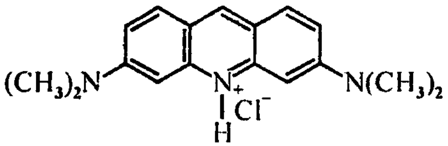


Capri blue GN

(*iv*) ***Acridine Dyes :*** These are derivatives of the heterocyclic ring called acridine. They also contain $-NH_2$ and $-NR_2$ groups as auxochromes. They are basic dyes used as salts mainly for leather.

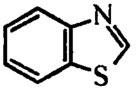


Acridine

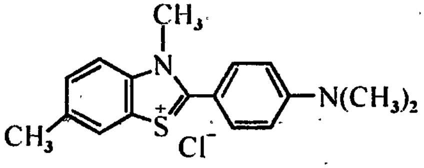


Acridine Orange R

(*v*) ***Thiazole Dyes :*** They are derivatives of the heterocyclic ring benzothiazole. They are basic dyes used as salts. They are suitable for cellulosic fibres and do not have good light fastness.

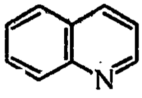


Benzothiazole

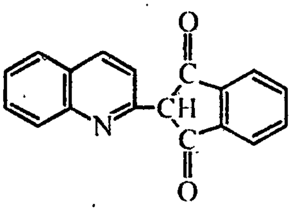


Methylene Yellow N

(*vi*) ***Quinoline Dyes :*** They are derived from quinoline ring and diketo indane ring. They are not suitable as dyes for fibres but used as, photographic sensitisers.

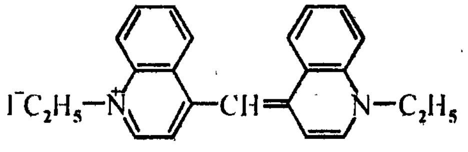


Quinoline

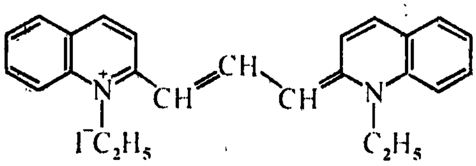


Quinoline Yellow

9. Cyanine Dyes : They contain two quinoline rings attached through a methine (=CH–) or polymethine (=CH–CH=CH–) groups. They are used as photographic sensitisers. They are further classified on the basis of the positions through which they are linked.



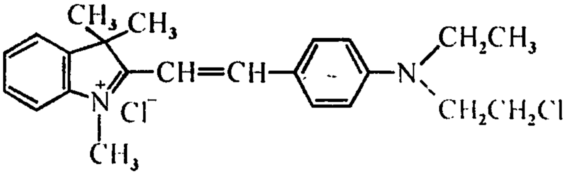
Cyanine



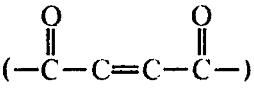
Pinacyanol

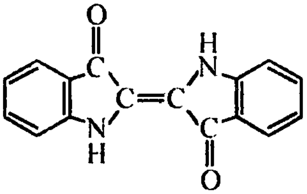
S. No.	*Type*	*Linkage*	*Position*	*Example*	*Sensitises to the colours*
(*i*)	Cyanine dyes	= CH–	4, 4′	Cyanine	Yellow, Orange, red.
(*ii*)	Isocyanine dyes	= CH–	2, 4′	Ethyl red	Green
(*iii*)	Pseudocyanine dyes	= CH–	2, 2′	Pseudo cyanine	Blue–green
(*iv*)	Carbocyanine dyes	= CH–CH=CH–	2, 2′	Pinacyanol	Red
(*v*)	Kryptocyanine dyes	= CH–CH=CH–	4, 4′	Kryptocyanine	

10. Polymethine Dyes : They consist of two aromatic or heterocyclic rings attached by one or more methine (=CH–) groups. They are basic dyes used for acrylic fibres.

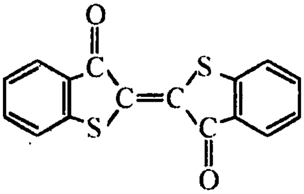


Astrazone Pink FG

11. Indigoid Dyes : They are derivatives of indiole and contain enedione  $(-\overset{O}{\overset{\|}{C}}-C=C-\overset{O}{\overset{\|}{C}}-)$ group as the chromophore Indigo is one of the oldest dye of this type and it is used extensively due to its special hue and very good fastness property. Many important derivatives of indigo have been prepared. They are important vat dyes.

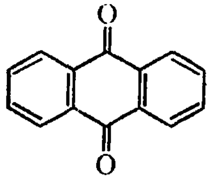


Indigo

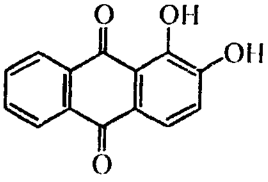


Thio indigo

12. Anthraquinone Dyes : They are derivatives of anthraquinone, with *p*-quinone system as the chromophore. It contains –OH, –NH_2, –NHR, –NHR, –NH, –Ar, –NHCOR groups as auxochromes. They are used as mordants as well as vat dyes. They have good fastness properties with textile fibres. They are also used for dyeing non-textile materials like paper, rubber, plastics, printing ink, etc.

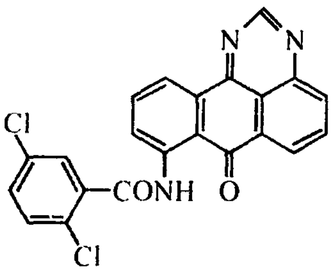


Anthraquinone



Alizarin

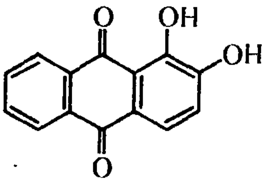
The derivatives of anthraquinone which contain heterocyclic rings and also acylamino groups are called indanthrene or Algol dyes. They are used for dyeing textiles including synthetics like nylon.



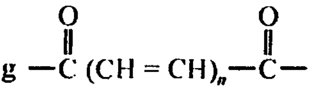
Indenthren Yellow 4GK

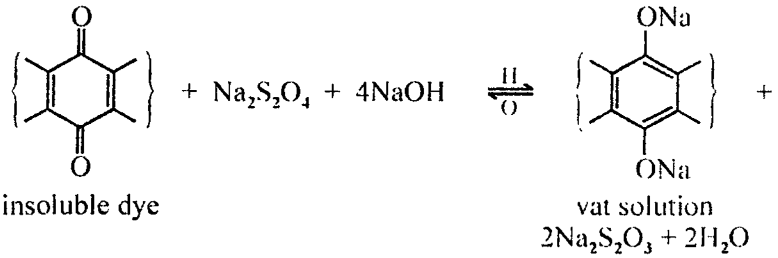
Anthraquinone dyes are further classified as follows :

(*i*) ***Anthraquinone mordant dyes :*** They contain groups such as hydroxyl or carboxyl group, which can combine with metal to form insoluble compounds called *lakes*.

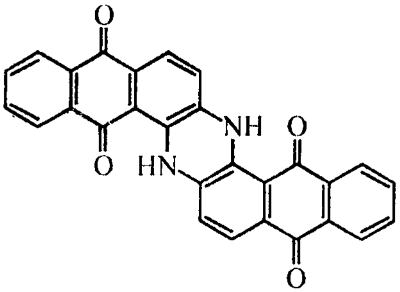


Alizarin
(Dye for cotton using $Al(OH)_3$ as mordant)

(*ii*) ***Anthraquinone vat dyes :*** These are vary important class of vat dyes. They are derivatives of anthraquinone containing heterocyclic or other poly cyclic rings. They may also contain the grouping  $-\overset{\displaystyle O}{\overset{\|}{C}}(CH=CH)_n-\overset{\displaystyle O}{\overset{\|}{C}}-$ attached to heterocyclic rings. They have high molecular weight and are insoluble in water. They are available in various brilliant colours and shades of exceptional fastness. They are mainly used for dyeing of cotton, wool, silk and nylon and also for printing. The anthraquinone vat dyes are first reduced by sodium hydrosulphite ($Na_2S_2O_4$) in alkaline medium to get a soluble form called 'vat.' Then the fabric is immersed in the vat solution. On exposure to air the dye is regenerated on the fabric by oxidation.



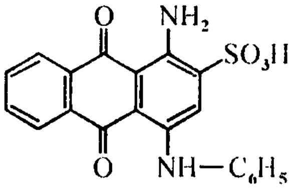
Example,



Indanthrone blue

(*iii*) ***Anthraquinone acid dyes :*** These are water soluble anthraquinone derivatives which have the solubilizing sodium sulphonate groups (SO_3Na). They are used for dyeing wool, silk, nylon leather and paper. These dyes are particularly fast when applied to wool in acidic medium.

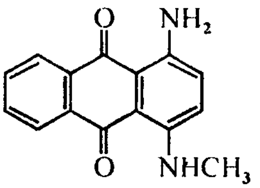
Example



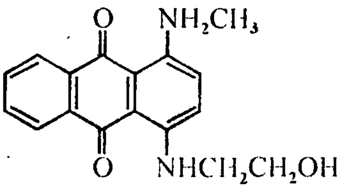
Solway ultra blue B

(*iv*) ***Anthraquinone disperse dyes :*** These are insoluble derivative of anthraquinone, mainly used for dyeing synthetic fibres like acetate, polyester and polyamide. They have good light fastness. However exposure to gas fumes causes fading and change of shade. This difficulty is overcome by substituting the ring with halogen, hydroxy, alkoxy, nitro, cyano groups.

Examples



Celliton fast violet 6B

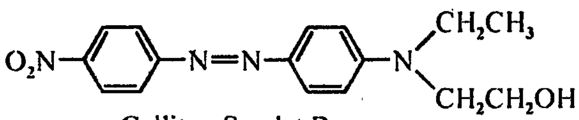


Dispersol blue

1. ***Reactive Dyes :*** The other class of dyes do not have good washing fastness when applied to cotton and cellulosic fibres. Hence reactive dyes were specially developed for those fibres. As the name suggests they actually react with the hydroxyl groups of cellulose through a fibre reactive system. Hence they will have good washing fastness when applied to cotton. They may be derived from azo, anthraquinone or other chromophoric system.

2. ***Disperse Dyes :*** The semi-synthetic and synthetic fibres like cellulose acetate, nylon polyester, rayon etc. are hydrophobic fibres. Hence they cannot be dyed by aqueous solution of dyes. Disperse dyes are insoluble but they are finely ground and dispersed in water using suitable dispersing agents. These microfine dispersions are applied to fibres by using organic carriers or by using high temperature and pressure. The fine particles of the dye diffuse into the material of the fabric and then held by adsorption. The disperse dyes may be nitro, azo or anthraquinone dyes. These dyes must have low molecular weight and should have groups like ethanol amine ($NHCH_2CH_2OH$) which help in the formation of dispersion.

Disperse azo dye



Celliton Scarlet B

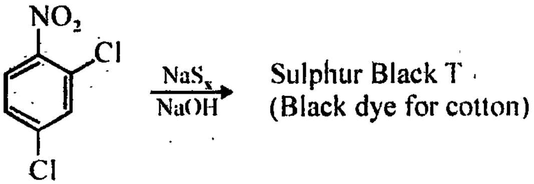
Disperse anthraquinone dye, example dispersol blue.

3. ***Basic Dyes :*** They are derivatives of heterocyclic rings containing $-NH_2$ and $-NR_2$ groups as auxochromes. The heterocyclic ring or a quinonoid system acts as a chromophore.

Their salts with acid are coloured (cationic dye). They can be directly applied to protein fibres like wool and silk. However they have poor affinity to cotton. Perkins mauve was the first synthetic basic dye prepared. They have brilliant shades but do not have good fastness to light. Hence they are used for dyeing leather, paper etc.

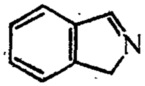
Examples : Triphenyl methane dyes (malachite green), xanthene dyes (Rhodamine B), thiazine dyes (methylene blue).

13. Sulphur Dyes : The structure of these dyes is not well established. When aromatic amines, aminophenols, chloronitro compounds, etc., are heated with sodium polysulphide, coloured compounds with complex structures are obtained, which are called sulphur dyes. They are insoluble and have fairly good washing and light fastness. They are prepared in large scale (next to azo dyes) as they give dark shades of blue, green, black and brown colours.

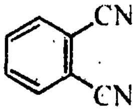


14. Phthalocynines : They are metal complexes of isoindoles and considered as the derivatives of the heterocyclic compounds called porphyrazine. Their colour (violet, blue, green) depends on the metal (Cu, Fe, Mg etc.) and also on the substitution in the ring.

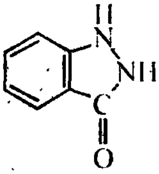
The first phthalocynine was formed as an impurity when phthalic anhydride was heated in an iron vessel. Copper phthalocyanine (Monastral Fast blue BS) was prepared by hearing phthalonitrile with cuprous chloride. The dyes can also be formed directly on the fibre by heating a precursor called phthalogen with Cu or Ni salts.



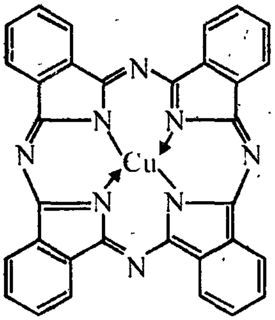
Isoindole



Phthalonitrile



Phthalogen



Monastral Fast Blue BS

These compounds are extremely stable to acid, alkalis, heat, light, etc. They are used as the pigments for paints, printing inks, plastics, rubber, fibres, etc. They can be made soluble by sulphonation and used as direct dyes.

5

CHAPTER

COLOUR AND CHEMICAL CONSTITUTION

5.1. Bathochromic and Hypsochromic Effects

If a structure change in a dye molecule shifts the absorption towards higher wavelengths, it will deepen the colour of the dye in accordance to the following sequence :

yellow → orange → red → purple → violet → blue → green

Any group or a factor that produces the deepening of the colour in accordance to the above sequence is known as *bathochrome* and the effect, *i.e.*, the deepening of colour, is known as *bathochromic* effect.

When a bathochromic group is introduced into a dye, it will increase the resonance which in turn decreases the energy gap of the *ground state-excited state transitions* with visible colour production. The shifting of the absorption towards higher wavelengths with the introduction of bathochromes has been illustrated in Fig. 5.1.

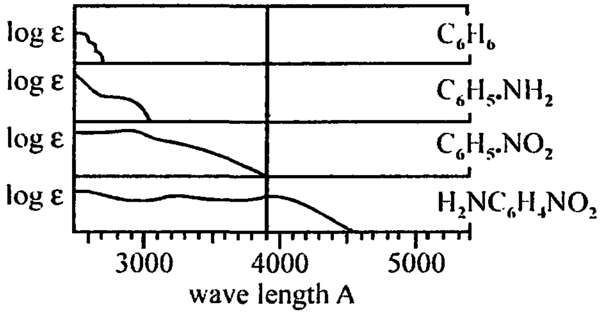


Fig. 5.1 : Absorption spectra of benzene, aniline, nitrobenzene. and *p*-nitroaniline.

If a structural change in a dye molecule shifts the absorption from higher to lower wavelength, it will lighten the colour of the dye in accordance to the following sequence :

green → blue → violet → purple → red → orange → yellow

Any group or a factor that will lighten the colour of the dye in accordance to the above sequence is known as *hypsochrome* and its effect produced is known as *hypsochromic effect.* The hypsochrome group diminishes resonance, often by forcing π-orbitals out of coplanarity.

Changes in the structure of a dye due to which the intensity of absorption increases are said to be *hyperchromic.* On the other hand, structural changes which decrease the intensity of absorption are termed as *hypochromic.*

Bathochromic, hypsochromic, hypochromic and hyperchromic effects are represented by the absorption spectra (Fig. 5.2) which are obtained by plotting the intensity of absorption against wavelength (λ).

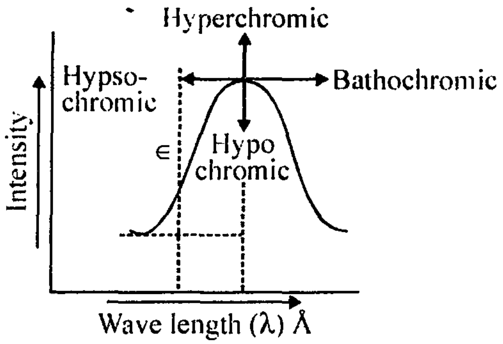
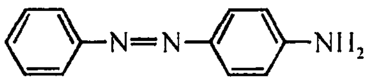


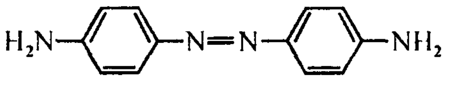
Fig. 5.2 : Absorption spectrum of a particular dye.

The introduction of certain groups in a dye molecule causes the bathochromic and hypsochromic effects. This is summarised in the following facts :

(*i*) The bathchromic effect is produced by the introduction of additional auxochromes such as –OH and $-NH_2$ groups in a dye molecule. For example, when an additional $-NH_2$ group comes in the aniline yellow, chrysodine is produced which is an orange coloured dye.



aniline yellow



chrysodine (orange)

(*ii*) In addition to the auxochromes, the *o*- and *p*- directing groups, when present on the aromatic ring, also deepen the colour. For example, alkyl, aryl and halogens deepen the colour and are therefore known as bathochromes.

(*iii*) When the alkylation of amino group is done, it produces the bathochromic effect. On the other hand, when the alkylation as well as acylation of phenolic groups are done, these will produce hypsochromic effect. A good example of illustrating the bathochromic effect is to introduce six methyl groups in pararosaniline (red dye) nucleus to give crystal violet (violet colour).

$-NH_2 \longrightarrow -N(CH_3)_2$ *bathochromic effect.*

$-OH \longrightarrow OCH_3$ or $-OCOCH_3$ *hypsochromic effect.*

(*iv*) The bathchromic effect is also produced by salt formation because it increases the possibility of resonance which is again due to the formation of dye ions.

$-NH_2 \longrightarrow NH_3^+Cl$ *bathochromic effects.*

$-OH \longrightarrow O\,Na^+$

5.2. Colour and Chemical Constitution

Colour : *The psychological sensation which is produced when the light of certain wavelength reaches the eye is known as the colour.* Thus, colour is dependent on and varies with the nature of the light illuminating the coloured substances.

The ordinary light consists of electromagnetic radiations of varying wavelengths which can be categorised in three headings :

Part of light	*Range of wavelength of light*
Ultraviolet light	1000–4000 Å
Visible part (white light)	4000–7500 Å
Infrared	7500–100,000,0 Å

The range of wavelength visible to human eyes is consisting of electromagnetic radiations covering rays of wavelength in the region 4000 to 8000 Å. Radiations below 4000 Å and above 8000 Å in the near vicinity are invisible and lie in ultraviolet (U.V.) and infrared (I.R.) regions respectively. Thus, the visible region is responsible for producing a definite colour to a particular substance. In the visible range of wavelength, light is composed of seven different colours namely, violet, indigo, blue, green, yellow, orange and red (VIBGYOR). The sequence of ultraviolet, visible (with specral colours) and infrared regions is shown in Fig. 5.3.

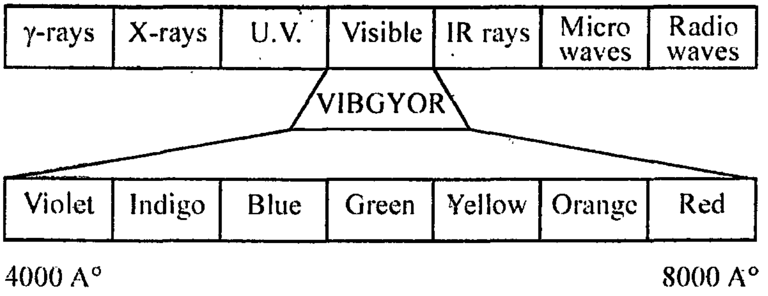


Fig. 5.3 : Sequence of UV, visible with spectral colours and IR.

The energy associated with a light wave is proportional to its frequency. Thus high frequency radiations have high energy. All radiations travel with same velocity. But they differ in the wavelength and frequency.

$E = h\nu$ Where h = Planck's constant

But $c = \nu\lambda$ c = Velocity of light

Therefore $E = hc/\lambda$ ν = frequency

λ = wavelength

When white light is incident on a substance, colour is obtained in the following different ways :

(*i*) If the white light is reflected completely, the substance will appear light.

(*ii*) If the white light is absorbed completely, the substance will appear black.

(*iii*) If all the wavelengths of white light are absorbed except a single narrow band which is reflected, the colour of the substance will be the colour of the reflected band. For example, if the substance absorbs all wavelengths except one single band say the blue (4500 Å) which is reflected, the substance will appear blue.

(*iv*) If only a single band of white light is absorbed, the substance will have the complementary colour of the absorbed band. For instance, blue colour is produced if light of 5900 Å (region of yellow colour) is absorbed because the composite of the remaining wavelengths which are reflected gives the psychological sensation of blue colour. Thus, blue and orange are said to be complementary colours because the absorption of one from white light gives the other. The relation of colour absorbed and colour visualised with respect to a given range of wavelength is given in Table 5.1.

Table 5.1 : Colour absorbed and colour visualised with respect to wavelength regions

Wavelength Å	*Colour absorbed*	*Colour visualised*
4000 – 4350	Violet	Yellow-green
4350 – 4800	Blue	Yellow
4800 – 4900	Green-blue	Orange
4900 – 5000	Blue-green	Red
5000 – 5600	Green	Purple
5600 – 5800	Yellow-green	Violet
5800 – 5950	Yellow	Blue
5950 – 6050	Orange	Green-blue
6050 – 7500	Red	Blue-green

5.3. Relation Between Colour and Chemical Constitution

The colour of a compound is related to its chemical constitution. It is evident from the following examples.

(*i*) Benzene is colourless while its isomer fulvene is coloured.

(*ii*) Reduction of coloured organic compounds results in the loss of colour and oxidation of the reduced compounds regenerates the original colour (Graebe and Libermann 1868).

$$\text{Coloured organic compound} \underset{\text{oxidation}}{\overset{\text{reduction}}{\rightleftharpoons}} \text{Colourless compound}$$

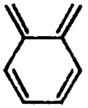
From this example, Graebe and Libermann concluded that unsaturation was responsible for the development of colour.

The relation between colour and chemical constitution of a substance has been explained by different theories which are described as follows :

1. Witt's Theory (Chromophore-auxochrome Theory) : According to this theory (1876). there existed a relationship between colour and chemical constitution of a compound and further a dye is made up of two parts, *chromophores* and *auxochromes*.

(*a*) ***Chromphores :*** The colour usually appears in an organic compounds if it contains certain unsaturated groups. Witt called these groups as the chromophores (Greek *chroma*-colour, and *phoros*, bearing). For example, diazomethane contains the unsaturated group, azo group, and is, therefore, yellow in colour. On reduction, the azo group is reduced and methylhydrazine is produced which is colourless because it does not contain unsaturated group. Some important chromophores are listed in Table 5.2.

Table 5.2 : Some Typical Chromophores

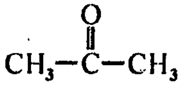
$-N=O$	nitroso		*o*-quinonoid
$>C=S$	thiocarbonyl	$-\overset{\vert\vert}{C}=N-$	azomethine
$-N=N$	azo	$-N\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O}$	nitro
$-N=N\rightarrow O$	azoxy		
$-N=N-NH$	azoamino	$>C=O$	carbonyl
	*p*-quinonoid	$>C=C<$	ethylenic

The chromophores listed in the above Table are of two types :

(*a*) *Independent chromophores :* This type includes such chromophores when a single chromophore is sufficient to impart colour to the compound. Examples of such chromophores are

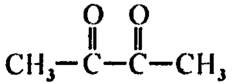
$-N=O$, $-NO_2$, $-N=N$, $-N=N\rightarrow O$, $-N=N-NH$, $-N=N\rightarrow O$, *p*-quinonoid, etc.

(*b*) *Dependent Chromophores :* This type includes such chromophores when more than one chromophore is required to impart colour. Examples of such chromophores are $>C=O$, $>C=C<$, etc. This type is exemplified by various examples. For example, acetone, containing one carbonyl groups, is yellow. A single C = C group does not produce colour in the compound but if a number of them are present in conjugation, the colour usually appears. For example, ethylene, $CH_2 = CH_2$ is colourless while $CH_3\ (CH_2)_6CH_3$ is yellow.



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

acetone

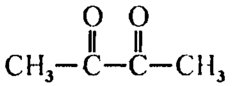


$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

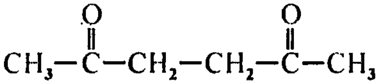
biacetyl

Diphenylpolyenes provide another example. The formula of these is $Ph\ (CH = CH)_nPh$. When n = 0, 1 or 2, the compound is colourless. However, when n is 3, the compound becomes yellow and when n is further increased, the colour gets deepened, *i.e.*, when n is 5, the colour is orange, when n is 7, the colour is copper-bronze and when n is 11, the colour is violet-black.

The shade of the colour is also influenced by the proximity of the chromophores. If these are separated by other groups, the compound becomes colourless. For example,



$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$ is yellow in colour while



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$ is a colourless compound.

Compounds containing a chromophoric group were called as **chromogens** by Witt.

(*b*) ***Auxochromes*** : A chromogen may be coloured but it does not represent a dye. Witt pointed out that the presence of certain groups in a chromogen leads to a deepening of the colour although these groups are not chromophores themselves and do not impart colour to the compound when present without the chromophore. Witt called these groups as **auxochromes** (Greek *auxein* to increase, and *chroma*-colour).

Witt had listed a number of auxochromes which are given in Table 5.3.

Table 5.3 : Some Typical Auxochromes

Name	*Group*	*Name*	*Group*
Amino	$-NH_2$	Chloro	$-Cl$
Methylamino	$-NHCH_3$	Methyl	$-CH_3$
Dimethyl amino	$-N(CH_3)_2$	Methoxy	$-OCH_3$
Sulphonic acid	$-SO_3H$	Cyano	$-CN$
Hydroxy	$-OH$	Acetyl	$-COCH_3$
Carboxylic acid	$-COOH$	Acetamido	$-CONH_2$

The auxochromes serve two functions, namely.

(*a*) *They increase the intensity of the colour* : This is illustrated by the following example :

(*i*) Benzene (no chromophore) is colourless.

(*ii*) Nitrobenzene ($-NO_2$ as a chromophore) is pale yellow.

(*iii*) *p*–Nitroaniline (NO_2 as a chromophore and $-NH_2$ as an auxochrome) is dark yellow.

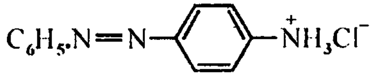
(*b*) *They make the chromogen a dye by fixing it to the fabric or the material to be dyed either by association or by salt formation.* The fixing of the dye to the fibre is generally due to the formation of chemical bond between the fibre and the auxochrome. This is best illustrated by the following example :

C_6H_6

benzene

$C_6H_5.N{=}N.C_6H_5$

azobenzene (coloured but not a dye)



p-aminoazobenzene hydrochloride (a dye, aniline yellow)

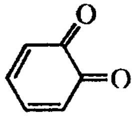
Auxochromes are mainly of two types :

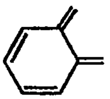
(*a*) **Bathochromic auxochromes** : These are the groups which increase the depth of the colour. These shift the absorption maxima from the violet towards the red and thereby bring about the deepening of the colour. It is called *red shift*. When the hydrogen atoms in an amino group $-NH_2$ are replaced by $-NHR$ or $-NR_2$, a bathochromic effect is produced.

(*b*) **Hypsochromic auxochromes :** These are the groups which decrease the depth of the colour. These shift the absorption maxima from the red to violet and this results in the fading of the colour. It is called *blue shift*. A hypsochromic effect is observed when $-OH$ or $-NH_2$ group of a dye is replaced by $-OCOCH_3$ or $-NHCOCH_3$ group respectively.

Witt's theory has been proved extremely useful empirical guide in developing many of the dyes.

2. Armstrong's Theory (1888) : The colour of a compound is due to the presence of quinonoid type of structure (ortho or para). This was based on the observation that benzene is colourless whereas benzoquinone is yellow coloured. Thus according to this theory the aromatic compounds (benzenoid structure) which can change into quinonoid structure are coloured. The quinonid ring is only a combination of the chromophores *i.e.*, C = C and C = O. Thus Armstrong's theory can be considered as an extension of chromophore theory. Hence this is called *quinonoid theory* to explain the cause of the colour in the compounds.


o-benzoquinone


o-quinonoid structure

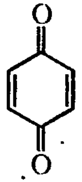

p-benzoquinone structure


p-quinonoid structure

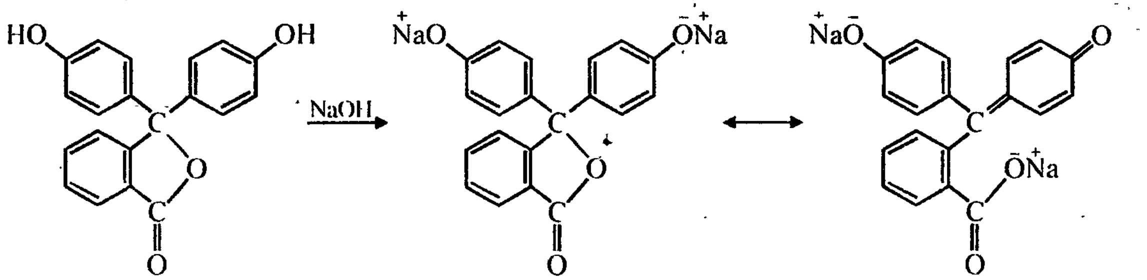
On the basis of this theory, it could be possible to explain the colouring properties of some of the important compounds. For example,

(*i*) Benzene is cloudless whereas benzo-quinones are coloured.


benzene (colourless)


p-benzoquinone (yellow).

(*ii*) For example, when phenolphthalein is present in benzenoid form, it is colourless. But its sodium salt can assume quinonoid structure. Hence it is coloured (pink) in alkaline medium.



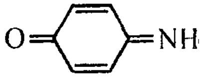
Phenolphthalein (colourless)

Na- salt (pink coloured)

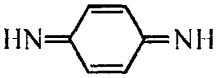
p-quinonoid

However, Armstrong's theory has the following limitations.

(*i*) The iminoquinone and di-iminoquinone have quinonoid structures, yet they are colourless.

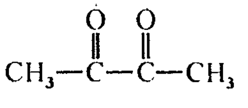


Iminoquione



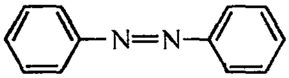
De-iminoquinone

(*ii*) There are large number of coloured compounds but they cannot be represented by quinonoid structures.



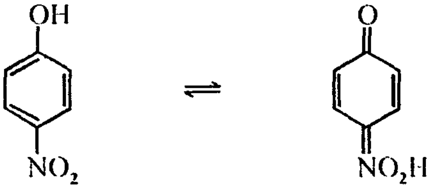
$$CH_3-\overset{\overset{O}{\parallel}}{C}-\overset{\overset{O}{\parallel}}{C}-CH_3$$

Diacetyl



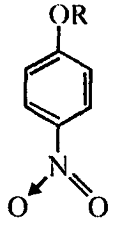
Azobenzene

(*iii*) Although this theory has a number of limitations, yet this theory stimulated further research on the problem of colour and constitution. It has found some practical applications in the dye industry. Armstrong attempted to explain the colour of *p*-nitrophenol (I) on the basis of a quinonoid structure (II) but there was no evidence for the existence of such a structure.

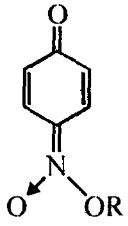


(I) (II)

The actual preparation of two series of ethers (III) and (IV) of *p*-nitrophenol by Hantzsch proved that there exists the phenomenon of tautomerism in nitrophenols.

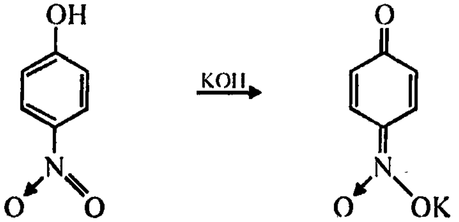


(III)
colourless



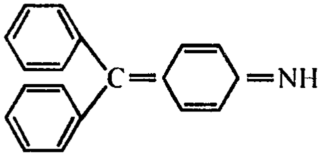
(IV)
coloured

Hantzsch presumed that a change in colour of a compound could be attributed to a change in structure from benzenoid to quinonoid or vice versa. However, Hantzsch also realised that *colour is an additive property.* It means that the state of the molecule as a whole should be taken into consideration for explaining the colour of a compound. For example, the groups $-NO_2$ and $-ONa$, if simultaneously present, impart visible colour but if present alone do not do so. It means that the two groups must be interacting to yield a new structure for the molecule. Thus, the change of colour is taken to be the evidence of the change of structure. This phenomenon is known as *chromoisomerism.*

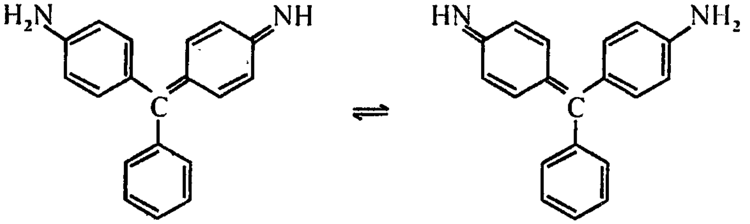


3. **Baeyer's theory** : According to this theory (1907), the colour might be due to the structural oscillation of the quinonoid condition between the two benzene rings. The change from one from to the other involved movement of electrons and not movement of atoms.

This theory is illustrated by considering fuchsonimine. It is a colourless. If an amino group is introduced in one of the benzene rings, it produces deeply coloured Deobner's violet. This colour is due to the structural oscillation of the quinonoid condition between the two benzene rings.



Fuchsonimine (colourless)



Deobner's violet (coloured)

4. **Nietzki's theory** : According to this theory, the colour of dye is deepened by the addition of substituents. Further the deepening of colour is proportional to the increase in molecular weight. For example, when benzene is replaced by naphthalene in azo dyes, the colour is deepened from yellow to red.

The Nietzki's rule is generally true but for the deepening of the colour the nature of the groups added is important and not the weight of it. This can be understood by considering the compound, CH_3 –$(CH_2)_a$ –X– $(CH_2)_b$ – CH_3 in which X is the chromophore. If X remains same but *a* and *b* are having different values, it is interesting to note that the depth of the colour is found to be independent of *a* and *b*.

5. **Watson's theory** : According to this theory, the depth of the colour depends upon many other factors besides the length of the conjugated chain. If the weight of the dye is increased without changing the length of conjugated chain the shade becomes deeper because vibrations become slower due to increase in molecular weight. For example, fluorescein on bromination gives eosin which has a much deeper hue than fluorescein,

Similar to other theories, this theory is only empirical.

5.4. Modern Theories of Colour and Constitution

The current and most important theories called *valence bond theory and molecular orbital theory* explain plausibly the relation between colour and constitution. These theories are based upon the following concepts :

1. **Quantisation of light energy** : Light is quantised in the units of energy called *light quanta* or *photons*.

2. **Absorption of radiation by molecules** : A compound appears coloured if it selectively absorbs light in the visible region and reflects the light of wavelengths in the rest of the visible region. The amount of light energy absorbed in the visible spectrum is the only responsible factor for the shade of the colour.

The main function of the absorbed energy is to raise the molecule from the ground state energy, E_0 to the excited state, E_1 and the difference of energy, ΔE is the quantum of energy given by quantum theory equation (1),

$$\Delta E = E_1 - E_0 = h\nu = h\frac{c}{\lambda} \tag{1}$$

where h = Planck's constant

c = velocity of light

λ = wavelength of the absorbed radiation

The amount of energy absorbed, ΔE, depends upon the structural configuration of that dye. In other words, ΔE depends upon how tightly the electrons are bound in the bonds and accordingly the absorption will occur in U.V. or a particular region of visible range. For instance,

(*i*) If the electron of a molecule are tightly bound as in saturated compounds, no light of visible region will be absorbed but only light of ultraviolet region will be absorbed and hence the compound will appear colourless.

(*ii*) If the electrons of a molecule are loosely bound as in saturated compounds, the absorption may occur in the visible region and the substance will then appear coloured. For a coloured region and the substance will then appear coloured. For a coloured substance the value of ΔE lie between 71 and 35.5 k cal/mole as we pass from 4000 to 8000 Å. It means that if an organic substance is to be coloured, it must have mobile electrons which can be raised from ground to excited state, the values of ΔE being between 71 and 35.5 k cal per mole.

Now the question arises how ΔE is responsible for producing colour. This has been explained as follows :

As the electrons occupy definite orbitals, it means that ΔE and hence frequency of light absorbed must have definite value. But each value of the frequency of the absorbed light is associated with a particular line in the spectrum. Therefore, the spectrum of a compound will consist of a large number of lines corresponding to a large number of excited states of the large number of molecules constituting the compound. The lines appear as a band because the values of ΔE are very close to each other. Now the existence of the bands in definite parts of the spectrum produces the colour.

3. **Dipole Moment :** The dipole moment plays a significant role in the transition of the molecule because a molecule can absorb light only if its dipole moment changes. For example, the more symmetrical the molecule, the smaller is the probability of transition dipole and, therefore, the light is absorbed by the molecule very slowly. Similarly, it is shown that the greater the transition dipole, the greater is the absorption of intensity. Thus, if the group, which is introduced in the molecule, decreases the symmetry of the molecule, the transition dipole and, therefore, the intensity of the absorbed light will also be increased.

We will now apply the above concepts in explaining the relation between colour and constitution by the two important theories called valence bond (V.B.) and molecular orbital (M.O.) theories. The former theory deals with electrons in pairs while the latter theory deals with electrons singly. Let us now discuss these theories one by one.

1. ***Valence bond theory (resonance theory)*** : The various postulates of this theory are as follows :

(*i*) Chromophores are groups of atoms, the π-electrons of which may get transferred from ground state to excited state by the absorption of radiation, thus producing the colour.

(*ii*) Auxochromes are groups which tend to increase resonance by interacting the unshared pair of electrons on nitrogen or oxygen atoms of the auxochromes with the π electrons of the aromatic ring. This increase in resonance increases the intensity of absorption of light and also shifts the absorption band to longer wavelength. Hence there occurs the deepening of the colour. From this it is evident that increase in resonance must deepen the colour and actually it has been found to be so.

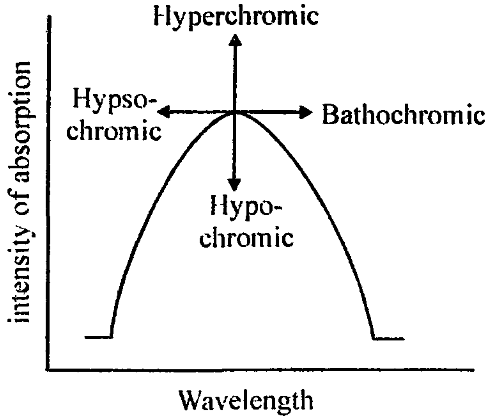


Fig. 5.4 : Absorption band in Visible Spectrum

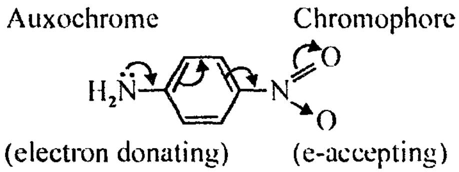
(*iii*) The dipole moment changes as a result of oscillation of electron pairs. The following order has been observed for the ease of excitation of different groups.

$$N = O > C = S > N = N > C = O > C = N > C = C$$

The colour deepens in the opposite direction.

(*iv*) Resonance theory explains the relation of the colour and the symmetry of the molecule or transition dipole of the molecule because as the number of charged canonical structures increases, the colour of the compound deepens. The more the possibility and longer the path for a charge to oscillate in a compound, the more longer wavelength of light will be absorbed and therefore more deeper would be the colour of the compound.

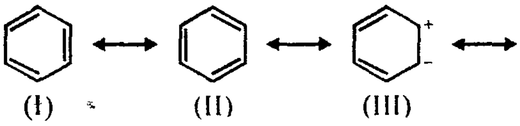
(*v*) In resonance theory the chromophore is considered as an electron withdrawing group and auxochrome as an electron donating group. When they are conjugated through double bonds (usually benzenoid systems) then electrons move from auxochrome to chromophore. This increases the resonance and also causes the change in dipole moment. Hence intensity of colour is increased. If the separation between chromophore and auxochrome is increased, the resonance increases, increasing the intensity of colour.



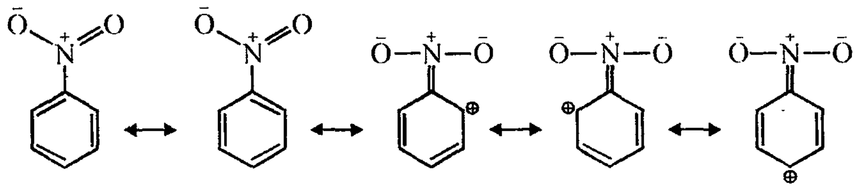
The development of colour in compounds can be explained with the help of resonance as follows :

(*a*) A simple and common example is that benzene is colourless, nitrobenzene is pale yellow and *p*-nitroaniline is dark yellow. This can be explained as follows :

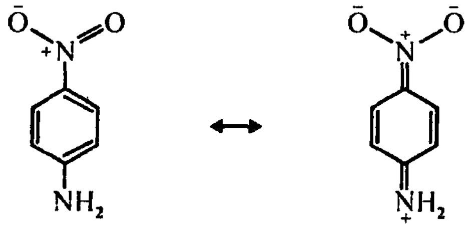
In benzene, two major structures contributing to its resonance hybrid are the two Kekule structures (I and II). In addition, a number of charged canonical structures of type III may be written but they contribute relatively little to either ground or excited state and thus benzene absorbs in the ultraviolet region. Also, the benzene molecule is symmetrical and, therefore, the absorption is weak.



In nitrobenzene, charged structures contribute much more in the case of benzene and, therefore, the absorption is shifted to longer wavelength (blue), thereby producing a pale yellow colour which is the complementary colour of the blue band. Also, the intensity of the absorption is increased in nitrobenzene due to the loss of symmetry of the molecule.



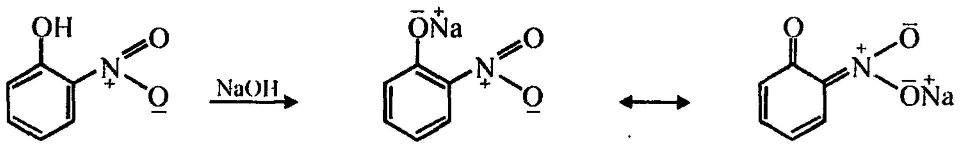
In *p*-nitroaniline, the contribution of the charged structure is still larger and hence the light of longer wavelength is absorbed, thus deepening the colour to the dark yellow.



p-Nitroaniline

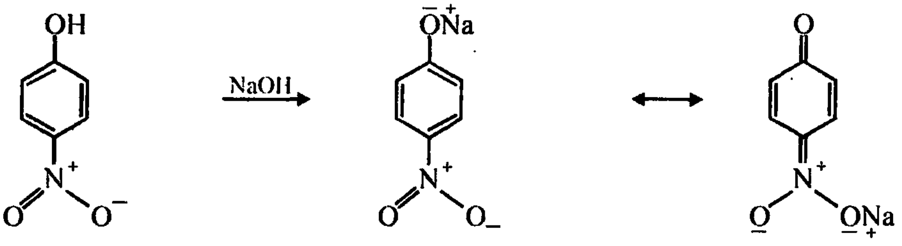
The comparison of dipole moments for nitrobenzene (0.21 D), aniline (1.48 D) and nitroaniline (6.1 D) also reveals that there occurs the relatively high contribution of the charged structure to the resonance hybrid of *p*-nitroaniline. The larger value (6.1 D) for *p*-nitroaniline over the sum of aniline and nitrobenzene (4.21 D + 1.48 D = 5.69 D) is due to the fact that each of amino and nitro groups cooperatively helps the other in shifting the actual state of the molecule in the direction of charged structure.

(*b*) Similarly, ortho and para-nitrophenols show dark colours in alkaline medium. In alkaline medium they form salts which have many charged resonance structures. They absorb strongly in visible region causing deep colour



o-Nitrophenol (pale yellow)

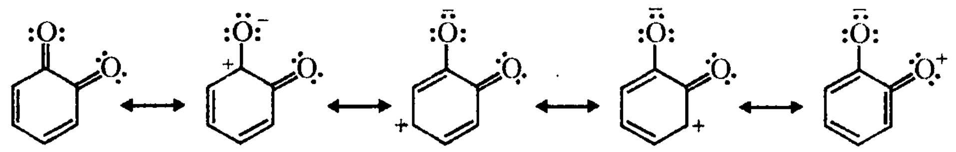
Sodium salt (orange red)



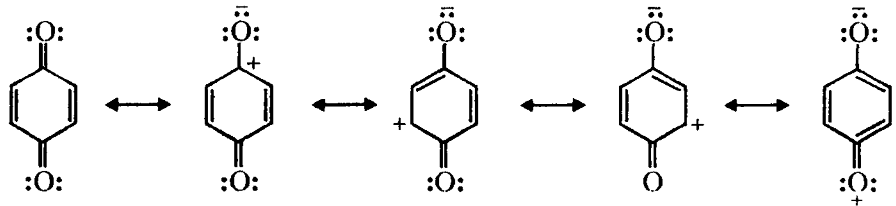
p-Nitrophenol

Sodium salt (Dark yellow)

(*i*) The resonance theory can also explain the colour of ortho and para quinones. There are many charged resonance structures which contribute to the resonance hybride. Hence, it strongly absorbs in visible region causing yellow colour.



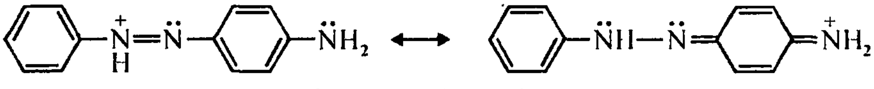
Resonance structures of *o*-quinone



Resonance structures of *p*-quinone

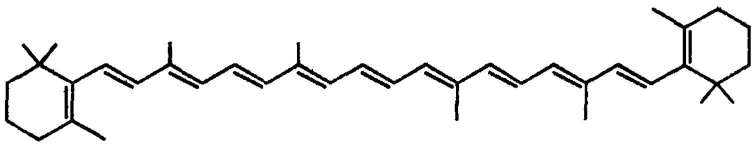
(*ii*) In many cases the colour of the dye changes with the nature of the medium. For example, *p*-aminoazobenzene is yellow in alkaline medium but in acidic solution it becomes violet. In alkaline or natural medium there is only one changed structure contributing to the resonance structure. It absorbs in the blue region and hence, shows yellow colour. In acidic medium it gets protonated and both the resonance structures are charged. Therefore, it absorbs at a longer wavelength in the yellow-green region and shows violet colour. This is an example of bathochromic shift.

Yellow (Alkaline or neutral medium)



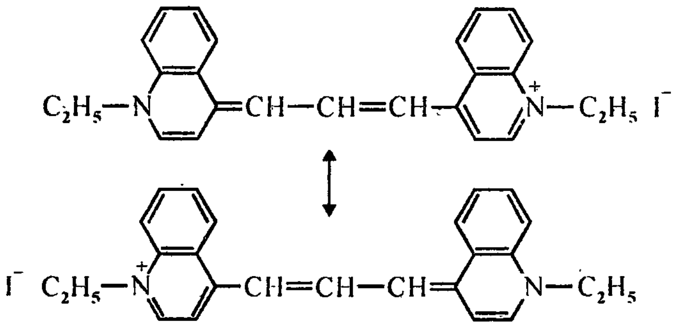
Violet (Acidic medium)

(*iii*) In case of diphenyl polyenes there is an extended conjugation and there is large dispersal of charge. There is a linear relation between the number of double bonds and the increase in the wavelength of absorption. Hence, there is a strong bathochromic shift and colour goes on deepening with increase in the number of double bonds. Another example of polyene, is β-carotene which is orange-red coloured natural product having eleven conjugated double bonds.



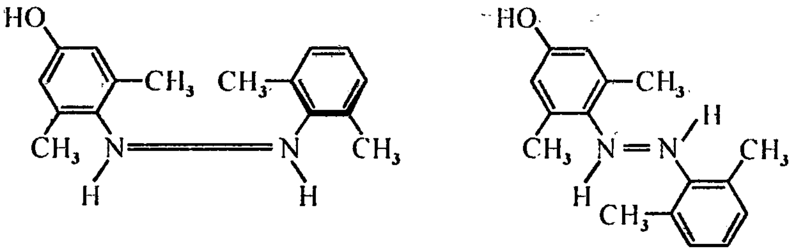
β-Carotene (Orange red)

The cyanine dyes are also very similar to diphenylpolyenes. They have two equivalent charged resonance structures. Hence they absorb strongly in visible region and show deeper colour.



Kreptocyanine

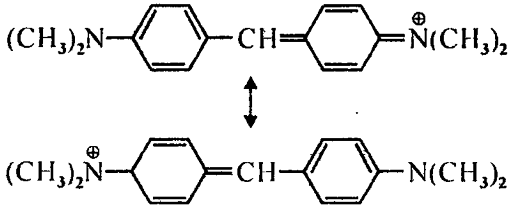
For the resonance to be effective the molecule should be planar. For example, the *cis*-isomer of the following azo dye is non-planar due to repulsion between two methyl groups which are close to each other. Thus the resonance is prevented and the compound is colourless. But the trans-isomer is planar and hence it is coloured due to resonance.



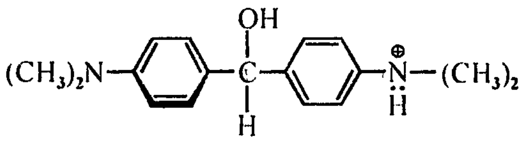
(2, 2, '6, 6'-Tetra methyl-4-hydroxy azobenzene)

cis-isomer (Non-planar, colourless) *trans*-isomer (Planar, coloured)

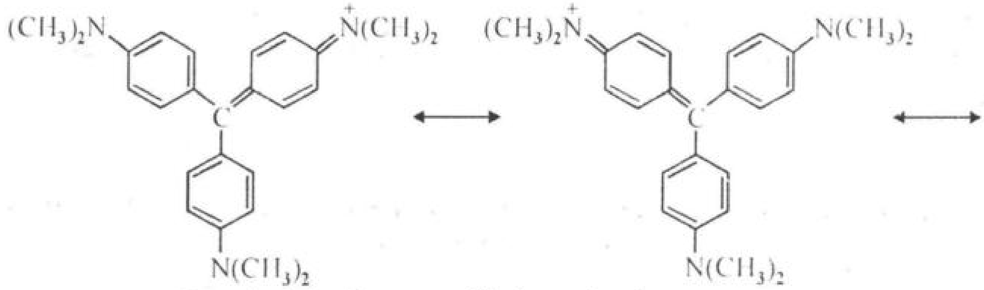
In case of Mischler's hydrol the π-electrons oscillate between the following two resonance structures, which are planar.



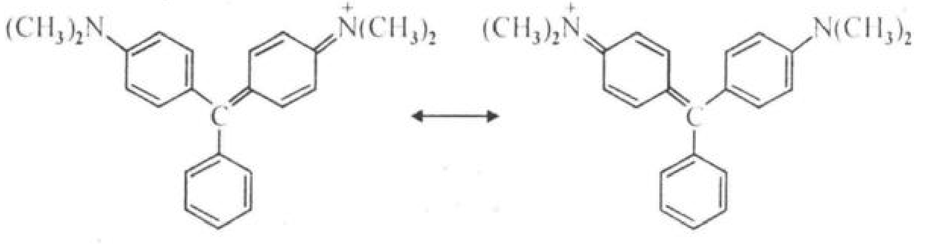
The compound has blue colour in acetic acid solution. If dilute hydrochloric acid is added it gets protonated. Due to the hydroxyl group at the central carbon atom the molecule becomes non-planar. Hence the colour disappears due to loss of extended resonance.



(*iv*) In triphenylmethane dyes all the three benzene rings are conjugated with each other. The three rings are planar and there is extensive resonance. Since all the structures are charged, they absorb strongly the longer wavelengths and hence show deeper colours.

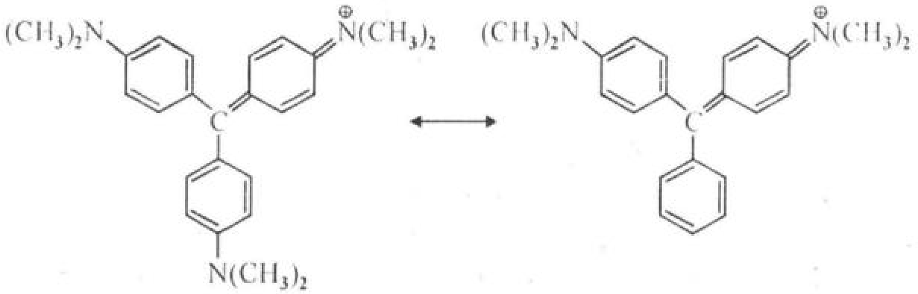


Crystal violet (3 way oscillations of π-electrons)



Malachite green (2 way oscillations of π-electrons)

In a dye molecule, there may occur oscillation of delocalised π electrons in more than one direction. If a dye is having a centre of symmetry as in crystal violet, in the cation of which all three benzene rings participate in resonance, polarisability becomes equal in all directions in the plane of the molecule and, therefore, there is only one principal absorption peak (λ_{max} 5900 Å). On the other hand, if a dye molecule is unsymmetrical as in malachite green, there are two axes of polarisability differing in degrees lying at right angles and therefore, there will be two absorption peaks (λ_{max} 4230 Å). Although the possibility for the oscillation for positive charge is more in crystal violet than in malachite green, yet the latter is more deeply coloured than the former.



Crystal Violet Malachite Green

It must be kept in mind that the amount of charge is also important. But the magnitude of the charge on each nitrogen atom in crystal violet is less that in malachite green. Therefore, crystal violet absorbs light of shorter wavelength than malachite green and hence colour of crystal violet will be lighter as compared to malachite green.

(*a*) ***Effect of Conjugation on Resonance :*** The longer the conjugation in a molecule, the deeper will be the colour because the conjugated system of double bonds (or of chromophores) provides a long path of resonance. Further, the absorption shifts progressively to longer and longer wavelengths with the increase in the number of C = C bonds in conjugated system

(Fig. 5.5). This has been observed in the case of a series of diphenylpolyenes, $C_6H_5-(CH = CH)_n-C_6H_5$ in benzene solution. In this case, *n* can have different values 1, 2, 3, 4 .... 15, etc. When *n* = 1 or 2, the compound is colourless. When *n* = 3, the compound is pure yellow. When *n* = 5, the compound is orange and so on. The shift in the absorption maxima with increasing values of *n* has been given in Table 5.4.

Table 5.4 : The shift in the Absorption Maxima of Diphenyl-polyenes, $C_6H_5-(CH = CH)_n-C_6H_5$ with Increasing Values of *n*.

Value of n	*Colour*	*Absorption maxima of characteristic band Å*
2	none	3520
3	pale-yellow	3770
4	greenish-yellow	4040
5	orange	4240
6	brownish-orange	4450
7	copper-bronze	4650
15	greenish-black	5700

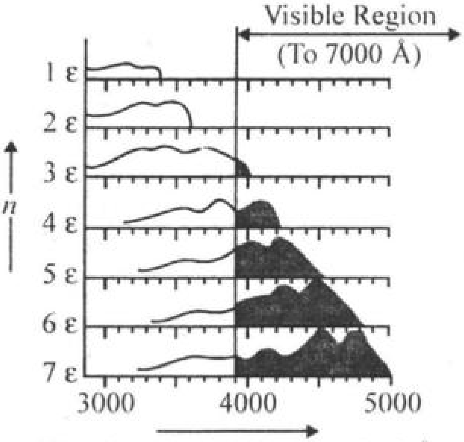
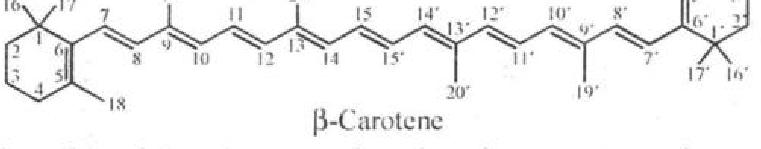


Fig. 5.5 : Change of wavelength and extinction coefficient with change of *n* in diphenylpolyene.

According to Lewis and Calvin, the deepening of the colour with the increase in the length of the conjugation has been attributed to the increase in the number of electrons which are participating in conjugation. The increase in conjugated system is also able to increase the deep colour of some compounds which do not have aromatic nucleus. For example, β-carotene, which contains a conjugated system of 11 ethylenic bonds, absorbs at 4510Å and is orange red in colour.



β-Carotene

As the number of fused rings increases, the colour deepens more and more. This is evident from the following example :

(*i*) Benzene is colourless.

(*ii*) Naphthalene having two benzene rings is colourless.

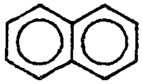
(*iii*) Anthracene having three benzene rings is colourless.

(*iv*) Naphthacene having four linearly fused rings is yellow in colour.

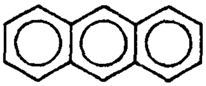
(*v*) Pentacene having five fused rings is blue.

(*vi*) Graphite, which is a sheet of benzene rings fused in all directions, is black as it absorbs almost all the colours.

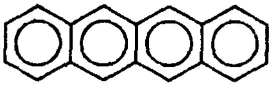
benzene (colourless)



naphthalene (colourless)

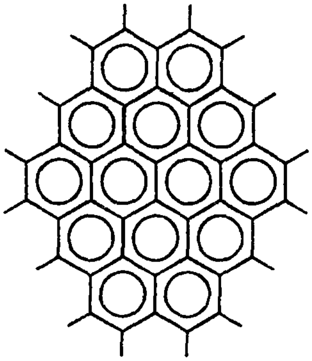


anthracene (colourless)



naphthacene (yellow)

pentacene (blue)



Graphite (Black)

If the conjugated system is also having atoms such as N, S, O, etc., it absorbs light of longer wavelengths than the corresponding compounds which consists of conjugated system of only the carbon atoms. There are two reasons for this which are as follows :

(*i*) The conjugated system having atoms such as N, S, O, etc. has a charge, while the conjugated system of only the carbon atoms does not have a charge.

$$O{=}C{-}C{=}C^{+}{-}O^{-} \qquad C{=}C{-}C{=}C{-}C$$

(*ii*) The conjugated system having atoms such as N, S, O, etc. is less symmetrical than the conjugated system of only the carbon atoms.

The qualitative application of the valence bond theory has led to many misunderstandings. On the one hand, mesomeric structures were repeatedly assumed to be different structures of the same compound and on the other hand the mesomeric structures were connected with excited states. However, the true low energy state lies between these two extremes.

2. Molecular Orbital Theory : According to this theory, the excitation of a molecule means the transference of one electron from an orbital of lower energy to that of higher energy.

These electrons may be σ, π or n (non-bonding) electrons. The higher energy states are commonly known as **antibonding orbitals.** The antibonding orbitals associated with σ and π bonds are called σ^* and π^* orbitals respectively. However, there are no antibonding orbitals associated with n (non-bonding) electrons because they do not form bonds. Fig. 5.6 shows, in the simplest form, the essential types of energy levels.

σ^*	Anti-bonding
π^*	Anti-bonding
n	Lone-pair, Non-bonding
π	Bonding
σ	Bonding

Fig. 5.6 : Scheme showing molecular orbitals.

The electronic transitions can occur by the absorption of ultraviolet and visible radiation. Although several transitions are possible, only the following types are allowed : (*i*) $\sigma \rightarrow \sigma^*$ (*ii*) $n \rightarrow \sigma^*$ (*iii*) $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$.

A $\sigma \rightarrow \sigma^*$ transition takes place when a bonding σ-electron is excited to an antibonding σ-orbital, *i.e.*, σ^*. This type of transition requires a very large amount of energy as σ-electrons are very tightly bond. Hence the compounds like saturated hydrocarbons which do not have any π or σ electrons may undergo only $\sigma \rightarrow \sigma^*$ transition. However, these transitions do not take place by absorbing in the ordinary ultra-violet region, *e.g.*, ethane absorbs at 135 mμ.

A $n \rightarrow \sigma^*$ transition takes place when one electron of a lone pair, *i.e.*, a non-bonding pair of electrons, is excited to an anti-bonding σ-orbital, *i.e.*, σ^*. Compounds having non-bonding electrons on heteroatom like O, N, S, etc. can undergo $n \rightarrow \sigma^*$ transitions also in addition to the $\sigma \rightarrow \sigma^*$ transitions. But the non-bonding, electrons are much more loosely held than the σ-electrons. Therefore, the energy required for $n \rightarrow \pi^*$ transitions will be much lower than that required for $\sigma \rightarrow \sigma^*$ transitions. Hence the compounds having non-bonding electrons usually absorb in the ordinary UV regin. For example, methyl iodide shows λ_{max} at 258 mμ while trimethylamine at 227 mμ.

Both transitions $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ are of lower energy than both the $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ transitions, and, therefore, take place at longer wavelengths. Furthermore, $\pi \rightarrow \pi^*$ transitions are of lower energy than the $n \rightarrow \sigma^*$ transitions but require more energy than the $n \rightarrow \sigma^*$ transitions. Acetaldehyde shows two absorptions, one at 180 mμ corresponding to a $\pi \rightarrow \pi^*$ transition while the other at 290 mμ corresponding to a $n \rightarrow \pi^*$ transition.

The various transitions may be arranged in their decreasing order of energy.

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

Let us now consider some examples.

(*a*) The $\pi \rightarrow \pi^*$ transitions for simple alkenes take place in the vacuum ultraviolet region. For example, ethylene absorbs at 175 mμ. Conjugation of double bonds decreases the energy required for $\pi \rightarrow \pi^*$ transition and, therefore, absorption shifts to longer wavelengths. For example, butadiene shows absorption at 217 mμ corresponding to a $\pi \rightarrow \pi^*$ transition. If a number of double bonds are present in a conjugation as in β-carotene, the absorption may even get shifted to visible region and the compound would be coloured. For example, β-carotene having eleven carbon-carbon double bonds in conjugation shows λ_{max} at 451 mμ corresponding to a $\pi \rightarrow \pi^*$ transition and is yellow in colour.

The above results have been summarised in the following table.

Compound	*Transition*	*Absorption band* (λ_{max})
$H_2C{=}CH_2$	$\sigma \rightarrow \sigma^*$	175 mμ
	$\pi \rightarrow \pi^*$	
$H_2C{=}CH{-}CH{=}CH_2$	$\pi \rightarrow \pi^*$	217 mμ
b-carotene	$\pi \rightarrow \pi^*$	451 mμ

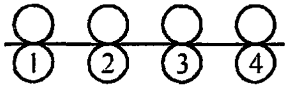
Ultraviolet spectrum of a compound is mainly used for detecting the presence of conjugation and also for determining the nature of the conjugated system. However, it is seldom used for detecting the presence of individual functional groups.

(*ii*) In order to explain the results of (*i*) consider the colourless conjugated compound butadiene, $CH_2{=}CH{-}CH{=}CH_2$. This study will help us to know the relation between colour and constitution on the basis of molecular orbital theory.

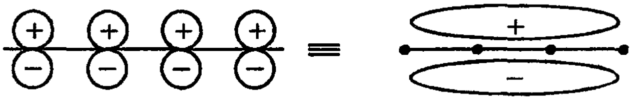
Fig. 5.7 (*a*) shows four p_z orbitals associated with four sp^2 hybridised carbon atoms of butadiene. All the four p_z orbitals are forming molecular orbitals which cover all the four carbon atoms. Two of four p_z electrons will occupy one molecular orbital [Fig. 5.7 (*b*)] and the remaining two the second molecular orbital [Fig. 5.7 (*c*)]. Fig. 5.7 (*d*) and Fig. 5.7 (*e*) represent the excited state of molecule.

When the butadiene is excited, four transitions from lower energy level to that of higher energy level are possible, *i.e.*, (*b*) to (*d*), (*b*) to (*e*), (*c*) to (*d*) or (*c*) to (*e*). If all these four transitions take place, four absorption bands would be produced. However if ΔE is calculated for all these transitions, it is found that ΔE for (*c*) → (*d*) transition is lowest than all the three other transitions and, thus, the absorption band of longest wavelength will correspond to such a transition.

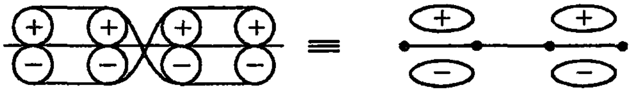
From the experimental work and calculation, it has been proved that as the conjugation increases, the energy difference between the highest level of the ground state and the lowest level of the excited state (*i.e.*, lowest ΔE among all the possible transitions in the molecule) decreases and, therefore, the absorption maximum of the compound increases. If the absorption maximum of the compound reaches the visible part of the spectrum, the compound tends to have a colour. Now consider the example of polyenes $CH_3{-}(CH{=}CH)_n{-}CH_3$. When the value of n is six, the absorption band appears in the blue region of the spectrum and the compound is, therefore, having yellow colour (complementary colour of blue). This is also the explanation for the deepening of colour of diphenylpolyenes.



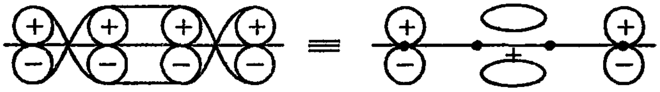
(*a*)



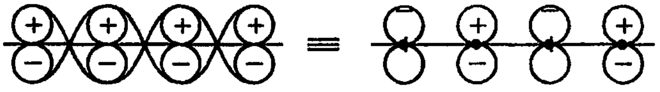
(*b*) Bonding



(*c*) Bonding



(*d*) Antibonding



(*e*) Antibonding

Fig. 5.7

(*iii*) Benzene which is symmetrical, possesses no transition dipole, does not absorb visible light and is colourless. In nitro-benzene the molecule is not symmetrical and thus its carbon atoms are unequally charged. The last property of the molecule creates a large transition dipole moment in the molecule and consequently strong absorption bonds are possible. Further, the introduction of nitro group in the benzene molecule extends its conjugation. This decreases the energy difference between the highest level of the ground state and the lowest level of the excited state and hence the strong absorption bands are expected at longer wavelength than that of benzene and thus nitrobenzene appears yellow while benzene colourless.

Suppose the aniline molecule is considered in which the lone pair of electrons present on nitrogen atom is in conjugation with the benzene ring and, therefore, the aniline molecule possesses dipole moment and consequently a transition dipole. Due to this, the aniline absorbs light of longer wavelength than that of benzene,

In acid solution, the lone pair of electrons present on nitrogen atom is co-ordinated with the proton. This destroys conjugation, then dipole moment and finally transition dipole. Due to this the absorption maximum of aniline is almost the same as that of benzene.

Two conjugated systems within a molecule are said to be insulated when the mobile electrons of the two systems are prevented from free interaction. Such systems absorb light as separate molecules.

From the above it is evident that conjugation is the important factor in producing colour. In general, any group conjugating with the benzene ring shifts the frequency of light to longer wavelength. It means that as the change in dipole moment of a compound increases, colour gets deeper and deeper. This may be realised by the presence of two or more polar groups which are connected through a conjugated system of the maximum possible distance.

Interaction of a dye with its environment involving aggregation, solvent`effects or absorption on a solvent may have a strong effect on the colour of the dye.

The valence bond approach for colour is satisfactory from a qualitative point of view whereas the molecular orbital method is more satisfactory from quantitative point of view.

6

CHAPTER

CHEMISTRY OF DYESTUFF INTERMEDIATES

6.1. Primaries

The raw materials used for the manufacture of dyes are mainly aromatic compounds, such as benzene, toluene, naphthalene, anthracene, pyrene, phenol, pyridine and carbazole. These raw materials are known as **primaries.**

In the past, the **primaries** came almost exclusively from the distillation of coal tar but in recent years increasing quantities of primaries, especially of benzene and toluene, have become available from petroleum and natural gas. The term "coal-tar dyes", still widely considered synonymous with synthetic dyes, is no longer an entirely correct description.

1. **Coal Tar :** When coal is subjected to destructive distillation, it yields *coal gas* and *coal tar.* Coal gas is mainly used as a fuel while coal tar when subjected to fractional distillation gives different products which are given in Table 6.1.

Table 6.1 : Fractional Distillation of Coal Tar

	Name of the Fraction	*Temperature*	*Main Constituents*
1.	Light oil or crude naphtha.	upto 170°C	Benzene, toluene and xylene.
2.	Middle oil or carbolic oil	170-230°C	Naphthalene and carbolic acid (phenol)
3.	Heavy oil or creosote oil	230-270°C	Cresols
4.	Anthracene oil or green oil	270-360°C	Anthracene, phenanthrene and carbazol.

The black residue, left in the still after the distillation is over, is called **pitch.** It contains 92-94 per cent of carbon and small amounts of pyrene and chrysene. The later compounds (*i.e.*, pyrene and chrysene) may be isolated from pitch by steam distillation followed by fractional distillation and crystallisation from solvent naphtha.

When **light oil** is subjected to fractional distillation, it yields three main fractions :

(*a*) ***Low Boiling Fraction :*** It contains acetonitrile, carbon disulphide and fatty hydrocarbons.

(*b*) ***High Boiling Fraction :*** It is mixed either with the carbolic or creosote oil.

(*c*) ***Middle Boiling Fraction :*** It is treated with cold conc. H_2SO_4 to remove basic substances, *e.g.*, pyridine, and then washed with water and treated with caustic soda to remove acidic substances, *i.e.*, phenol and excess sulphuric acid. It is then washed with water and subjected to fractional distillation when the following fractions are obtained :

(*i*) *90% Benzol (80-110°C) :* It contains benzene and toluene. It contains 70% of benzene.

(*ii*) *50% Benzol (110-140°C) :* It contains the same two hydrocarbons in two different proportions along with xylene. It contains 46% of benzene.

(*iii*) *Solvent Naphtha or Benzine (140-170°C) :* It contains xyline. mesitylene, etc.

The various benzols and benzine on fractional distillation yield benzene, toluene and xylenes.

Middle oil contains mainly naphthalene and phenol. This layer on keeping for sometime deposits naphthalene which is separated by centrifuging and pressing. The residue is treated with caustic soda and the aqueous solution is separated and treated with dil. sulphuric acid to regenerate phenol.

Crude naphthalene is first washed with sodium hydroxide, then with conc. sulphuric acid to remove bases and finally with very dilute caustic soda. It is next purified by sublimation.

Heavy oil contains mainly cresols. It is used as such for the preparation of dyes.

Anthracene oil contains anthracene and phenanthrene which are deposited as crystals on cooling.

1. **Petroleum :** In recent years, petroleum source has become important especially for the production of primaries such as benzene, toluene, xylene, naphthalene, etc. Potentially important developments in the production of these primaries lie in the cracking and hydrogenation processes.
2. **Other Sources :** In recent years it has become a common practice to obtain aromatic hydrocarbons from water gas, methane and olefins by catalytic processes.
3. **Inorganic Raw Materials :** A great variety of inorganic materials are required by the dye industry. These include sulphuric acid, oleum, nitric acid, chlorine, bromine, caustic soda, sodium nitrite, hydrochloric acid, sodium carbonate, sodium hydrosulphite, sodium sulphide, aluminium chloride, sodium dichromate. and manganese dioxide.

6.2. Intermediates

The *primaries* for dyes are almost never directly useful in dye synthesis. It is necessary to convert them to a variety of derivates which are in turn made into dyes. These derivatives are called *intermediates*. They are called such because they are really intermediates between the primaries and the final dyestuffs.

Intermediates are produced by reactions such as nitration, reduction, sulphonation, halogenation, oxidation and condensation. Most of these reactions lead to the formation of substituted hydrocarbons which are functional in nature, *i.e.*, they bear groups which are capable of undergoing further chemical reactions.

6.3. Unit Process

This denotes a synthetic step in organic synthesis of a compound on a large scale. The common unit processes involved in the dyes-tuff production are sulphonation, nitration, amination by reduction, ammonolysis, oxidation, halogenation, hydrolysis, dehydration, Friedel-Crafts reaction, etc.

It is important that all unit processes should be well-planned and controlled. Some of the processes like nitration are inherently dangerous. For these reasons, close supervision by technically trained men is the rule in plants where intermediates are manufactured.

6.4. Manufacture of Intermediates

Various intermediates required for the manufacture of dyes have been divided into three main groups :

(*i*) Aliphatic compounds,

(*ii*) Aromatic compounds, and

(*iii*) Heterocyclic compounds

Let us discuss these one by one.

6.5. Aliphatic Compounds as Dyestuff Intermediates

The main uses of aliphatic compounds in dyestuff industry are as follows :

(*i*) They are mainly used as solvents

(*ii*) Some are used as reagents or reactants

The various aliphatic compounds used as dyestuff intermediates include alcohols, chloroderivatives, carboxylic acids and esters, aldehydes and ketones, amines and miscellaneous aliphatic compounds.

Alcohols

These are manufactured by the following methods :

(*i*) By hydrolysis of alkyl halides.

(*ii*) By treatment of alkenes with sulphuric acid and subsequent hydrolysis.

(*iii*) By reduction of aldehydes and ketones with iron and acetic acid or with zinc and sodium hydroxide solution or with lithium aluminium hydride.

(*iv*) By treating Grignard's reagent with aldehydes, ketones, esters and cyclic oxides (such as ethylene oxide) and subsequent hydrolysis.

Methyl Alcohol : It is manufactured by reaching hydrogen and carbon monoxide gases in 2:1 proportion at 350-400°C and at 250 kg/sq. cm pressure.

$$CO + 2H_2 \xrightarrow[250 \text{ Kg/sq. cm}]{350-400°C} CH_3OH$$

It is used as a solvent and a reactant. It also finds use in the manufacture of sodium methoxide, dimethyl sulphate, formaldehyde, formic acid, nitroanisoles, dimethylaniline and many other useful intermediates.

Ethyl Alcohol : It is mainly manufactured form molasses by the fermentation in the presence of yeast.

$$\underset{\text{Sucrose Molasses}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{in yeast}]{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{yeast}]{\text{Zymase in}} 2\,C_2H_5OH + 2\,CO_2$$

It is also manufactured from ethylene compressed to 15-30 atmospheres pressure (obtained from cracked petroleum) by treatment with sulphuric acid (98%) at 70-80°C. The ethyl hydrogen sulphate or diethyl sulphate is formed. This on hydrolysis with warm water produces ethyl alcohol.

$$\begin{aligned} C_2H_4 + H_2SO_4 &\longrightarrow C_2H_5HSO_4 \\ C_2H_4 + C_2H_5HSO_4 &\longrightarrow (C_2H_5)_2SO_4 \\ C_2H_5HSO_4 + HOH &\longrightarrow C_2H_5OH + H_2SO_4 \\ (C_2H_5)_2SO_4 + 2HOH &\longrightarrow 2C_2H_5OH + H_2SO_4 \end{aligned}$$

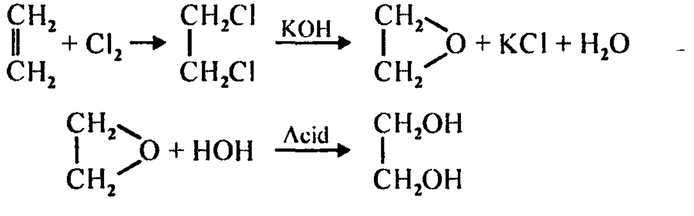
Ethyl alcohol is used as a solvent as well as a reactant. It is also used in the manufacture of sodium ethoxide, diethyl sulphate, diethyl ether, ethyl chloride, esters, acetaldehyde, acetic acid, nitrophenetoles and several intermediates.

Butyl Alcohols : These are obtained from C_4 cut of fractional distillation of petroleum by sulphuric acid treatment and subsequent hydrolysis. Butyl alcohols are mainly used as solvents.

Amyl Alcohols : These are obtained from C_5 cut of fractional distillation of petroleum by chlorination, fractional distillation of products and subsequent hydrolysis.

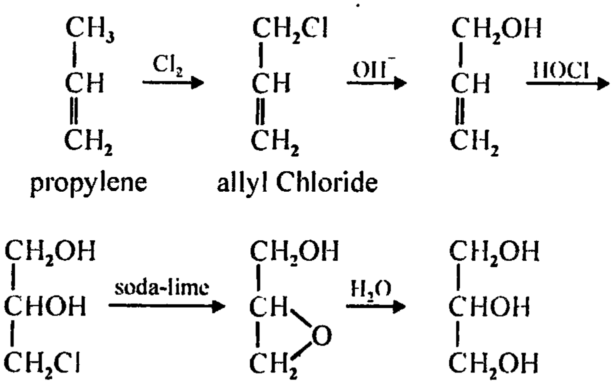
Amyl alcohols are mainly used as solvents.

Ethylene Glycol : It is obtained from ethylene by chlorination and subsequent alkaline hydrolysis or from ethylene oxide by acid hydrolysis.



Ethylene glycol is mainly used as a solvent and especially as an antifreezing agent for refrigeration.

Glycerol : It is manufactured by splitting of fats (which are esters of long chain carboxylic acids with glycerol) by hydrolysis. It is also manufactured from propylene by chlorination and subsequent treatment with hydrochloric acid and then with soda-lime followed by hydrolysis.



Glycerol is mainly useful in Skraup's synthesis of benzanthrone from anthraquinone and of quinolines, *e.g.*, 8-hydroxyquinoline from *o*-aminophenol.

Halogen Compounds of Aliphatic Series

The chlorine compounds are manufactured by the following methods :

(*i*) By the chlorination of hydrocarbons.

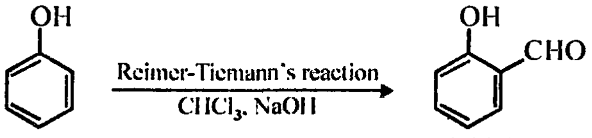
(*ii*) By the treatment of alcohols with chlorinating agents such as PCl_3, PCl_5 and $SOCl_2$, in certain cases (*t*-butyl and allyl alcohols) by the action of hydrochloric acid, etc.

The bromo compounds are manufactured in the same manners as chloro compounds and also by the treatment of alcohol with sodium bromide and sulphuric acid.

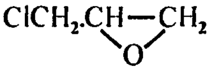
Many more methods are also known but they are of little importance in the production of halogen compounds.

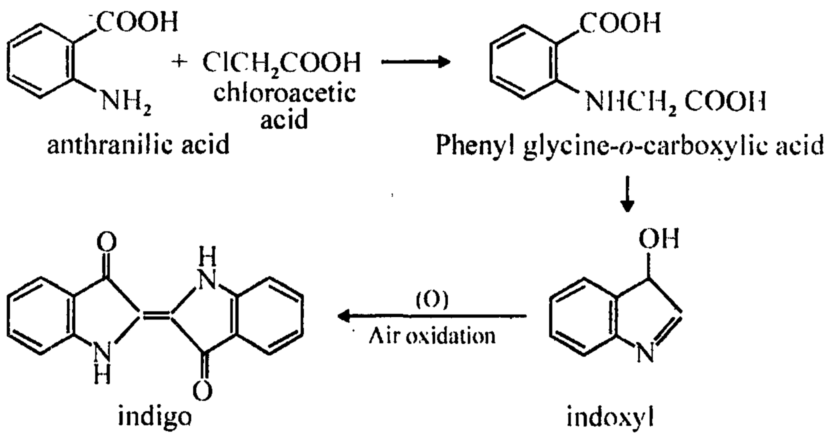
Methyl chloride, dichloromethane, ethylene dichloride, trichloro-ethylene, carbon tetrachloride, chloroform, etc., are mainly used as solvents.

Chloroform is also used as a reagent in many reactions such as Reimer-Tiemann reaction which involves conversion of phenol to corresponding phenolic aldehyde using chloroform and potassium hydroxide.



Salicylaldehyde

Many aliphatic chloro compounds like vinyl chloride, chloroacetic acid, chloral, phosgene, thiophosgene ($CSCl_2$) and epichlorohydrin  $ClCH_2.CH{-}CH_2$ (epoxide, $-O-$) are used in various condensation reactions to obtain aromatic and heterocyclic intermediates and dyes. For example chloroacetic acid on condensation with anthranilic acid yields a product which is cryclised to get indoxyl which by air oxidation gets converted to the dye called indigo.



Chloral is used in the production of isatin.

Phosgene is used to condense two moles of an intermediate or a dye having free amino group to get a urea linkage. Thus, two dyes of the same class are condensed with phosgene to obtain a combined effect. For example, a yellow dye and a blue due, each having free amino group for the condensation when suitably condensed with phosgene yield a green (yellow + blue) dye.

$$\underset{\text{yellow dye}}{D_Y - NH_2} + COCl_2 + \underset{\text{blue dye}}{H_2N - D_B}$$
$$\downarrow$$
$$\underset{\text{green dye with urea linkage}}{D_Y - NHCONH - D_B}$$

Aliphatic or Aromatic Carboxylic Acids and Esters

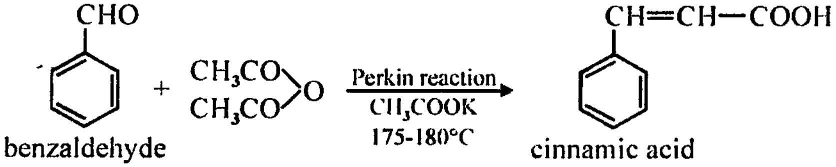
Acids are manufactured by the following methods :

(*i*) The oxidation of aldehydes, ketones, alcohols, etc., with various oxidising agents such as $KMn0_4$ and sulphuric acid, dilute nitric acid, sodium hypobromite, etc.

(*ii*) Replacement of halogen atom in alkyl halides *either* by the action of Grignard's reagent followed by passing carbon dioxide and subsequent hydrolysis *or* by the action of potassium cyanide to get alkyl cyanide (0_5 nitrile) and subsequent hydrolysis.

Various esters are manufactured by acid-catalysed esterification of the carboxylic acid and the alcohols.

Many of the carboxylic acids and their esters such as formic acid, acetic acid, ethyl acetate, etc., are mainly used as solvents. Most of the acids such as formic acid, acetic acid, malonic acid, maleic acid, succinic acid, etc., find importance in various condensation reactions either themselves or in the form of anhydrides or esters. For example, benzaldehyde can be condensed with acetic anhydride using potassium acetate at 175-180°C following Perkin reaction to obtain cinnamic acid.



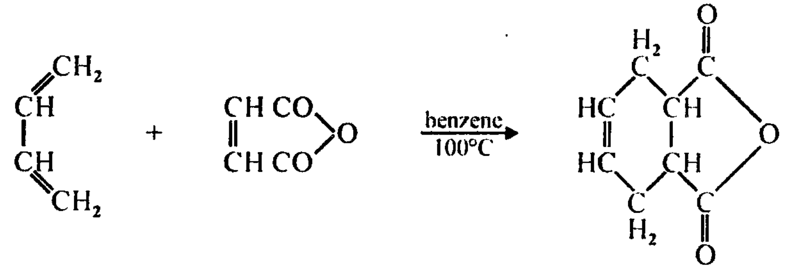
Two moles of ethyl acetate can be self condensed in the presence of a base such as sodium ethoxide to yield sodioaceto acetic ester which gets hydrolysed by an acid to yield acetoacetic ethyl ester.

$$\begin{tikzcd} 2\,CH_3\,COOC_2H_5 \arrow[r, "NaOC_2H_5"] & \overset{\oplus}{Na}\ (CH_3CO\overset{\ominus}{C}H\,COOC_2H_5) \arrow[d, "HCl"] \\ & CH_3COCH_2COOC_2H_5 \end{tikzcd}$$

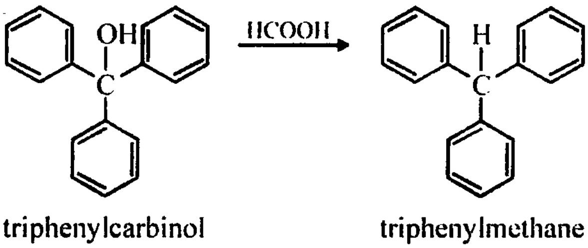
ethyl Acetate — sodium acetoacetic ester

acetoacetic ethyl ester

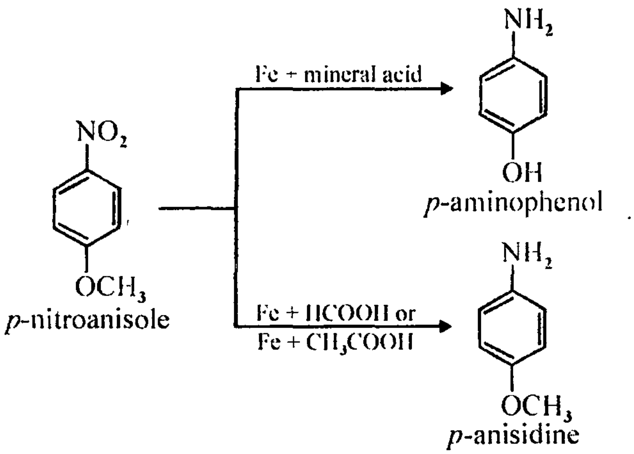
Butadiene and similar compounds condense with maleic anhydride under Diels-Aider reaction by 1, 4-addition giving a cyclic compound like *cis*-tetrahydrophthalic anhydride.



Formic acid finds use in the reduction of certain organic compounds. For example, triphenylcarbinol on treatment with formic acid can be converted into triphenylmethane.



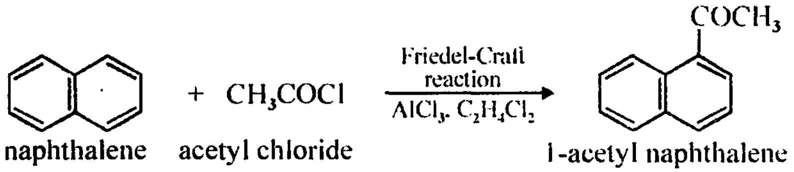
There are certain carboxylic acids which also find use as reagents. For example, formic and acetic acids are widely used for the reduction in the place of mineral acids in *Bechamp reduction* (making use of catalytic amount of an acid and iron for reducing aryl nitro compounds to arylamines). If mineral acids are used, they can bring about the hydrolysis of the methoxy group during Bechamp reduction of *p*-nitroanisole giving *p*-aminophenol. On the other hand, if formic or acetic acid is used, it smoothy converts nitro-anisole to anisidine without causing hydrolysis to take place.



Acid Chlorides

Acetyl chloride and other acid chlorides are prepared by treating corresponding acids with a chlorinating agent such as PCl_3, PCl_5, $SOCl_2$, etc.

Acid chlorides find uses in many organic reactions such as Friedel-Craft reaction in the production of intermediates. For example, acetylation of naphthalene with acetyl chloride or acetic anhydride in ethylene dichloride solvent gives rise to the formation of 1-acetylnaphthalene under Friedel-Craft's conditions.



Aldehydes and Ketones

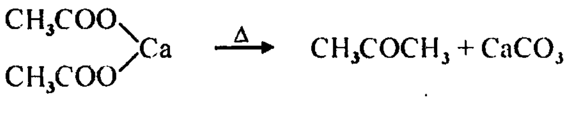
These are prepared by the following methods :

(*i*) By control oxidation of corresponding alcohols using oxidising agent such as potassium dichromate and sulphuric acid, aluminium *t*-butoxide, lead tetra-acetate, periodic acid etc.

(*ii*) By dehydrogenation of alcohols using copper at elevated temperatures.

(*iii*) By ozonolysis of alkenes followed by hydrolysis.

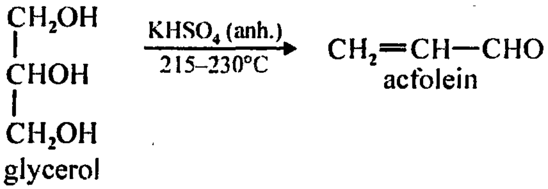
(*iv*) By hydrolysis of metal anhydrides (*e.g.*, acetone from calcium acetate).



$$\begin{matrix} CH_3COO \diagdown \\ \quad Ca \\ CH_3COO \diagup \end{matrix} \xrightarrow{\Delta} CH_3COCH_3 + CaCO_3$$

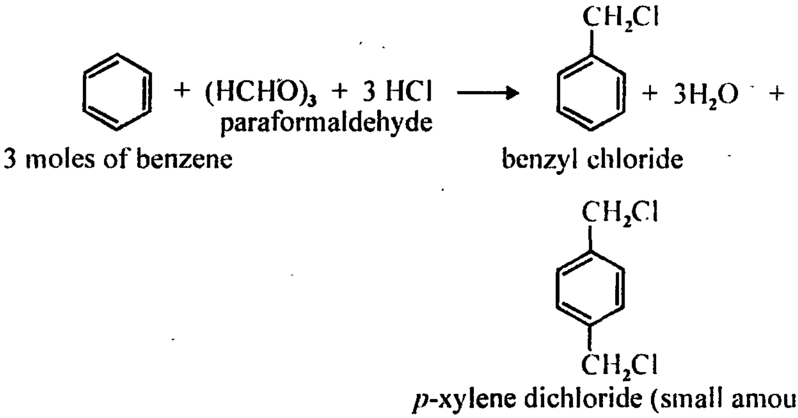
(*v*) By using Rosenmund reaction which involves catalytic hydrogenation of corresponding acid chlorides, etc.

(*vi*) By special methods. For example, aetaldehyde is prepared by catalysed hydration of acetylene; acetone is prepared by bacterial fermentation of sugars; chloral is prepared by the action of chlorine on ethanol; acrolein is prepared by dehydration of glycerol using acidic reagents.

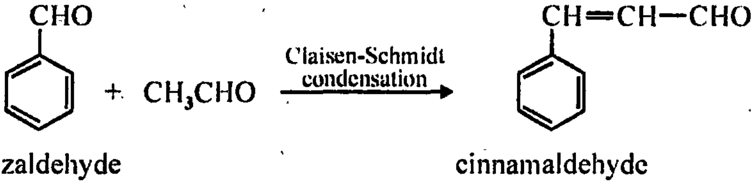


$$\underset{\text{glycerol}}{\begin{array}{c}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}} \xrightarrow[215\text{–}230°C]{KHSO_4\,(anh.)} \underset{\text{acrolein}}{CH_2{=}CH{-}CHO}$$

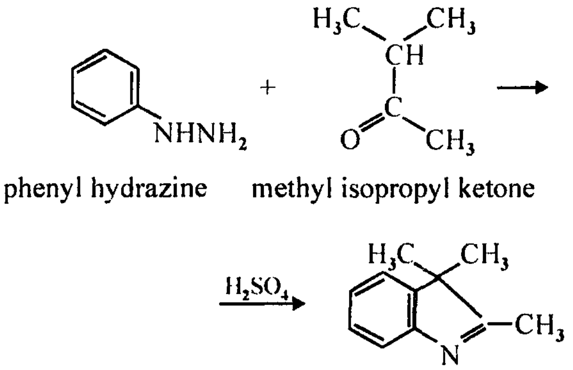
Aldehydes and ketones are mainly used in the manufacture of ranges of intermediates. For example, paraformaldehyde (a trimer of formaldehyde) when treated with benzene (three moles) using three moles of hydrochloric acid in the presence of a catalysts like zinc chloride or aluminium chloride under Blanc reaction conditions yields benzyl chloride with a small amount of *p*-xylene dichloride.



Acetaldehyde and benzaldehyde in aqueous alkali react at room temperature under Claisen Schmidt condensation to yield cinnamaldehyde.



When methyl isopropyl ketone is condensed with phenylhydrazine, the corresponding phenylhydrazone, is obtained which is cyclised with sulphuric acid (Fischer synthesis) to yield 2, 3, 3-trimethyl indolenine, an important indole derivative which finds uses in the synthesis of well known astrazones (cationic dyes).



Aliphatic Amines

They are prepared by the following methods :

(*a*) Primary, secondary, tertiary and quaternary amines may be prepared by the action of ammonia on alkyl halides or on alcohols in stages.

(*b*) (*i*) Primary amines may also be prepared by the reduction of corresponding nitriles or oxines with sodium and alcohol or lithium aluminium hydride or by hydrogenation with Raney nickel as catalyst.

(*ii*) Primary amines are also obtained by the action of sodium hypobromite in alkali on amides (Hofmann reaction).

(*iii*) Primary amines may also be prepared from acid hydrazides by Curtius reaction. In this reaction, acid hydrazides are treated with sodium nitrite to get acid azides which are heated to yield isocyanate and subsequently hydrolysed under alkaline conditions.

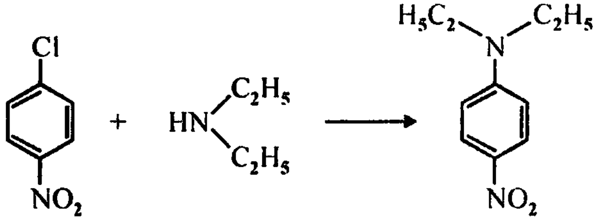
(*iv*) Primary amines may also be prepared from alkyl halides by reacting with potassium phthalimide under Gabriel synthesis conditions to yield alkyl phthalimides which get subsequently hydrolysed under alkaline conditions at boil.

(*c*) Secondary amines may be prepared by reducing acid amides ($R–NHCOCH_3$) with lithium aluminium hydride or by carrying out Hofmann reaction as in the case of primary amines.

(*d*) The diamines may be prepared in the same manner as primary amines. The starting materials are alkyl dihalides, alkyl dicyanides, etc.

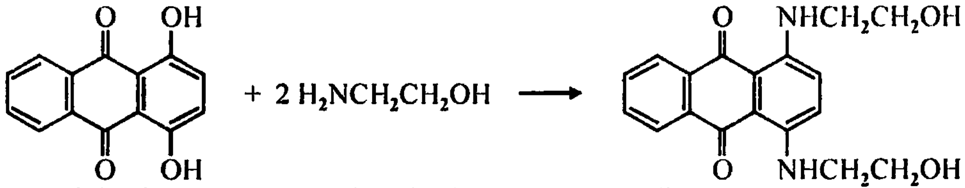
(*e*) Monoethanolamine, diethanolamine and triethanolamine are prepared by carrying out the ammonolysis of ethylene oxide and separating the mixture of ethanolamines by fractional distillation.

Aliphatic amines find use as versatile reagents. They undergo facile condensation reactions with many aromatic compounds having active chloro or phenolic groups. For example, *o*- and *p*-nitro-chloro-benzenes and similar derivatives react with secondary amines, *e.g.*, diethylamine to yield corresponding *o*- and *p*-substituted amino-nitrobenzenes.



p-nitrochlorobenzene *p*-diethylaminonitrobenzene

Monoethanolamine reacts with quinizarin to yield a disperse dye under suitable conditions.



quinizarin monoethanolamine disperse dye

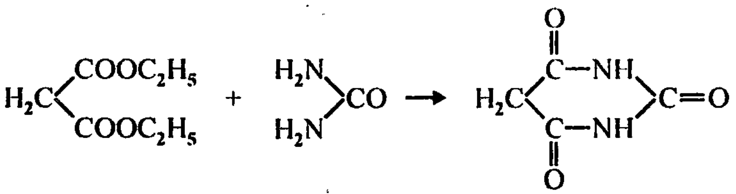
Methylamine reacts with sodium salt of chloroacetic acid to yield sarcosine which is used for stabilising diazonium salt needed for rapidogen class of azoic colours.

$$\underset{\text{methylamine}}{CH_3NH_2} + ClCH_2COONa \rightarrow \underset{\text{sarcosine}}{CH_3NHCH_2COONa}$$

Miscellaneous Aliphatic Compounds

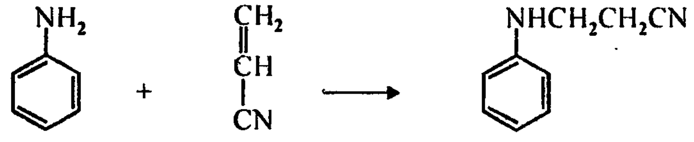
Many aliphatic compounds such as ethylene oxide, acetonitrile, urea, thiourea, acrylic acid, acrylonitrile, dimethyl sulphate, etc., are frequently used in the production of intermediates and dyes. Some examples of these uses are as follows :

(*i*) Urea finds use in the synthesis of barbituric acid by the condensation with malonic ester using sodium ethoxide as condensing agent.

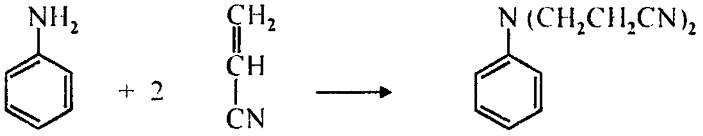


barbituric acid

(*ii*) Aniline condenses with acrylonitrile to give mono (cyano-ethyl) aniline and bis (cyanoethyl) aniline when one and two moles of acrylonitrile are used respectively. This reaction is known as cyanoethylatin.

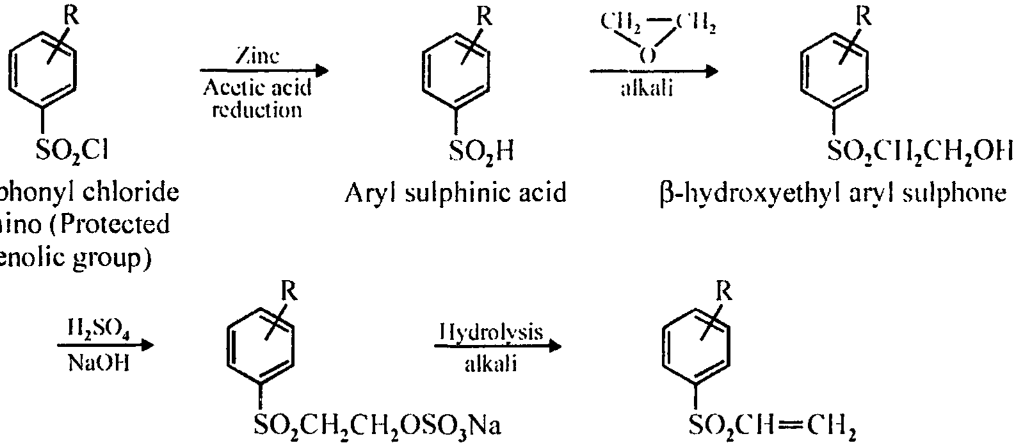


aniline acrylonitrile mono (cyanoethyl) aniline



bis (cyanoethyl) aniline

(*iii*) Ethylene oxide finds used in the synthesis of vinyl sulphone reactive systems in which a sulphonyl chloride is first reduced with zinc and acetic acid to corresponding sulphinic acid which is reacted with ethylene oxide giving β-hydroxyethyl sulphone and subsequently sulphated to yield a vinyl sulphone derivative.



Arylsulphonyl chloride
R is amino (Protected or phenolic group)

Aryl sulphinic acid

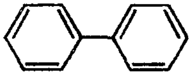
β-hydroxyethyl aryl sulphone

β-sulphato ethyl aryl sulphone

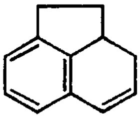
aryl vinyl sulphone

6.6. Aromatic Compounds as Dyestuff Intermediates

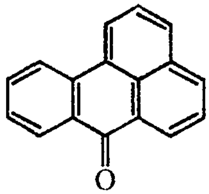
The aromatic dyestuff intermediates are mainly prepared from benzene, naphthalene, and antraquinone. However, certain aromatic dyestuff intermediates are less frequently obtained from biphenyl, acenaphthene, benzanthrone, pyrene, perylene, etc.



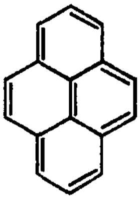
biphenyl



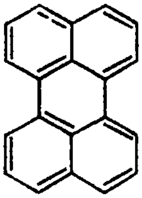
acenaphthene



benzanthrone



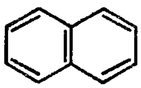
pyrene



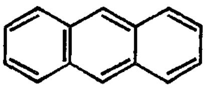
perylene

The reactivity of aromatic compounds has been found to depend upon the availability of π electrons cloud on the system. The increase of π electron cloud occurs as we proceed from benzene to anthracene.

6π



10π



14π

The reactivity has been found to increase in the sequence towards electrophiles but decreases in the same sequence towards nucleophiles. The presence of electron donating groups in the aromatic hydrocarbons eases the attack of an electrophile and resists the attack of a nucleophile as compared to the unsubstituted hydrocarbon because of the extension of π electron clouds in the ring system. Examples of electron donating groups are amino ($-NH_2$), phenolic ($-OH$), thiol ($-SH$), and methyl group.

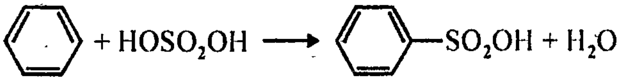
The presence of electron withdrawing groups in the aromatic hydrocarbons resists the attack of an electrophile but eases the attack of a nucleophile as compared to the unsubstituted hydrocarbon because of the removal of π electron cloud away from the aromatic ring. Some examples of electron-withdrawing groups are nitro ($-NO_2$), cyano ($-CN$), aldehyde ($-CHO$), sulphonic acid ($-SO_3H$) and carboxylic acid ($-COOH$).

Due to the conjugative effect, the presence of electron donating groups in the benzene ring favours further substitution in ortho and para positions, while electron withdrawing groups favour meta position. Chlorine in chlorobenzene is more electronegative than the carbon atom to which it is attached, and therefore chorine atom becomes electron withdrawing. Methyl group in toluene is electron donating due to inductive effect. Whatever may be the reason, the electron rich and electron deficient positions in benzene and other aromatic compounds get attached by electrophiles and nucleophiles respectively. The conditions of entering species have to be forced according to the site is weak or strong in electron richness or electron deficiency.

Here we shall give more discussion about the manufacture of aromatic compounds which are more frequently employed in dyestuff production.

Sulphonation : The introduction of the sulphonic acid group in an aromatic nucleus is known as *sulphonation*. This group is introduced to render intermediates soluble in water or to provide a route to other substituents, such as the hydroxyl group which is obtained by subsequent alkaline fusion.

Sulphonation of aromatic compounds is carried out by heating the compound with the sulphonating reagent during which water is eliminated. The water must be removed from the reaction mixture so that the sulphonating reagent does not get diluted and smooth reaction occurs. The sulphonation of benzene with sulphuric acid is illustrated by the following equation.



Direct sulphonation is achieved with the following reagents :

(*i*) Strong sulphuric acid

(*ii*) Oleum (sulphuric acid plus sulphur trioxide).

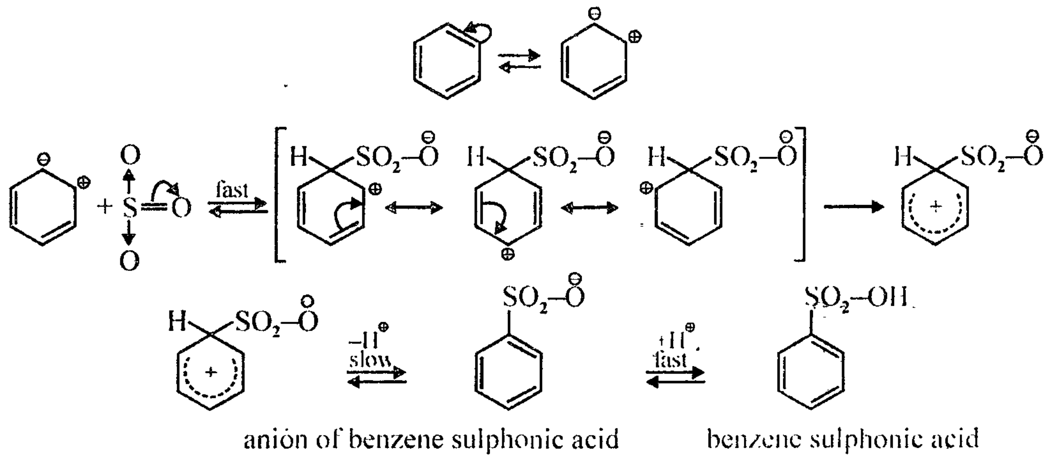
(*iii*) Sulphur trioxide in organic solvent or as a complex.

(*iv*) Chlorosulphonic acid.

Mechanism of Sulphonation : Various mechanisms have been proposed for sulphonation. However, the accepted mechanism is that sulphonation proceeds with free SO_3 which is produced as follows :

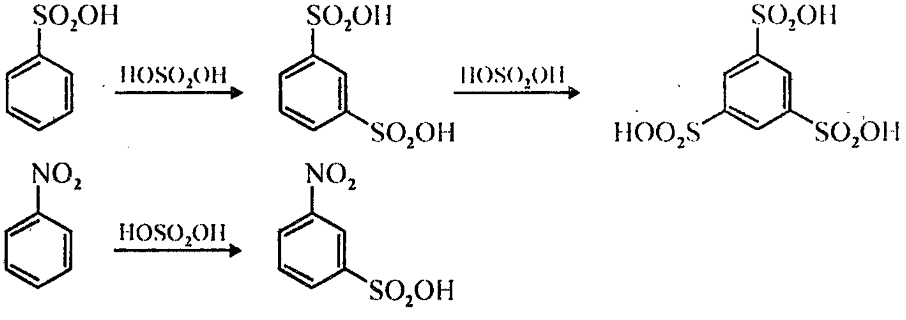
$$2H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4 + SO_3$$

The SO_3 is electrophilic reagent. It attacks the benzene ring to form the intermediate carbocation. Then, this loses a proton to form the resonance-stabilised substitution product, the anion of benzene sulphonic acid, which takes a proton to give benzene sulphonic acid. The step involving the loss of proton by carbocation is slow and, therefore, becomes the rate determining step.

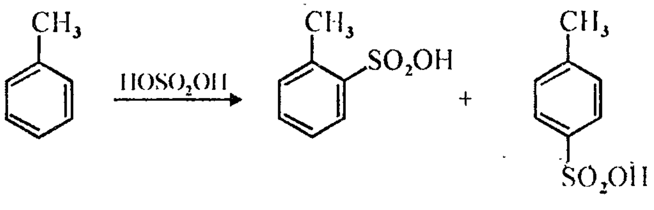


Substitution Rules : These rules for sulphonation are similar to those of nitration. However, these rules are as follows :

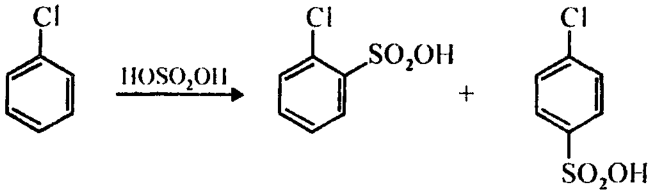
(*i*) The groups $-NO_2$, $-COOH$ and $-SO_3H$ direct the entering group to the *meta* position, *e.g.*,



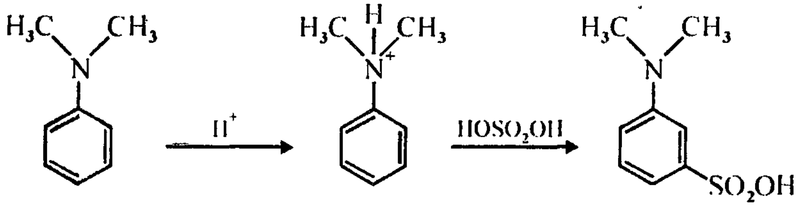
(*ii*) The alkyl groups (*e.g.*, methyl) direct the entering group predominantly to the *ortho* and *para* positions. Generally, a mixture of isomers is obtained.



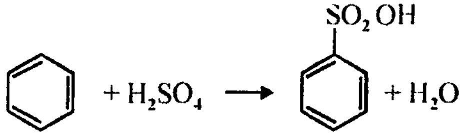
(*iii*) The chlorine is similar to the methyl group in its effect on orientation but gives less of the *ortho* isomer.



(*iv*) The directing effect of amino groups depends on their basicity. The less basic amines are *ortho-para* directing. Aniline is an example of this type. However, more basic amines (*e.g.*, dimethyl amine) form *meta*-directing salts in acid (why?).

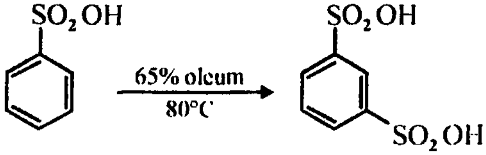


Sulphonation of Benzene : It is carried out by heating benzene (1 part) with 100% sulphuric acid (2 parts). In carrying out this reaction, oleum containing 8 per cent free sulphur trixode is added slowly to offset the dilution caused by the water formed in this process. When the reaction is complete, the charge is diluted by running it into water, and the product is precipitated by adding salt. It is isolated by filtration as the sodium benzene sulphonate.



(1 part) (2 parts)

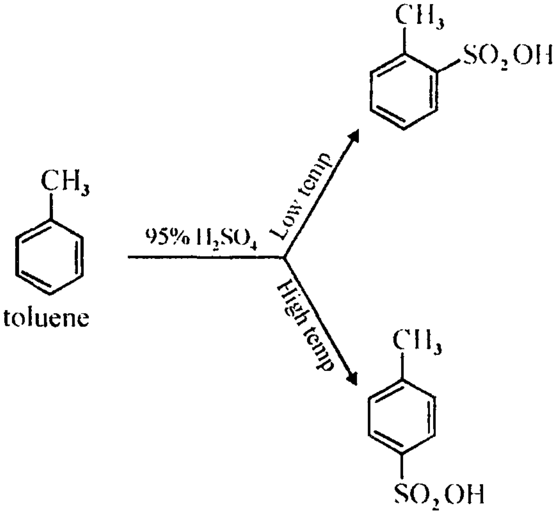
Benzene monosulphonic acid obtained in the above process on further sulphonation yields benzene-1, 3-disulphonic acid. The sulphonation is carried out by keeping the reaction mixture of benzene mono-sulphonic acid and 65% oleum at 80°C for 3 hours. After the reaction is complete, the sulphonated mass is added to ice cold water and neutralised by adding powdered calcium carbonate. Insoluble calcium sulphate is removed by filtration while to the filtrate sodium carbonate is added till no more calcium carbonate is precipitated. The solution is again filtered and evaporated to dryness when disodium salt of benzene-1, 3-disulphonic acid is formed.



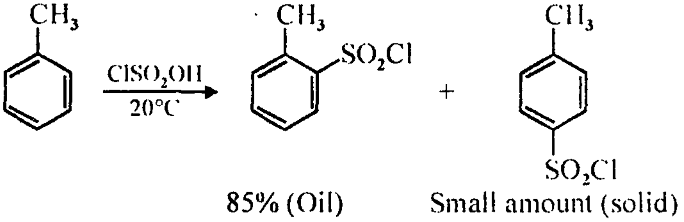
benzene-1, 3-disulphonic acid

It is used in the manufacture of resorcinol.

Sulphonation of Toluene : This takes place more readily than benzene to yield a mixture of *o*- and *p*-toluene sulphonic acids. Low temperatures favour the formation of the *o*-isomer while high temperatures favour the formation of the *p*-isomer. About 85% of *p*-toluene sulphonic acid is produced using 84% sulphuric acid at 100°C.



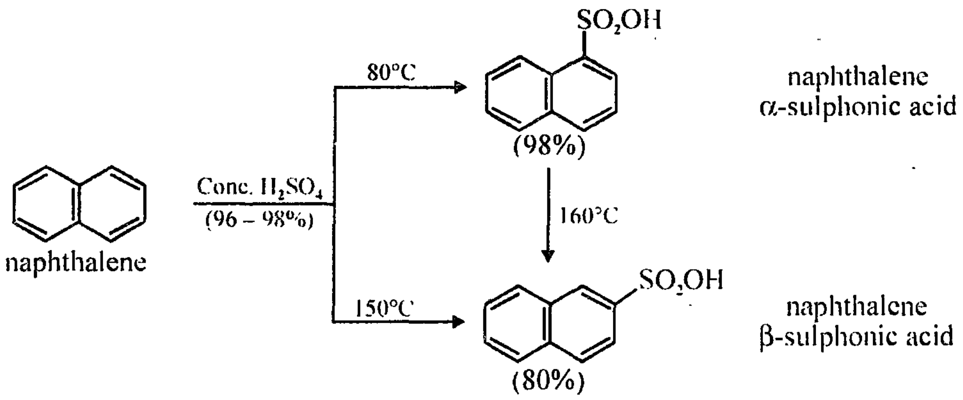
A much better yield of the *o*-isomer may be obtained in another way. Toluene on treatment with chlorosulphonic acid at low temperature, about 20°C, yields a mixture of toluene *ortho-* and *para*-sulphonyl chlorides. The solid *para*-isomer is filtered off from the mixture of acid chlorides obtained.



The two chlorides are separated by filtration and converted into the corresponding sulphonic acid by heating with alkali and then acidifying the solution.

Sulphonation of Naphthalene : The sulphonation of naphthalene yields a number of isomers. The product obtained may be controlled to some extent by the choice of agent. With any one reagent, temperature and time of reaction determine the result. It is rarely possible to obtain a single isomer. However, effort is directed towards forming a preponderant amount of one isomer. For example, naphthalene on direct sulphonation with sulphuric acid at 80°C for eight hours yields 96% 1-naphthalene sulphonic acid. As the temperature is raised, correspondingly less of this isomer is formed and more of the 2-sulphonic acid. For example, at 150°C, 8 per cent of the 1-isomer is formed and over 80 per cent of the 2-isomer is formed.

When sulphonation of naphthalene is carried out, the acid is run into the melted naphthalene to avoid disulphonation. The amount of acid added is the calculated amount for one sulphonic acid group. The water formed during the reaction retards but does not prevent it. Oleum may be added towards the end to hasten the reaction.



Naphthalene-1-Sulphonic Acid : When naphthalene is sulphonated with sulphuric acid at 80°C for eight hours, 96% of the 1-isomer and 4% of 2-isomer are obtained. The reaction mixture is diluted, treated with lime and filtered, the filtrate contains almost pure salt of the 1-sulphonic acid because it is more soluble than the calcium salt of the 2-suphonic acid. It is important to remember that no further purification is necessary.

Naphthalene-2-Sulphonic Acid : When 96% sulphuric acid is added to molten naphthalene and initially the temperature is maintained at 110-125°C and then the temperature is raised to 160°C and maintained there at least for 3 hours, naphthalene 2-sulphonic acid is the main product. Unsulphonated naphthalene is removed by steam distillation. Naphthalene-2-sulphonic acid is isolated as sodium salt by the addition of sodium chloride.

The sodium salt of naphthalene-2-sulphonic acid is mainly used for the manufacture of β-naphthol and "Cleve acids".

Naphthalene Disulphonic Acids : These can be prepared either by the action of oleum on naphthalene or by further sulphonation of naphthalene monosulphonic acids with concentrated sulphuric acid. The relative proportions of disulphonic acids formed have been found to depend upon temperature.

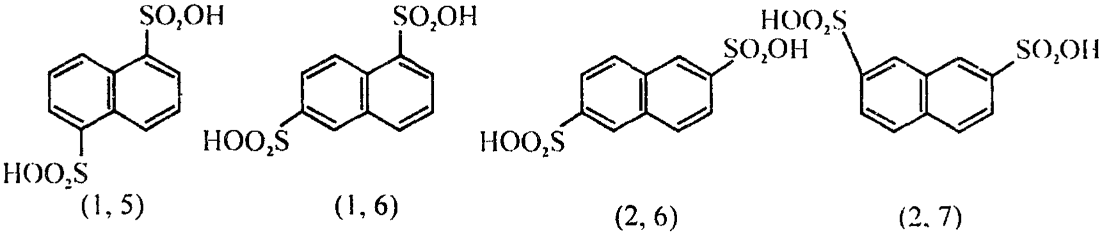
When the second sulphonic group enters, its position is governed by the following rules :

(*i*) At low temperatures, the entering group will occupy the most distant α-position from the already present sulphonic acid group.

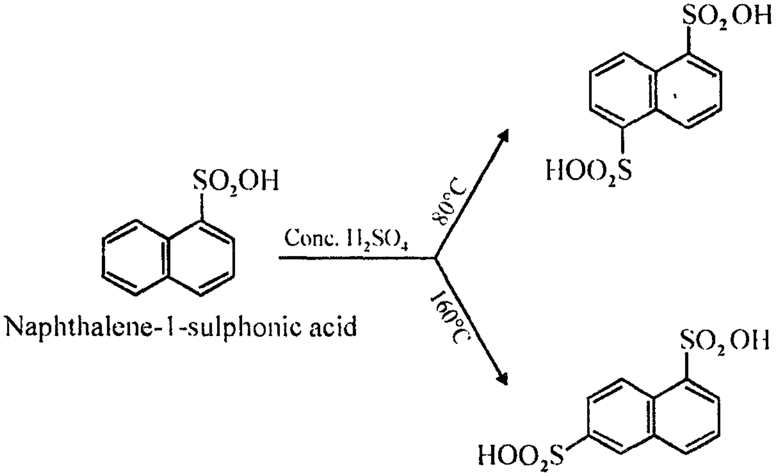
(*ii*) At high temperature, the entering group takes the most distant β-position from the already present sulphonic acid group.

(*iii*) The entering group does not take up the *ortho* (1, 2 or 2, 3), *para* (1, 4) or *peri* (1, 8) position with respect to the already present sulphonic group.

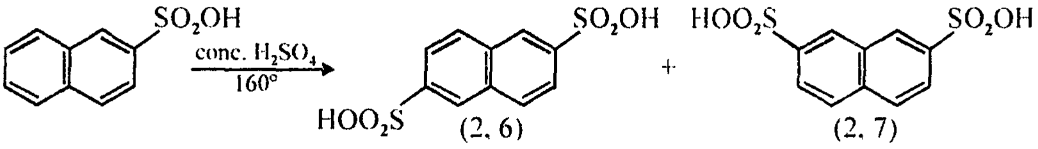
Theoretically, six naphthalene disulphonic acids are possible. All the six have been actually isolated among the products of the sulphonation of naphthalene. However, the following four are important intermediates in dye manufacture.



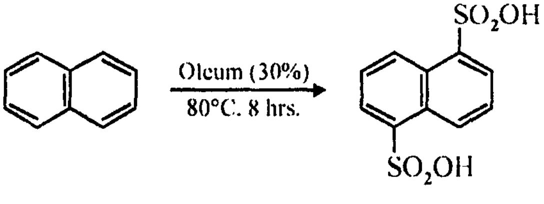
Naphthalene, 1, 5. and 1, 6 disulphonic acids are obtained by the sulphonation of naphthalene-1-sulphonic acid with conc. H_2SO_4 at 80°C and 160°C respectively.



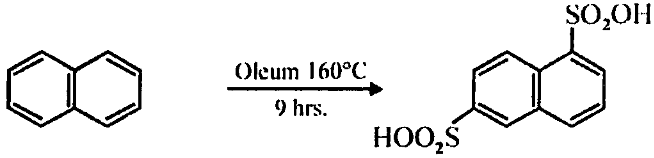
Naphthalene-2, 6-and 2, 7-disulphonic acids are obtained by the sulphonation of naphthalene-2-sulphonic acid at 160°.

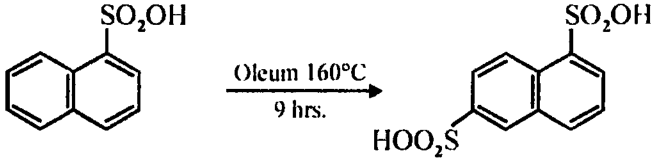


Naphthalene-1, 5-Disulphonic Acid : It is very important in the preparation of stabilised diazonium salts. It is most conveniently prepared by sulphonating naphthalene (1 part) with 30% oleum (4 or 5 parts) at 80°C for 8 hours. On dilution with about four parts of water, the 1, 5-acid crystallises out which is removed and used without its further purification.

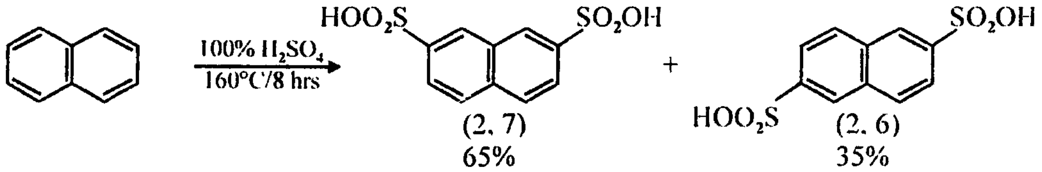


Naphthalene-1, 6-Disulphonic Acid : It is obtained along with 1, 5-acid by sulphonating naphthalene or naphthalene-1-sulphonic acid with oleum at 160°C for 9 hours. To the reaction mixture, barium carbonate is added when sparingly soluble barium salt of naphthalene-1, 6-disulphonic acid is formed which is removed. To the filtrate, sodium carbonate is added when 1, 6-disulphonic acid is obtained as sodium salt which is filtered and concentrated.

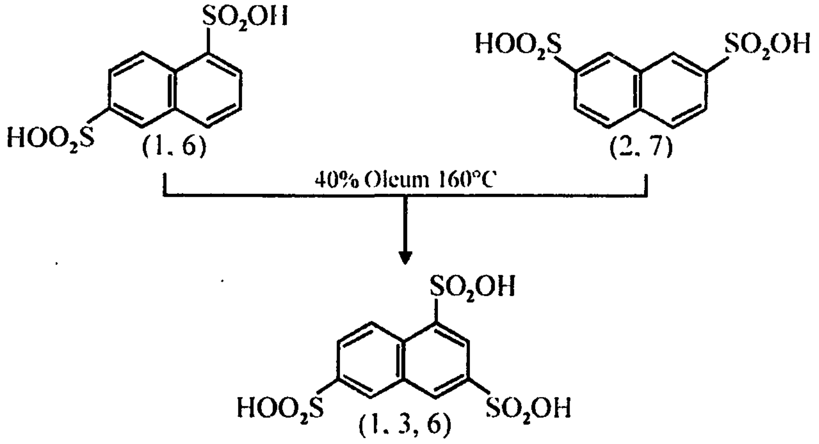




Naphthalene-2, 6-and-2, 7-Disulphonic Acids : These are obtained by sulphonating naphthalene (1 part) with 100% sulphuric acid (5 parts) at 160°C for 8 hours. 2, 6-disulphonic acid is separated from 2, 7-disulphonic acid as insoluble barium salt.



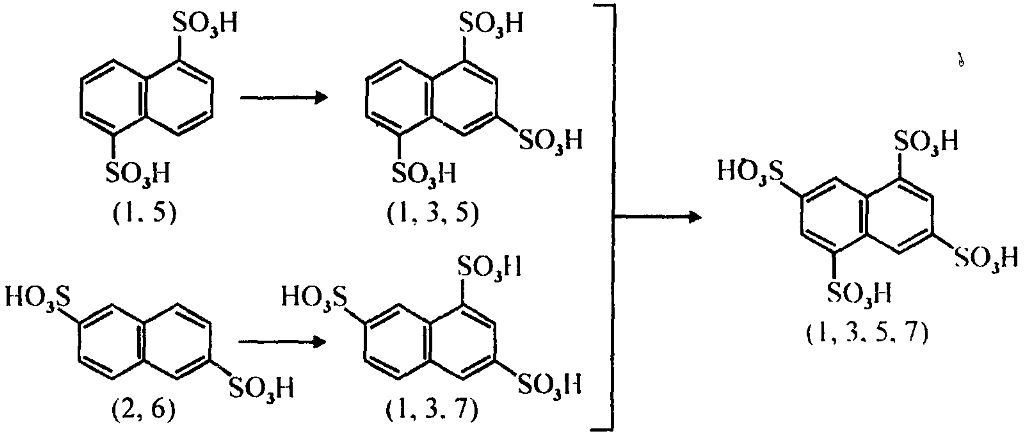
Naphthalene tri-and tetra-sulphonic acids : Naphthalene 1, 3, 6-trisulphonic acid may be obtained by trisulphonation of naphthalene with stronger oleum at 170°C. It may also be obtained by sulphonation of naphthalene-1, 6-and-2, 7-disulphonic acids with 40% oleum at 160°C.



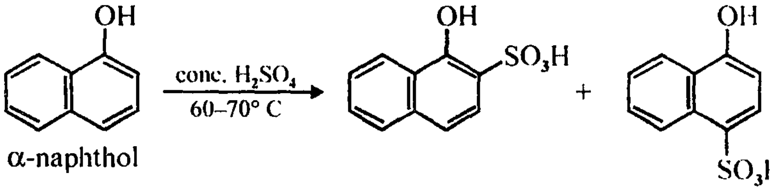
Naphthalene-1, 3, 6-trisulphonic acid is an important intermediate in the preparation of H-acid which is 8-amino-1-naphthol-3, 6-disulphonic acid.

Naphthalene-1, 3, 6-trisulphonic acid can be sulphonated further.

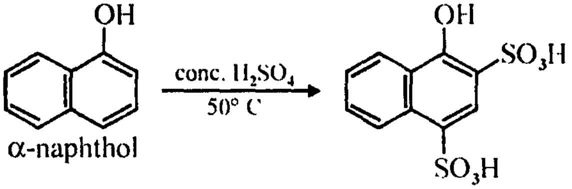
Naphthalene-1, 5-disulphonic acid on further sulphonation yields naphthalene-1, 3, 5-trisulphonic acid. On the other hand, naphthalene-2, 6-disulphonic acid on further sulphonation yields naphthalene-1, 3, 7-trisulphonic acid. Both 1, 3, 5 and 1, 3, 7-isomers on further sulphonation yield the same naphthalene-1, 3, 5, 7-tetrasulphonic acid.



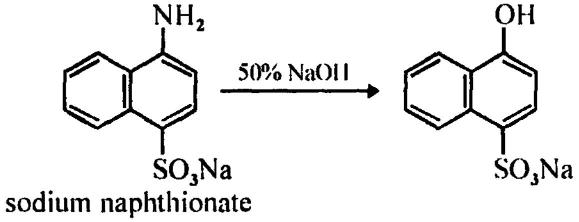
Naphthol Sulphonic Acids : These acids are prepared by sulphonation of naphthols. If α-naphthol is sulphonated with equal weight of conc. sulphuric acid at 60-70°C, 1-naphthol 2-sulphonic acid is the main product, a small amount of 1-naph-thol-4-sulphonic acid is also formed.

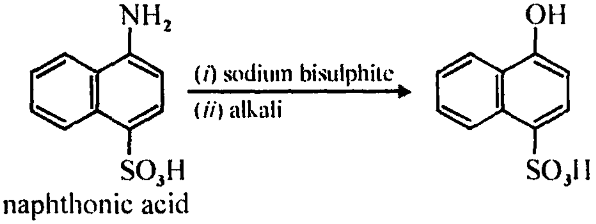


If the sulphonation of α-naphthol is carried out with twice amount of sulphuric acid, 1-naphthol-2, 4-disulphonic acid is the main product.

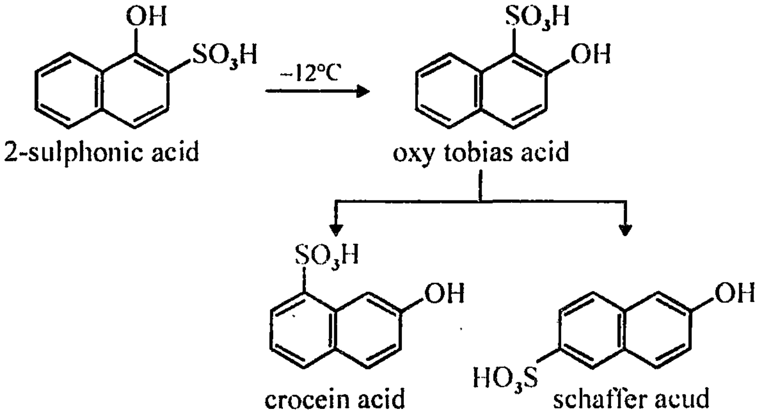


1-Naphthol-4-Sulphonic Acid : It is also known Nevile and Winther's Acid (NW–Acid). It is obtained (*a*) by heating sodium naphthionate with 50% aqueous NaOH in an autoclave or (*b*) by heating naphthionic acid with sodium bisulphite and decomposing the product with alkali.



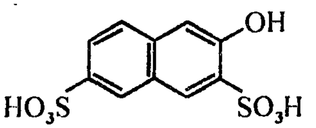


β-Naphthol Sulphonic Acid : The sulphonation of β-naphthol yields various products depending upon temperature and proportion of sulphuric acid. If the sulphonation is carried out at −12°C, 2-hydroxynaphthalene-1-sulphonic acid (oxy tobias acid) is the product. But at 20°C 7-hydroxynaphthalene-1-sulphonic acid (crocein acid) is the main product. The probable mechanism is that the 2-sulphonic ester undergoes rearrangement at low temperatures to yield 1-sulphonic acid, migration taking place at higher temperatures, as follows :

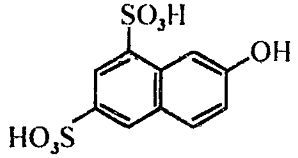


β-Naphthol Disulphonic Acid : If the amount of sulphuric acid is increased, disulphonic acids are obtained. The quantity of acids formed depends upon the temperature at which the sulphonation is taking place. At a low temperature mainly "G-Acid" (β-naphthol-6, 8-disulphonic acid) is obtained while at a higher temperature "R-Acid" (β-naphthol-3, 6-disulphonic acid) is the main product. Both these are very important azo dye intermediates.

When β-naphthol is heated for several hours with three times its weight of sulphuric acid at 110°C, the main product is R-acid which separates as sodium salt on pouring the sulphonation product into brine, whereas G-acid remaining in solution. G-acid may be separated from R-acid by precipitation of G-acid as the potassium salt.

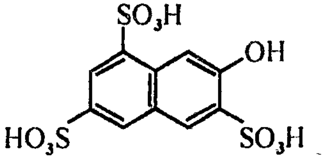


β-naphthol-3, 6-disulphonic acid (R-Acid)



β-naphthol-6, 8-disulphonic acid (G-Acid)

β-Naphthol Trisulphonic Acid : The β-naphthol 3, 6, 8 trisulphonic acid is obtained by the further sulphonation of either G-Acid or R-Acid or by the sulphonation of β-naphthol with 40% oleum at about 120°C.



β-naphthol-3. 6, 8-trisulphonic acid

Naphthylamine Sulphonic Acids : These are prepared by the following methods :

(1) By sulphonation of naphthylamine, (2) By sulphonation and subsequent reduction of nitronaphthalene, and (3) By nitration and reduction of naphthalenesulphonic acid.

The course of sulphonation of the naphthylamines is being shown in Charts 6.1 and 6.2.

Chart 6.1 : Sulphonation of α-naphthylamine

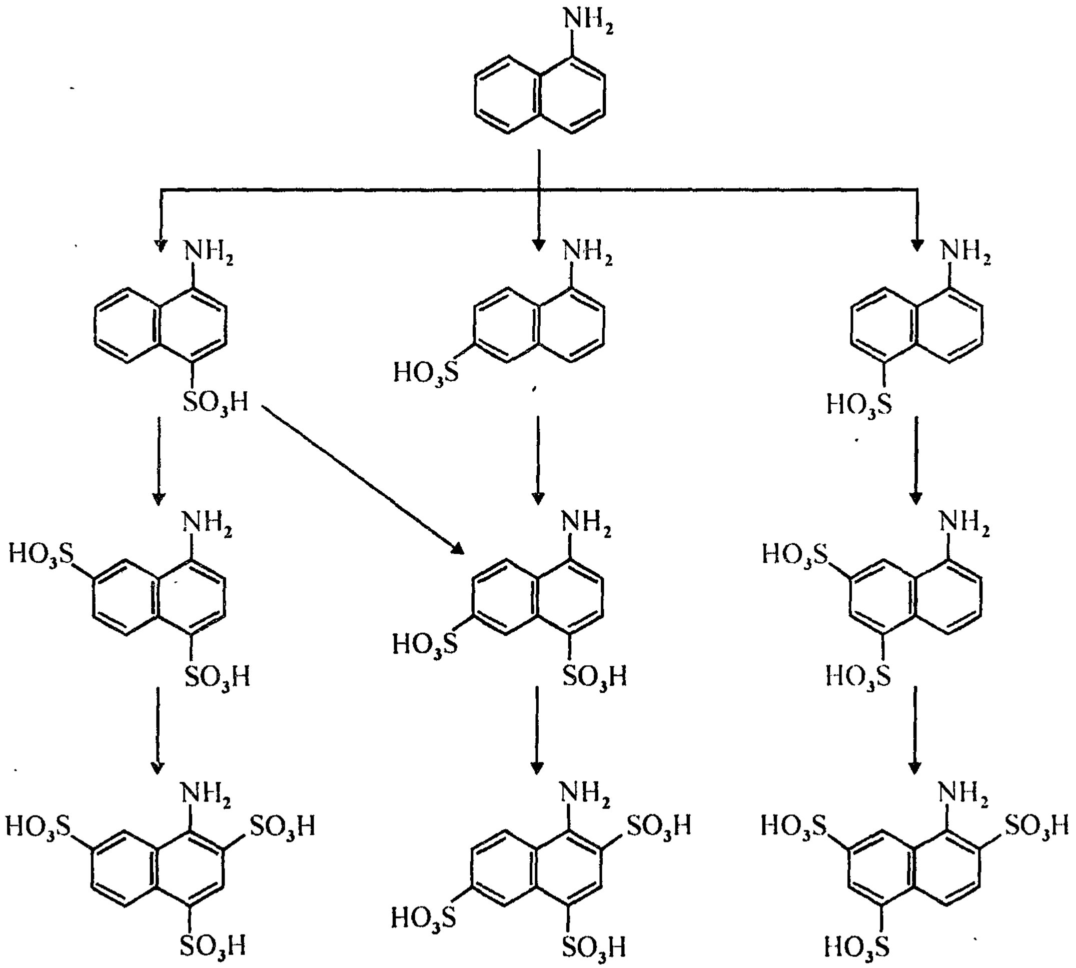
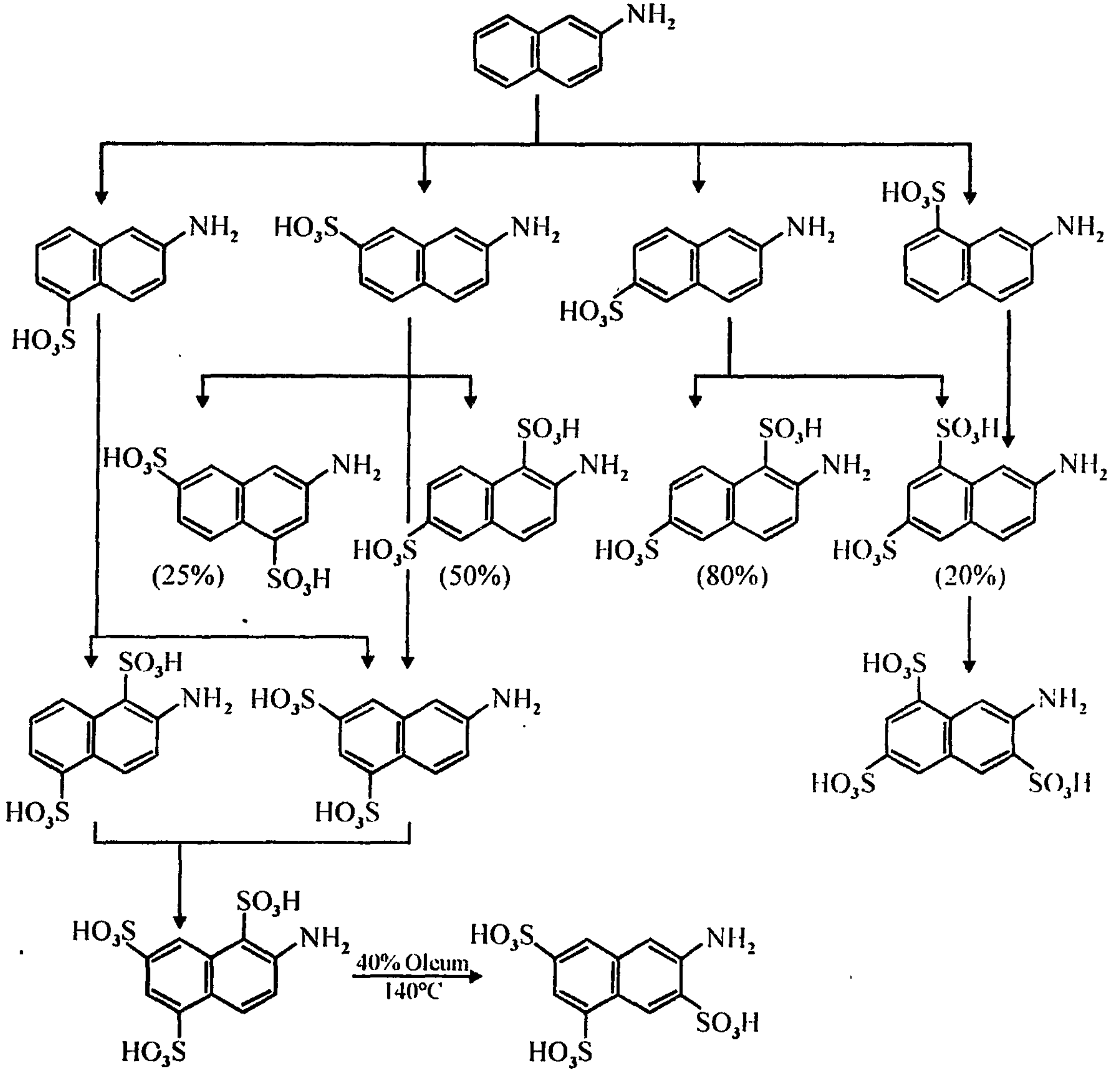
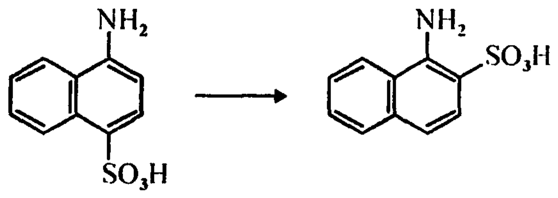


Chart 6.2 : Sulphonation of β-naphthylamine (*See* page 6.23)

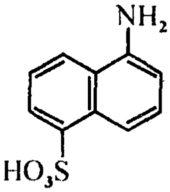


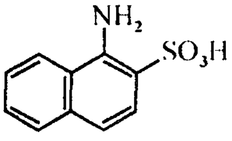
Naphthionic Acid : It is obtained by heating α-naphthylamine acid sulphate mixed with about 3% of its weight of oxalic acid at 170-180°C in vacuum. The acid is used mainly as a secondary component for benzidine dyes and also as a coupling component in azo dyes *e.g.*, congo red and benzopurpurine. Naphthionic acid isomerises to the 2-sulphonic acid if its sodium salt is heated with four parts of naphthalene, at about 200°C for a few hours.



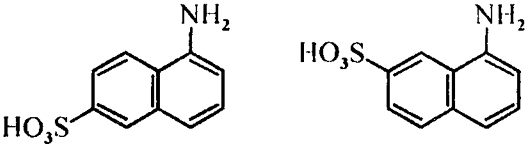
naphthionic acid *ortho*-naphthionic acid

By the cold nitration and subsequent reduction of naphthalene-α-sulphonic acid, a mixture of *peri-acid* (*α-naphthylamine*-8 sulphonic acid) and *laurent acid* (α-naphthylamine-5-sulphonic acid) is obtained. The peri acid is used in the form of its N-phenyl or N-tolyl derivative as an end-component for dark azo-dyes. It gets separated from the laurent acid as its sparingly soluble sodium salt.

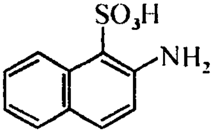

laurent acid


peri-acid

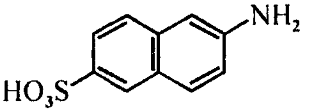
When naphthalene-β-sulphonic acid is nitrated, it yields a mixture of 1-nitro-naphthalene-6 and 7-sulphonic acids which on reduction give a mixture of cleve acids. These are important azo dye intermediates especially in the manufacture of blue trisazo dyes.

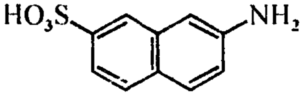

cleve acids

2-Naphthylamine-1-sulphonic acid (tobias acid) is obtained by heating 2-naphthol-1-sulphonic acid with ammonia and ammonium sulphate at 150°C for 30 hours and 10 atm. pressure. After removing ammonia, tobias acid gets precipitated by hydrochloric acid. It is useful for the manufacture of azo colour lakes.


tobias acids

The 2-naphthylamine-6-sulphonic acid (Bronner acid) and 2-naphthylamine-7-sulphonic acid (Cassella acid F) are prepared by treating β-naphthylamine with thrice its weight of concentrated sulphuric acid at 160-180°C for 2 hours. They may be separated from each other in the form of their sodium salts.

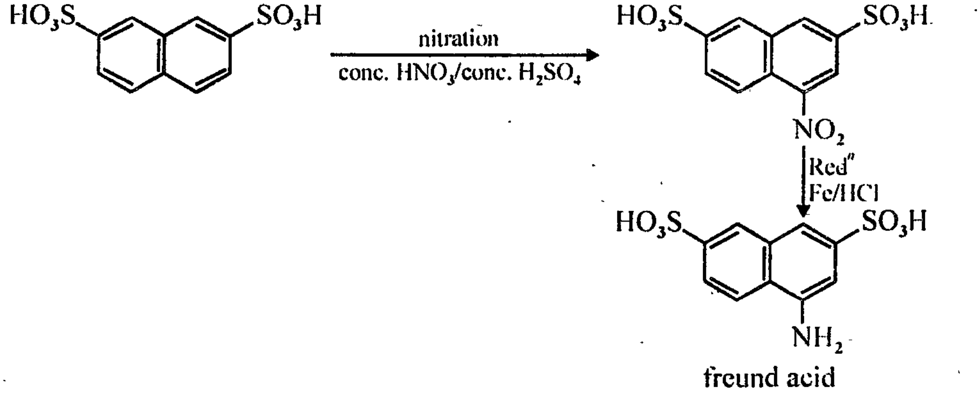

Bronner acids


Cassella acid F

These acids are used as a first and as an end-component for azo-dyes respectively.

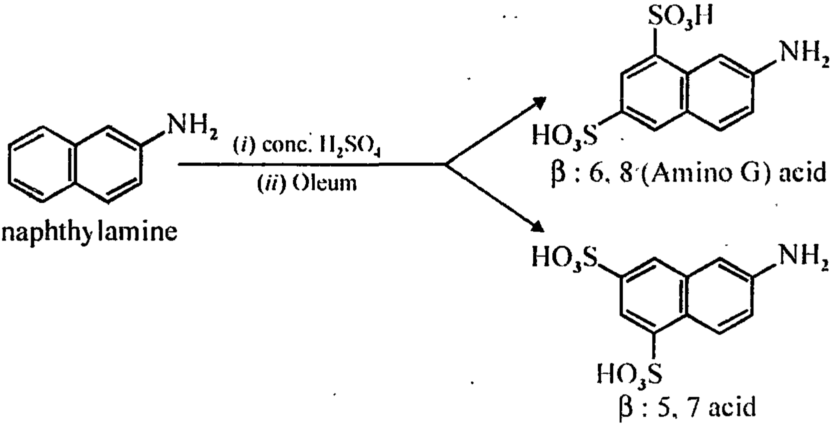
Of the polysulphonic acids of the two naphtylamines, the following are very important :

1. **1-Naphthylamine 3, 6 Disulphonic Acid (Freund Acid) :** It may be prepared as follows :



It is mainly used for the preparation of 'wool blacks' (azo-dyestuffs).

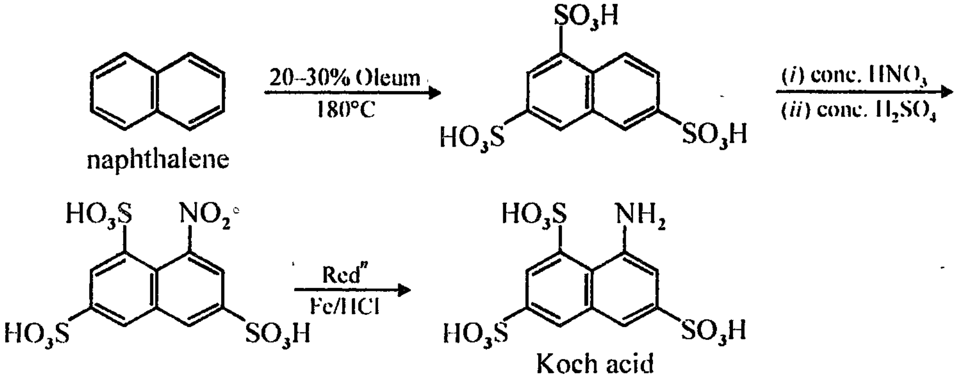
2. **2-Naphthylamine-6, 8 Disulphonic Acid (Amino G acid) and 2-Naphthylamine-5, 7 Disulphonic Acid :** These are prepared by the sulphonation of β-naphthylamine with fuming sulphuric acid.



These acids are intermediates in the manufacture of 'γ-acid' and 'J-acid' respectively.

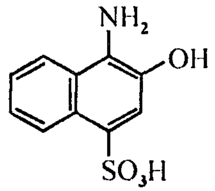
3. **1-Naphtylamine 3, 6, 8-Trisulphonic Acid (Koch Acid) :** It is obtained by nitration and subsequent reduction of the 3, 6, 8 naphthalenetrisulphonic acid.

It is used for the preparation of 'H-Acid'.

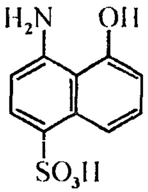


Aminonaphthol Sulphonic Acids : The following are the principal aminonaphtholsulphonic acids :

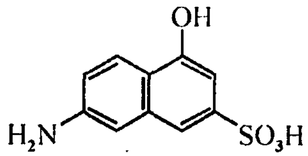
1. **1-Amino-2-Naphthol-4-Sulphonic Acid :** It is obtained by treating 1-nitroso-2-naphthol with sodium bisulphite at 18-20°C, followed by addition of sulphuric acid and the mixture is heated to 40-50°C. The product crystallises out and is filtered off. It is used for making modern black 3.
2. **8-Amino-1-Naphthol-5-Sulphonic Acid (S-Acid) :** It is obtained by melting 1-naphthylamine-4, 8-disulphonic acid with caustic soda. It is used for making blue azo-dyes.
3. **6-Amino-1-Naphthol-3-Sulphonic Acid (J-Acid) :** It is obtained by heating 2-naphthylamine 5, 7-disulphonic acid with concentrated caustic soda solution. It is used for the production of direct cotton dyes.
4. **7-Amino-1-naphthol-3-sulphonic Acid (γ-Acid) :** It is obtained by heating 2-naphthylamine-6, 8-disulphonic acid with concentrated caustic soda solution in an autoclave. It is an intermediate for acid azo dyes.
5. **8-Amino-1-Naphthol-3, 6-Disulphonic Acid (H-Acid) :** It is obtained by heating 1-naphthylamine 3, 6, 8-trisulphonic acid with 35% aqueous caustic soda in an autoclave at 180-190°C. It is isolated by its sparingly soluble acid sodium salt. It is a valuable azo-dye intermediate.
6. **8-Amino-1-Naphthol-3, 5 Disulphonic Acid (K-Acid) :** It is obtained by heating 1-naphthylamine-4, 6, 8-trisulphonic acid with 75% aqueous caustic soda at 170°C. It is used for making blue azo-dyes for cotton.



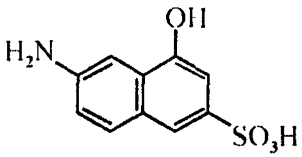
1-amino-2-naphthol-4-sulphonic acid



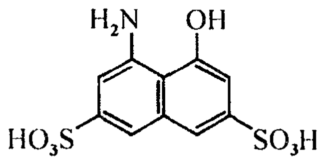
S-acid



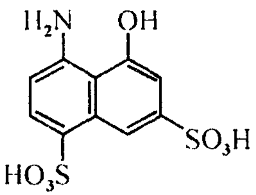
J-acid



γ-acid



H-acid



K-acid

Anthraquinone Sulphonic Acids : These are vary important intermediates in the manufacture of dyes because their sulphonic groups can be replaced directly by hydroxyl, chlorine, amino and even by methoxyl groups.

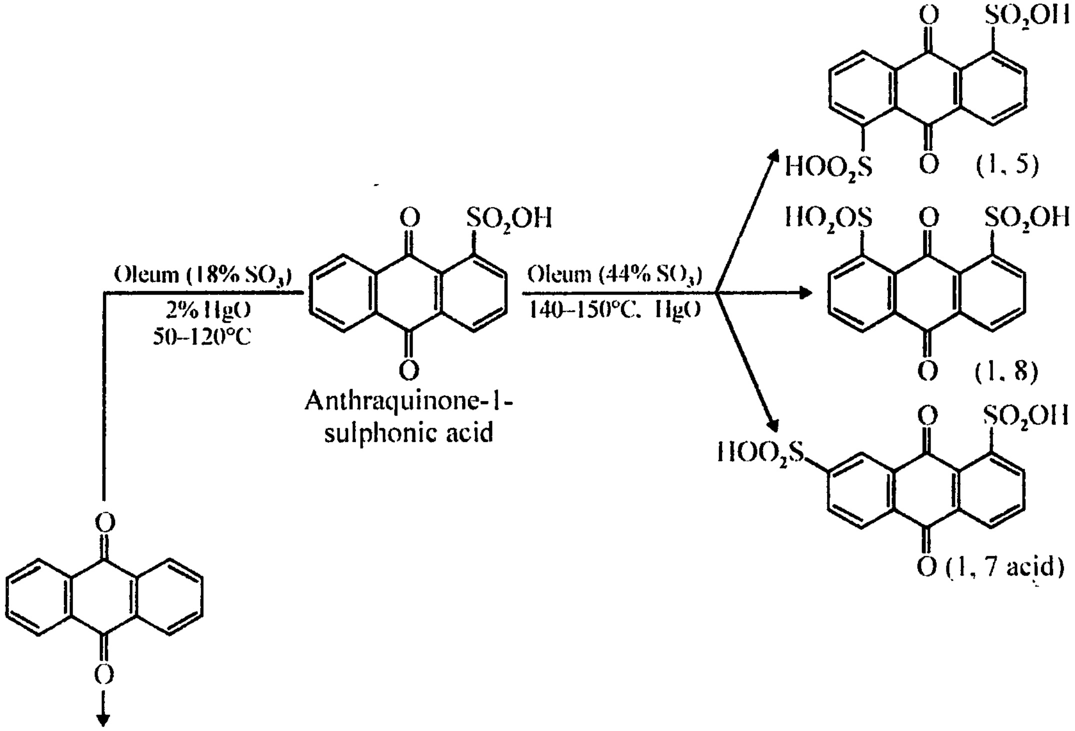
(*a*) **Anthraquinone-2-Sulphonic Acid :** This is obtained by heating anthraquinone with oleum containing 45 per cent free sulphur trioxide at 150°C for one hour. The resulting melt is run into water and neutralised with sodium hydroxide while still hot. On cooling, the sodium salt of anthraquinone-2-sulphonic acid separates out.

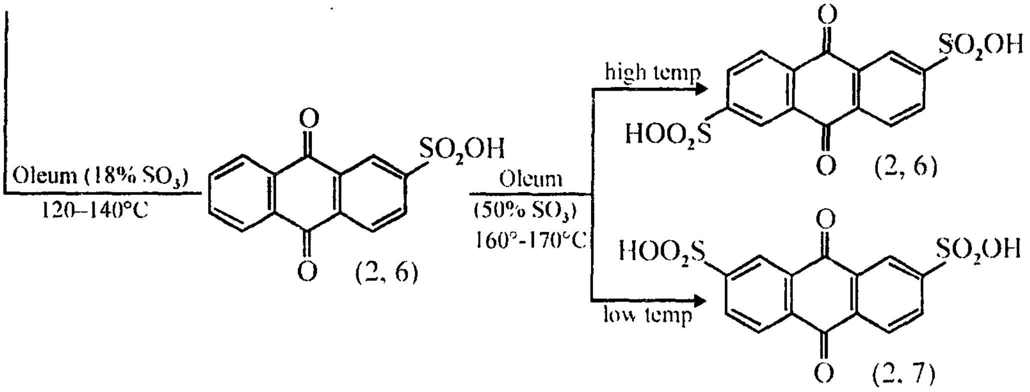
(*b*) **Anthraquinone-2, 6-and-2, 7-Disulphonic Acids :** These are obtained by further sulphonation of anthraquinone-2-sulphonic acid with 50% oleum at 160-170°C in the absence of mercury. At higher temperature, the 2, 6-isomer is the main isomer while at lower temperatures the 2, 7-isomer is predominant. The 2, 6-and 2, 7-isomers are separated as the sodium salts. The 2, 6-isomer is mainly used for the manufacturing of flavopurpurin while the 2, 7-isomer for anthrapurpurin.

(*c*) **Anthraquinone-1-Sulphonic Acid :** It is obtained by heating anthraquinone containing 18% free sulphur trioxide and about 2% of finely powdered mercuric oxide (*i.e.*, mercuric sulphate) at about 50-120°C. The unsulphonated anthraquinone is removed by filtration and 1-sulphonic acid is isolated as its sparingly soluble potassium salt. It is used for the production of 1-aminoanthraquinone and other intermediates.

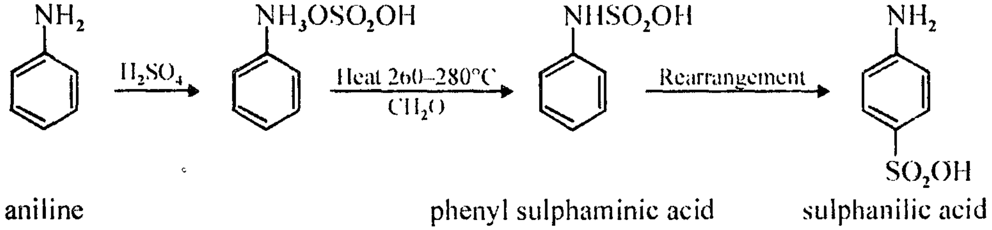
(*d*) **Anthraquinone-1, 5 and-1, 8-Disulphonic Acids :** These are obtained as a mixture by further sulphonation of anthraquinone 1-sulphonic acid. The 1, 5-isomer is salted out from the more soluble 1, 8-isomer after diluting the sulphonation mass.

The above reactions of anthraquinone are given in the following scheme :

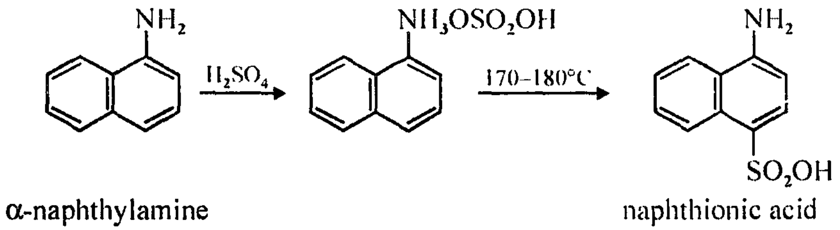




Sulphonation by Baking Process : In this process, amines may be sulphonated by baking their sulphates at elevated temperatures. This procedure offers the advantage of giving fewer isomers. For example, the baking of aniline sulphate at 260-280°C gives high yield of the para sulphonic acid, *i.e.*, sulphanilic acid.

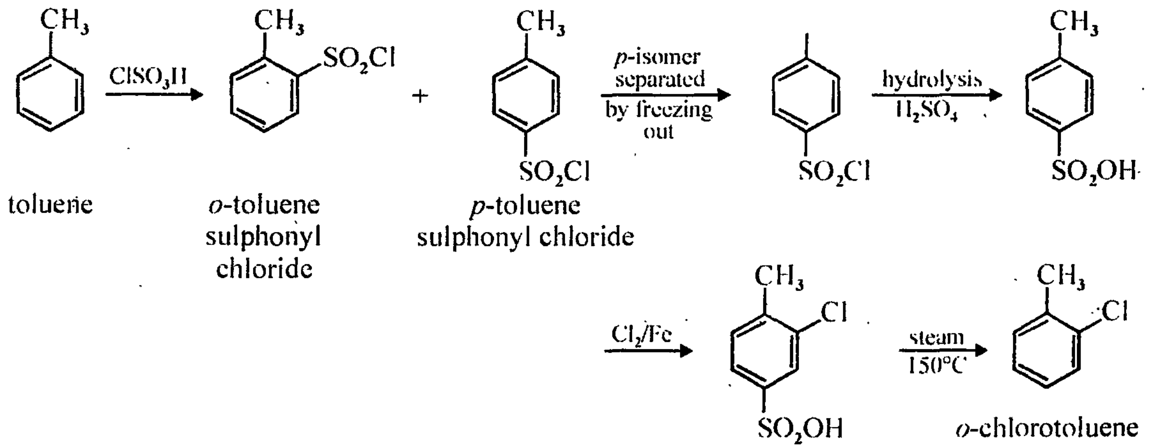


Similarly, naphthionic acid is prepared by heating α-naphthylamine sulphate at 170-180°C under vacuum.

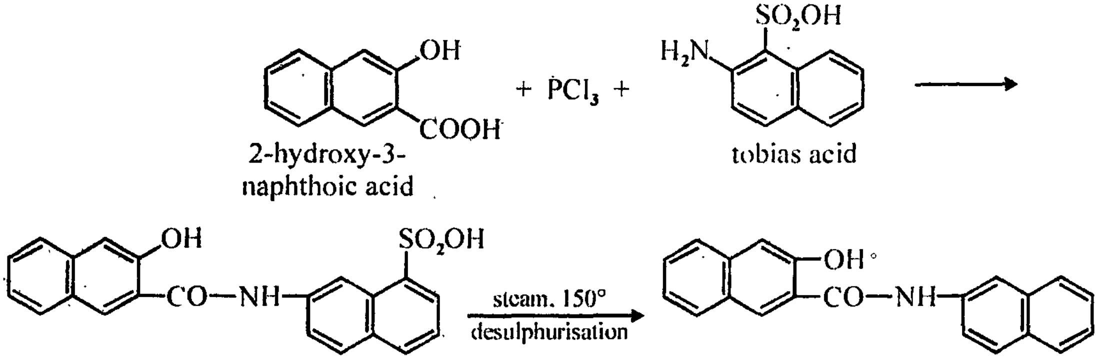


Desulphonation : The reverse of sulphonation is sometimes called desulphonation. In this process the sulphonic acid group is replaced by a hydrogen atom. Desulphonation of certain aromatic sulphonic acids will take place especially when the sulphonic acid group present is staggering with other groups present in the aromatic compound.

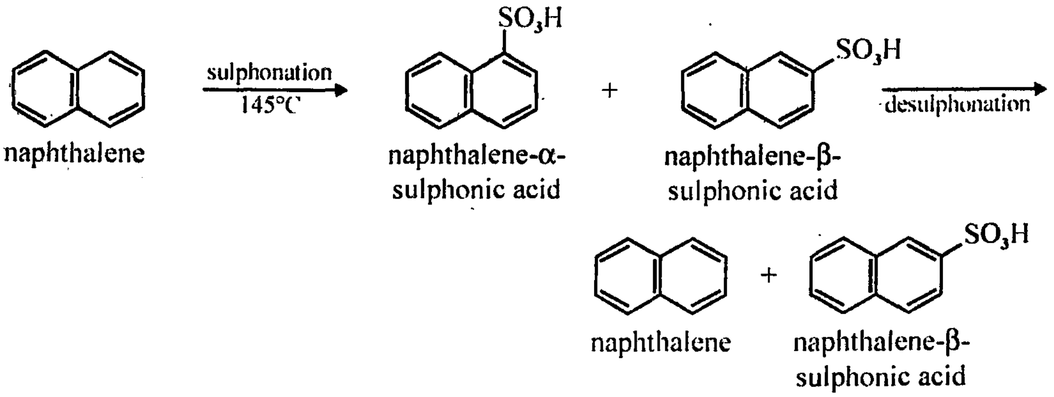
Desulphonation is a useful method for synthesising dye intermediates which could not be prepared by other methods. This method is illustrated by the desulphonation of 2-chloro-1-methyl benzene-4-sulphonic acid in superheated steam at 150°C to *o*-chlorotoluene.



The process of desulphonation is also useful in another way. It avoids the use of carcinogenic 2-naphthylamine but in place of it non-carcinogenic 2-amino-naphthalene-1-sulphonic acid (tobias acid), followed by desulphonation to yield naphthol AS-SW.



The process of desulphonation is also useful for the separation of naphthalene-β-sulphonic acid from naphthalene-α-sulphonic acid. This mixture is obtained on sulphonation of naphthalene at 145°C. When this mixture is worked up for desulphonation, only naphthalene-α-sulphonic acid is converted to naphthalene which can be removed along with steam leaving behind pure naphthalene-β-sulphonic acid.



Amination

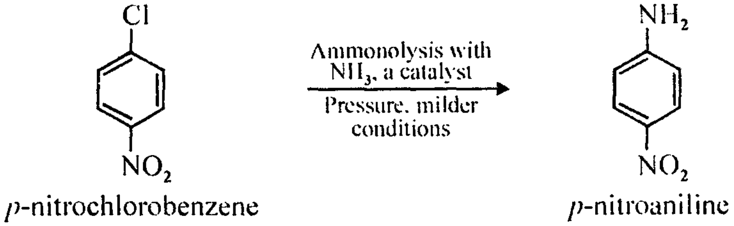
The introduction of an amino group into an aromatic nucleus by replacement of another functional group is called *amination.* This reaction generally takes place in the presence of a catalyst. The primary amines and ammonia act as nucleophilic reagents replacing groups in amination.

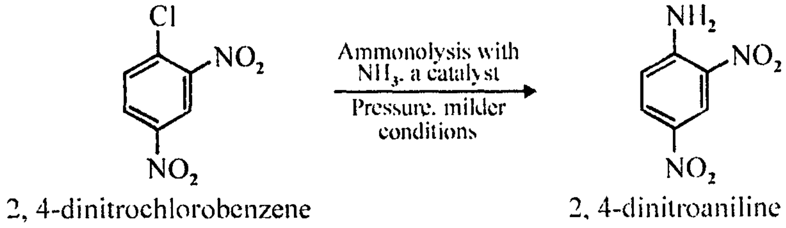
Amination by amines and ammonolysis is important. Ammonolysis generally takes place under pressure. Ammonolysis may be carried out by using gaseous ammonia or liquid ammonia or aqueous ammonia. However, aqueous ammonia is preferred but it gives phenols as by-products. Thus, it reduces the yield of aromatic amines.

In ammonolysis, a metallic catalyst like copper oxide, cuprous oxide or cupric chloride is to be used. However, the choice of a catalyst depends upon the type of the compound handled. For example, a reducing catalyst like cuprous chloride is preferred when the compound like aniline is likely to get oxidised easily. On the other hand, an oxidising catalyst like cupric chloride is preferred when the compound like aminoanthraquinone is likely to get reduced readily. Sometimes sulphites have been used as catalysts in liquid phase while alumina has been used in gaseous phase in ammonolysis.

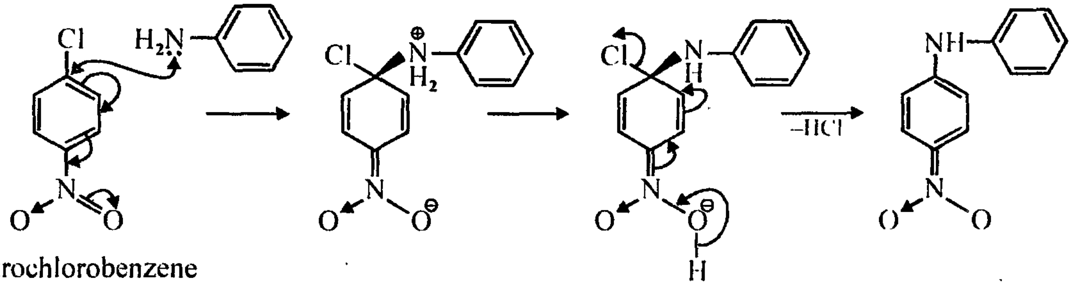
Some examples of amination reactions are as follows :

(*a*) An interesting example of amination in the benzene series is the conversion of *p*-nitrochlorobenzene to *p*-nitroaniline with ammonia. This reaction may be carried out continuously with 40 per cent aqueous ammonia under 200 atmosphere pressure at 235-240°C. Similarly, amination of 2, 4-dinitro-chlorobenzene is effected under much milder conditions because the chlorine atom is more labile.



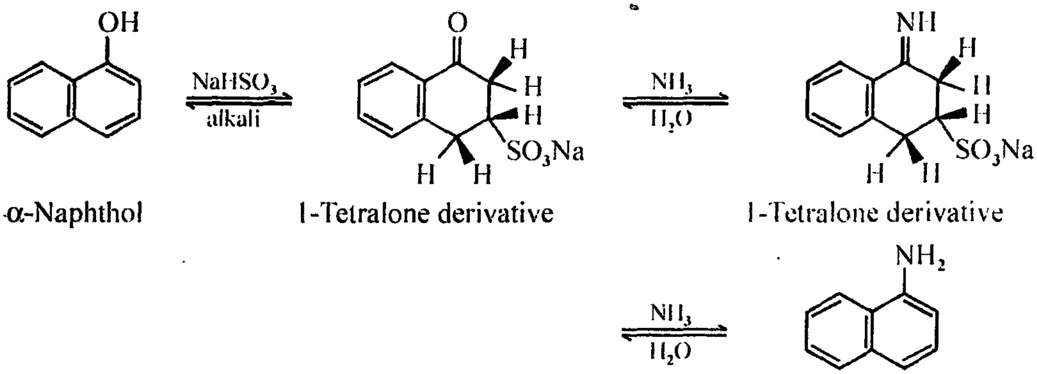


The mechanism of amination of *p*-nitrochlorobenzene by aniline may be given as follows :



p-Nitrochlorobenzene

(*b*) **Bucherer reaction** illustrates amination in the naphthalene series. A naphthol is heated under pressure (6 atm) with ammonium sulphite or ammonia and alkali metal bisulphite at 100-150°C. The result is replacement of the hydroxyl group by an amino group probably by way of a bisulphite addition product of the keto form of the naphthol.



α-Naphthol

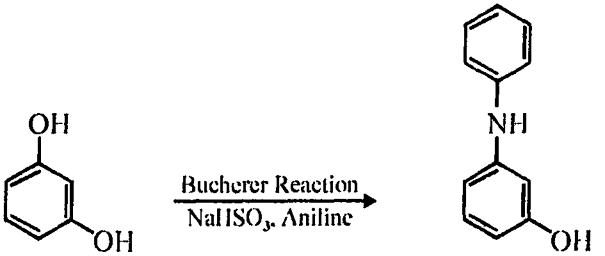
1-Tetralone derivative

1-Tetralone derivative

α-Naphthylamine

Bucherer reaction is reversible and may be used to convert naphthylamines to phenols.

Bucherer reaction is also applicable to resorcinol in benzene series. For example, amination of resorcinol under Bucherer reaction with aniline yields hydroxydiphenylamine.



resorcinol

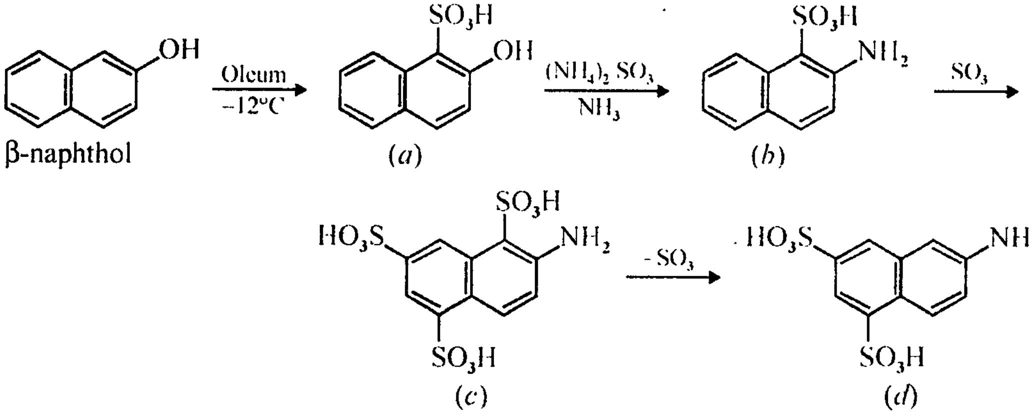
3-hydroxydiphenylamine

By Bucherer reaction, it is possible to convert 1-naphthol 4-sulphonic acid into 1-amino-naphthalene-4-sulphonic acid (naphthionic acid) and vice versa.

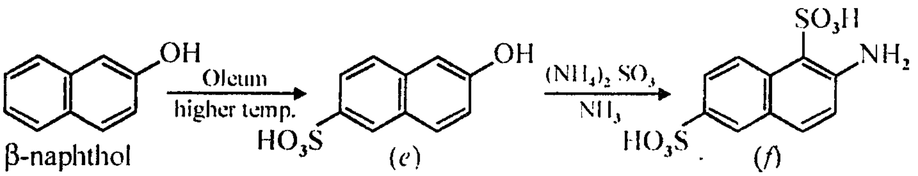
By Bucherer reaction, it is also possible to prepare two important aminosulphonic acids like amino *J* acid and amino *G* acid. These acids are azo dye intermediates.

Amino J-Acid : β-Naphthol on sulphonation yields oxytobias acid (*a*) which is converted into tobias acid (*b*) by the Bucherer reaction. Then tobias acid is sulphonated to form

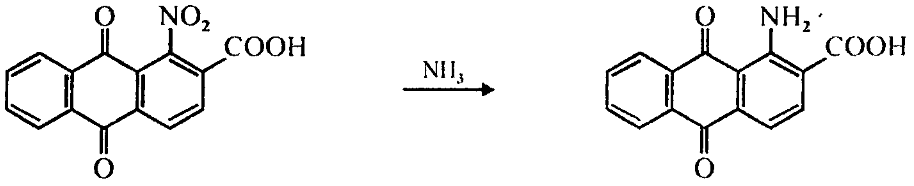
2-aminonaphthalene-1, 5, 7-trisulphonic acid (*c*) which on desulphonation yields 6-amino-naphthalene-1, 3-disulphonic acid (*d*) *i.e.*, amino J-acid.



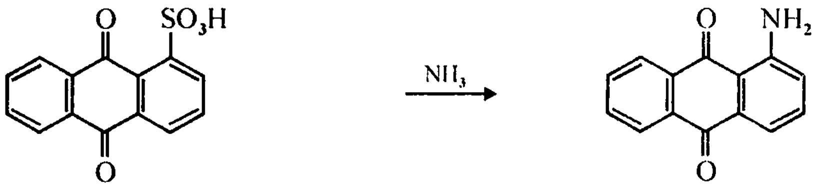
Amino G-Acid : β-Naphthol on sulphonation at a higher temperature yields 2-naphthol-6, 8-disulphonic acid (*e*) which on amination by Bucherer reaction yields 7-aminonaphthalene-1, 3-disulphonic acid (*f*) *i.e.*, amino G-acid.



(*c*) In the anthraquinone series amination is frequently a convenient means of preparing amines. 1-Aminoanthraquinone-2-carboxylic acid can be obtained by the reaction of 1-nitro anthrauinone-2-carboxylic acid with aqueous ammonia at 130°C. The nitro group is displaced but not reduced. In a similar manner, 1-anthraquinone sulphonic acid can be aminated to form 1-aminoanthraquinone or if desired, ammonia may be replaced by methylamine to yield 1-N-methylaminoanthraquinone.



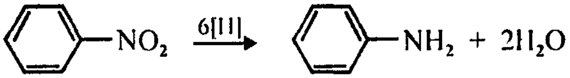
1-nitroanthraquinone-2-carboxylic acid 1-aminoanthraquinone-2-carboxylic acid



1-anthraquinone sulphonic acid 1-aminoanthraquinone

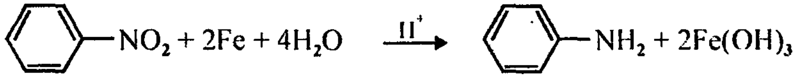
Reduction

The most common reduction method in the manufacture of dye intermediates is the conversion of a nitro compound to the corresponding amine. This reaction is illustrated by the reduction of nitrobenzene to aniline.



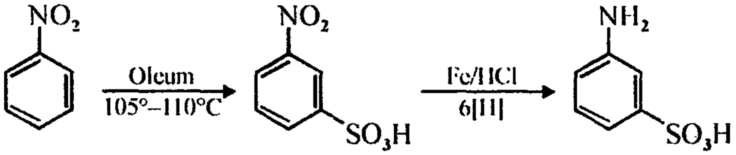
Reduction of nitro compounds may be accomplished by the following methods depending upon the type of reducing agent or system used.

(*a*) **Bechamp Reduction :** This is employed on a large scale because of its simplicity. The effective reducing agent is nascent hydrogen which is produced by the reaction of grey iron and water having a small amount of hydrochloric acid, formic acid or acetic acid to promote reaction. The overall reaction may be illustrated for nitrobenzene as follows :



Iron reduction of nitro compounds is being de-emphasized in favour of catalytic reduction which is more efficient in a labour industry such as dyes.

Bechamp reduction method can also be used in reducing the nitro derivatives of sulphonic acids. This can be illustrated by the manufacture of metanilic acid from nitrobenzene. The starting substance is nitrobenzene which on sulphonation with oleum at 105-110°C yields *m*-nitrobenzenesulphonic acid. The resulting mixture is neutralized by $CaCO_3$ and filtered to remove calcium sulphate. The solution of calcium salt of *m*-nitrobenzenesulphonic acid is reduced with iron-water in the presence of an acid (Bechamp reduction). The reduction liquor is made alkaline with caustic soda solution, filtered from iron sludge. The solution is first evaporated to 50% strength as sodium metanilate and then precipitated by acidification as metanilic acid.



Nitrobenzene *m*-Nitrobenzene-sulphonic acid Metanilic acid

Bechamp reduction method is also used in the manufacture of 1-naphthylamine sulphonic acids.

A few applications of Bechamp reduction method are summarised in Table 6.2.

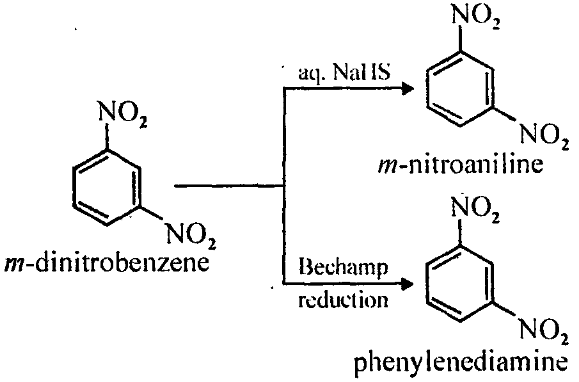
Table 6.2 : Applications of Bechamp Reduction

Starting substance	*Product*	*Acid use*
p-nitrophenol	*p*-aminophenol	acetic acid
p-nitroaniline	*p*-phenylenediamine	$FeCl_3/HCl$
p-nitrobenzoic acid	*p*-aminobenzoic acid	HCl

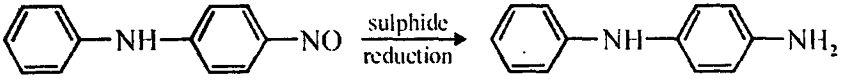
(Contd...)

Starting substance	*Product*	*Acid use*
m-nitrotoluene	*m*-toluidine	Formic acid
1-chloro-3-nitrobenzene	*m*-chloroaniline	Formic acid
2-chloro-6-nitrotoluene	3-chloro-*o*-toluidine	Formic acid
2-chloro-4-nitrobenzoic acid	5-amino-2-chlorobenzoic acid	HCl
1, 3-dichloro-4-nitrobenzene	2, 4-dichloroaniline	HCl

(*b*) **Sulphide Reduction :** Another useful method of reduction of nitro group to amino group is reduction using sodium sulphide (Na_2S), sodium hydrosulphide (NaHS) or sodium polysulphide (Na_2S_x). An important feature of this type of reducing system is its adaptability to bring about step-wise reduction of dinitro compounds. Partial reduction is illustrated with *m*-dinitrobenzene which can be reduced to *m*-nitroaniline with sodium sulphide at 95°C under controlled conditions. However, for getting *m*-phenylene diamine, Bechamp reduction is to be followed.



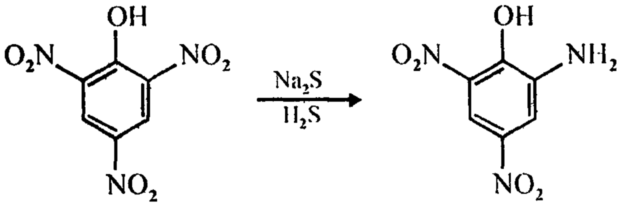
Sulphide reduction is also used to reduce some nitroso compounds, *e.g.*, 4-nitrosodiphenylamine to 4-aminodiphenylamine.



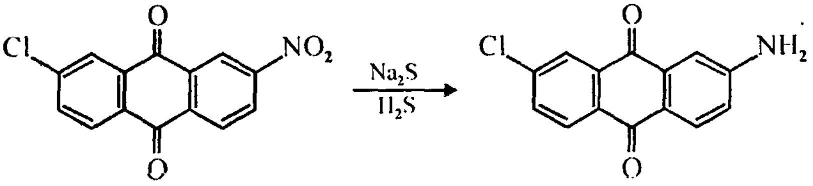
4-nitroso diphenylamine 4-amino diphenylamine

Other examples of sulphide reduction method are as follows :

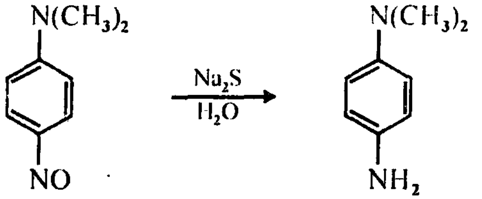
(*i*) Picric acid is reduced to picramic acid.



(*ii*) 2-Chloro-7-nitro anthraquinone is also reduced.



(*iii*) *p*-Nitrosodimethylaniline is reduced to *p*-aminodimethyl-aniline.

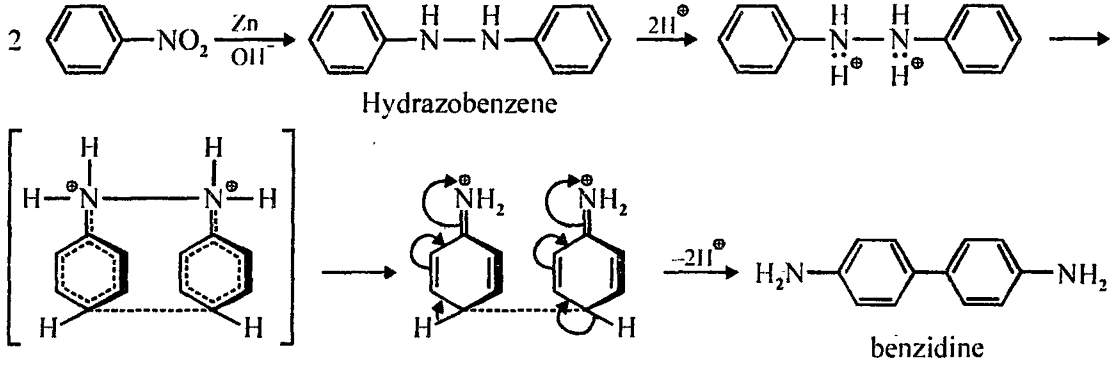


Some other examples of sulphide reduction method are given in Table 6.3.

Table 6.3 : Some Applications of Sulphide Reduction Method

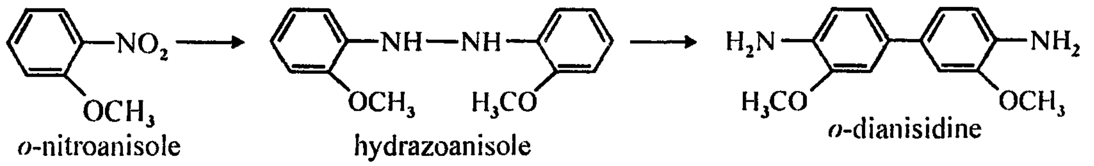
Starting substance	*Product*	*Reducing Agent*
o-nitroaniline	*o*-phenylene diamine	Na_2S
p-nitroanisole	*p*-anisidine	Na_2S
1, 4-dimethoxy-2-nitrobenzene	2, 5-dimethoxyaniline	NaSH
3, 5-dinitro-*p*-toluene sulphonic acid	3-amino-5-nitro- *p*-toluene sulphonic acid	NaSH/MgO
5-phenylazosalicylic acid	5-aminosalicylic acid	Na_2S_x

(*c*) **Zinc Reduction** : The zinc reduction in alkaline aqueous or alcoholic medium is especially useful to bring about bimolecular reduction. This kind of reaction is illustrated by the conversion of nitrobenzene to hydrazobenzene. Rearrangement of hydrazo-benzene with acid gives benzidine. The reaction mechanism is given as follows :



This mechanism leads to C–C linking but also leads to N–N bond breaking originally present in hydrazobenzene and can give rise to 4, 4′-product, *i.e.*, benzidine.

In a similar manner, *o*-nitroanisole is first converted to hydrazoanisole and then to *o*-dianisidine.

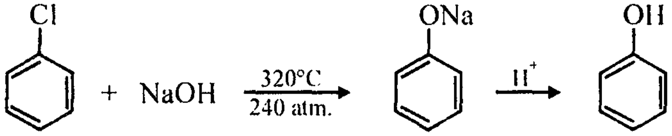


(*d*) **Catalytic Reduction** : Generally, where the reaction is carried out on a large scale, the catalytic procedure is best. Catalytic reduction requires a catalyst such as nickel, copper, platinum, molybdenum or tungsten. Reduction conditions vary widely, depending on the nature of nitro compound and the catalyst. Reduction may be carried out in solvent, in the vapour phase or in the liquid phase. Aniline can be manufactured by continuous vapour phase reduction of nitrobenzene at 350-460°C at nearly atmospheric pressure.

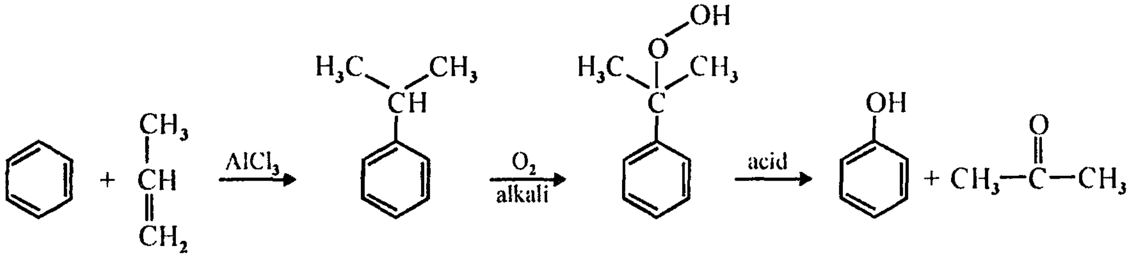
The place of hydrogen as a reducing gas may be taken by water gas, producer gas or an alcohol.

Hydroxylation : Aromatic hydroxy compounds are used extensively as coupling components in the manufacture of azo dyes. The hydroxyl group may be introduced into the aromatic nucleus by the following methods :

(*a*) **Dow Process** : In this process, chlorobenzene and aqueous caustic soda are heated to 320°C under pressure of 240 atmospheres when phenol is obtained. This is used extensively in dyes and plastic industry.



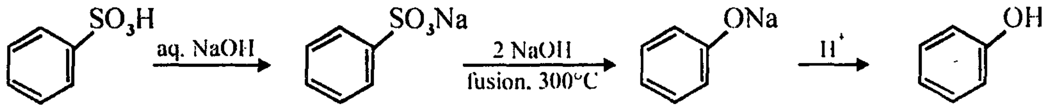
(*b*) **Cumene Process** : It is the modern process for the manufacture of phenol. In this process, benzene and propene combine in the presence of aluminium chloride to give cumene which is air-oxidised to cumene hydroperoxide. The latter on treatment which acid gets decomposed into acetone and phenol.



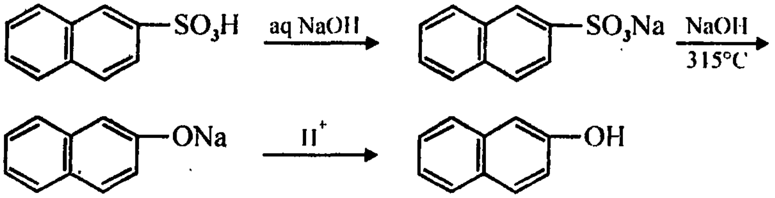
Similarly, *p*-cresol may be prepared by using the above method.

(*c*) **Alkali Fusion** : It is an important procedure for the hydroxylation of aromatic compounds. In this method, a sulphonic acid group is replaced by a hydroxyl group. This reaction cannot be used when nitro or chloro groups are present but is applicable to amino compounds.

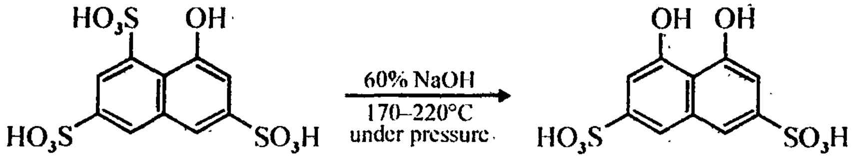
Alkali fusion is usually carried out with a concentrated solution of sodium hydroxide in a cost-iron pot which is equipped with a scraping agitator and heated externally. The water is evaporated and then the mass fuses. The reaction mixture is heated between 190-350°C, depending on the reactivity of the sulphonic acid group.



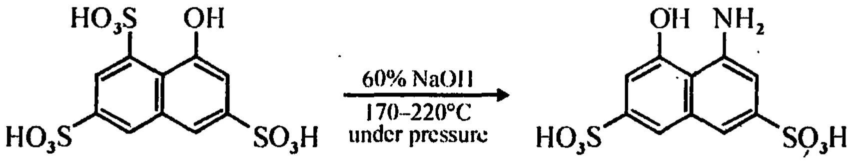
By this process, 2-naphthol is obtained from naphthalene-2-sulphonate.



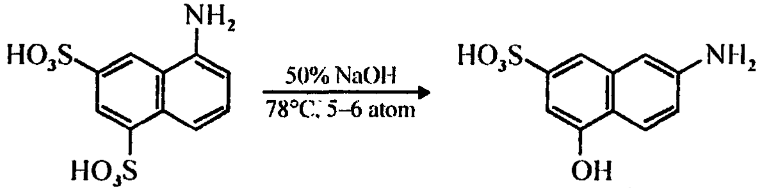
A sulphonic acid group is also replaced by a hydroxyl group by heating it with aqueous alkali under pressure. For example, in the following manner :



Similarly, H-acid is prepared from 1-aminonaphthalene-3, 6-8-sulphonic acid (Koch acid) in the following manner :

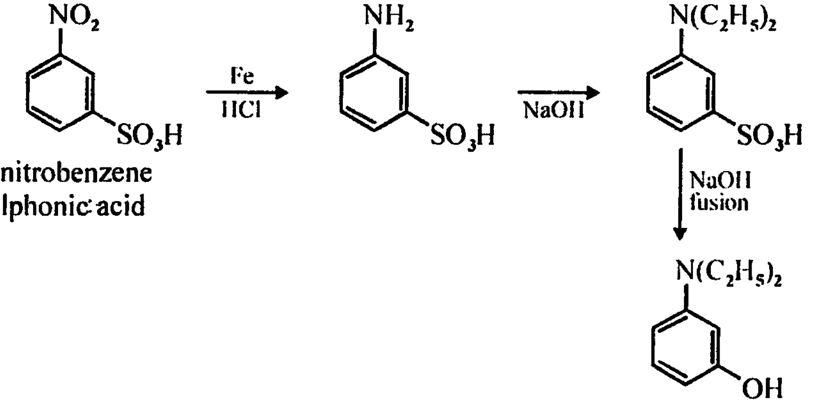


Also, 1-aminonaphthalene-5, 7-disulphonic acid is converted into *J*-acid in the following way:



J-acid

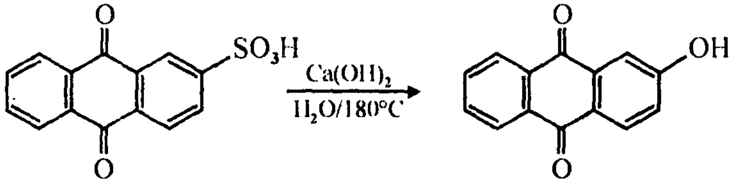
Aqueous alkali method is used in the manufacture of *m*-diethylaminophenol which is used in the manufacture of sulphorhodamine B and certain brightening agents.

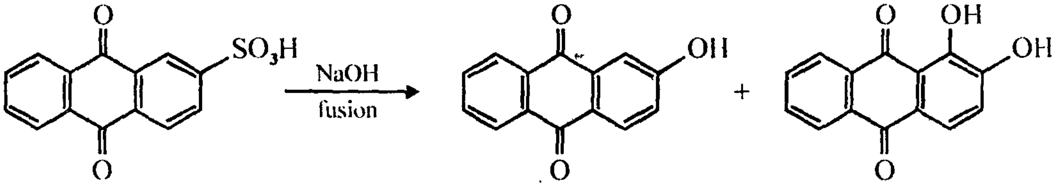


m-nitrobenzene sulphonic acid

m-diethylaminophenol

In the anthraquinone series, 2-anthraquinonesulphonic acid can be converted to the hydroxy compound by heating with calcium hydroxide in water. Alkaline fusion of the same sulphonic acid gives alizarin in addition to β-hydroxy anthraquinone.

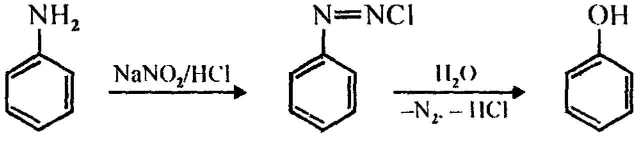




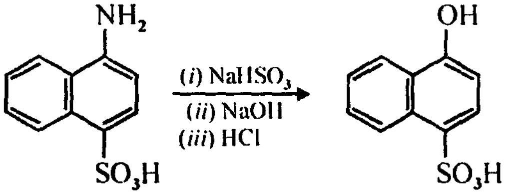
Alizarin

(*d*) **Replacement of $-NH_2$ Group by –OH Group** : It may be done by the following methods :

(*i*) By boiling the diazo salt with water.

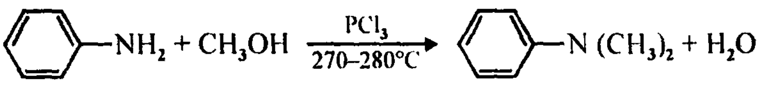


(*ii*) By the reverse Bucherer reaction, *e.g.*, Nevile and Winther's acid may be obtained from 1-amino-naphthalene-4-sulphonic acid.



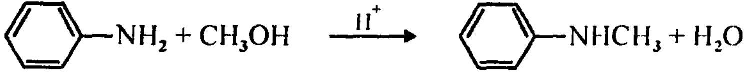
Alkylation of Aromatic Amines : Alkylation refers to the introduction of an aliphatic group, such as methyl, into an organic molecule. Alkylation may occur on carbon, nitrogen, oxygen or sulphur. Of these possibilities, alkylation on nitrogen and oxygen are important in the manufacture of dye intermediates. The alkylating reagents usually are chlorides, alcohols or sulphates.

An example of alkylation is that N, N-dimethylaniline is made by reacting aniline with methanol in the presence of PCl_3 in chromium-molybdenum steel autoclaves at 270-280°C under pressure of 70-100 atm. The product is purified by distillation in vacuum.



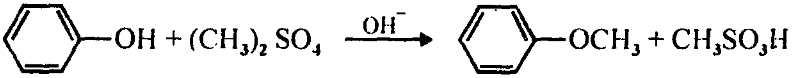
N–N-dimethylaniline

However, a methyl group may be introduced into the amino group of aniline by heating with methyl alcohol under pressure in the presence of a mineral acid.



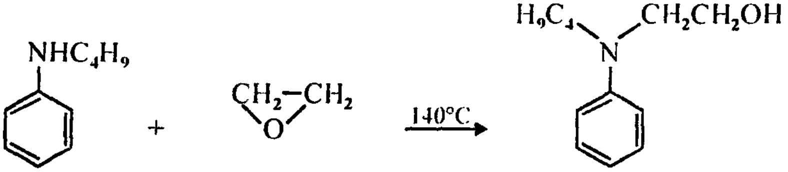
N-methylaniline

Phenol may be methylated with methyl sulphate in cold alkaline medium to give anisole.



anisole

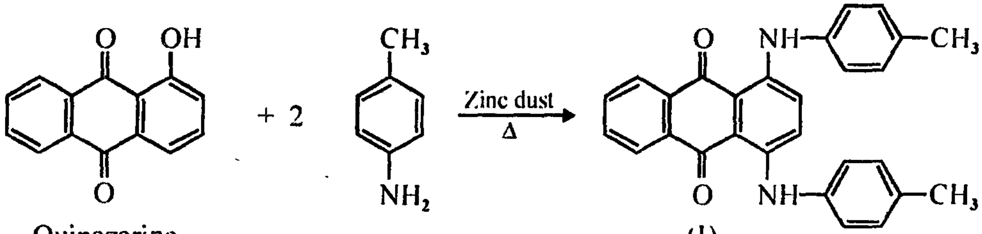
Hydroxyethylation is carried out on primary or secondary amines and is very important for disperse dyes.



N-n-butylaniline ethylene oxide N-n-butyl-N-2-hydroxyethylaniline

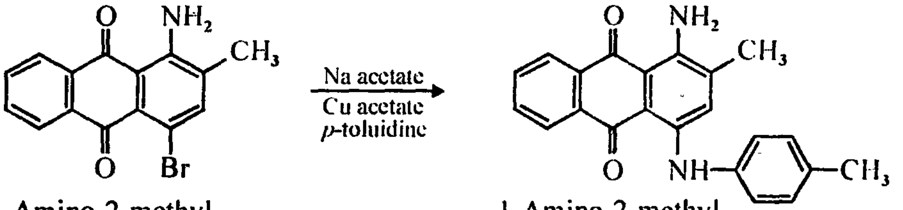
The product is purified by distillation and is used as an azo coupling component.

Arylation of Amines : This is a very important reaction in anthraquinone intermediates. One way is replacement of hydroxyl group by arylamine group. For example, the condensation of two molecules of *p*-toluidine with one molecule of quinazarine in the presence of small quantity of zinc dust yields 1, 4-di-*p*-tolylaminoanthraquinone (I).



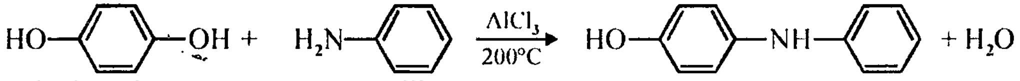
Quinazarine (I)

Arylamino groups are introduced also by replacement of halogens, *e.g.*,



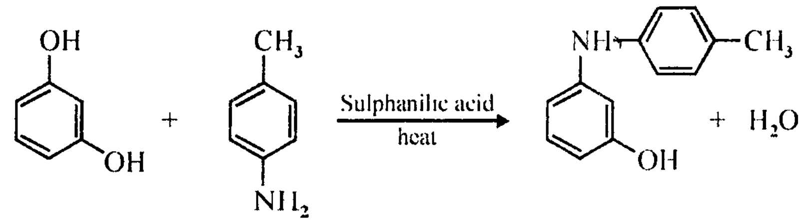
1-Amino-2-methyl-4-bromo anthraquinone 1-Amino-2-methyl-4-*p*-toluidine anthraquinone

4-Hydroxydiphenylamine is obtained by heating hydroquinone with excess of aniline in the presence of aluminium chloride as catalyst at 200°C.



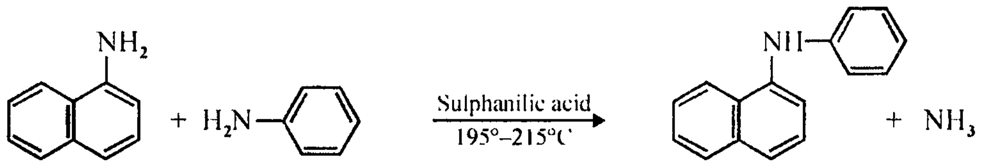
hydroquinone aniline

Some more reactions are as follows :



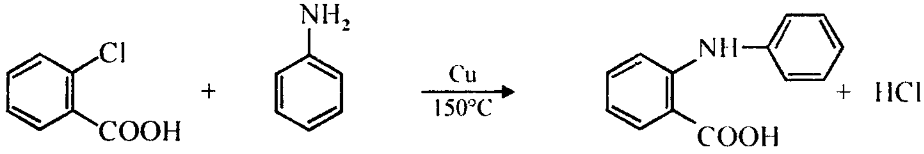
resorcinol *p*-toluidine

It is used in making triphenylmethane dye.



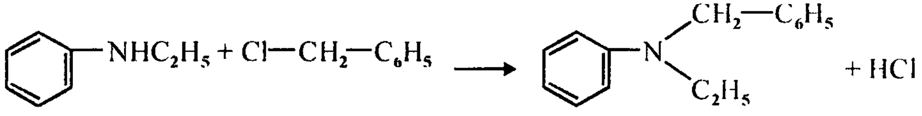
α-naphthylamine aniline N-phenyl-1-naphthalene

It is used in the manufacture of victoria blue B

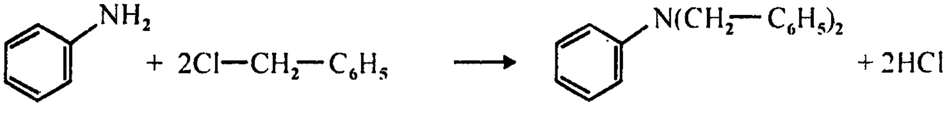


o-chlorobenzoic acid aniline N-phenyl anthranilic acid

N-benzyl-N-ethyl-aniline and N, N-dibenzylaniline are obtained by the action of benzyl chloride on N-ethylaniline and aniline respectively.



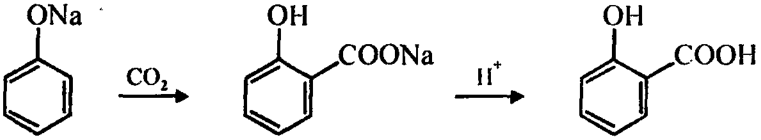
N-benzyl-N-ethylaniline



N-N-dibenzylaniline

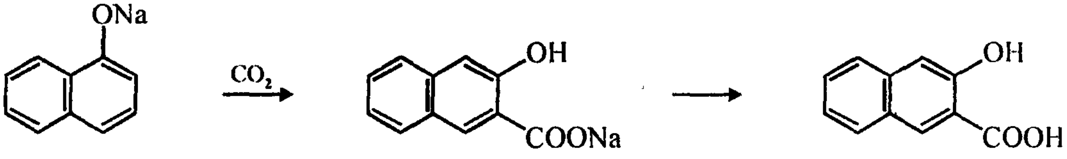
N-benzyl-N-ethylaniline is used for the preparation of acid dyes of the triphenyl-methane series.

Carboxylation : The carboxylic acid group may be introduced by side chain oxidation as described above. In addition it may be introduced by direct action of carbon dioxide on certain compounds through Kolbe's reaction. In this reaction, sodium phenolate is treated with carbon dioxide under pressure at about 150°C when sodium salicylate is formed. Acidification of the salicylate gives the free acid which may be purified by vacuum distillation.



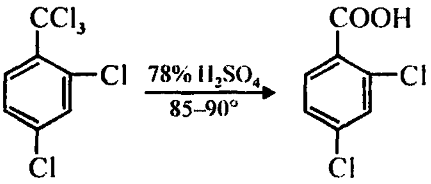
salicylic acid

2-Hydroxy-3-naphthoic acid, an intermediate for azo dyes is made from sodium 2-naphtholate by Kolbe's reaction.



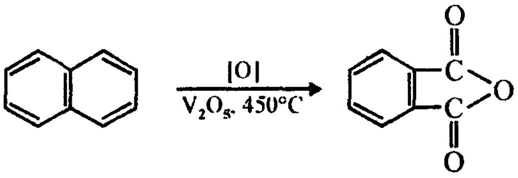
sodium 2-naphtholate 2-hydroxy-3-naphthoic acid

2, 4-Dichlorobenzoic acid is obtained in good yield by hydrolysis of 2, 4-dichlorobenzotrichloride with 78% sulphuric acid at 85-90°C.

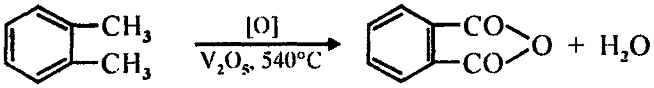


Oxidation : It may be affected by air in the presence of a catalyst or by a variety of chemical oxidants such as manganese dioxide and potassium permanganate.

Catalytic Vapour-Phase Oxidation : It is illustrated by the conversion of naphthalene to phthalic anhydride. This reaction is carried out over a vandadium pentoxide catalyst at 450°C.

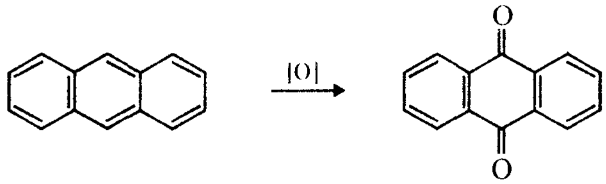


Another route to phthalic anhydride is oxidation of *o*-xylene, a product of the petroleum industry. The conditions for this reaction are similar to those for naphthalene oxidation, except that the temperature is higher, *i.e.*, 540°C.



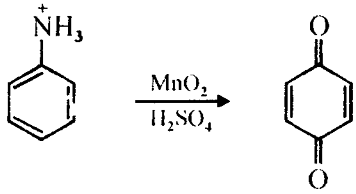
Phthalic anhydride plays a significant role in dye chemistry.

A lot of anthracene is available as by-product of coal tar distillation. Anthracene on oxidation with air in the presence of V_2O_5 (catalyst) yields anthraquinone.



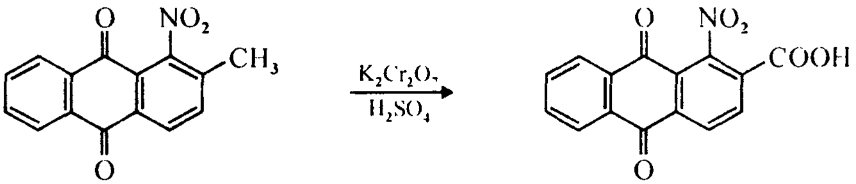
anthraquinone

Oxidation with Chemical Oxidants : Aniline sulphate can be chemically oxidised with manganese dioxide in sulphuric acid. The product is *p*-quinone.



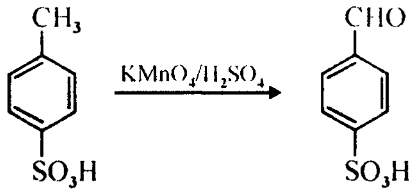
p-quinone

The use of potassium dichromate in sulphuric acid affects the oxidation of 1-nitro-2-methylanthraquinone to the corresponding carboxylic acid. This reaction illustrates side-chain oxidation, an important route to the carboxylic acids.

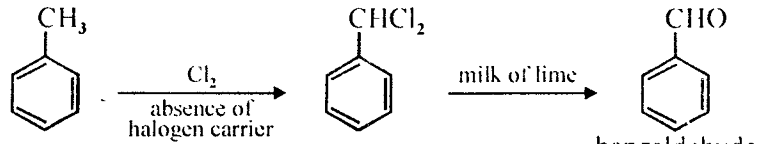


1-nitro-2-methylanthraquinone 1-nitro-2-anthraquinone carboxylic acid

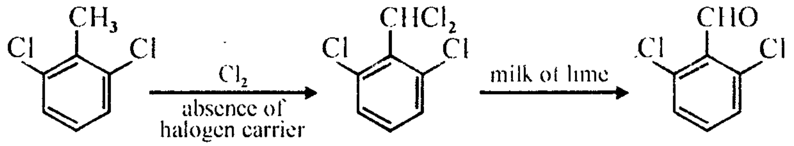
Benzaldehyde-4-sulphonic acid required for triarylmethane dyes is made from *p*-toluene sulphonic acid by oxidation with permanganate in sulphuric acid.



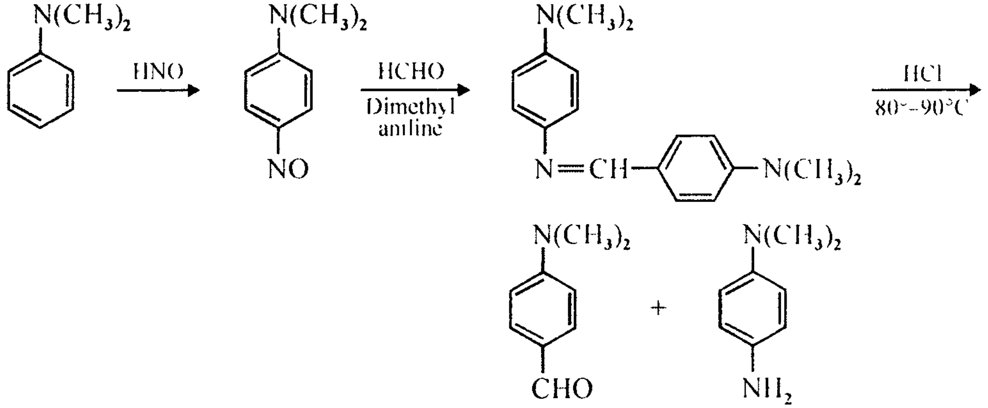
Formylation : Introduction of –CHO group into the aromatic nucleus is called *formylation*. It is carried out by the hydrolysis of dichloromethyl group which is introduced into the benzene nucleus by the chlorination of side chain $-CH_3$ in the absence of halogen carrier. For example, toluene on chlorination in the absence of halogen carrier yields benzal chloride which upon hydrolysis with milk of line yields benzaldehyde. Toluene derivatives also undergo similar type of reactions. For instance, 2, 6-dichlorotoluene yields 2, 6-dichlorobenzaldehyde.



benzaldehyde

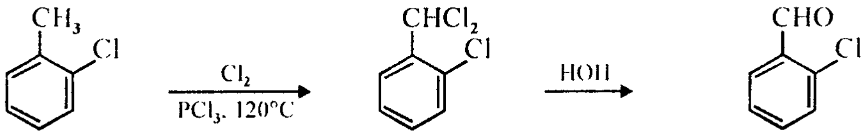


Formylation of tertiary amines can be carried out by nitrosation followed by reaction with formaldehyde. The product is separated by filtration after neutralising the reaction mixture while the diamine remains in solution.



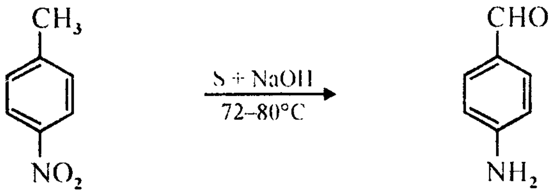
4-dimethylamino-benzaldehyde

The *o*-chlorobenzaldehyde is obtained from *o*-chlorotoluene through the following sequence of reactions :



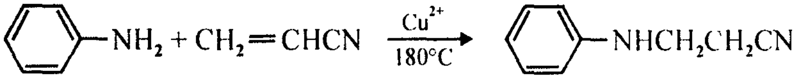
o-chlorotoluene *o*-chlorobenzaldehyde

The *p*-aminobenzaldehyde is obtained by heating *p*-nitrotoluene with sulphur and sodium hydroxide at 72-80°C (intermolecular oxidation-reduction).



p-nitrotoluene *p*-aminobenzaldehyde

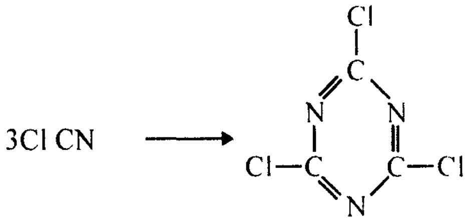
Cyanoethylation : Reaction of a primary or secondary aromatic amine with acrylonitrile results in N-cyanoethylation. An example is the cyanoethylation of aniline with cupric sulphate catalyst.



N-cyanoethylaniline

The products produced by cyanoethylation are useful intermediates for azo and basic dyes.

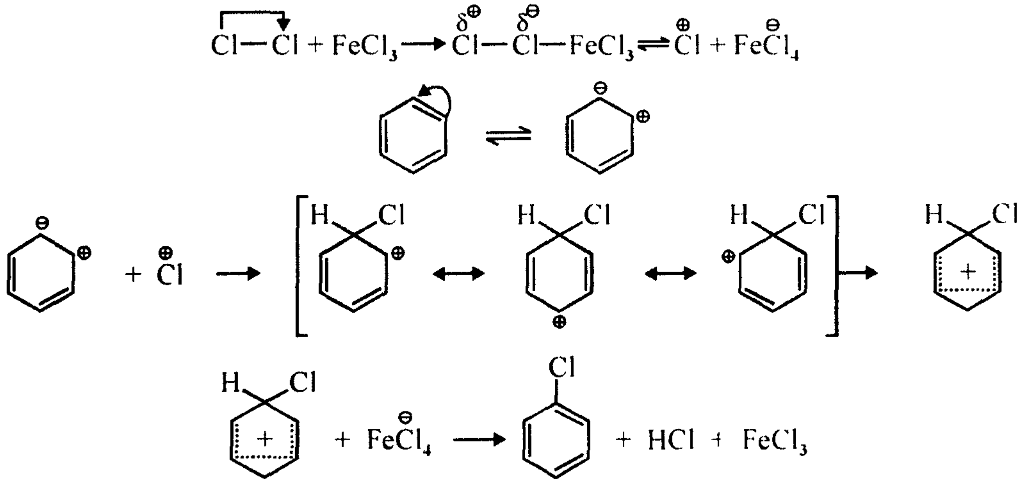
Addition : An intermediate called cyanuric chloride is obtained by the addition of cyanogen chloride to itself. This reaction is catalysed by a small amount of free chlorine.



cyanogen chloride cyanuric chloride

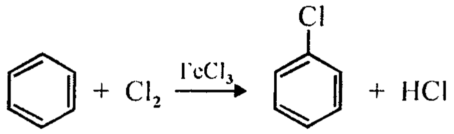
Halogenation

Chlorination : Chlorine is the most widely used of the halogens because it is comparatively economical. Generally, chlorination is performed by dried chlorine gas *i.e.*, by direct chlorination with or without a catalyst. In a few cases, chlorination may be achieved with reagents such as thionyl chloride, phosphorus oxychloride, phosphorus pentachloride or sulphuryl chloride. The mechanism of chlorination of benzene is as follows :



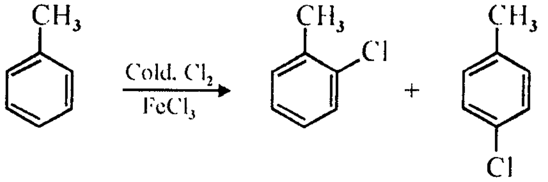
chlorobenzene

Chlorination of Benzene : Chlorobenzene is made by passing a stream of dried chlorine into benzene in the presence of ferric chloride; some *p*-dichlorobenzene is formed at the same time. To produce monochlorobenzene as the sole product excess benzene is only partially converted and unreacted benzene is recycled. Even so, some polychlorobenzene is obtained.



Chlorobenzene formed is purified by fractional distillation. Chlorobenzene is converted into phenol, aniline, D.D.T. and many other products.

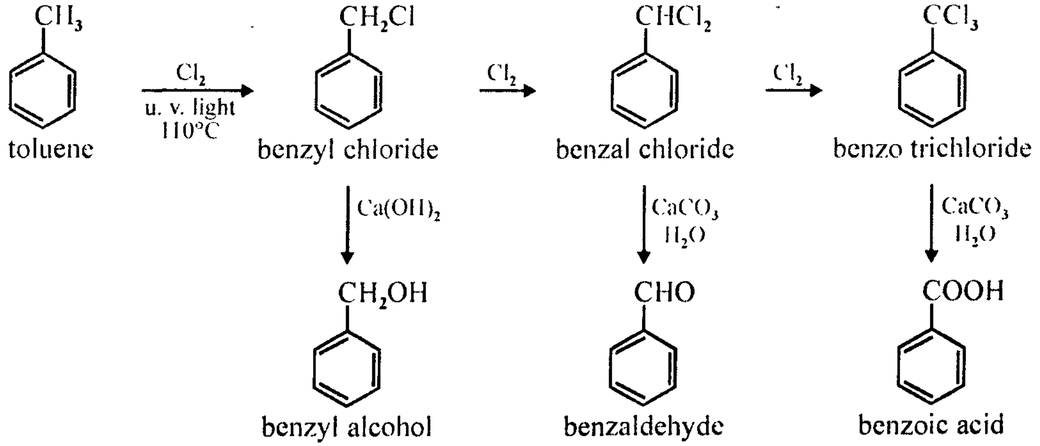
Chlorination of Toluene : Chlorination of alkylated aromatic compounds, for example, toluene, can occur either in the aromatic ring or in the side chain. The use of an iron catalyst directs the chlorine to the aromatic ring, probably by inducing formation of the Cl^+ cation as the active agent.



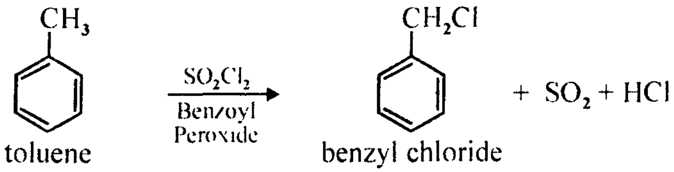
The hydrogen chloride formed is usually neutralised by a suspension of calcium carbonate.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

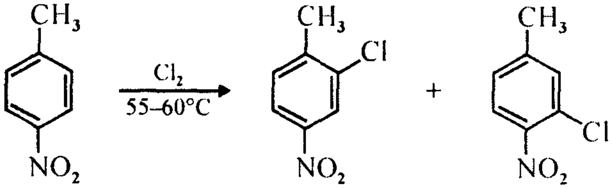
Chlorination of toluene in the complete absence of iron produces side chain chlorination products. These are benzyl chloride, benzal chloride and benzotrichloride. All these compounds are valuable, although the reaction is difficult to stop to produce pure intermediate products with calcium carbonate. Benzal chloride is converted to benzaldehyde with calcium carbonate in water, while benzotrichloride gives benzoic acid under the same conditions.



It is also possible to carry out the side-chain chlorination of toluene in the absence of light by the action of sulphuryl chloride on boiling toluene in the presence of benzoyl peroxide.

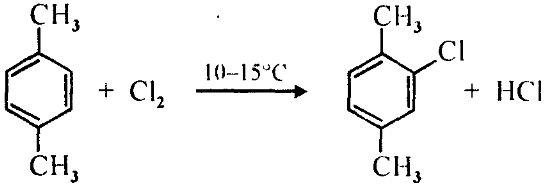


When *p*-nitrotoluene is chlorinated at 55-60°C, it yields a mixture of two isomers. These are purified by fractional distillation.

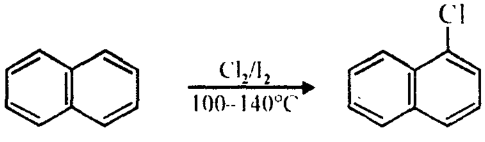


p-nitrotoluene

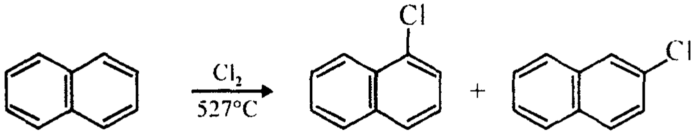
Chlorination of Xylenes : Among the xylenes, chlorination of *p*-xylene is important. The chlorination of *p*-xylene directly at 10 to 15°C yields 2-chloro-*p*-xylene. This product is purified by fractional distillation.



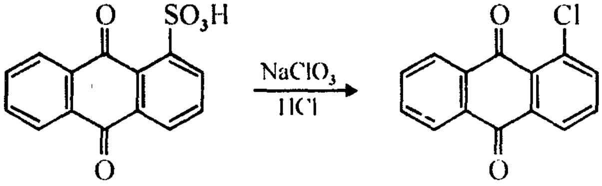
Chlorination of Naphthalene : When chlorine is passed through molten naphthalene at 100-140°C in the presence of iodine (catalyst), the main product is α-chloronaphthalene and a small amount of β-chloronaphthalene (8%) is also formed.



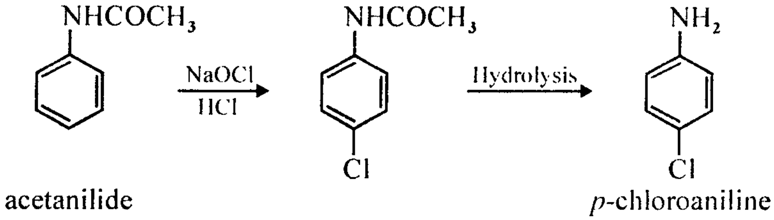
When the above reaction is carried out at higher temperatures, *i.e.*, in the vapour phase, α- and β-isomers are obtained in equal proportions.



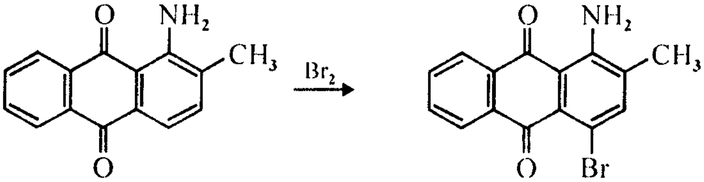
Chlorination of Anthraquinone : In the anthraquinone series, both direct and indirect chlorinations are employed. An example of the indirect chlorination is the conversion of 1-anthraquinone sulphonic acid to the corresponding chloro compound. This reaction is carried out at approximately 100°C with sodium or potassium chlorate in hydrochloric acid.



Chlorination of Acetanilide : Acetanilide on treatment with sodium hypochlorite in the presence of mineral acid yields *p*-chloroacetanilide which on hydrolysis yields *p*-chloroaniline.

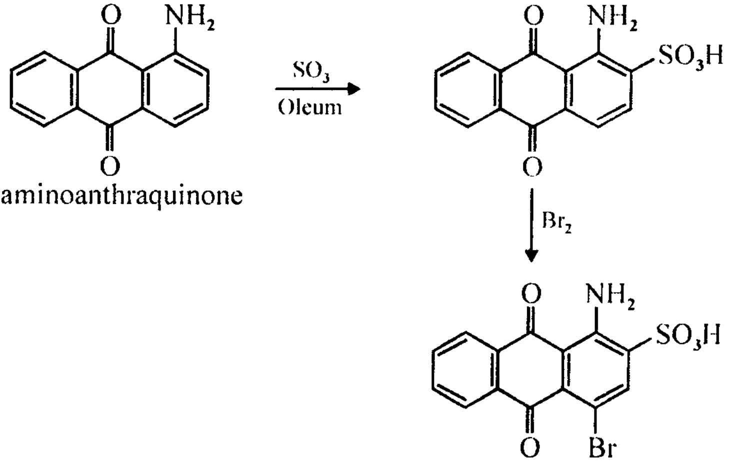


Bromination : It may be done similar to chlorination by using liquid bromine. It is carried out in the anthraquinone compounds due to higher reactivity of bromo compounds compared with the corresponding chloro compounds. For example, 1-amino-2-methyl-anthraquinone on treatment with aqueous bromine yields 1-amino-4-bromo-2-methylanthraquinone (I). This compound is used in the manufacture of alizarin light blue 4 GL.



(I)

Similarly, 1-amino-4-bromoanthraquinone-2-sulphonic acid (II) may be synthesised as follows:



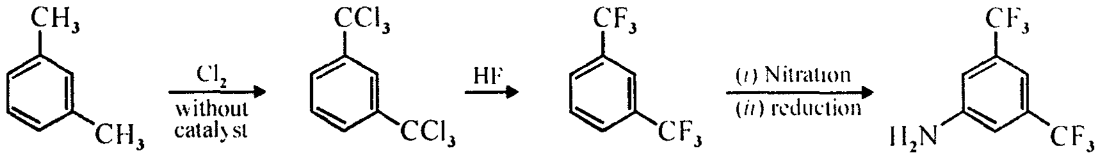
(II)

The compound (II) is an important intermediate in the manufacture of acid dyes.

Fluorination : The fluorination of organic compounds with the reactive elemental fluorine is difficult to be carried out. However, it is carried out by adding dry nitrite to a stirred dry mixture of hydrogen fluoride and an amine hydrochloride.

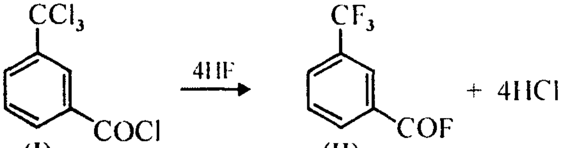
$$RNH_2.HCl + HF + NaNO_2 \longrightarrow R - F + NaCl + N_2 + 2H_2O.$$

It is interesting to note that dyes having trifluoromethyl group (CF_3) increases brightness of shade. The fluoro group is introduced by treating the corresponding chloro compound with 98% hydrofluoric acid under pressure. For example, fast orange GGD base is synthesised as follows :



fast orange GGD base

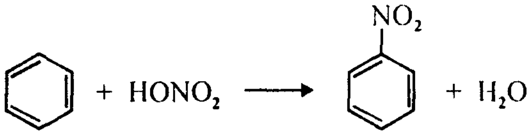
m-Trichloromethyl benzoyl chloride, on heating with anhydrous hydrofluoric acid at about 30 atm pressure initially at 30°C and then at 80°C, yields *m*-trifluoromethyl benzoyl fluoride. This is used for the preparation of some anthraquinone vat dyes.



(I) (II)

Nitration : It involves the replacement of one or more ring hydrogen atoms by the nitro group. The nitration of aromatic hydrocarbons is a fundamental operation in the manufacture of many dye intermediates.

Nitration of benzene is an example.



nitrobenzene

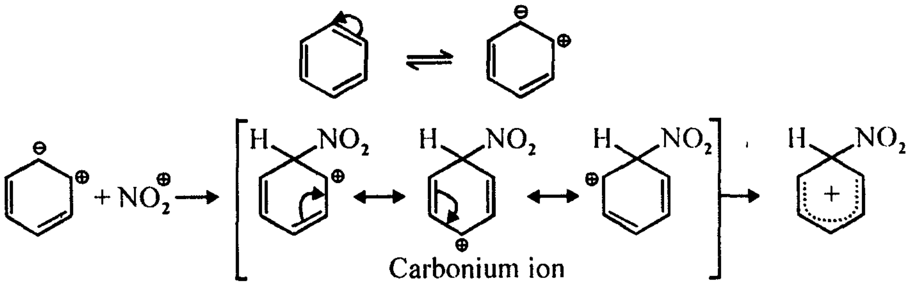
Nitration of compounds of high reactivity is carried out with nitric acid in water or organic solvent. Less reactive compounds are nitrated in a combination of nitric and sulphuric acids ("*mixed acids*").

Mechanism : The mechanism of nitration may involve the following steps :

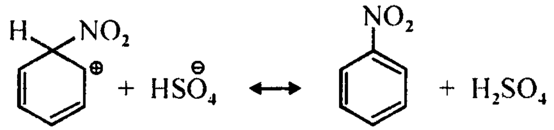
(*i*) The sulphuric acid facilitates nitration by reaction with nitric acid to form the nitronium ion (NO_2^+).

$$HONO_2 + 2H_2SO_4 \longrightarrow H_3O^+ + 2HSO_4^- + NO_2^+$$

(*ii*) The nitronium ion is electrophilic and attacks benzene molecule to form a transition state carrying a positive charge, called carbonium ion.



(*iii*) The carbonium ion reacts further with HSO_4^- to form nitrobenzene.



$$H_3\overset{\oplus}{O} + HS\overset{\ominus}{O}_4 \longrightarrow H_2SO_4 + H_2O$$

Thus, the functions of sulphuric acid are as follows :

(*i*) It serves as a solvent for the reaction.

(*ii*) It facilitates nitration by reaction with nitric acid to form the nitronium ion, generally believed to be the active nitrating agent.

(*iii*) It also serves to maintain the strength of the nitrating mixture by combining with the water, which is formed.

Orientation of Nitro-Compounds : When benzene derivatives are nitrated, nitration takes place in suitable positions depending upon the directing properties of the group already present. Thus, if the benzene nucleus contains one of the $-CH_3$, –Cl, –Br, –I, –OH, $-NH_2$, etc. groups, the nitro group enters in the *ortho* and *para* positions. On the other hand, if the benzene group contains one of the $-NO_2$, –COOH, –CHO, –CN or $-SO_3H$ groups, the nitro group enters in the meta position. Some functional groups such as the amino group, in compounds to be nitrated must be protected against oxidative destruction by acetylation. The acetyl group is removed by hydrolysis when nitration is complete.

Nitration of Benzene (Nitrobenzene) : It is carried out in a cast iron vessel fitted with a propeller type of stirrer with revolutions per minute of not less than 60. This vessel also contains thermometer pocket, inlet for mixed acid, cooling jacket, bottom discharge and sometime cooling coils inside the vessel.

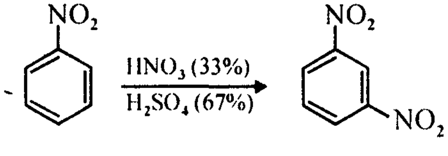
In the manufacture of nitrobenzene, the benzene is first run in the vessel followed by slow addition of mixed acid to keep the temperature in the range of 25-30°C. At the end of acid addition, the temperature is allowed to go up to 60-70°C. The composition of the reaction is checked by measuring the density of nitrobenzene layer or by finding the percentage of nitric acid in the acid layer.

When the reaction is complete, the agitation is stopped and the nitrobenzene separates as an oily layer over the acid. This oil is drawn off and agitated with water or dilute alkali to remove residual acid. It may then be redistilled if pure nitrobenzene is required. The spent acid is concentrated and reused.

Nitrobenzene is used in the manufacture of aniline, phenyl hydrazine, benzidine, metanilic acid, etc.

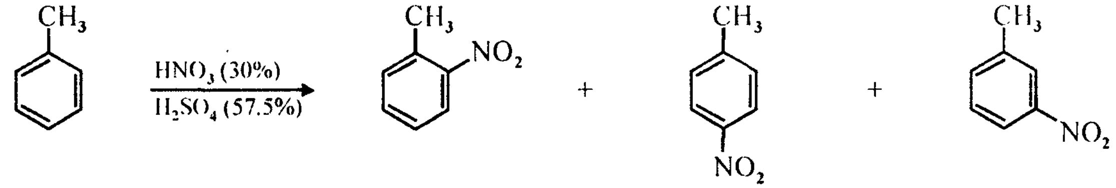
***m*-Dinitrobenzene :** It is obtained by nitration of crude nitrobenzene with fuming nitric acid and strong sulphuric acid or with mixed acid containing HNO_3 (33%) and H_2SO_4 (67%). The crude product contains 85-90% *m*-dinitrobenzene together with small quantities of *o*- and *p*-dinitrobenzene.

The *o*-and *p*-dinitrobenzenes present in *m*-dinitrobenzene are removed as water soluble products by treating the nitration products with aqueous sodium sulphite; soluble sodium *o*-and *p*-dinitrobenzene sulphonates being formed. The residual *m*-dinitrobenzene is separated from the aqueous layer, washed with water and finally dried.



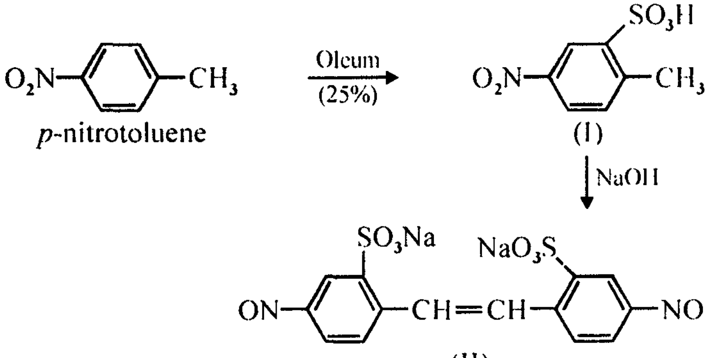
m-dinitrobenzene is used for making *m*-nitroaniline and *m*-phenylenediamine.

Nitration of Toluene : When nitration of toluenel is carried out with mixed acid of composition, HNO_3 (30%), H_2SO_4 (57.5%) and H_2O (12.5%) at temperature below 30°C, a mixture of three isomers of nitrotoluene is obtained. This mixture consists of 62-63% *ortho*-, 33-34% *para* and 3-4% *meta*-nitrotoluene. The mixture is separated by fractional distillation at 15 mm mercury. The crude *p*-nitrotoluene is purified by crystallisation at 18°C. In dye industry *p*-nitrotoluene is the important isomer.



toluene *ortho*-(62–63%) *para*-(33–34%) *meta*-(3–4%)

p-Nitrotoluene on sulphonation with 25% oleum is used to make *p*-nitrotoluene *o*-sulphonic acid (I), an intermediate for stilbene dyes. The intermediate (I) reacts with caustic soda to yield dinitrosostilbenedisulphonate (II) which is further used in the manufacture of dyes under the names of *stilbene* and *mikado yellow*.



p-nitrotoluene

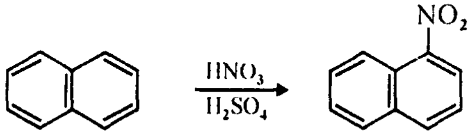
(I)

(II)

When *o*- and *p*-nitrotoluenes are further nitrated, both yield mainly 2, 4-dinitrotoluene together with little of the 2, 6-dinitrotoluene which can be separated as an oil when the product is cooled.

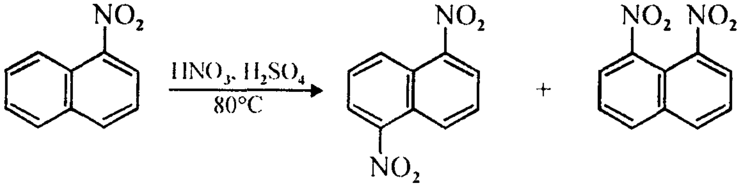
2, 4-Dinitrotoluene is mainly used for the preparation of *m*-tolulylenediamine.

Nitration of Naphthalene : When naphthalene is nitrated with mixed acid having 28% HNO_3, 57% H_2SO_4 and 15% H_2O, 1-nitronaphthalene is the main product.



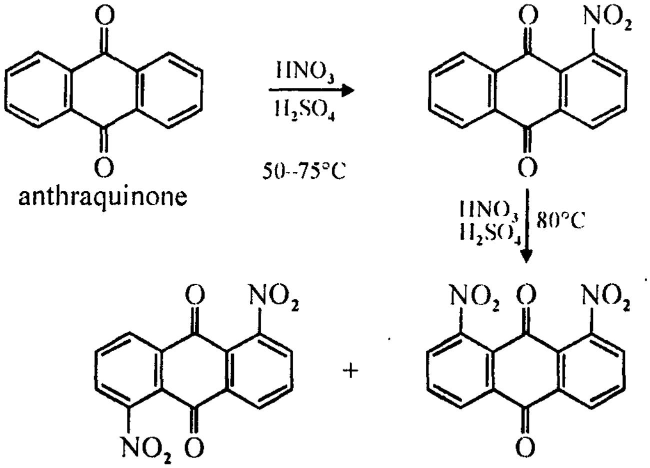
1-Nitronaphthalene is used for making 1-aminonaphthalene. However, 2-nitronaphthalene is not made by nitration.

When 1-nitronaphthalene is further nitrated, a mixture of 1, 5-and 1, 8-dinitronaphhalenes is obtained. The 1, 5-compound is separated from its 1, 8-compound by crystallisation from pyridine in which it is much less soluble.



(1, 5) (1, 8)

Nitration of Anthraquinone : The nitration of anthraquinone does not give pure mononitro compound. However, mononitration of anthraquinane at about 50°C gives mainly 1-nitro-anthraquinone. At 80-95°C, dinitration occurs to give a mixture of the 1, 5-and 1, 8-isomers. In some cases the mixture is used; in others, isomer separation is necessary. Nitroanthraquinones are used in the preparation of corresponding amino compounds.

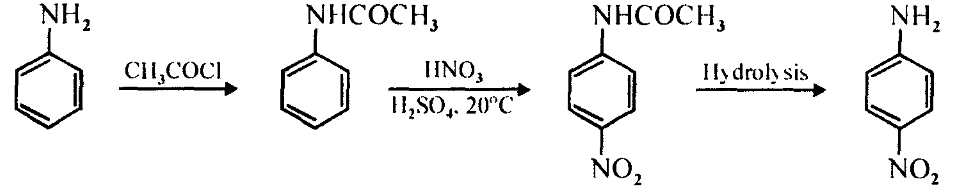


(1; 5) (1; 8)

These nitrations are carried out in cast iron or steel vessels with steel agitators. Since the starting materials are solids, they are first dissolved in sulphuric acid and then treated with mixed acids; the products are also solids.

Nitration of Aromatic Amines : It is not carried out directly due to sensitivity of NH_2 groups to oxidation. The NH_2 group is acetylated or protected by other means.

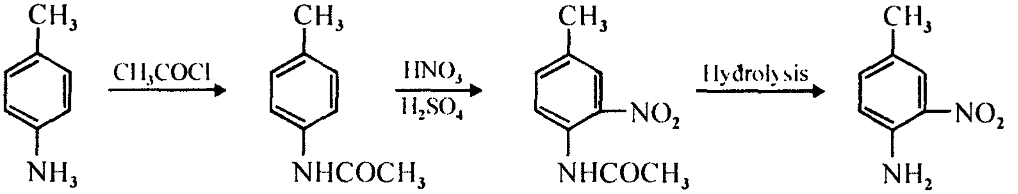
Acetanilide on nitration with mixed acid below 20°C yields a mixture of about 75% of the *p*-nitro compound and 20% of the *o*-isomer.



Aniline Acetanilide *p*-Nitroaniline

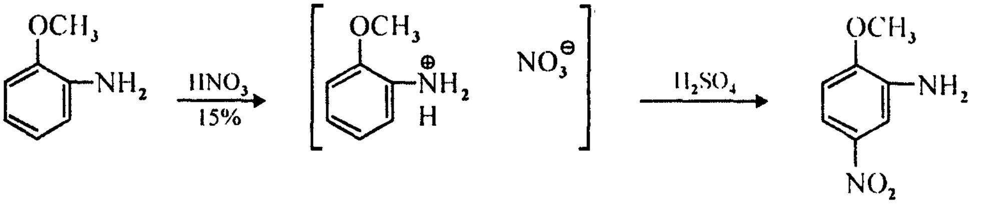
p-Nitroaniline is used for the preparation of azo dyes and pigments.

***p*-Toluidines :** When N-acetyl-*p*-toluidine is nitrated, followed by hydrolysis, it yields 4-amino-3-nitrotoluene which finds use as a diazo component in the preparation of pigments.

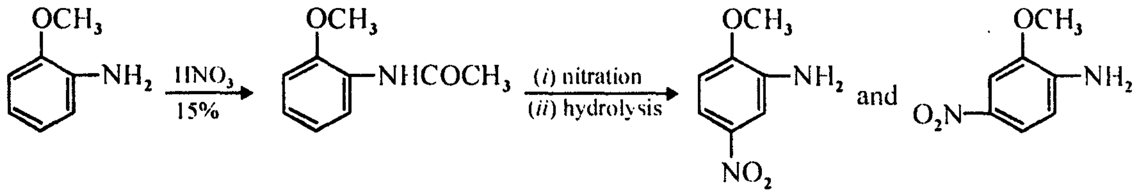


4-amino-3-nitrotoluene

***o*-Anisidine :** Nitration of *o*-anisidine may be done directly with 15% nitric acid to form a nitrate. The aminonitrate on treatment with 95% H_2SO_4 at 0-5°C gives 2-amino-1-methoxy-4-nitrobenzene. It is used for azo dyes and as an azoic diazo component.



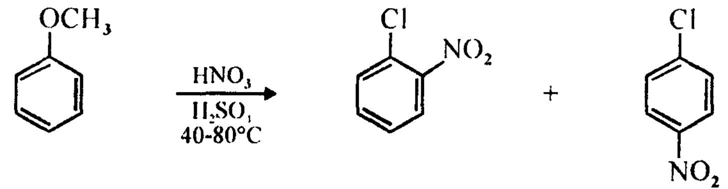
N-Acetylated-*o*-anisidine on nitration at 25°C with mixed acid (HNO_3 12%, H_2SO_4 30%) followed by hydrolysis yields a mixture of two nitro compounds, *i.e.*, 2-amino-1-methoxy-4-nitro-benzene (I) and 2-amino-1-methoxy-5-nitrobenzene.



(I) (II)

Nitration of Chloro Derivatives : As the nitro groups in positions 2-and 4-relative to chlorine have an activating effect, the nitration of chlorobenzene, dichlorobenzene and chlorotoluenes yields substances of considerable value in dye chemistry.

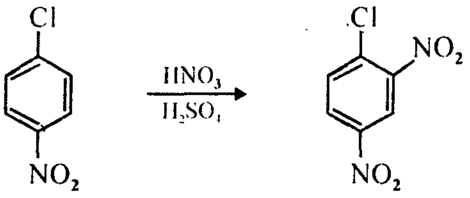
When chlorobenzene is nitrated with a mixed acid, HNO_3 35%, H_2O 12% and H_2SO_4 53%, at 40-80°C, it yields a mixture of 35% of *o*-chloronitro-benzene and 65% of *p*-chloronitrobenzene. The two isomers are separated by fractional distillation in vacuum.



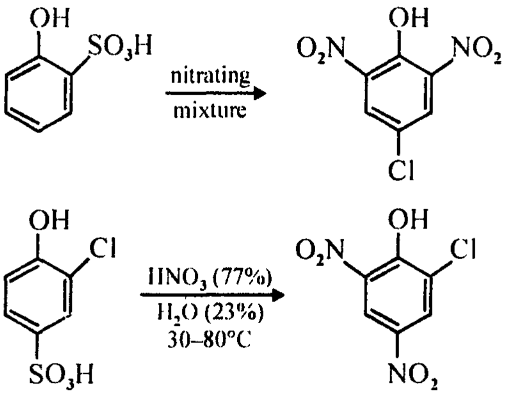
chlorobenzene *ortho* (35%) *para* (65%)

Both *o*-chloro-and *p*-chloro nitrobenzenes are used in making the nitrophenols, nitroanisoles, nitrophenetoles and nitroanilines. They are also useful intermediates for sulphur dyes.

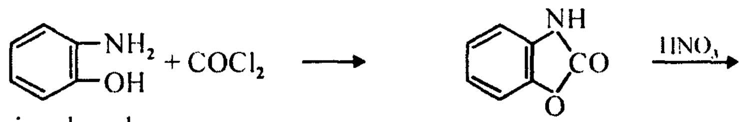
When the nitration of *p*-nitrochlorobenzene is carried out with mixed acid (HNO_3 35% and 65% H_2SO_4) at 95°C, followed by reduction of temperature at a later stage to 45-55°C, 1-chloro-2, 4-dinitrobenzene is obtained. The chlorine atom in this compound is very reactive. This is an important intermediate in the synthesis of certain disperse dyes.



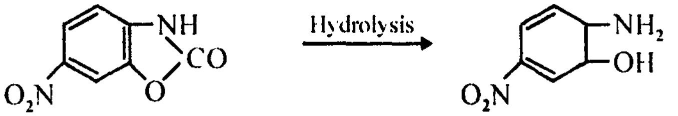
Nitration of Aromatic Sulphonic Acids : It is generally carried out by adding the nitrating agent to the sulphonation mass. Thus, both the nitration and the sulphonation can be achieved in one-step operation. In some cases, nitro group replaces the sulphonic group during the nitration. For example, 4-chloro-1-phenol-2-sulphonic acid yields 4-chloro-2, 6-dinitrophenol whereas 2-chloro-1-phenol-4-sulphonic acid yields 2-chloro-4, 6-dinitrophenol.



Nitration of *o*-aminophenol : Both the amino and phenolic groups are active and are protected by the treatment of *o*-amino-phenol with phosgene to give the benzoxazole. This on nitration followed by hydrolysis yields 2-amino-5-nitrophenol.

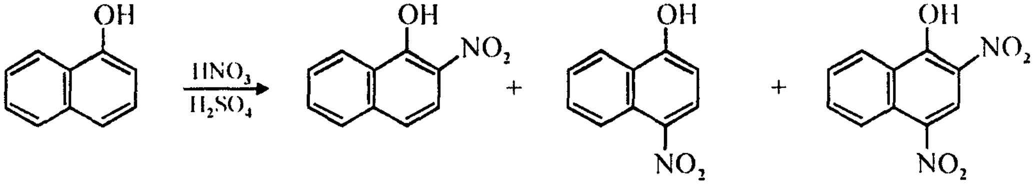


o-aminophenol

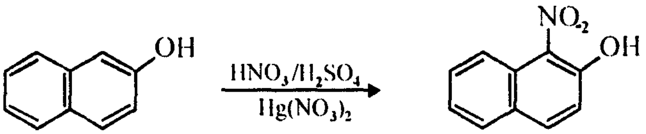


2-amino-5-nitrophenol

Nitration of α-naphthol : When α-naphthol is nitrated, it yields a mixture of 2-nitro-and 4-nitro-1-naphthol along with some amount of 2, 4-dinitro-1-naphthol.

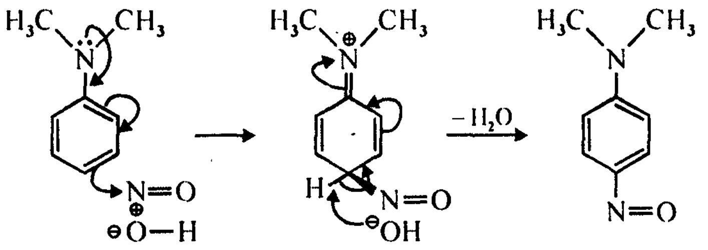


Nitration of β-naphthol : When β-naphthol is nitrated in the presence of mercuric nitrate, 1-nitro-2-naphthol is obtained.

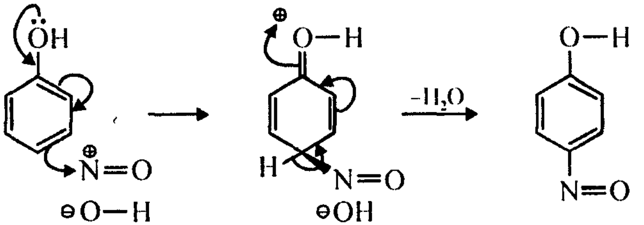


Nitrosation Reaction : This reaction is mainly used for getting nitrosation intermediates. Nitrosation of dimethyl aniline and phenol is carried out by sodium nitrite and an acid such as dil. HCl or dil. H_2SO_4 in cold. The nitroso $\overset{\oplus}{N}=O$ electrophile is an attacking species as shown below:

$$NaNO_2 + HCl \longrightarrow H-O-N=O + NaCl$$
$$H-O-N=O \longrightarrow \overset{\ominus}{O}H + \overset{\oplus}{N}=O$$



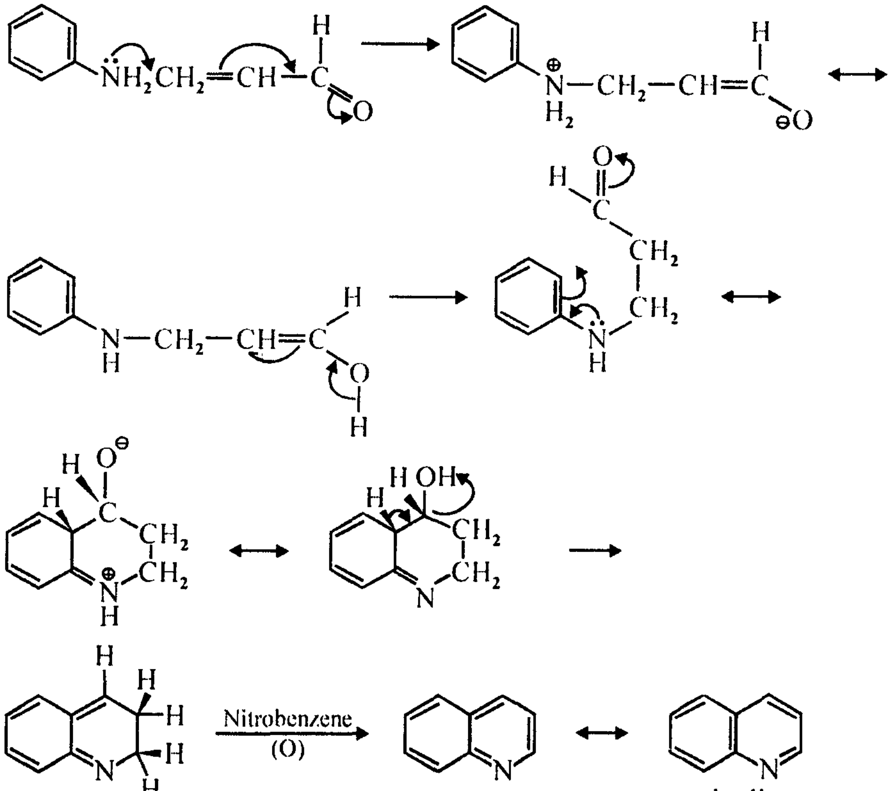
dimethylaniline p-nitrosodimethylaniline



p-nitrosophenol

Skraup's Synthesis : This reaction involves the treatment of an arylamine in the presence of corresponding arylnitro compound with acrolein obtained *in situ* by dehydration of glycerol, iron and sulphuric acid to get quinoline derivative or the fused pyridine derivative. The following reaction sequence explains the formation of fused ring.

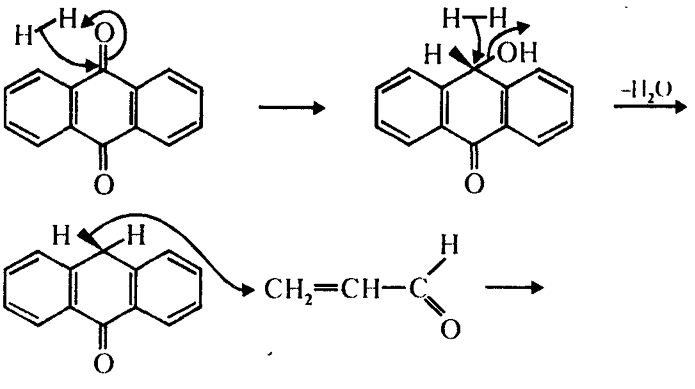
$$\underset{\text{glycerol}}{CH_2OH-CHOH-CH_2OH} \xrightarrow{\text{dehydration}} CH_2{=}CH-CHO$$

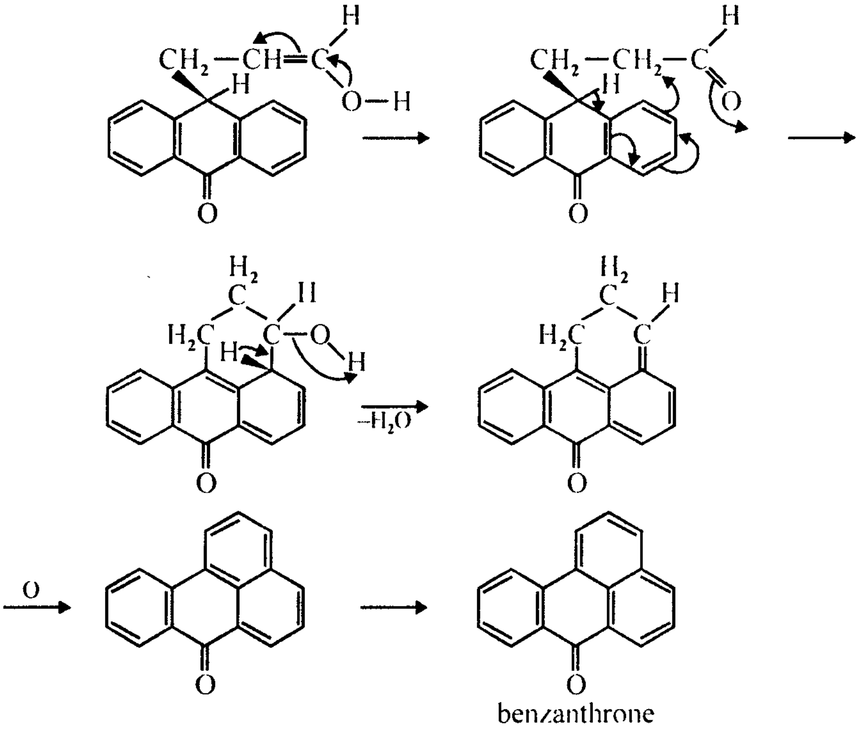


quinoline

A similar synthesis as described above is the preparation of benzanthrone from anthraquinone. In this reaction there occurs the formation of anthrone which reacts with acrolein to effect cyclisation with the formation of fused ring to the anthracene structure.

$$CH_2OH-CHOH-CH_2OH \xrightarrow{\text{dehydration}} CH_2{=}CH-CHO$$

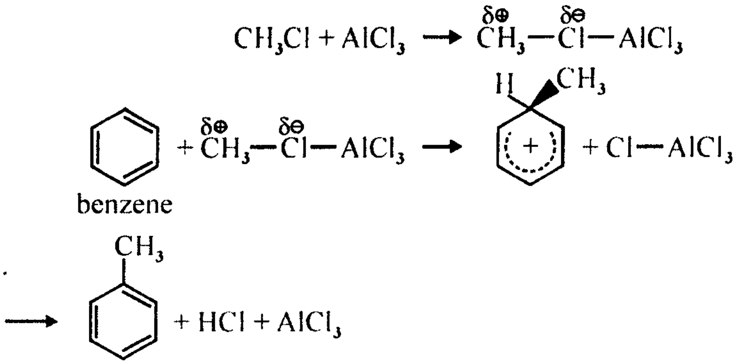




Friedel-Craft's Reaction

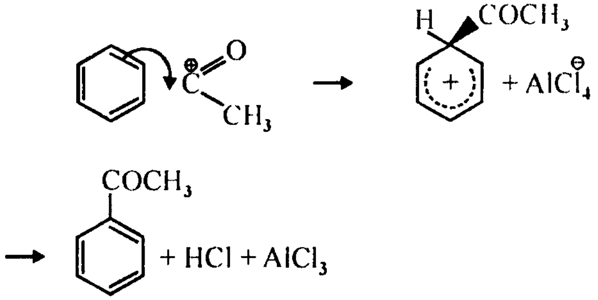
This reaction is used to form carbon-carbon bond. In this reaction, there occurs the reaction of hydrocarbon such as benzene with alkyl chloride (alkylation) or acyl chloride (acylation) or aroyl chloride (aroylation) or with acid anhydride (acylation or aroylation) depending upon whether the acid anhydride is aliphatic or aromatic in the presence of a Lewis acid catalyst like aluminium chloride, aluminium bromide or boron trifluoride. Acylation with acetyl chloride or acetic anhydride is known as acetylation and aroylation with benzoyl chloride is known as benzoylation.

Alkylation

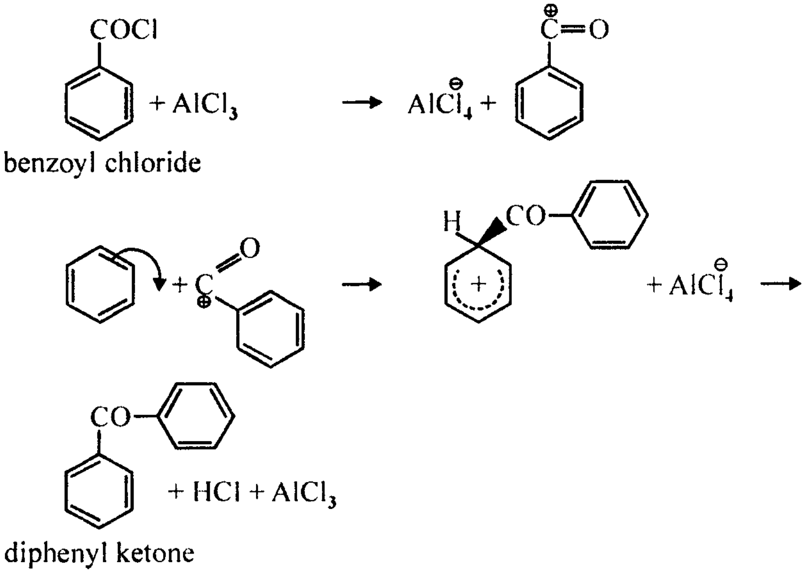


Acylation

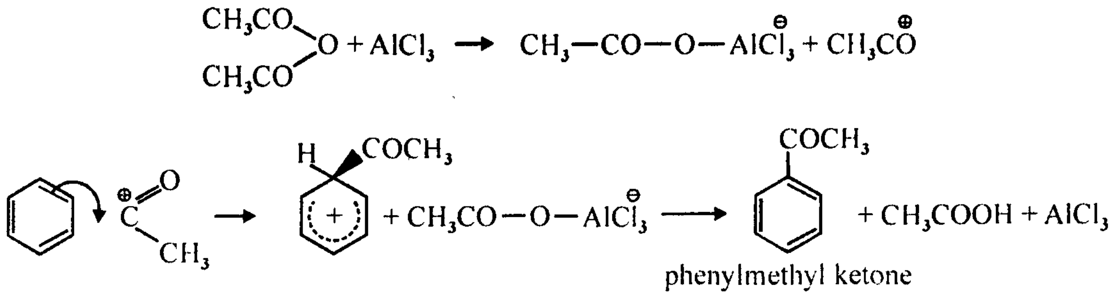
$$CH_3COCl + AlCl_3 \longrightarrow \overset{\ominus}{AlCl_4} + CH_3\overset{\oplus}{C}{=}O$$



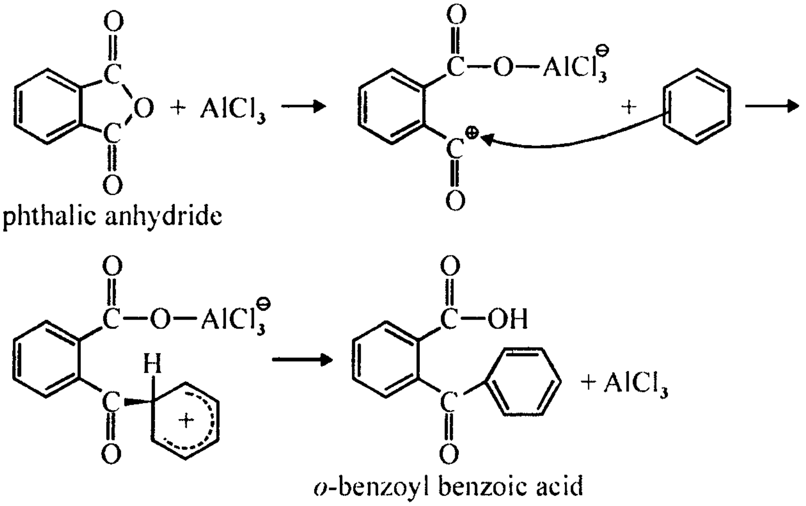
Aroylation



Acylation with Aliphatic Acid Anhydride



Aroylation with Aromatic Acid Anhydride



6.6. Heterocyclic Intermediates

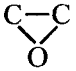
Many heterocyclic intermediates find use in the dyestuff industry. Some important heterocyclic systems commonly involved in this industry have been given in Table 6.1 in accordance to the total number of members present in the heterocyclic rings. In this table, some examples of intermediates belonging to the specific heterocyclic systems have also been included.

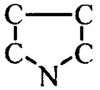
Table 6.1 : Heterocyclic Systems Used in Dyestuff Intermediates

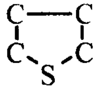
S.No.	*Members present in Heterocyclic Ring*		*Name*	*Examples*
	Total	*Hetero atoms*		
1	*2*		*3*	*4*
1	3	1–O	Ethylene oxide	Ethylene oxide
2	5	1–N	Pyrrole	Indoles, Phthalimides, Naphthostyril, Carbazole
3	5	1–S	Thiophene	Thioindoles
4	5	1–O, 1–N	Oxazole	2-Methyl and 2-amino benzoxazoles
5	5	1–N, 1–S	Thiazole	2-Methyl and 2-amino benzthiazoles
6	5	2–N	Imidazole	2-Methyl and 2-amino benzimidazoles
7	5	2–N	Pyrazole	1-Phenyl-3-methyl-pyrazol-(5)-one
8	5	3–N	Triazole	Benzotriazoles
9	6	1–O	Pyran	Coumarins, Xanthenes
10	6	1–N	Pyridine	Pyridine derivatives, Quinoline derivatives, Naphthalimides, Acridines
11	6	2–N	Pyrimidine	Barbituric acid, Amino-pyrimidines.

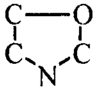
1	*2*		*3*	*4*
12	6	3–N	Triazine	Cynuric chloride
13	6	2–N	Azine	Azine derivatives
14	6	1–O, 1–N	Oxazine	Oxazine derivatives
15	6	1–N, 1–S	Thiazine	Thiazine derivatives.

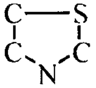
The heterocyclic system in the above Table 6.3 includes the following skeletons.

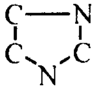

ethylene oxide skeleton

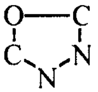

pyrrole skeleton


thiophene skeleton

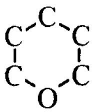

oxazole skeleton

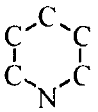

thiazole skeleton


imidazole skeleton

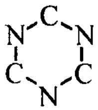

pyrazole skeleton

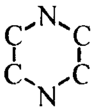

triazole skeleton

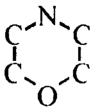

pyran skeleton

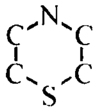

pyridine skeleton


pyrimidine skeleton

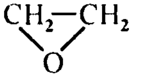

triazine skeleton

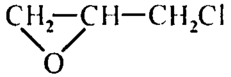

azine skeleton


oxazine skeleton

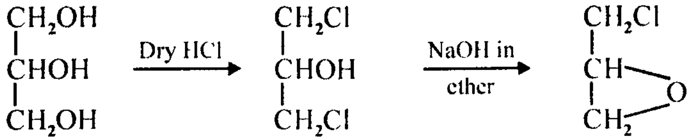

thiazine skeleton

Among three membered heterocyclic ring systems the important is ethylene oxide ring system. Epichlorohydrin is another important example.


ethylene oxide

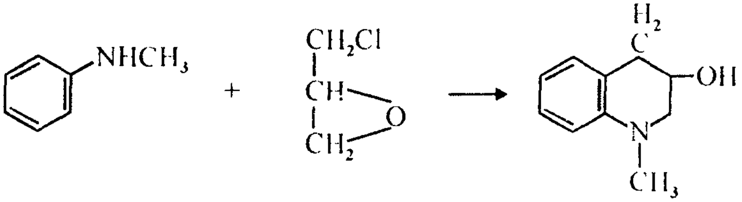

epichlorohydrin

The ethylene oxide finds use in the synthesis of vinyl sulphone reactive systems and in mono and bis (β-hydroxy ethyl) anilines. Ethylene oxide is prepared by the direct combination of ethylene and oxygen under high pressure and temperature in the presence of silver salts. It is also prepared by the action of soda lime on ethylene chlorohydrin (HO–CH_2–CH_2Cl). Epichlorohydrin is prepared from glycerol by chlorination with dry hydrochloric acid to obtain glycerol–1, 3-dichlorohydrin and subsequent treatment with caustic soda in a solvent such as ether.

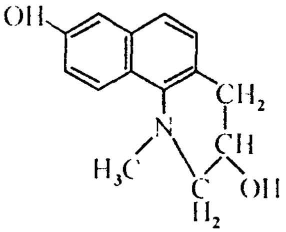


glycerol glycerol-1, 3-dichlorohydrin epichlorohydrin

Epichlorohydrin is used in the synthesis of coupling components for cellulose acetate dyes. The coupling components are prepared by the condensation of a primary arylamine or a secondary alkylarylamine with epichlorohydrin to yield tetrahydroquinoline and tetrahydrobenzoquinoline derivatives.

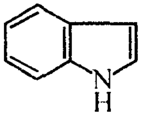


monomethylaniline epichlorohydrin N-methyl-3-hydroxy tetrahydro quinoline

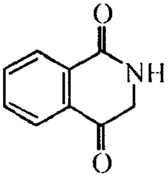


N-methyl-3, 8-dihydroxy tetrahydro benzoquinoline

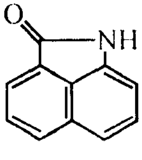
The five membered heterocyclic systems include pyrrole, thiophene, oxazole, thiazole, imidazole and thiazole rings. Indoles phthalimides, naphthostyril and carboazoles belong to pyrrole class and are important.



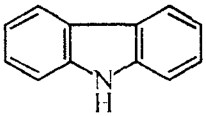
indole



phthalimide

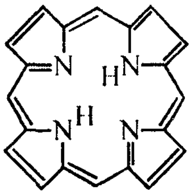


naphthostyril

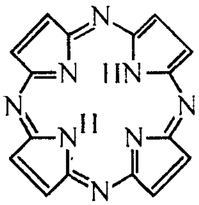


carbazole

Phthalocyanines, phthalogens and some natural colouring matters like chlorophyll possess pyrrole rings in the form of tetrazaporphin and porphin ring structures.

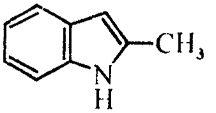


tetrazaporphin

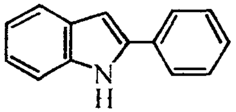


porphin

Indoles find use in the indigoid vat dyes. Anthranilic acid and chloroacetic acid get condensed, cyclised to indoxyl and subsequently air oxidised to yield indigo. 2-Methyl and 2-phenyl indoles, may get coupled at three positions with diazonium salts to obtain azo dyes, or get converted to styril dyes.



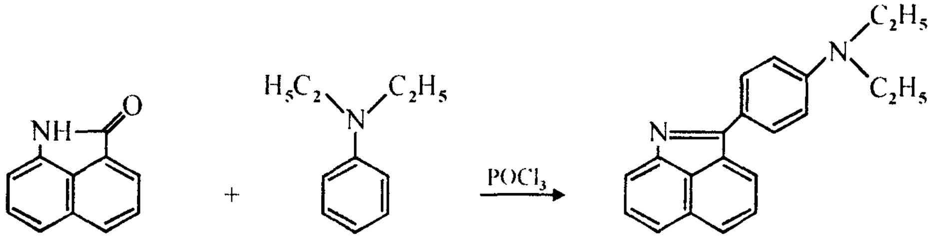
2-methyl indole



2-phenyl indole

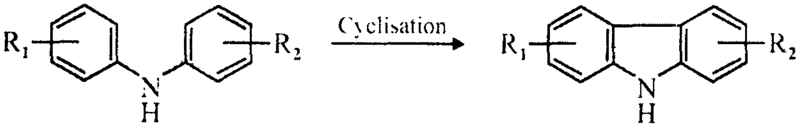
They are prepared by following *Fischer indole synthesis* in which there occurs the cyclisation of phenyl hydrazones of acetone and phenyl methyl ketone respectively.

Phthalimide finds use in the manufacture of many anthranilic acid derivatives and phthalocyanines and phthalogens. Naphthostyril acts as a useful intermediate for disperse and cationic dyes, such as a disperse dye which could be prepared by the condensation of naphthostyril with diethylaniline in the presence of phosphorus oxychloride.



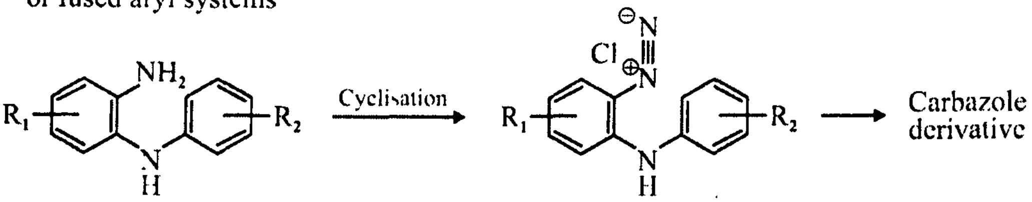
naphthostyril diethyl aniline disperse dye

Carbazole structure is found in many anthraquinonoid vat dyes and sulphurised vat dyes like Hydron Blue. The general methods used for the preparation of carbazole derivatives start from the corresponding diarylamine. Thus the diarylamino compound gets cyclised in concentrated sulphuric acid at suitable temperature to yield carbazole derivative. It can be synthesised in good yields by arylation of the corresponding ortho substituted diazonium salt of diarylamino compound which is prepared from *o*-amino diarylamino derivative.



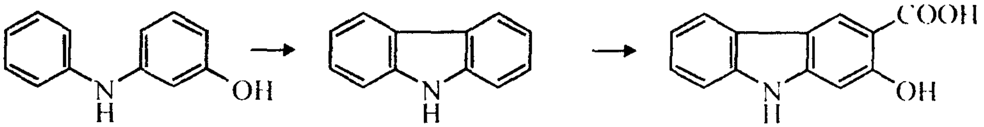
diarylamino compound
R_1, R_2 are substituents
or fused aryl systems

carbazole derivatives R_1, R_2
as in diarylamino compound



o-amino diarylamine *o*-diazonium diarylamine salt

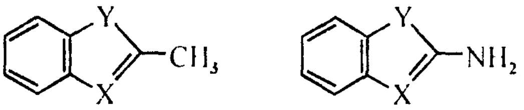
3-Hydroxy diphenylamine is prepared by the Bucherer reaction of resorcinol with aniline. It gets cyclised to yield 3-hydroxy carbazole which on carboxylation under *Kolbe-Schmidt* reaction yields 3-hydroxycarbazole-4-carboxylic acid which finds use as a naphthol coupling component in certain azoic colours, after converting it to the acid chloride and further condensing with arylamines.



3-hydroxy diphenylamine 3-hydroxy carbazole 3-OH-carbazole-4-carboxylic acid

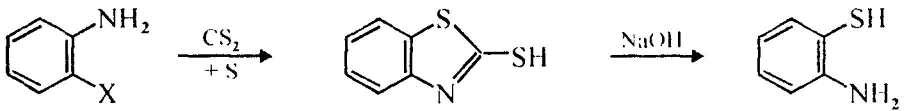
Thiophene skeleton is found in thioindoles.

Oxazoles, thiazole and imidazole skeletons are found in compounds such as 2-methyl and 2-amino benzoxazoles, benzthiazoles and benzimidazoles.



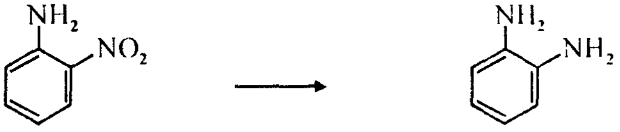
X is N,	Y is O	X is N	Y is O
X is N,	Y is S	X is N,	Y is S
X is N,	Y is NH	X is N,	X is NH

2-Methyl derivatives are obtained by the condensation of suitable ortho substituted aromatic amines such as orthoaminophenol, ortho-aminothiophenol and orthophenylenediamine with acetyl chloride or acetic anhydride under anhydrous conditions. Ortho amino thiophenol is obtained from aniline by the action of carbon disulphide and sulphur to obtain 2-mercapto benzthiazole and subsequent alkaline hydrolysis.



aniline 2-mercapto benzthiazole

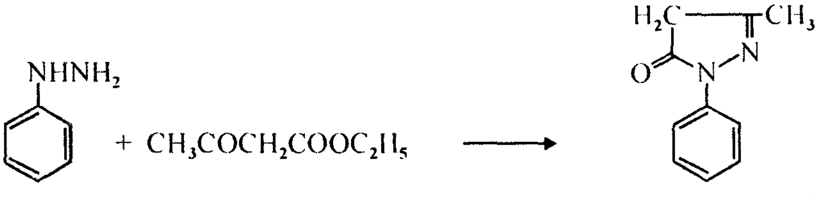
Orthophenylenediamine is prepared by Bechamp reduction of *o*-nitroaniline.



ortho nitroaniline ortho phenylene diamine

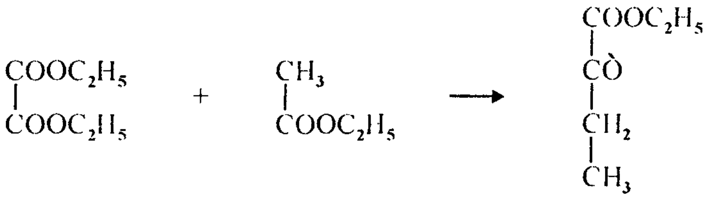
2-Aminobenzoxazole, 2-aminobenzthiazole and 2-aminobenzimiadzole are obtained from orthoaminophenol, orthoaminothiophenol and orthophenylenediamine by different methods.

1-Phenyl-3-methyl-pyrazol-(5)-one and various other pyrazolones have been found to be useful intermediates for azo dyes. 1-Phenyl-3-methyl-pyrazol-(5)-one is prepared by the condensation of phenylhydrazine with acetoacetic ester.

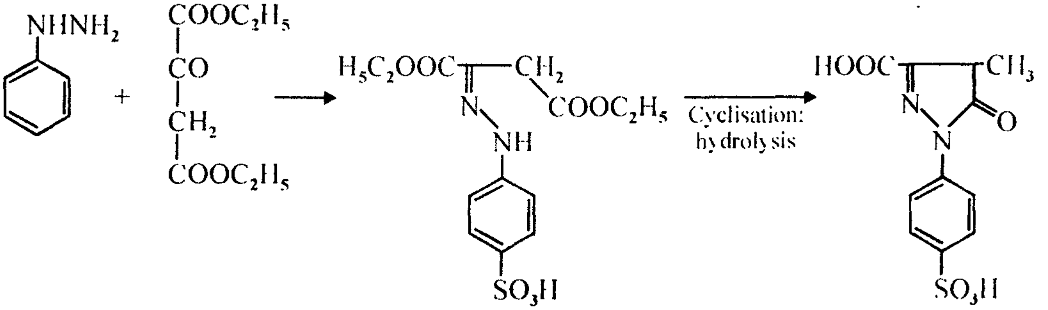


phenylhydrazine acetoacetic ester 1-phenyl-3-methyl-pyrazol-(5)-one

1-Para sulpho phenyl-pyrazol-(5)-one-3-carboxylic acid is prepared by the condensation of phenylhydrazine-p-sulphonic acid obtained from sulphanilic acid with oxaloacetic ester obtained from ethyl oxalate, ethyl acetate and sodium metal in benzene, followed by further cyclisation and hydrolysis.



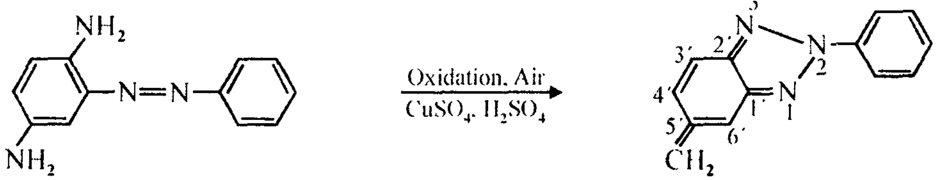
ethyl oxalate ethyl acetate oxaloacetic ester



phenyl hydrazine *p*-sulphonic acid phenyl hydrazone 1-(*p*-sulhophenyl)-pyrazol-(5) -one-3-carboxylic acid (pyrazolone)

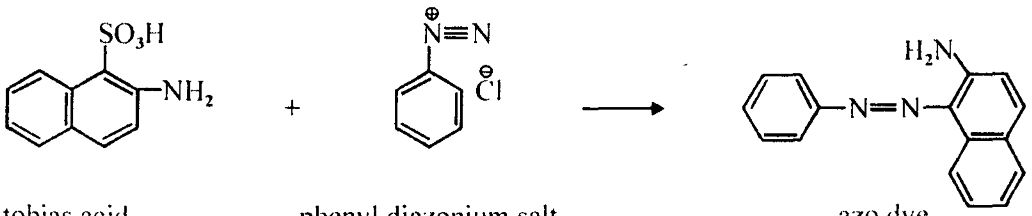
The pyrazolone finds use in the synthesis of azo dyes like tartrazine.

Benzotriazoles find use in a number of important fluorescent brighteners. They are prepared from ortho amino azo dyes by air oxidation using copper sulphate and dilute sulphuric acid.

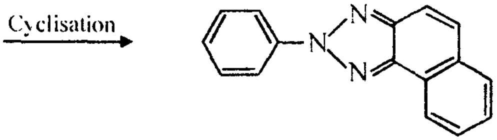


o-aminoazo dye 1, 3-(5-toluyl)-2-phenyl-triazole

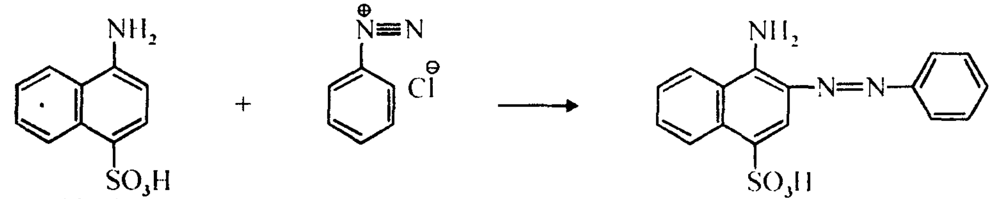
Naphthotriazoles have been similarly prepared form coupling components like tobias acid and naphthionic acid and cyclisation of the corresponding azo dyes.



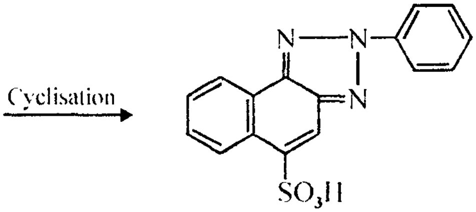
tobias acid phenyl diazonium salt azo dye



1, 3-(1', 2'-nyphthyl)-2-phenyl triazole



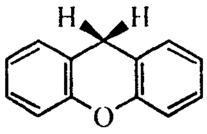
naphthionic acid phenyl diazonium salt azo dye



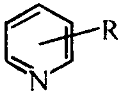
1, 3-(1', 3'-nyphthyl-4'-sulphonic acid)-2-phenyl triazole

Amongst pyran heterocyclic intermediates,·coumarin and xanthene have been important. Coumarin structure is found in many fluorescent brighteners and xanthene structure is found in a number of basic dyes such as rhodamines.

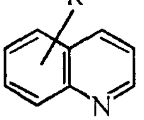
Pyridine skeleton is found in important pyridine derivatives, quinoline derivatives, naphthalimides and acridines.



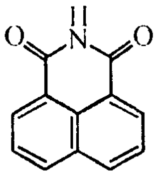
xanthene



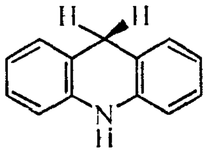
pyridines



quinolines

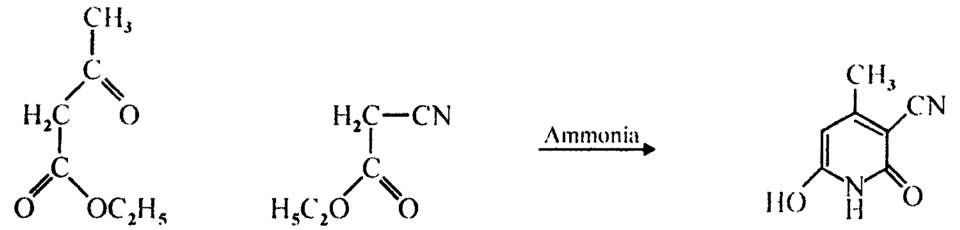


naphthalimide



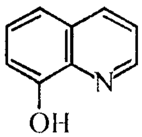
acridine

Pyridine derivatives like amino derivatives find use as diazonium components for disperse and cationic dyes. However, 2-amino and 4-amino pyridine derivatives are difficult to diazotise because nitrous acid needed for the diazotisation of these amines attacks pyridine nucleus and bring about oxidation. 3-Amino pyridines can be diazotised without bringing about oxidation. A number of pyriding derivatives find use as coupling components. An example is 2-hydroxy-4-methyl-5-cyano-pyrid-(6)-one which is obtained by the condensation of aceto acetic ester, cyano acetic ester and ammonia.

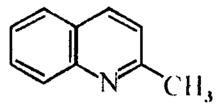


acetoacetic ester cyanoacetic ester 2-hydroxy-4-methyl-5-cyano-pyrid-(6)-one

Quinoline derivatives consist of a number of coupling components like 8-hydroxy quinoline which is prepared by Skraup synthesis starting with ortho amino phenol, as given in the case of quinoline.



8-hydroxy quinoline

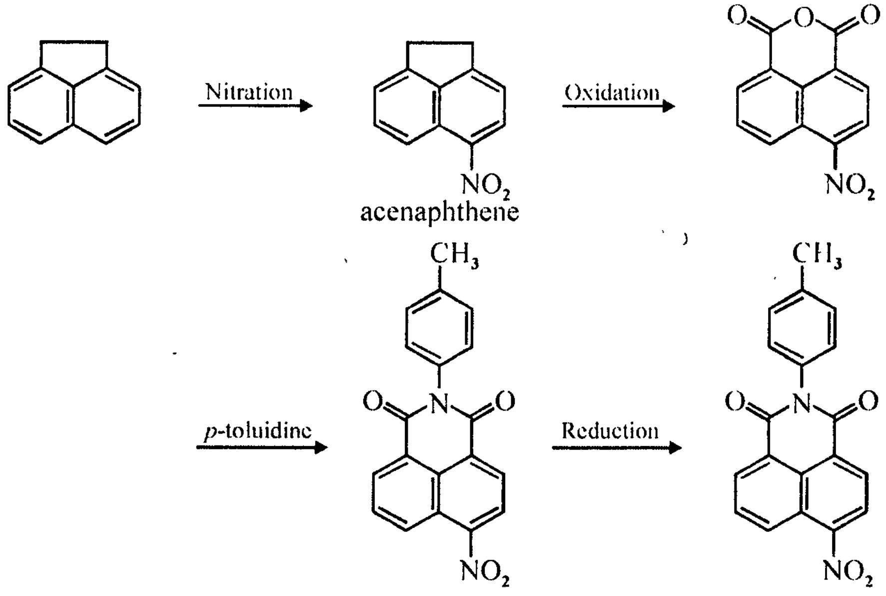


2-methyl quinoline

Tetrahydroquinoline and tetrahydrobenzoquinoline derivatives find use as coupling components. 2-Methylquinoline with condensed with phthalic anhydride yield quinoline yellow on sulphonation.

Naphthalimide dyes like 5-aminonapthalimide derivatives are useful fluorescent dyes. For example, sulphonation of 5-amino naphthal-(*p*-toluyl)-imide yields acid dye with greenish yellow fluorescence.

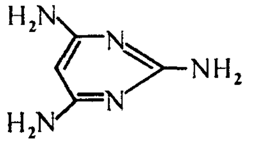
The naphthalimide is obtained from acenaphthene by following nitration, oxidation, condensation with *p*-toluidine and reduction.



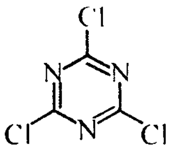
acenaphthene

5-amino naphthal-(*p*-toluyl)-imide

Pyrimidine skeleton is found in a number of coupling components barbituric acid and amino pyrimidines). It is also found in some anthraquinonoid dyes.

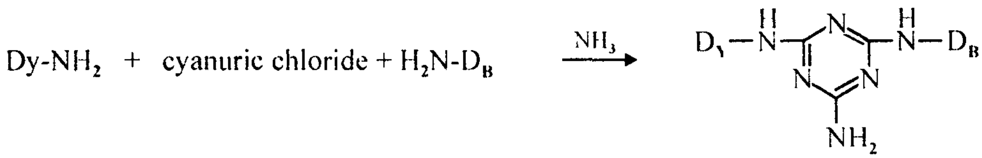


2, 4, 6-triamino pyriomidine



cyanuric chloride

Cyanuric chloride has been a useful intermediate from triazine skeleton. Cyanuric chloride finds use in the production of various triazine reactive dyes like reactive red B, which reacts on cotton. Triazine reactive dyes are mainly used for dyeing cotton and wool. A pure green dye can be obtained by the condensation of a yellow dye and a blue dye, both having a free amino group with cyanuric chloride as in the case of phosgene ($COCl_2$). A triazine bridging linkage is formed with cryanuric chloride.



A yellow dye A blue dye A green dye with triazine linkage

The condensation of an amine or alcohol or phenol, etc. with cyanuric chloride occurs by replacing three chloro groups in cyanuric chloride in stages, generally, first chloro group can be replaced at lower temperature (0-5°C), second at about 40-50°C and the third at about 100°C and, therefore, it is possible to obtain variety of triazine derivatives having no chlorine atom, one chlorine atom or two chlorine atoms.

Azine, oxazine and thiazine systems are found in azine, oxazine and thiazine classes of dyes. For example, methylene blue belongs to thiazine class.

7

CHAPTER

NITRO DYES

7.1. Introduction

Nitro dyes are the nitro derivatives of phenols having at least one nitro group in the *o*-or *p*-position to the hydroxyl group. They have the nitro group as the *chromophore* and the hydroxyl group as the *auxochrome.*

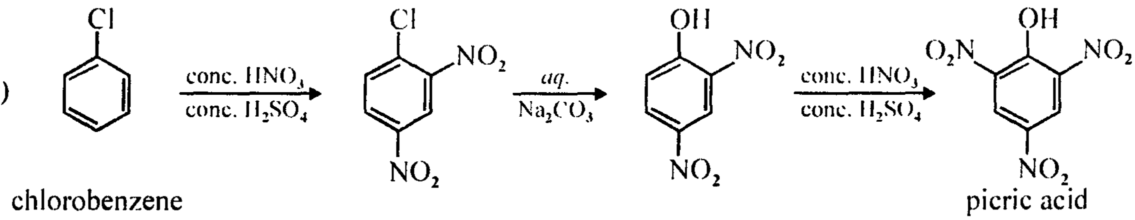
Nitro dyes are of two types, namely, **acid dyes** and **disperse dyes.** *Acid dyes* are having a solubilising group such as sulphonic acid. An example of acid dyes is naphthol yellow *S. Disperse dyes* do not have any solubilising group and generally have *o*-nitro-diphenylamine structure. An example of disperse dyes is disperse yellow.

These dyes are not very fast and hence have very little commercial importance. These dyes have greenish yellow to yellowish brown colour. Some examples of nitro dyes are described in Art. 7.2.

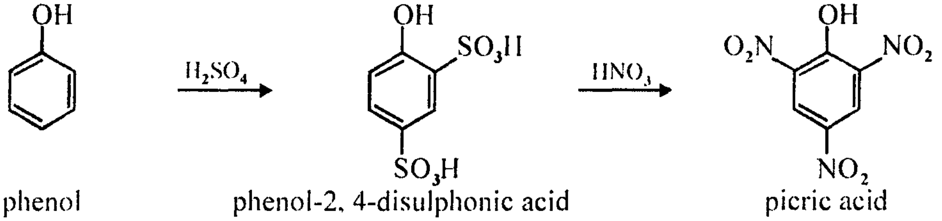
7.2. Different Examples of Nitro Dyes

1. **Picric Acid (2, 4, 6-trinitrophenol)** : It is the simplest member of this class. It is the oldest artificial dyestuff, prepared by Woulff (1771) by the action of nitric acid on indigo. However, it is now prepared from chlorobenzene or phenol by the following sequence of reactions:

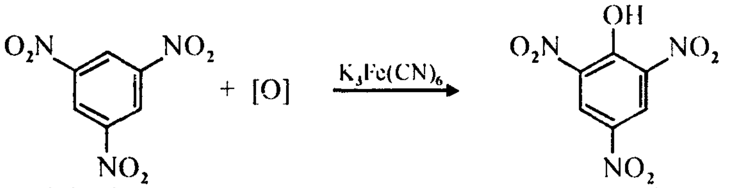
(*a*)



(*b*)



(*c*) It is also prepared by oxidising *s*-trinitrobenzene with potassium ferricyanide.

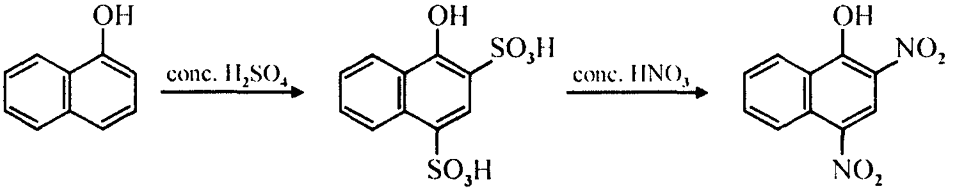


s-trinitrobenzene picric acid

It is a yellow crystalline solid, m.p. 122°C, with a bitter taste (Greek : *pikros*, bitter). The yellow colour is probably due to the presence of quinonoid structure.

It is generally used to dye silk and wool yellow. But the colour is fugitive. Therefore, it is mainly used as an explosive.

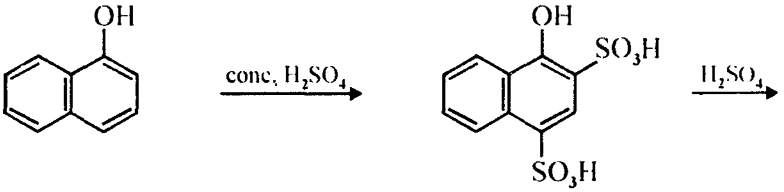
2. **Martius Yellow** : (Manchester yellow or 2, 4-dinitro-1-naphthol). It is generally used as sodium, calcium or ammonium salt. It is prepared from 1-naphthol by the following sequences of reactions :



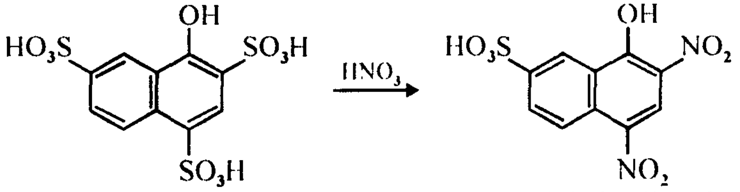
1-naphthol 1-naphthol-2, 4-disulphonic acid martius yellow

It dyes silk and wool in an acid bath. It is also used as a pigment colour and for colouring soap. It is fugitive and sublimes off the fibre.

3. **Naphthol Yellow-S** : (2, 4-dinitro-1-naphthol-7-sulphonic acid). It is obtained by the nitration of 1-naphthol-1, 4, 7-trisulphonic acid. The latter is obtained by the nitration of 1-naphthol.

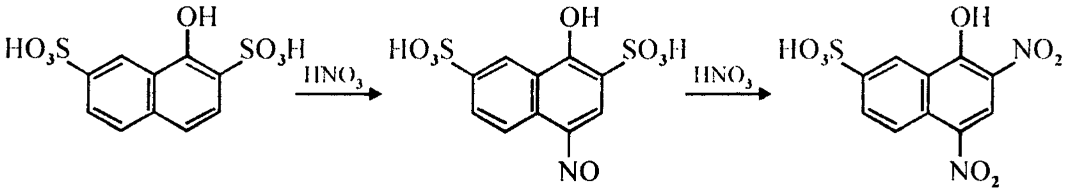


1-naphthol 1-naphthol-2, 4-disulphonic acid



1-naphthol-2, 4, 7-trisulphonic acid naphthol yellow S

It is also obtained by the nitration of 4-nitroso-1-naphthol-2, 7-disulphonic acid.



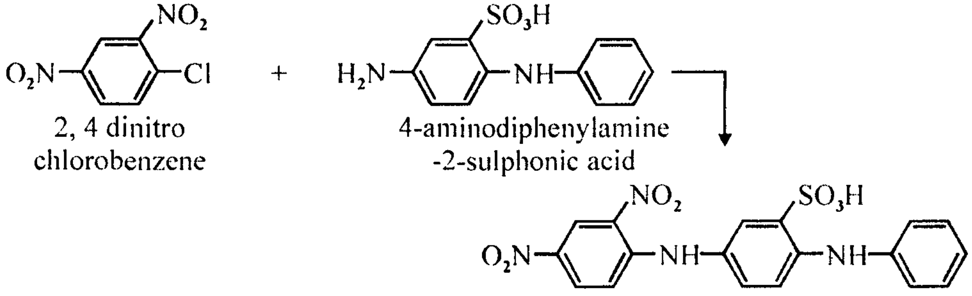
1-naphthol-2, 7-disulphonic acid

4-nitroso-1-naphthol-2, 7-disulphonic acid

naphthol yellow S

It is used as the sodium or potassium salt. It is a cheap dye for wool and silk in an acid bath, giving pure yellow shades. Unlike martius yellow, it is non-poisonous and is used as a food colour.

4. **Amido Yellow-E :** It is prepared by the condensation of 4-amino-4′-methyl-diphenyl amine-2-sulphonic acid with 1-chloro-2, 4-dinitrobenzene.



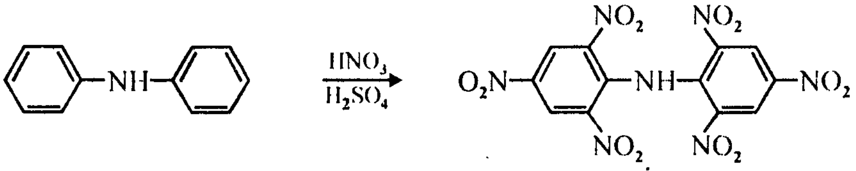
2, 4 dinitro chlorobenzene

4-aminodiphenylamine -2-sulphonic acid

Amido Yellow E

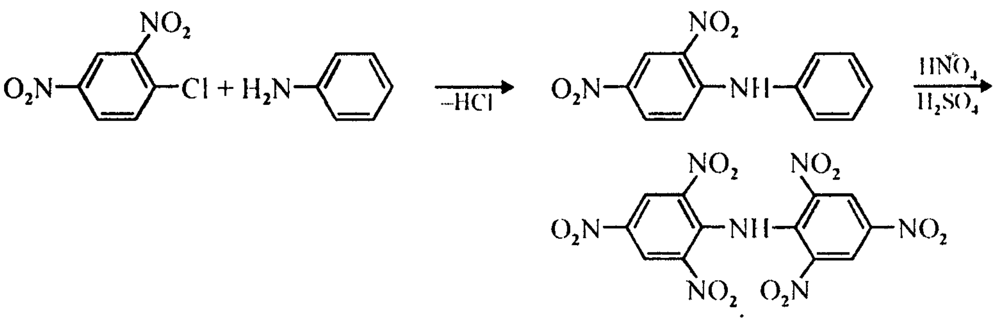
It dyes silk and wool just on the lines of naphthol yellows. It gives yellow shades which are moderately fast to light and washing but not to alkali.

5. **Aurantia (hexanitrodiphenylamine) :** It may be prepared by nitration of diphenyl amine :



aurantia

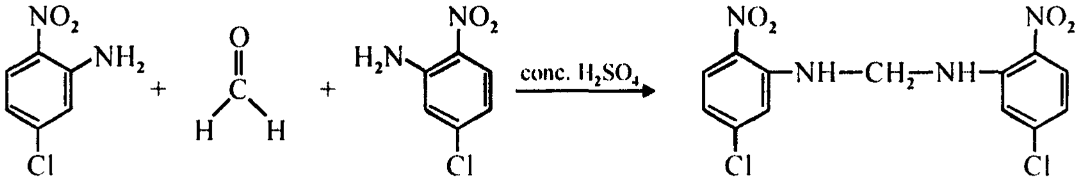
It may also be obtained by condensing dinitrochlorobenzene with aniline and nitrating and nitrating the product.



aurantia

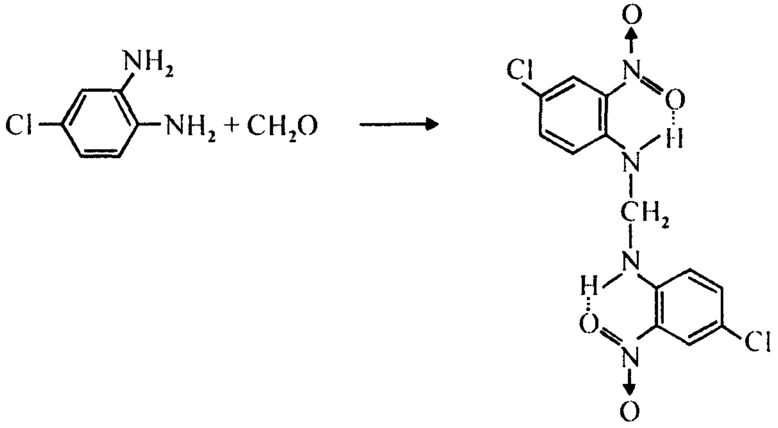
Its ammonium salt is generally used. It is a bright orange yellow substance.

6. **Pigment Chlorine GG :** It may be prepared by condensing formaldehyde with *o*-nitro-*m*-chloroaniline in the presence of sulphuric acid.



It is a pigment and is insoluble in water. It is used as a colour lake for paints and varnishes.

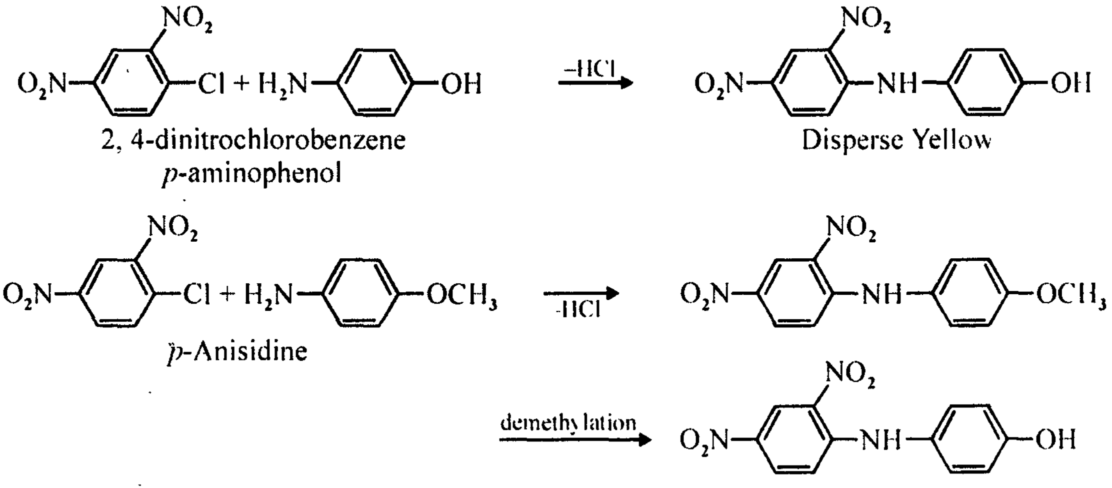
7. **Lithol Fast Yellow GG :** It is an isomer of pigment chlorine GG. It may be prepared by the condensation of *p*-chloro-*o*-nitroaniline with formaldehyde.



Lithol Yellow G

It is a non-poisonous substitute for chrome yellow. (lead chromate).

8. **Disperse Yellow :** It is obtained by the condensation of 2-4-dinitrochlorobenzine with *p*-aminophenol or with *p*-anisidine and demethylation.



2, 4-dinitrochlorobenzene
p-aminophenol

Disperse Yellow

p-Anisidine

Disperse Yellow

8

CHAPTER

NITROSO DYES

8.1. Introduction

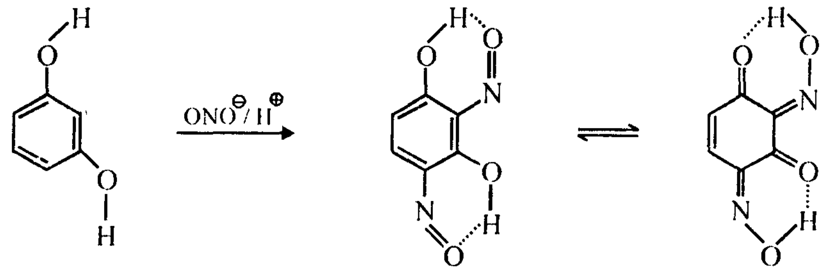
In these dyes, nitroso group being the chromophore and generally hydroxy (phenolic) group being as auxochrome in the *ortho* position with respect to each other. Nitroso dyes are obtained by the action of nitrous acid on phenols or naphthols.

Nitroso dyes are generally used in dyeing and calicoprinting in the form of lakes (mostly iron which gives green lake).

The tautomeric oxime form is mainly involved in the formation of lakes or metallic derivative because this form gets stabilised by hydrogen bonding. Some important nitroso azo dyes are described in Art. 8.2.

8.2. Some Examples of Nitroso Dyes

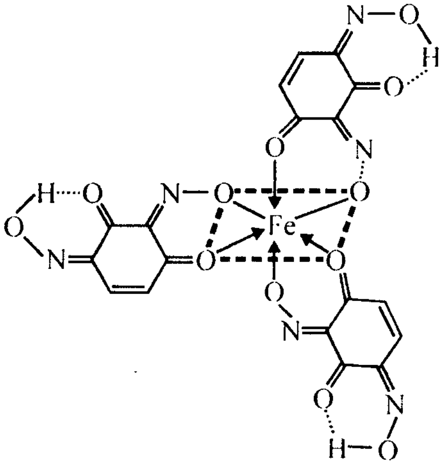
1. **Fast Green O** (***dinitroso resorcinol***) : It is obtained by the action of nitrous acid on resorcinol.



Resorcinol

Fast Green O

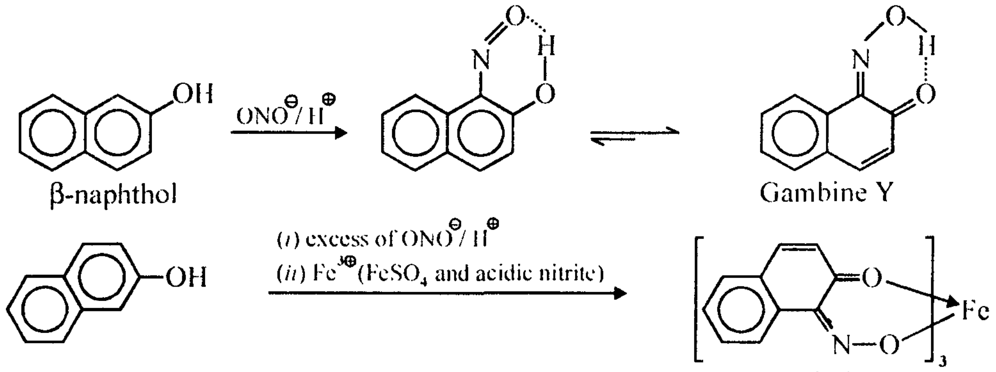
Fast Green O forms a green lake with iron III which is fast to light and washing.



Iron green lake of fast green O

Iron green lake of fast green was one time important in calico printing.

2. **Naphthol Green Y or Gambine Y** : It is α-nitroso-β-naphthol. With iron III, it forms a green lake which is known as Fast Printing Green. This α-nitroso-β-naphthol is also used for the detection of cobalt in the presence of nickel.



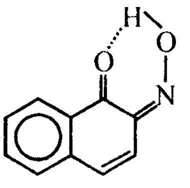
β-naphthol

Gambine Y

β-naphthol

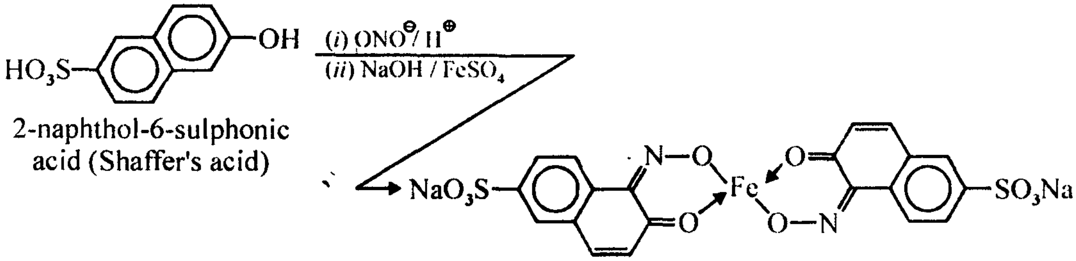
Fast Printing Green

The β-nitroso-α-naphthol is known as Gambine R.



Gambine R

3. **Naphthol Green β** : The ferrous complex of 6-sulphonic acid derivative of α-nitroso-β-naphthol in the form of sodium sulphonate is named as Naphthol Green-β. It is prepared by the treatment of ferrous sulphate, lime and sodium carbonate with α-nitroso-β-naphthol 6-sulphonic acid which is prepared by the actin of HNO_2 on β-naphthol-6-sulphonic acid (Shaffer's acid). It dyes wool to give fast green in an acid bath. [Octahedral ferric complex is named as Naphthol Green B; $(C_{30}H_{15}FeN_3Na_3O_{15}S_3]$.



2-naphthol-6-sulphonic acid (Shaffer's acid)

Naphthol Green-β

9

CHAPTER

AZO DYES

9.1. Introduction

The azo dyes and pigments form the largest group of all the synthetic colorants. The chromophoric system of these dyes is the azo group, –N = N –, in association with one or more aromatic systems. There may be more than one azo group present in the dye molecule and thus one speaks of mono azo, disazo, trisazo, tetrakisazo and polyazo dyes according to whether there are one, two, three, four or more azo group present in the dye molecule. Thus hues covered by azo dyes are very wide.

9.2. Diazotisation

In 1858, Peter Griess, a German Chemist, discovered that when a primary aromatic amino compound such as aniline, toluidine, etc., is acted on in aqueous acid medium by ice-cold nitrous acid, a second nitrogen atom has been introduced into the molecule, giving the new compound ArN_2Cl. This new compound ArN_2Cl is called *diazo compound* and the formation of this compound is called *diazotisation*. This process may be envisaged as taking place as follows :

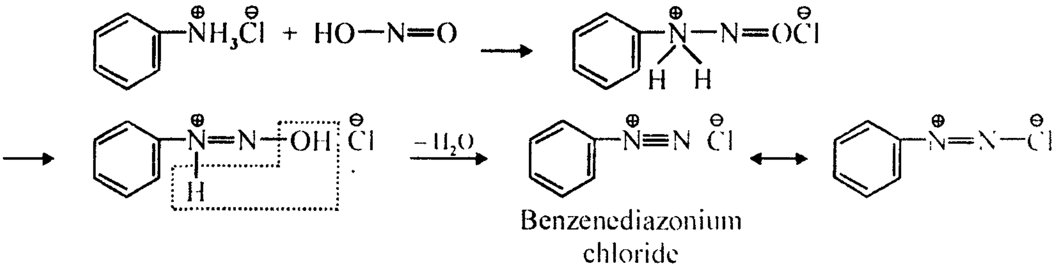
$$\underset{\text{Primary amine}}{Ar-NH_2} + HNO_2 + HCl \xrightarrow{\text{Cold}} ArN_2Cl + 2H_2O$$

or

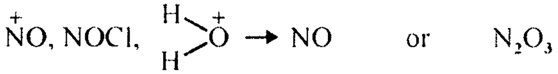
$$ArNH_2 + NaNO_2 + 2HCl \longrightarrow ArN_2Cl + NaCl + H_2O$$

The diazotisation is believed to take place through the following steps :

$$NaNO_2 + HCl \xrightarrow{-NaCl} HNO_2 \longleftrightarrow HO-N=O$$



The actual nitrosating species has been found to vary according to condition and may be

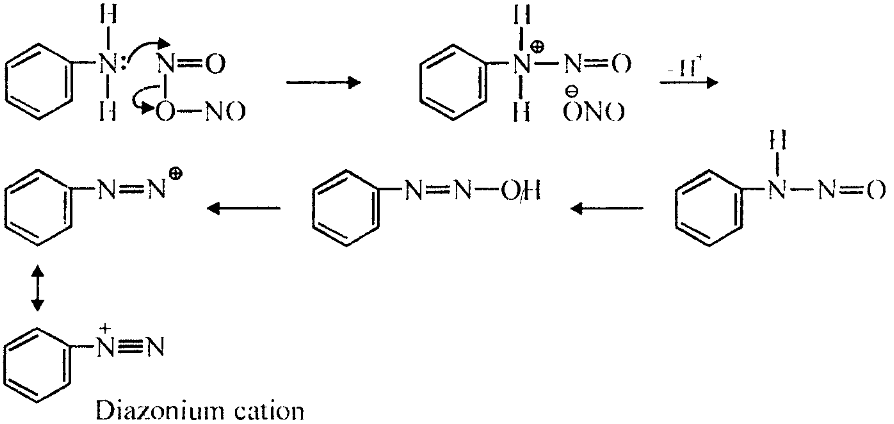


$$\overset{+}{N}O,\ NOCl,\ H_2\overset{+}{O}\text{—}NO \rightarrow \overset{+}{N}O \quad \text{or} \quad N_2O_3$$

At low acidities, it is probable that N_2O_3 is the effective reagent. This may be arising from the equilibrium.

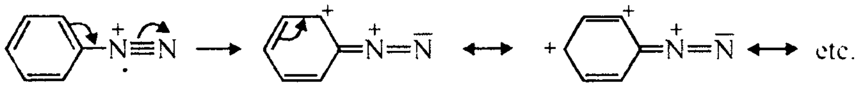
$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

The mechanism with N_2O_3 in the case of aniline being as follows :



Diazonium cation

The primary aliphatic amines do not form stable diazonium cations and on treatment with nitrous acid, breakdown occurs with the formation of non-nitrogenous products, nitrogen gas being evolved. On the other hand the relative stability of the aromatic diazonium cation is the result of delocalisation of the positive charge by the π-electron system, thus



Effects of Substituents on Diazotisation : The readiness with which an aromatic amine may be diazotised has been found to depend upon the nature and position of substituents in the nucleus as affecting the basicity of the amine. For instance, relative to aniline, *p*-nitroaniline and 2, 4-dinitroaniline are much less basic due to the presence of electron-withdrawing NO_2 groups and therefore, require special methods for their diazotisation. For example, weakly basic amines, *e.g.*, 2, 4-dinitroaniline and 1-, 2-aminoanthraquinone are diazotised by adding the solid amine to nitrosylsulphuric acid.

Diazotisation may also give rise to difficulties through low solubility in aquenous acid, the presence of easily replaceable groups such as $-SO_3H$, $-NO_2$, or the presence of easily oxidizable groups such as -OH, -CHO. Accordingly, a number of methods have been developed to overcome these difficulties.

Methods of Diazotisation : Diazotisation can be carried out by different methods which are as follows :

(*i*) ***Direct Method :*** Direct diazotisation can be carried out by treating one mole of the aromatic amine with about 3 moles of hydrochloric acid, ice is added to lower the temperature to 0-5°C and the theoretical quantity of nitrite is now added as an aqueous solution. If aniline is diazotised with only one mole of acid present, then a diazoamino compound results (N-coupling).

$$\text{Ar—NH}_2 + \text{ArNO}_2 + \text{HCl} \longrightarrow \text{ArN}_2^{\oplus}\text{Cl}^{\ominus} + \text{NaCl}$$

$$\text{Ar—NH}_2 + \text{Ar}\overset{\oplus}{\text{N}}_2 \longrightarrow \text{Ar—N=N—NH—Ar}$$

Completion of diazotisation and a slight excess of nitrous acid may be tested by starch-iodide paper. The diazonium salt solution is then used for coupling as soon as it is produced. The excess of nitrous acid at the end of diazotiation process may be destroyed either by urea or sulphamic acid because nitrous acid reacts with the second component.

$$\text{CO(NH}_2)_2 + 2\text{HNO}_2 \longrightarrow \text{CO}_2\uparrow + 2\text{N}_2\uparrow + 3\text{H}_2\text{O}$$

$$\text{NH}_2\text{–SO}_2\text{OH} + \text{HNO}_2 \longrightarrow \text{N}_2 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$$

As the diazonium ion decomposes in the presence of metals, the diazotisation is carried out in wooden vats or rubber-lined steel vessels or glass-lined steel vessels.

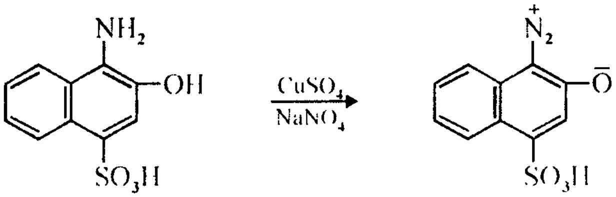
For nitrosubstituted compounds, diazotisation is carried out in enamelled glass vessels.

The naphthylamines are diazotised by direct method at 10-12°C. While naphthylamine sulphonic acids are diazotised by first precipitating the free sulphonic acid in an acid solution followed by reaction with the sodium nitrite.

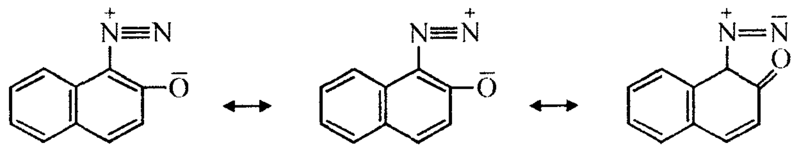
The direct diazotisation may also be carried out in acetic acid with amyl or ethyl nitrite. This is largely a laboratory method.

(*ii*) ***Reverse Method :*** In the reverse method, a solution of amine and solution of sodium nitrite are run into the solution of the acid. This method is used for naphthylamine sulphonic acids which give insoluble diazo salts due to the formation of zwitter ions. The diazonium salts are explosive and care must be exercised in handling them.

(*iii*) ***Special Method :*** Aminophenols are readily oxidised by nitrous acid to the quinones and, therefore, special methods are developed for diazotisation. The diazotisation of aminophenols is carried out in the presence of copper sulphate and absence of mineral acids. For example, 1-amino-2-naphthol-4-sulphonic acid is made into a 25% solution cooled to 20°C. To the solution is added copper sulphate followed by sodium nitrite.

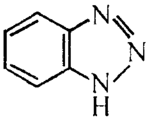


The diazo-oxide obtained is more stable than other diazo ions and may be subjected to even further reactions such as nitration, halogenation, etc. The diazo-oxides also undergo coupling reaction. Their stability has been ascribed to resonance structures.



Similarly, 1. 4-aminophenols form diazo-oxides. However, 1, 3-aminophenols do not form diazo-oxides.

Diazotisation of Diamines : Whenever an attempt is made to prepare a diazo or tetrazo derivative of *o*-phenylenediamine, there occurs ring closure with formation of benztriazole which does not couple. *m*-Phenylenediamine can be diazotised but strongly acid conditions are essential if coupling with unchanged *m*-phenylenediamine is to be avoided.

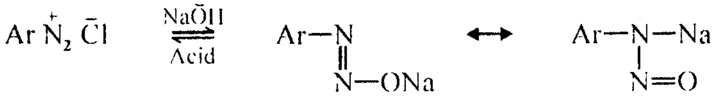


p-Phenylene diamine is easily diazotised but less easily tetrazotised. However, the tetrazo compound is very unstable.

Benzidine derivatives such as dichlorobenzidines, toluidines and dianisidines can be smoothly tetrazotised and the products are stable in solution.

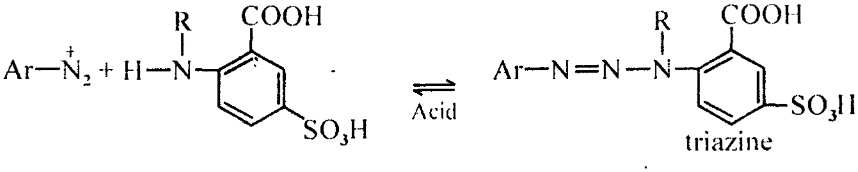
Stabilised Azo Compound : Most of the diazonium salts are not very stable except the nitro substituted benzene diazonium salts, diazo oxides and zwitter ions. Almost all the dry diazonium salts are explosive. However, there is a great need for the dyer and printer for the diazonium salts to produce different shades on the fibre by coupling. A number of methods have been developed to make stable diazonium compounds.

iso-Diazotates or nitrosoamines are produced when diazo solutions are poured into warm dilute caustic soda. These compounds are reasonably stable and are converted back to the diazo salt by treatment with acids.



iso- or *anti*-diazotate nitrosoamine

Diazoamino compounds are produced by reacting a diazonium salt with a primary or secondary amine. From these compounds, diazonium salt may be regenerated by treatment with acid. The amines employed are both aliphatic as well as aromatic. Aliphatic amines used are sarcosine, CH_3NHCH_2COOH and other amino acids. The aromatic amines used are sulphoanthranilic acid or 2-alkylamino-5-sulphobenzoic acids.



The triazenes obtained are used as rapidogen dyes (IG) in combination with coupling components in printing pastes.

Diazosulphonates are obtained when diazonium solution is treated with naphthalene-1, 5-disulphonic acid, *e.g.*,

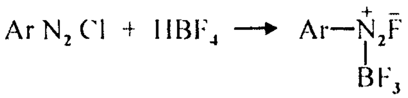
$$Ar\overset{+}{N_2}\overset{-}{Cl} + HO_3S - Ar' \longrightarrow Ar - N = N - O - O_2S - Ar' + HCl$$

The diazoarylsulphonate on redissolving in water is in equilibrium with the diazosalt. On coupling the diazoaryl sulphonate further breaks up. Diazoarylsulphonates are prepared from diazonium salts which do not yield stable antidiazotate or diazoamino compounds, *e.g.*, *p*-amino-diphenyl-amine diazonium salt, variamine blue B and blue BB.

Diazonium compounds are also prepared by isolating sulphate or chloride and drying the diazonium salt below 50°C. These salts are used on a large scale, *e.g.*, nitroanilines, chloroanilines, etc.

Double salts are obtained by treatment of diazonium solution with zinc chloride solution when the double salt $(ArN_2Cl)_2\ ZnCl_2$ is formed and crystalisted out, *e.g.*, benzidine, aminoazo, benzene, etc.

Stabilised fluoborates are also obtained by treatment of diazonium solution with fluoboric acid.

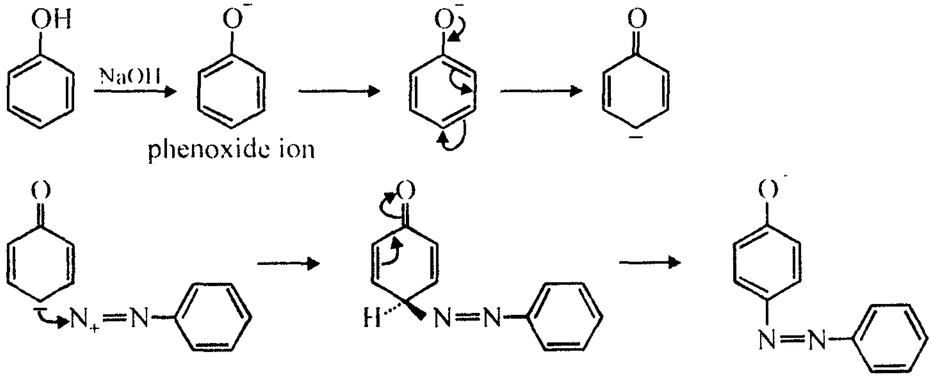


$$ArN_2Cl + HBF_4 \longrightarrow Ar{-}\overset{+}{N_2}\overset{-}{F}\ (\text{with } BF_3 \text{ below } N)$$

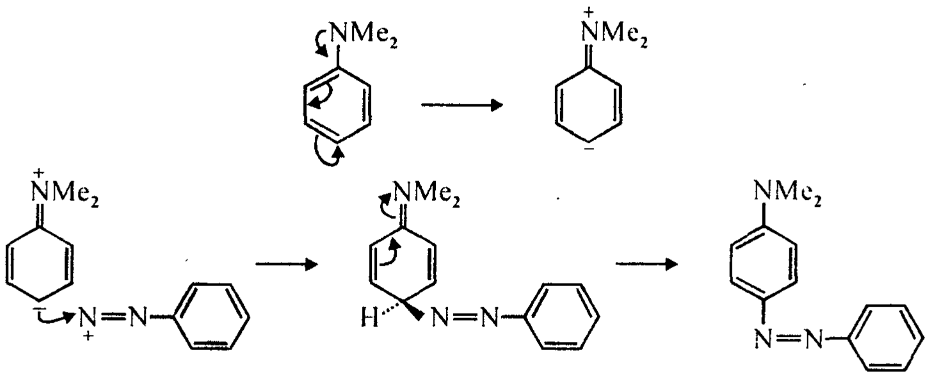
The stabilised diazonium compounds of the above types are very important and are marketed as fast salts, double salts or as components in rapid fast, rapidogen and rapidazol dyes.

Diazo Coupling

It may be regarded as an electrophilic substitution by a diazo group. Thus, normally coupling reaction takes place at sites of increased electron density. The coupling takes place in aromatic or heterocyclic systems having aromatic character or at activated carbon atoms in aliphatic systems such as acetoacetanilide. The diazo ion compared tonitronium ion or SO_3 is a weak electrophile. It reacts only when the aromatic nucleus possesses powerful electrondonating groups like OH or NH_2. The mechanism of coupling may be depicted as follows :

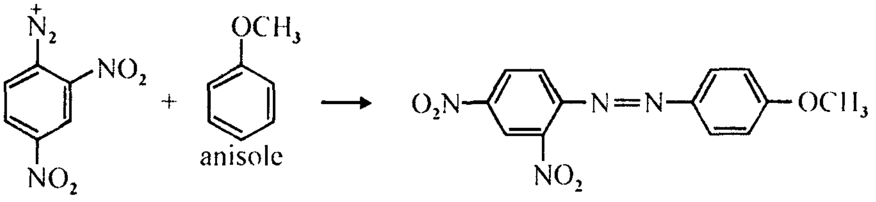


With tertiary amines a similar situation arises :



Coupling with phenols are usually carried out under alkaline conditions while the coupling with amines are carried out under slightly acidic conditions.

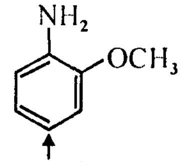
The electron-withdrawing groups such as nitro in *o*-and *p*-position to the diazo ion increases its electrophilic character and the coupling reaction takes place even with weak electron donating groups in the aromatic nucleus, *e.g.*, anisole.



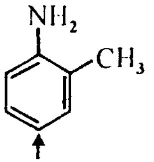
Coupling Components

Benzene Derivatives

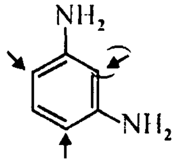
Amines : Primary aromatic amines are useful as coupling components. Some important examples are as follows :



o-anisidine

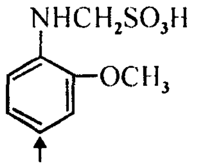


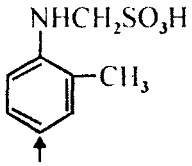
o-toluidine



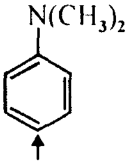
m-phenyl enediamine

The arrows indicate the usual coupling position. Coupling is generally carried out under acid condition with an energetic diazo component. If less energetic diazo components are to be coupled with the amine, the amino group has to be protected by first forming the methanesulphonic acid by reacting the amine with formaldehyde and bisulphite. The resulting compounds may be coupled under alkaline conditions. However, the methanesulphonic acid group is subsequently removed by hydrolysis.

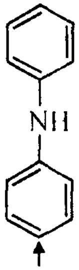




Examples of secondary and tertiary amines used as coupling components are as follows:



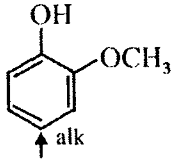
N-dimethylaniline



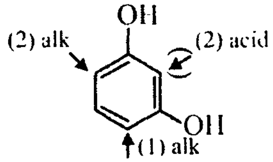
diphenylamine

Hydroxy Derivatives

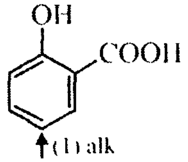
Phenol couples under alkaline conditions principally in the 4-position. In resorcinol, coupling takes place in the 4-position and then according to the pH at which the coupling is done, *e.g.*, pH 5–8, position 2; pH > 8, position 6. Resorcinol couples principally in the 4-position.



phenol



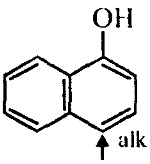
resorcinol



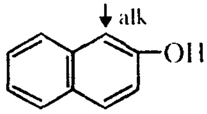
salicylic acid

Naphthalene Derivatives

Naphthols : Their coupling positions are shown as below :



1-naphthol

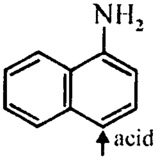


2-naphthol

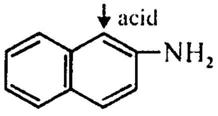
1-Naphthol will couple with diazo-oxides in the 2-position under alkaline conditions. The derivative 2-hydroxyl-3-naphthoic acid of 2-naphthol is used in development colours and gives rise to the widely used 2-hydroxy-3-naphtharylamides.

Naphthylamines

Coupling is carried out under acid conditions in both the cases :



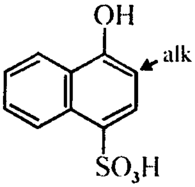
1-naphthylamine



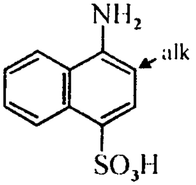
2-naphthylamine

2-Naphthylamine is no longer manufactured because it is a known powerful carcinogen.

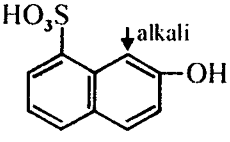
Naphtholmonosulphonic Acids



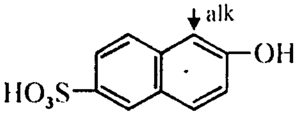
nevile and winther's acid



1-naphthol-5-sulphonic acid

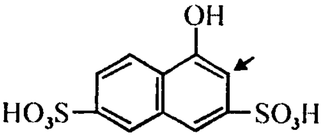


crocein acid

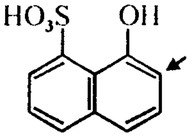


schaffer's acid

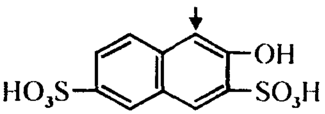
Naphtholdisulphonic Acids



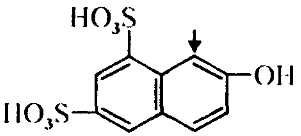
1-naphthol-3, -6-disulphonic acid



epsilon acid

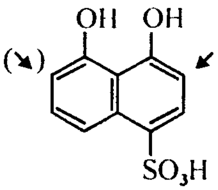


R-acid

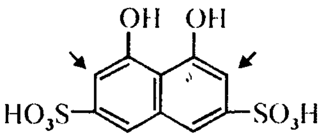


G-acid

Dihydroxynaphthalenesulphonic Acids



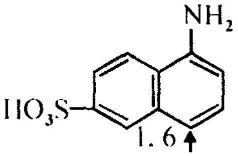
4, 5-dihydroxynaphthalene
-1-sulphonic acid

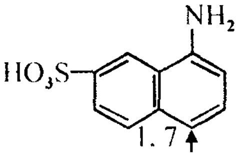


chromotropic acid

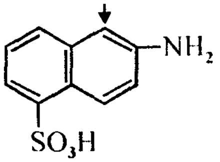
Naphthylaminesulphonic Acids

naphthionic acid

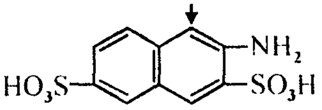




cleve's acid



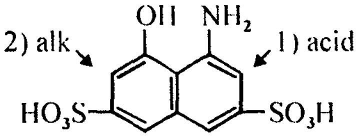
2-aminonaphthalene
-5-sulphonic acid



2-aminonaphthalene
3, 6-disulphonic acid

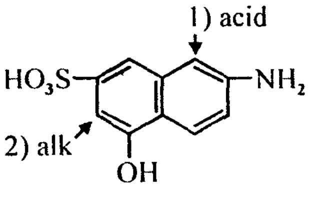
Aminonaphthol Sulphonic Acids

An example of these is H-acid from which hundreds of azo dyes are prepared which are widely used for dyeing wool, cotton and leather dyes.

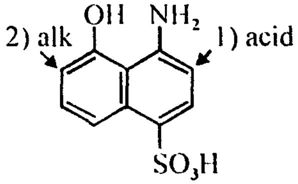


H-acid

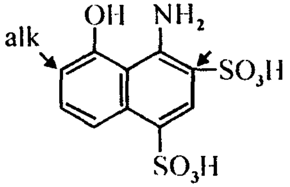
Other examples are as follows :



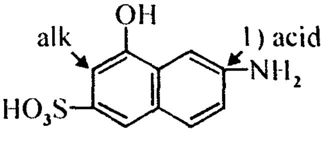
J-acid



S-acid



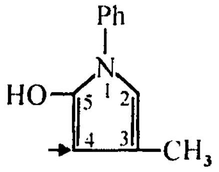
S-acid



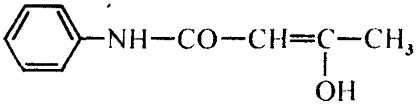
gamma acid

Methylphenyl Pyrazolone

It couples at position 4. It is used in the manufacture of direct and acid dyes and especially in mordant dyes.

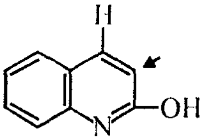


Acetoacetanilide

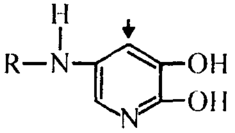


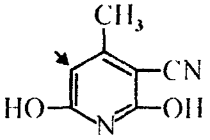
It is used for making a number of direct and acid dyes.

Quinoline-2, 4-diol



Dihydroxypyridines





where R = alkyl

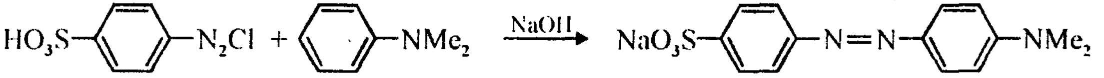
9.3. Types of Azo Dyes

The azo dyes prepared and used are very large in number, also their structures are largely varied and so they are further classified according to the fibre as follows :

1. Acidic Azo Dyes : These dyes have been characterised by the presence of an acidic group such as $-SO_3H$, $-COOH$ or phenolic $-OH$ group. This acidic group makes the dye more soluble and is also used as the reactive point for fixing the dye. The acidic groups act as auxochromes in these dyes.

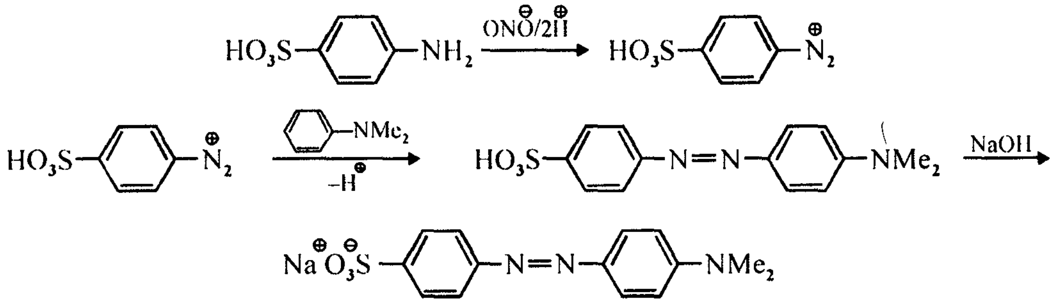
***(a) Methyl Orange** : (Orange III, sodium p-dimethylamino azobenzene -p′-sulphonate).*

It is obtained by coupling diazotised sulphanilic acid with dimethylaniline. This dye is generally isolated as the sodium salt. The hydrochloride of methyl orange is called *helianthin*.



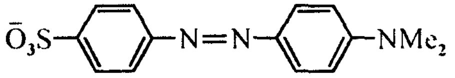
methyl orange (orange III)

Mechanism

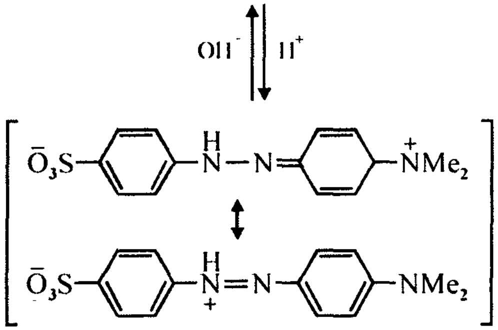


Methyl Orange (Orange III)

Methyl orange is not used as a dye because it is sufficiently fast to light or soap. However, its sodium salt is used as the indicator in acidimetry and alkalimetry because its colour change is sharp over a small pH change. It gives yellow colour in alkaline solution, *i.e.*, above pH 4.4, and red in acidic solution *i.e.*, below pH 3.1. The change in colour of the compound in different media has been ascribed to the difference in its structure in the two media.



negative ion in alkaline medium, pH 5–14 (yellow)

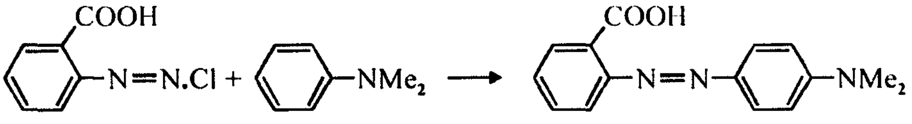


dipolar ion in acidic medium, pH 0–3.0 (red)

Since methyl orange is not sufficiently fast to light or soap solution, it is not used as a dye. However, it is a common acid-base indicator. Methyl orange gives yellow colour in alkaline and red in acidic solution. The cause of this change in colour is the difference in its structure in the two media.

Cango red is a valuable dye which is intense red in alkaline medium, and changes to deep blue in strong mineral acid; hence methyl orange and congo red are similar as regards the property of giving two different colours in two different media.

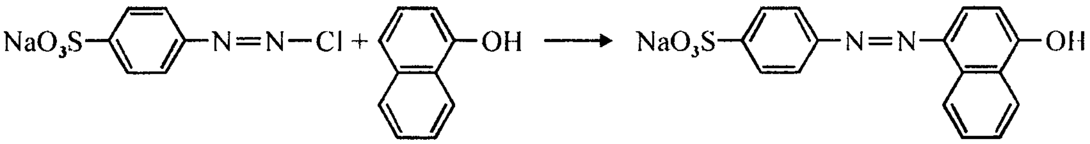
(b) Methyl Red : It may be obtained by the coupling of diazotised anthranilic acid with dimethylaniline.



Methyl red

It is not used as a dye but is used as an indicator in acid-alkali titrations. It gives an intense red colour in strongly acidic solution (saturation with carbon dioxide deepens the colour.)

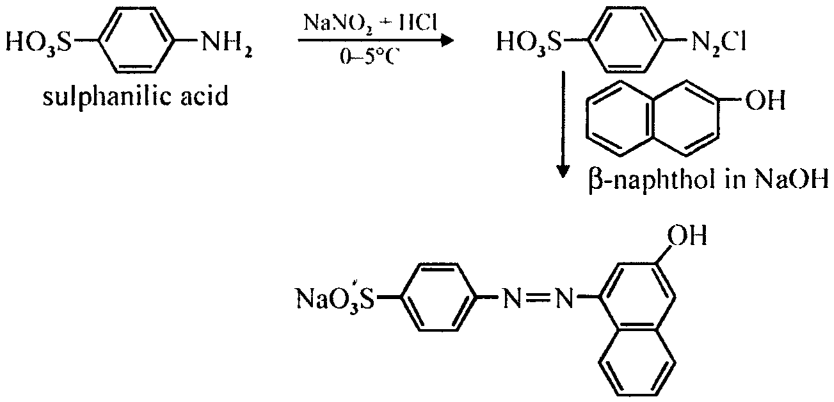
(*c*) *Orange I :* (*α-Naphthol Orange*). It is obtained by coupling α-naphthol with diazotised sulphanilic acid.



orange I or α-naphthol orange

Orange I is used widely for dyeing wool and cotton fibres.

(*d*) *Orange II :* (β-*Naphthol orange*). It is obtained by coupling β-naphthol with diazotised sulphanilic acid.

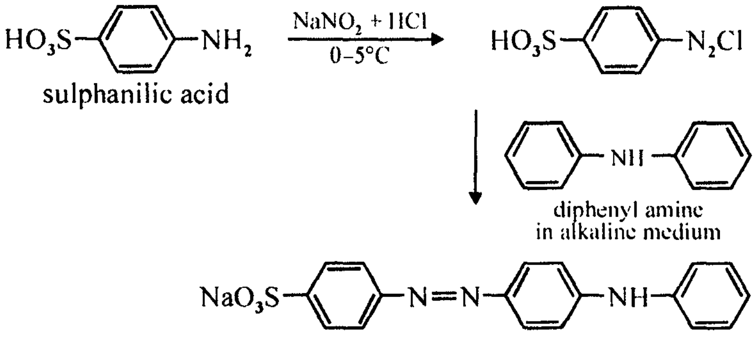


orange II

Procedure : Sulphanilic acid is diazotised with sodium nitrite and hydrochloric acid at 5–8°C. Now the diazotised sulphanilic acid is run into a solution of β-naphththol having caustic soda, soda ash and common salt at 8°C. After stirring the contents for 2 hours, the temperature is raised from 8 to 16°C. The pH of the solution rises from 9.1 to 9.4 which is lowered by acidifying with HCl. The salted dye is filtered and dried.

Orange II is used widely for dyeing wool, cotton fibres, silk, paper and leather.

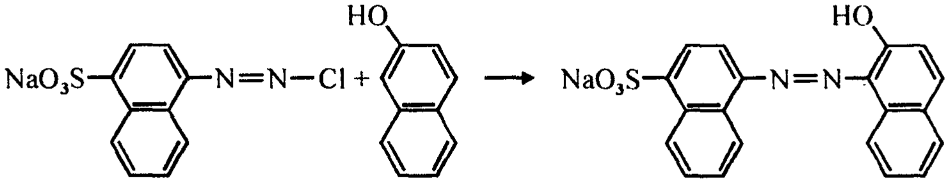
(*e*) *Orange IV :* It is obtained by coupling diazotised sulphanilic acid with diphenylamine in alkaline solution. But diphenylamine is insoluble in water. Therefore, it is to be emulsified in water before coupling is carried out.



orange IV

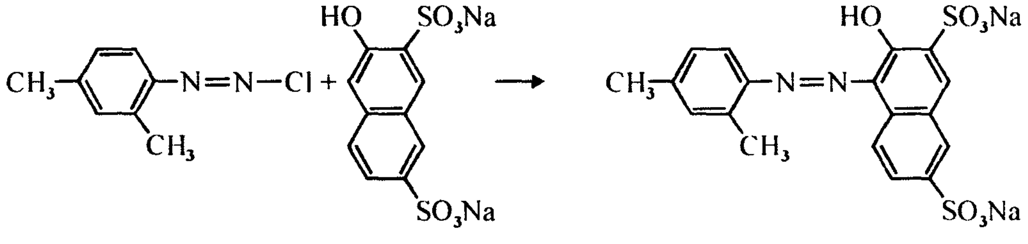
It is an acid azo dye. It is mainly used for dyeing wool and cotton fabrics. In acid medium, it possesses limited fastness.

(*f*) ***Fast Red A*** : It was the first red azo dye and is still important due to its cheapness and adequacy for many purposes. It is obtained by the condensation of diazotised naphthoic acid (1-naphthylamine-4-sulphonic acid) with β-naphthol.



Fast Red A

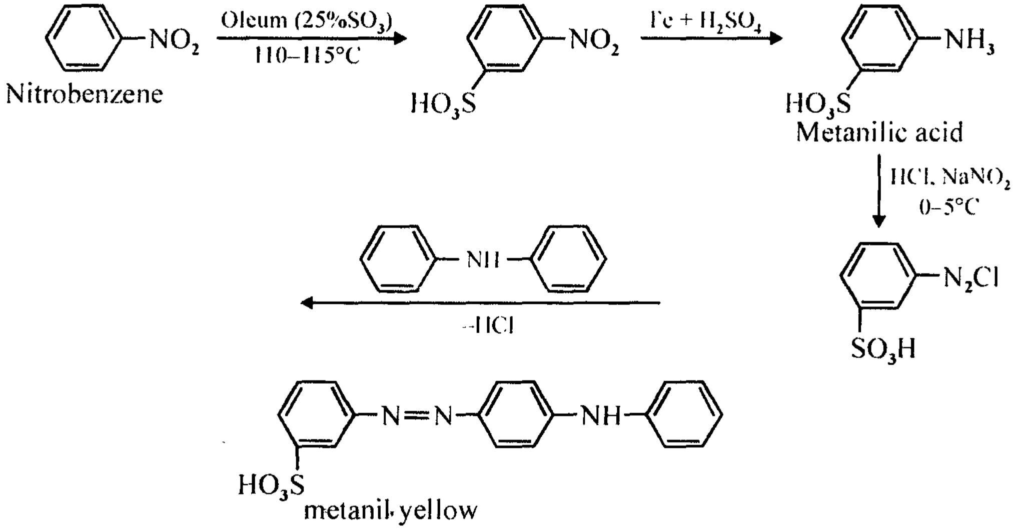
(*g*) ***Ponceau '2R'*** : It is obtained by coupling diazotised *m*-xylidene with the R acid (2-naphthol-3, 6-disulphonic acid).



ponceau '2R'

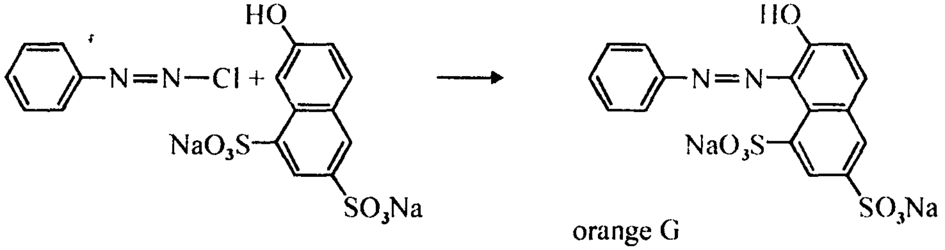
It is favourable scarlet dye. It has good fastness to light and washing.

(*h*) ***Metanil Yellow*** : The starting compound for this acid azo dye is nitrobenzene. It is sulphonated followed by reduction with iron and sulphuric acid when metanilic acid is produced. This acid is now diazotised and then coupled with diphenylamine when metanil yellow is obtained. Since diphenylamine is insoluble in water, the coupling reaction has to be carried out by emulsifying diphenylamine in water before coupling.

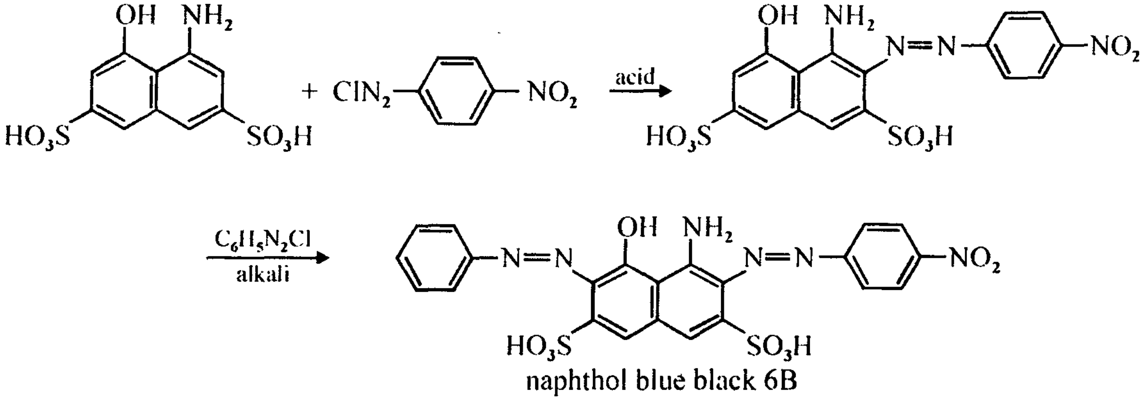


It is used for dyeing silk and cotton fibres.

(*i*) ***Orange G*** : It is obtained by coupling diazotised aniline with the G-acid (2-naphthol-6, 8-disulphonic acid).

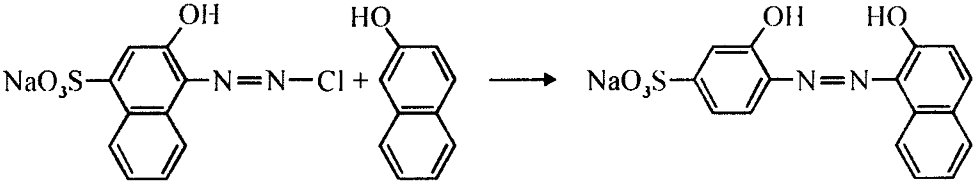


(*j*) ***Naphthol Blue Black 6B*** : (*amino black 10 B*). It is obtained by coupling H-acid (1-amino-8-naphthol-3, 6-disulphonic acid) with one molecule of diazotised *p*-nitroaniline in an acid medium followed by coupling of the product with one molecule of benzene diazonium chloride in an alkaline medium).



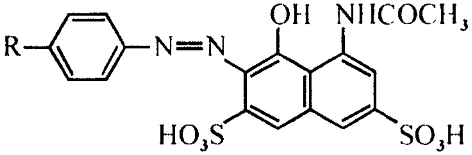
It is an important acid dye which is generally used for dyeing wool for black shades of moderate fastness.

(k) Chrome Blue Black R : It is prepared by coupling diazotised 1-amino-2-naphthol-4-sulphonic acid with β-naphthol.



chrome blue black R

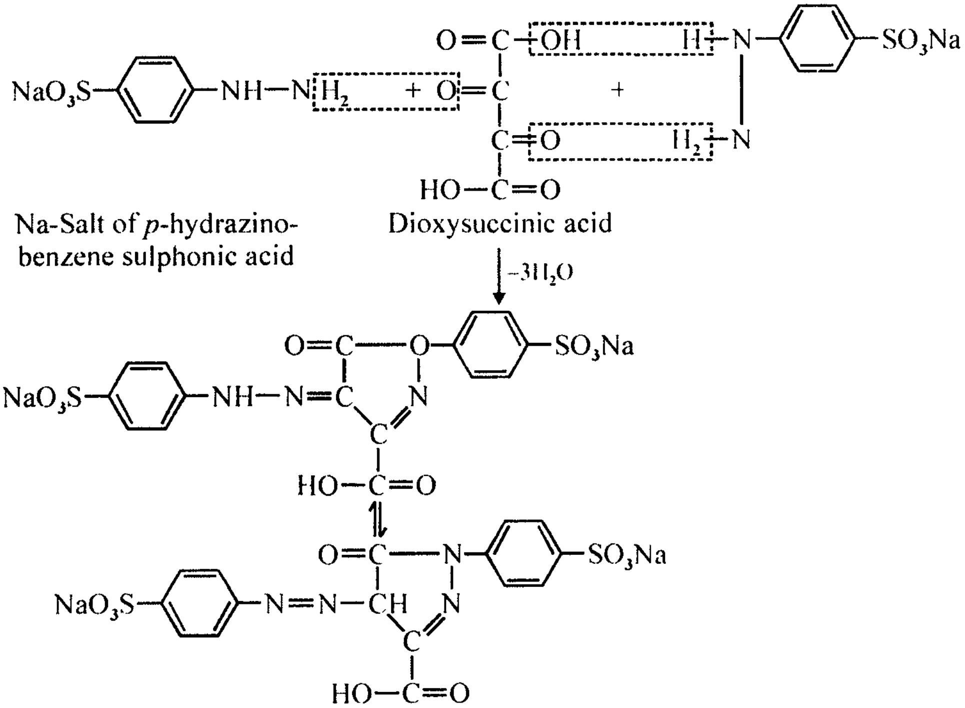
(l) Carabolan Dyes : The main drawback of the above described dyes is that they are readily washed away with water. This drawback has been overcome by another group of acid azo dyes called *carbolan dyes;* the general formula of these dyes is depicted as follows :

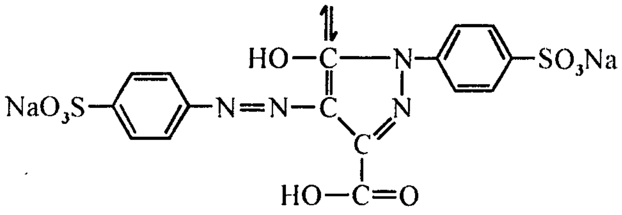


In the above formula, R denotes a long-chain alkyl group (*e.g.*, $C_{12}H_{25}$). but this group is hydrophobic in nature. Therefore, it prevents the removal of the dye by water and thus makes the dye resistant to washings.

(m) Tartrazine : It is an acid azo dye which may be prepared by the following two method:

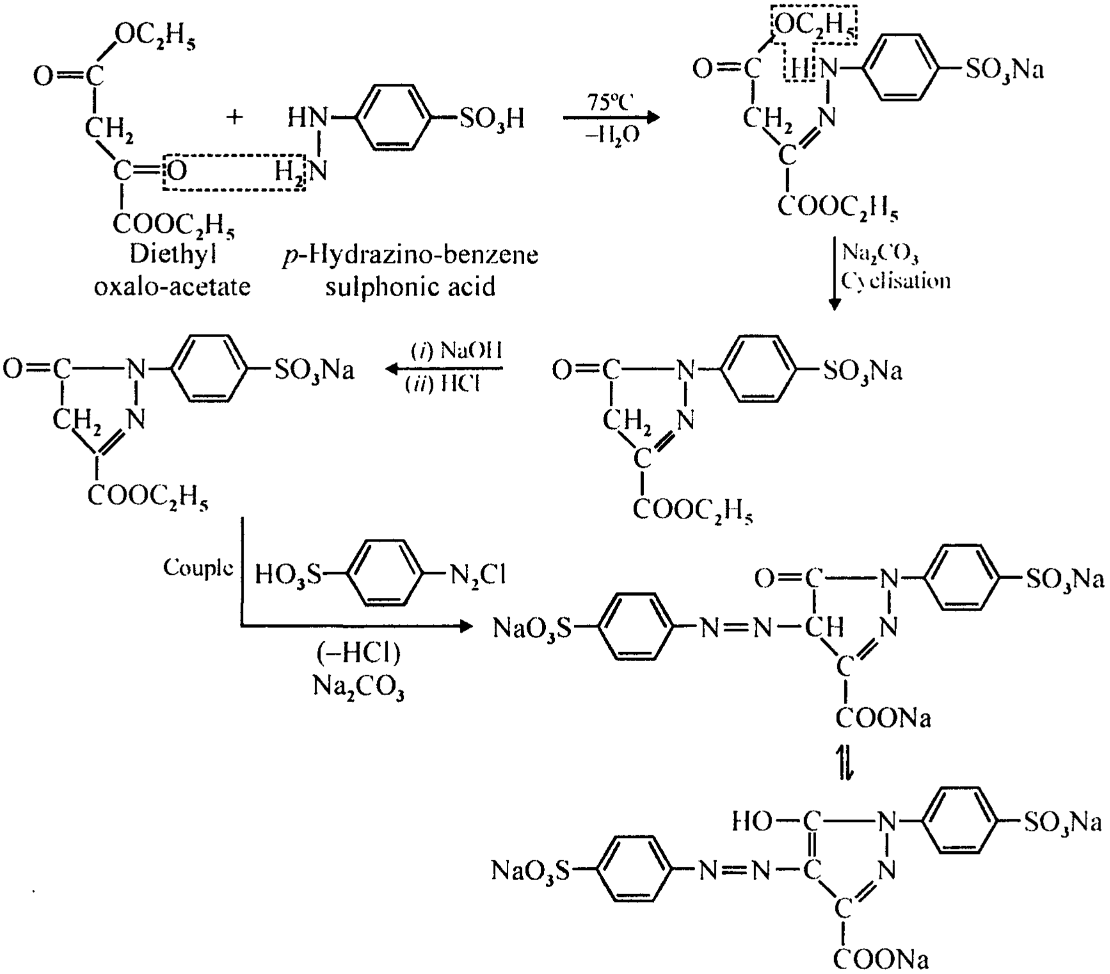
(*i*) If may be prepared by condensing two molecules of *p*-hydrazinobenzene sulphonic acid with one molecule of dioxysucinic acid.





Tartrazine

(*ii*) It may also be prepared by condensing one molecule of *p*-hydrazinobenzene sulphonic acid with one mole of diethyloxaloacetate. The product so obtained on coupling with diazotised sulphonic acid yields tartrazine.



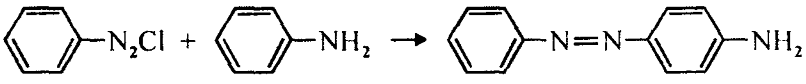
Tatrazine

It is mainly used for dyeing wool fabrics yellow with moderate fastness and silk fibres with poor fastness.

2. Basic Azo Dyes : These dyes have $-NH_2$ or $-NR_2$ group as the auxochrome. The chromophoric system is present as a cation. Only few basic azo dyes are known. These dyes are not much used and they are, therefore, not of much significance industrially.

Some of the basic azo dyes are described as follows :

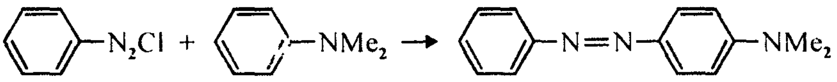
(*a*) ***Aniline Yellow :*** It is the simplest and the first azo dye that was made. It is obtained by coupling diazotised aniline with aniline.



aniline yellow (*p*-amino azobenzene)

As this dye is acid-sensitive, it is not of much significance industrially. However, it is used as an intermediate in the synthesis of other dyes.

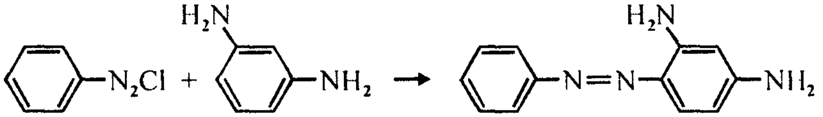
(*b*) ***Butter Yellow :*** It is obtained by coupling dimethylaniline with diazotised aniline.



butter yellow or
p-dimethylaminoazobenzene

It is used for colouring butter, oils and margarine.

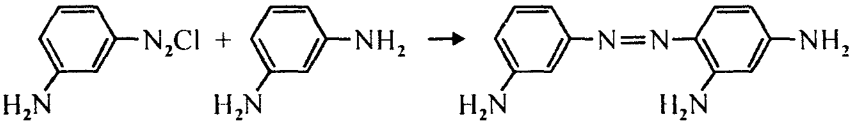
(*c*) ***Chrysodine G (2, 4-diaminoazobenzene) :*** It is a cationic dye. It is obtained by coupling *m*-diphenylenediamine with benzene diazonium chloride.



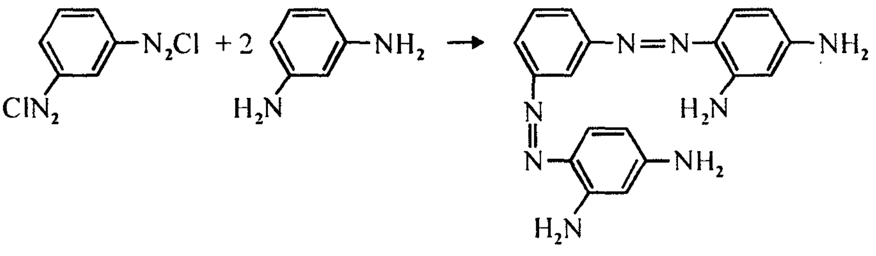
chrysodine G

It is an orange dye. It is generally used to dye silk, woll, cotton, leather and paper.

(*d*) ***Bismark Brown (Phenylene Brown) :*** It is one of the oldest dyes which is a mixture of mainly two compounds, I and II. This mixture is obtained by the action of HNO_2 on excess of *m*-phenylenediamine *i.e.*, by the diazotisation and coupling by *m*-phenylenediamine



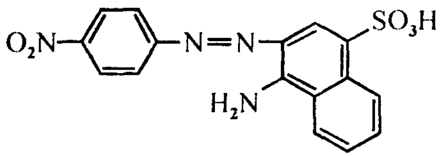
monoazo compound, I



bisazo compound, II

It is a brown dye. It is mainly used for dyeing leather on a tannin mordant.

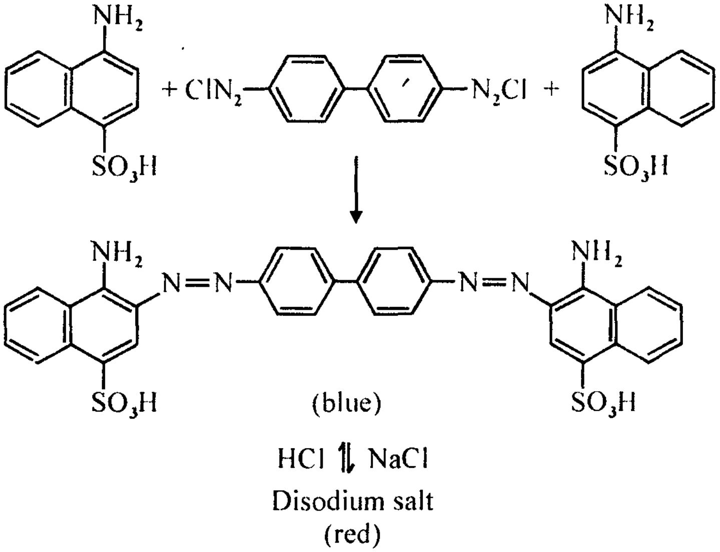
(*e*) ***Acid Red :*** It is obtained by coupling diazotised *p*-nitroaniline with naphthionic acid.



Acid Red

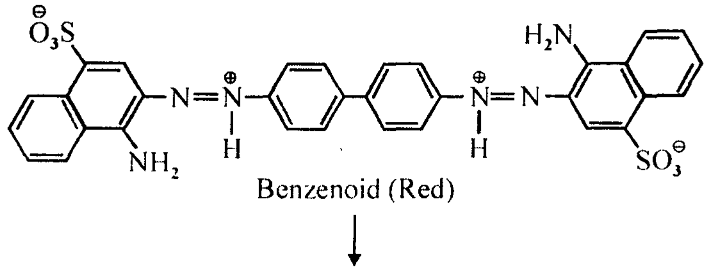
3. Direct or Substantive Azo Dyes : The azo dyes described earlier are used to dye the proteinous fibres (*e.g.*, wool, silk and leather) directly but they need mordant for dyeing cellulosic fibres (*e.g.*, cotton, linen, paper, etc.,). However, certain azo dyes are known which could dye directly the cellulosic fibres without a mordant. Such azo dyes are called firect or substantive azo dyes. Some important direct azo dyes are described as follows :

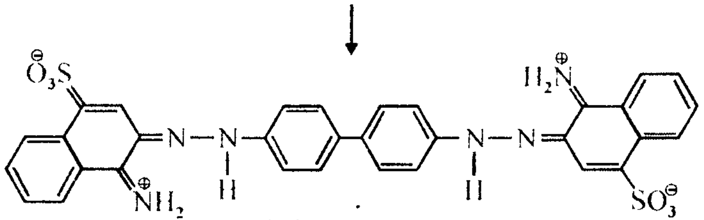
(*a*) ***Congo Red :*** It is a simple benzidine bisazo-dye stuff. It is obtained by coupling tetrazotised (*bis*-diazotised) benzidine with two molecules of naphthionic acid. The blue dye so obtained is converted into its red disodium salt during its salting out with sodium chloride.



The red salt is capable of dyeing cotton directly.

The red salt is very sensitive to acids, the colour turns from red to deep blue in the presence of strong mineral acids and to dull purple by organic acids. The change in colour from red to blue in the presence of inorganic acids may be explained due to the occurrence of resonance as follows:

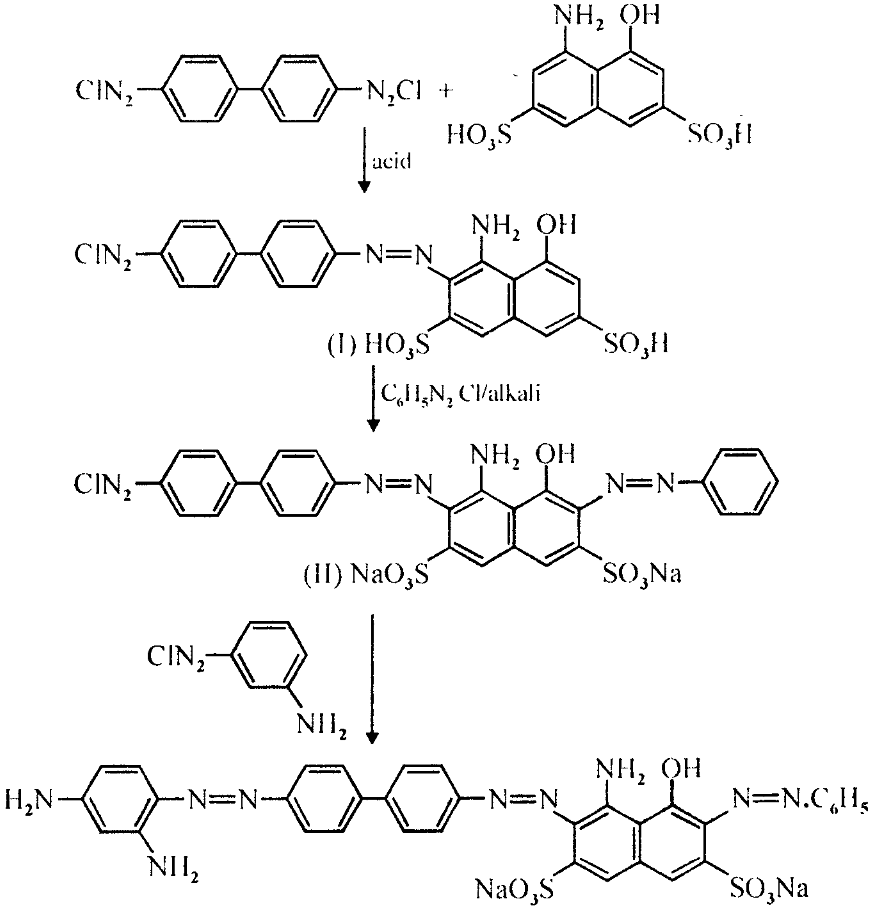




o-Quinonoid (Blue)

Congo red is used as an indicator in acid-alkali titrations. Congo paper is used for testing acidity of the solution.

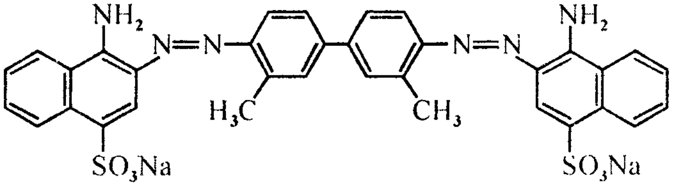
(b) Direct Deep Black : It is trisazo dye and is obtained by following series of coupling reactions in a particular order. First of all, the *bis*-diazotised benzidine is coupled with one mole of H-acid (1-amino-8-naphthol-3, 6-disulphonic acid) in acid medium to yield a product, I. Then this product, I, is coupled with one molecule of benzene diazonium chloride in alkaline medium to yield the product II. Finally, the product, II, is coupled with *m*-phenylenediamine to yield direct deep black.



direct deep black

It is the most widely used black dye.

(*c*) ***Benzopurpurin :*** It is obtained by coupling *bis*-diazotised *o*-toluidine with two molecules of naphthionic acid.

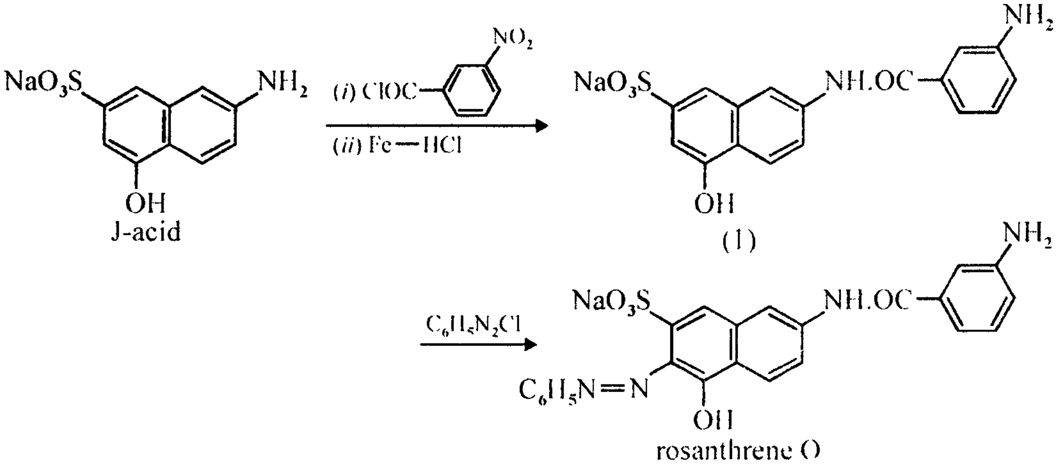


It is interesting to note that this dye exhibits similar colour changes. However, it is less sensitive towards acids. It is also a largely used dye for pink on cotton and scarlet on wool.

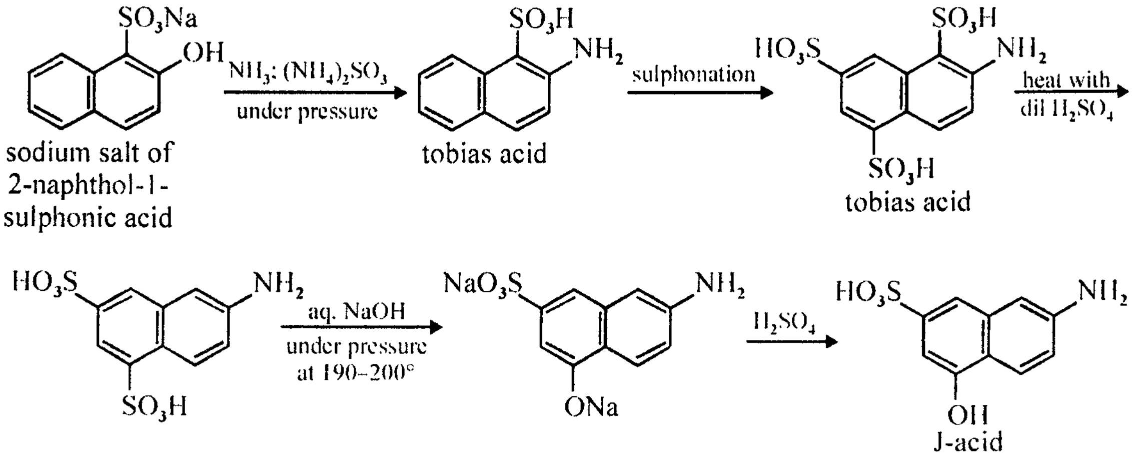
(*d*) ***Rosanthrene O :*** The preparation of this dye involves the following steps;

(*i*) First of the *J*-acid is condensed with *m*-nitrobenzoyl chloride in the presence of sodium acetate to yield a product which is then reduced with iron and dilute hydrochloric acid to yield the product I.

(*ii*) The product (1) on coupling with benzene-diazonium chloride yields rosanthrene O.

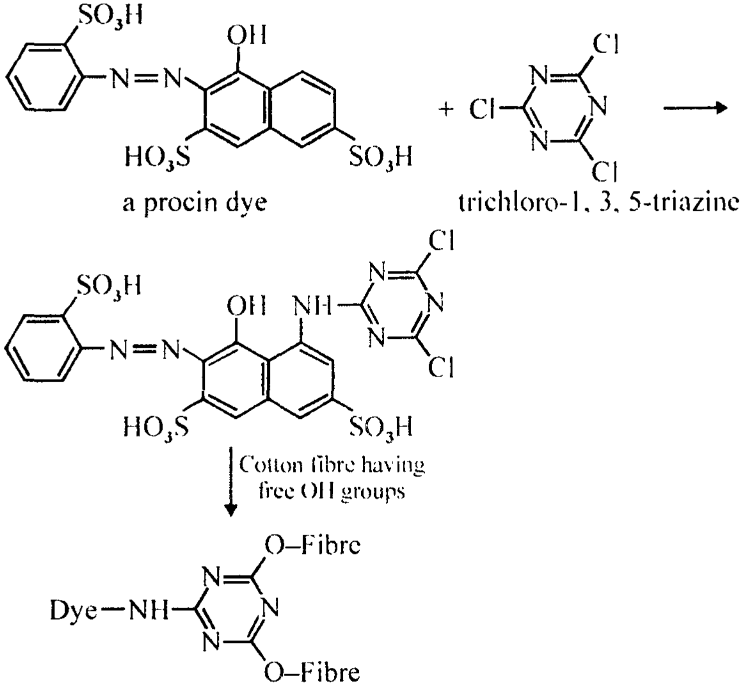


(*iii*) The *J*-acid required for step (*i*) is prepared from tobias acid in the following manner:

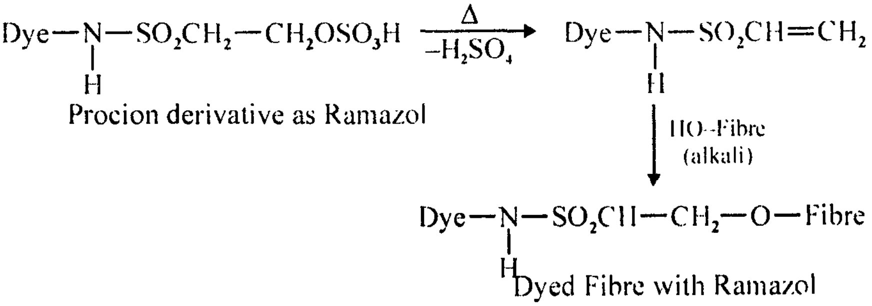


The *J*-acid as well as its N-phenyl and N-methyl derivatives are important intermediates of direct dyes for cellulosic fibres.

(*e*) *Procion Dyes* : The direct azo dyes described above have been found to attach themselves to the fibres by hydrogen bonds. However, certain direct azo dyes are known which are water soluble and get attached to the fibres through chloro-1, 3, 5-triazine molecule. Such dyes are called *procion dyes* An example of these dyes is given as follows :



(*f*) *Ramazol* : Similar to procion dyes, there is another group of dyes called ramazol, *e.g.*,



$$\text{Dye}-\underset{\text{H}}{\underset{|}{\text{N}}}-SO_2CH_2-CH_2OSO_3H \xrightarrow[-H_2SO_4]{\Delta} \text{Dye}-\underset{\text{H}}{\underset{|}{\text{N}}}-SO_2CH=CH_2$$

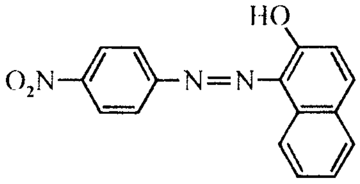
Procion derivative as Ramazol

$$\Big\downarrow \text{HO-Fibre (alkali)}$$

$$\text{Dye}-\underset{\text{H}}{\underset{|}{\text{N}}}-SO_2CH-CH_2-O-\text{Fibre}$$

Dyed Fibre with Ramazol

4. Ingrain Azo Dyes : These are water insoluble azo dyes which are formed on the fibre. They are prepared by dipping the fabric in an alkaline solution of 2-naphthol containing turkey red oil, drying it and then immersing in a solution of the diazotised amine. The most important example of this group is para red (diazotised para-nitroaniline).



para red

Some other ingrain azo dyes along with their both the components are given as follows :

2-naphthol + *m*-nitroaniline = Nitroaniline orange.

2-naphthol + 2, 4-dinitroaniline = Permanent red 2R,

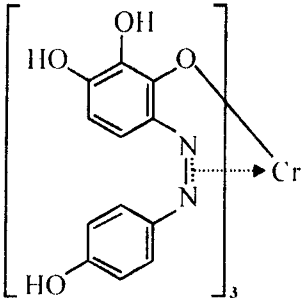
2-naphthol + dianisidine = Dianisine blue.

Some authors consider aniline black as a special case of ingrain dyes. In order to dye fabrics black with aniline, the first step is to cover the fabrics with aniline hydrochloride (aniline salt) and then these fabrics are treated with a solution of potassium dichromate, sulphuric acid and other substances. In conclusion, they are subjected to special treatment called ageing.

5. Mordant Azo Dyes : These are the azo dyes, which, when fixed on the fibre, are capable of forming complex metallic compounds when after treated with metallic salts such as sodium dichromate, sodium chromate or chromium fluoride. A considerable molecular-surface increases and often significant solubility decrease results. Such treatment usually produces a bathochromic effect and yields dyeings of improved fastness properties. Chromium is the most widely used metal in mordant azo dyes. The chromium salts can be applied to the fibre before dyeing (chrome-mordant or chrome-bottom method), together with the dye (metachrome method), or after dyeing (afterchrome method).

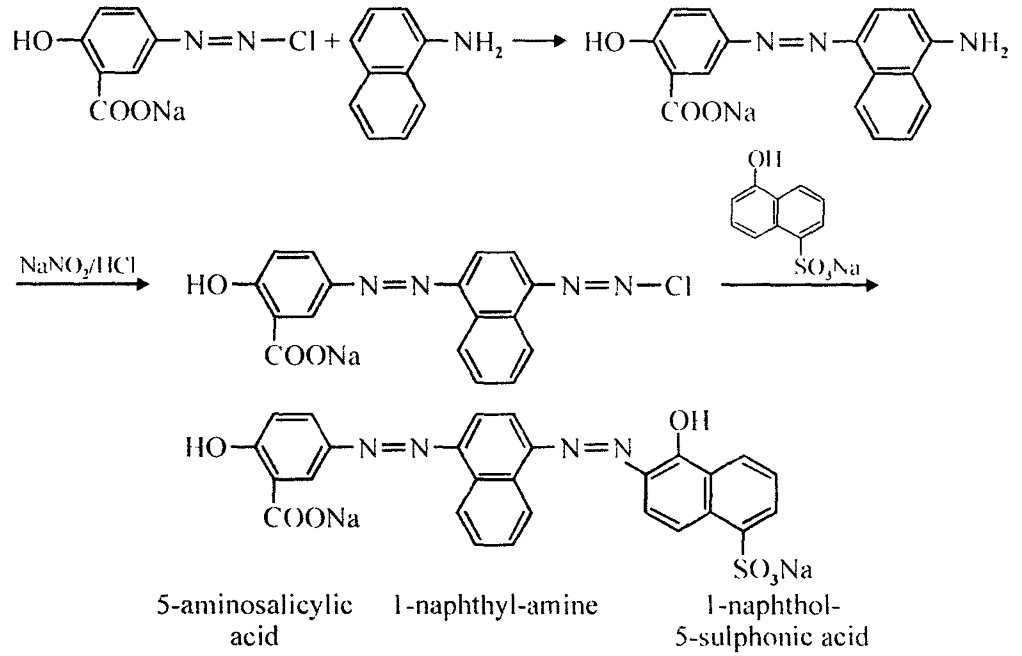
Most of the dyes belonging to this group are monoazo dyes but they include a few disazo dyes. Their great importance is due to their high fastness to light and washing.

The characteristic structural feature in all mordant azo-dyes is the presence of a hydroxyl group ortho- to the azo-group. Chromium is the most important mordanting metal–the dyes so produced are usually called azochrome mordant dyes. The fibre is mordanted by boiling with potassium dichromate solution, generally in the presence of a reducer like formic, lactic or oxalic acid. In this operation, the Cr (VI) is changed into Cr (III). The mordanted fibre is now dipped in a solution of the dye so as to precipitate the insoluble coloured lake (metal complex) on the fibre, *e.g.*, 'mordant brown' (formed by coupling diazotised *p*-aminophenol with pyrogallol). Some important mordant azo dyes are as follows :



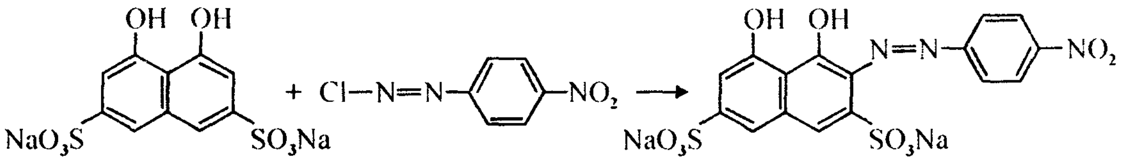
Modrant Brown

(*a*) ***Diamond Black F :*** It is disazo mordant dye. It is one of the earliest chrome dyes. It is obtained by coupling diazotised 5-amino salicylic acid with 1-naphthylamine and amino azo dyestuff thus produced is diazotised and coupled with 1-naphthol-4- or 5-sulphonic acid.



diamond black F

(*b*) ***Chromotrope 2B :*** It is obtained by coupling diazotised *p*-nitro-aniline with chromotropic acid (1, 8-dihydroxy-naphthalene-3,6-disulphonlc acid).

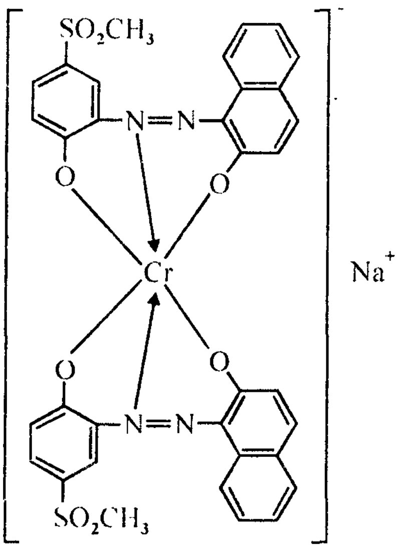


It is interesting to note that this dye is first applied to the fibre and then this dyed fibre is mordanted with boiling sodium dichromate in the presence of reducing agent (chromed). This method changes the colour completely. For example, chromotrope 2B dyes wool a bluish red but it gets changed into blue to black by 'after chroming.'

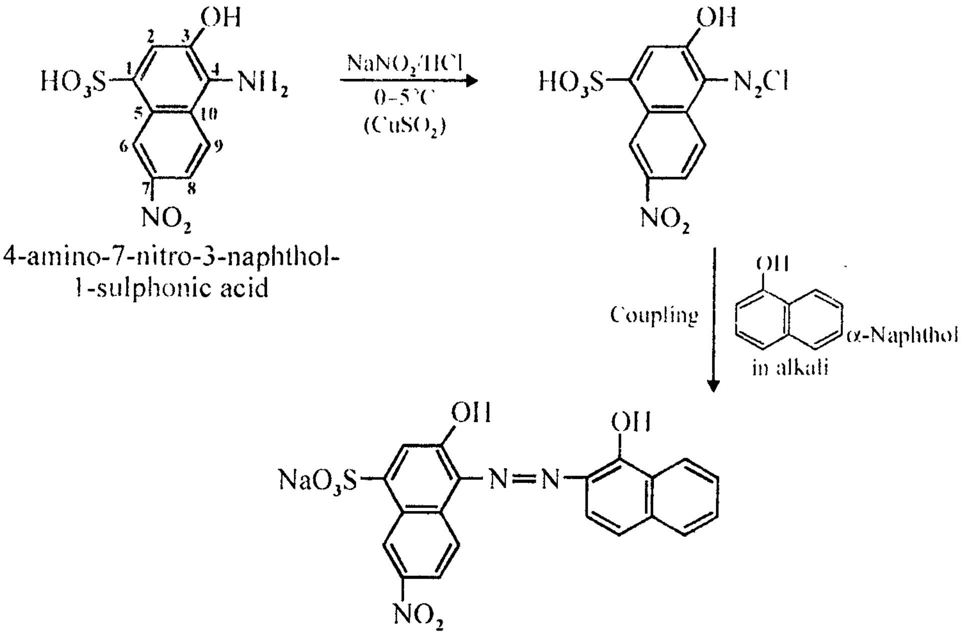
(*c*) ***Irgalans :*** It is a group of mordant azo dyes which are obtained by the coordination of two molecules of dye with the chromium atom (*i.e.*, these are 2 : 1 complexes). For example, irgalan brownviolet is 2 : 1 complex. Its structure is shown on next page.

The main advantage of this dye over the above two dyes is that this does not damage the fibre while the above dyes may do.

Irgalans dye wool in neutral solution. The colours produced by this group of dyes are fast to light and washing. It is possible to replace chromium metal by cobalt.



(*d*) ***Eriochrome Black T :*** It is used in large quantities on account of its high light and wet fastness. It is prepared by diazotising 4-amino-7-nitro-3-naphthol-1-sulphonic acid in the presence of a small quantity of copper sulphate followed by coupling the product with β-naphthol.

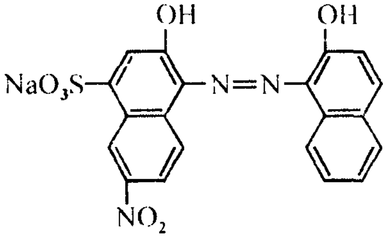


4-amino-7-nitro-3-naphthol-1-sulphonic acid

Eriochrome Black T

It is mainly used as an indicater in EDTA titrations.

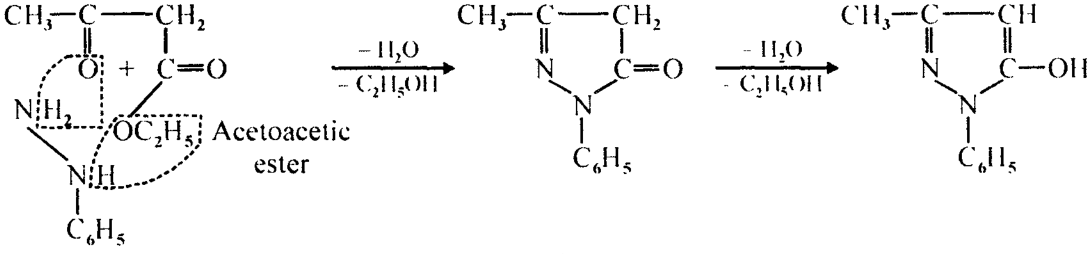
(*e*) ***Eriochrome Black A :*** It may be prepared in the similar manner as that of eriochrome black T except that coupling in this case is done with β-naphthol.



eriochrome black A

It is an azo chrome dyes. It is applied to wool by different methods.

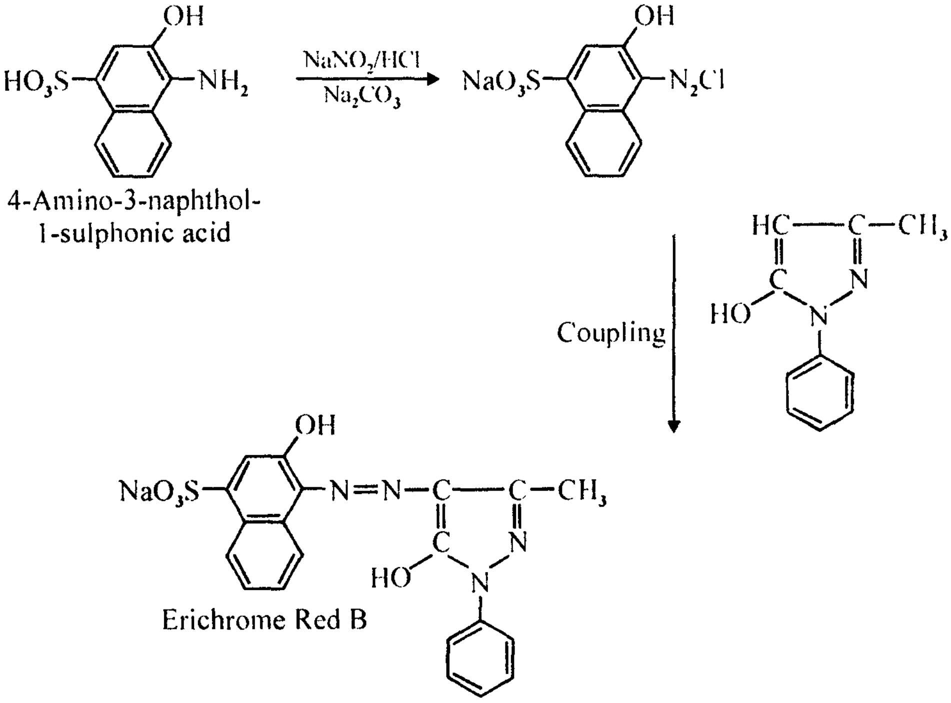
(*f*) ***Eriochrome Red B :*** It is a chrome azodye which is prepared by coupling 3-methyl-1-phenylpyrazolone (obtained by condensation of acetoacetic ester with phenylhydrazine) with diazotised 4-amino-3-naphthol-1-sulphonic acid.



Acetoacetic ester

Phenyl hydrazine

3-Methyl-1-phenyl-pyrazolone



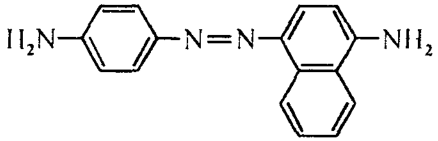
4-Amino-3-naphthol-1-sulphonic acid

Erichrome Red B

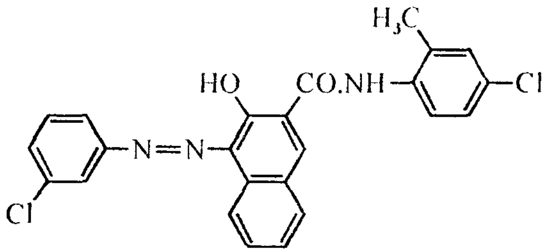
It is also a chrome dye. However, it is fast to light and washing.

6. Synthetic Fibre Dyes : Several dyes are known which are used to dye synthetic fibres such as rayon, terylene, nylon, polyacrylonitrile, etc. These may be **acidic, basic** or **disperse** dyes.

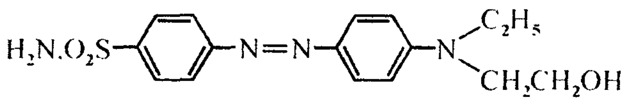
In disperse dyeing the first job is to convert the insoluble dye into a state of uniform fine dispersion by means of the dispersing agents in the dye bath. Then, the next job is to dip the synthetic fibre into this dye bath. Some of the main dyes used for dyeing synthetic fibres are as follows:



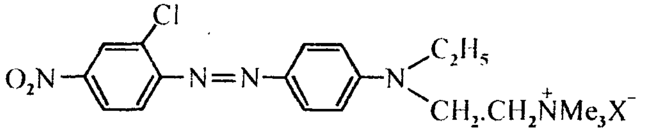
It dyes rayon orange, but black when used as ingrain dye with 3-hydroxy-2-naphthionic acid



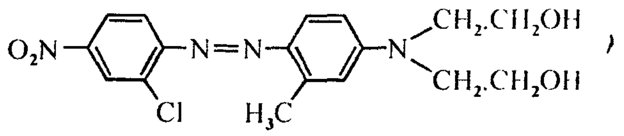
red disperse dye (used for terylene)



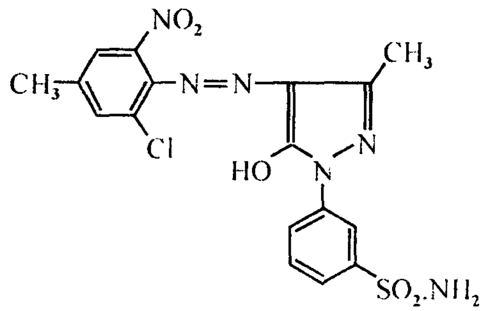
red disperse dye (used for nylon)



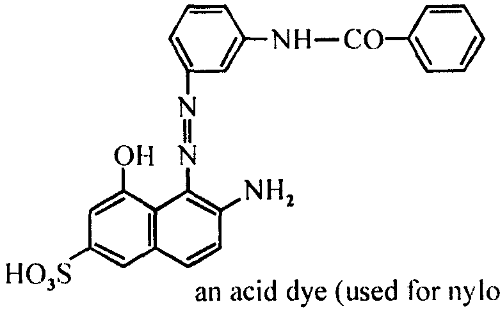
a cationic dye (astrazone red GTL) (used for polyacrylonitrile fibres)



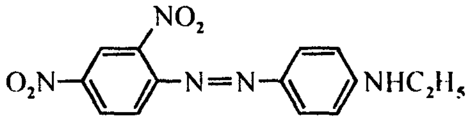
a cationic dye (astrazone red GTL) (used for polyacrylonitrile fibres)



yellow disperse dye (used for terylene)

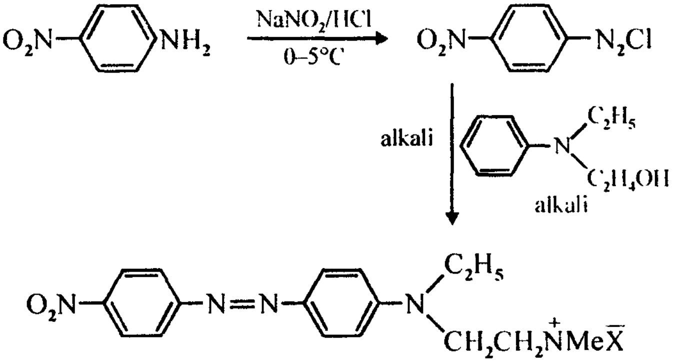


an acid dye (used for nylon)



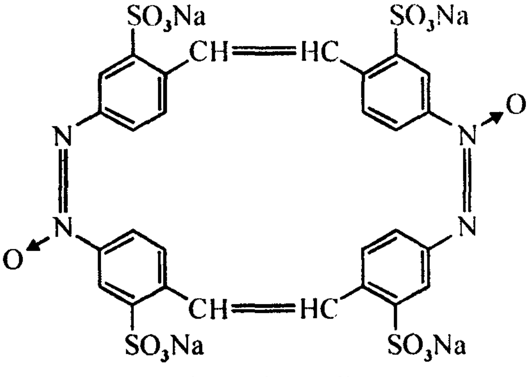
ionamine red KA (used for rayon)

Cellitone Scarlet B : It is a disperse azo dye which is prepared by coupling diazotised *p*-nitroaniline with N-ethyl–N (β-hydroxyethyl)-aniline in alkaline medium.



It is mainly used for dyeing cellulose acetate and nylon. The group 2-hydroxyethyl is responsible for introducing dispersiblity in the dye.

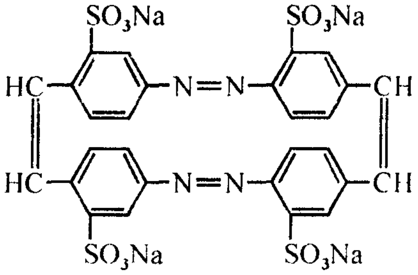
7. Stilbene-azo Dyes : These are yellow and orange direct azo dyes used for cellulosic fibres. Although these dyes have azo groups, they are not prepared by the processes of diazotication and coupling. Some examples of stilbene-azo-dyes are as follows :



Naphthamine Yellow

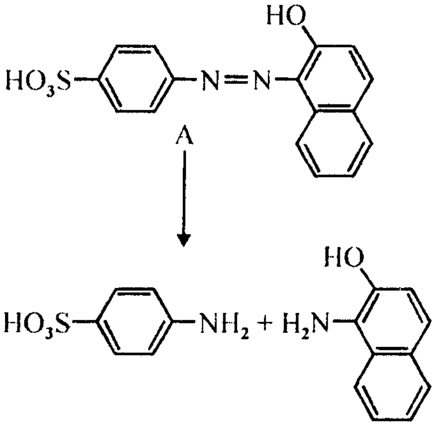
(*a*) ***Napthamine Yellow*** : It is prepared by heating 4-nitrotoluene-2-sulphonic acid with aqueous sodium hydroxide solution.

(*b*) ***Mikado Orange*** : It is prepared by heating 4-nitrotoluene 2-sulphonic acid with aqueous sodium hydroxide solution in the presence of a reducing agent such as glucose.



mikado orange

8. Determination of the Structure of an Azo Dye : In order to determine the structure of an azo dye, the usual method is to reduce the azo dye with sodium hydrosulphite to primary amines which are isolated and identified. For example, orange II when reduced yields a mixture of sulphanilic acid and 1-amino-2-naphthol. This clearly reveals that the structure of orange II is A.



sulphanilic acid 1-amino-2-naphthol

The reduction products of the azodye also indicate its possible synthesis.

9.4. Nomenclature Used in the Subclasses of Azo Dyes

In the following discussion of various subclasses of azo dyes, Lapworth's system is used to represent general structure of azo dyes. In this system we use the following notations :

(*i*) **A** : It represents an arylamine used as diazonium components, further such components used are denoted by A_1, A_2, etc. Examples of A are aniline, *o*-toluidine, etc.

(*ii*) **D** : It is an aryldiamine like benzidine having two diazotisable groups. Examples of D are benzidine, 4, 4′-diaminostilbene-2, 2′-disulphonic acid, etc.

(*iii*) **E** : It is the second component or coupling component. Examples of E are phenol, β-naphthol, dimethylaniline, etc.

(vi) **Z** : It is a coupling component having dual coupling positions. Examples of Z are H-acid, gamma acid, J-acid, etc.

(v) **T** : It is a coupling component having three coupling positions. Examples of T are resorcinal, meta-phenylene diamine, etc.

(vi) **M** : It is the middle component having one coupling position and one diazotisable amine which can further couple with a coupling component. Examples of M are 1-naphthylamine, J-acid, etc.

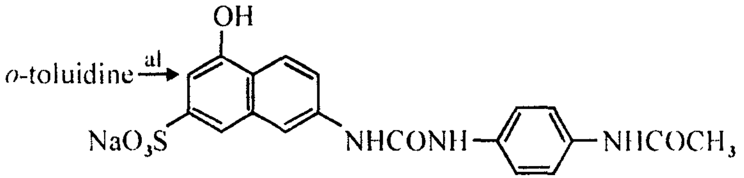
7.5. Subclasses of Azo Dyes

Azodyes can also be put into various subclasses such as monoazo, bisazo, trisazo, polyazo, mordant azo, stilbene azo and pyrazolone. We shall discuss these one by one.

Monoazo Dyes

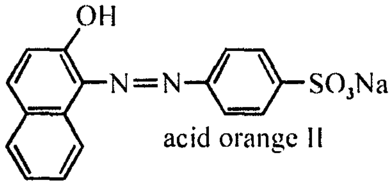
They are considered to be a large group of dyes belonging to many application classes and are of A → E type, coupling is done either in acidic or in alkaline pH.

Monoazo Direct Dyes : A few direct dyes from monoazo subclass have been commercially used. Only useful dyes of this type have been derived from J-acid derivatives as coupling component. An example is C.I. direct red 65 (C.I. No. 17870). (C.I. represents colour Index).

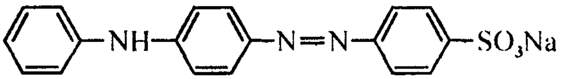


C.I. direct red 65

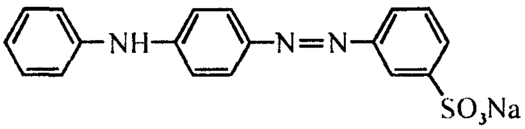
Monoazo Acid Dyes : Monoazo acid dyes having a variety of coupling components are known. Thus, naphthols, arylamino derivatives, pyrazolones, etc., having sufficient sulphonic acid or carboxylic acid groups get coupled with aryldiazonium salts derived from arylamino sulphonic acids. Acid orange II, acid orange IV and metanil yellow have been typical examples.



acid orange II



acid orange IV

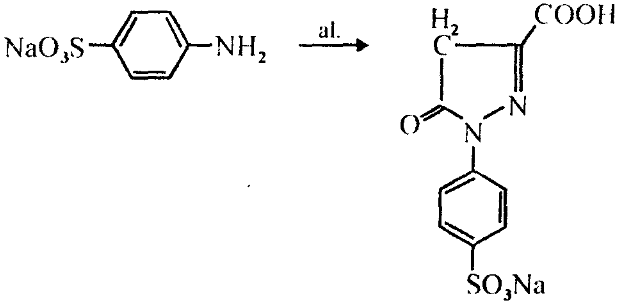


metanil yellow

Acid orange II is obtained by the reverse diazotisation of sulphanilic acid and slow addition of the resulting diazonium salt to alkaline solution of β-naphthol having caustic, soda ash and salt at 6–8°C. At the end of coupling, temperature is brouth to 15°C and pH 9.0 to 9.5. After strirring for a few hours, hydrochloric acid has to be added to bring pH slightly alkaline and the salted out dye is filtered and dried.

Acid orange IV and metanil yellow are obtained by the diazotisation of sulphanilic acid by the reverse method and of metanilic acid by direct method respectively and coupling with diphenylamine. As diphenylamine is very weakly basic and insoluble in water as well as dilute hydrochloric acid. the coupling is done with an emulsion of diphenylamine or in alcoholic solution or using pyridine. For example, in the preparation of metanil yellow metanilic acid is diazotised with sodium nitrite and hydrochloric acid solutions at 5°C and after the diazotisation gets completed the diazonium salt solution is made acidic and slowly added to the emulsion of diphenylamine obtained by intimately mixing a mixture of diphenylamine, water and small quantities of glue and dispersing agent. The coupling is slow and needs very long time to complete. After the coupling has been completed, salt solution is added and the mixture has been stirred at room temperature for few hours if the dye is precipitated out.

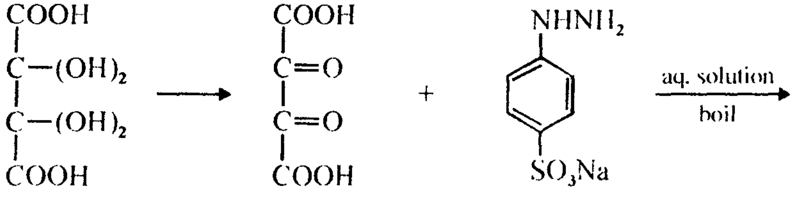
Monoazo Food Colours : Among the food colours which are permitted to use for addition to foodstuffs, tartrazine belonging to monoazo subclass has been important. It is obtained from sulphanilic acid as diazonium component and 1-(*p*-sulphophenyl)-pyrazol-(5)-one-3-carboxylic acid as the coupling component, the coupling takes place at the active methylene group in the four positions of the pyrazolone under alkaline conditions.



sulphanilc acid

1-(*p*-sulphophenyl) pyrazol-(5)-one 3-carboxylic acid

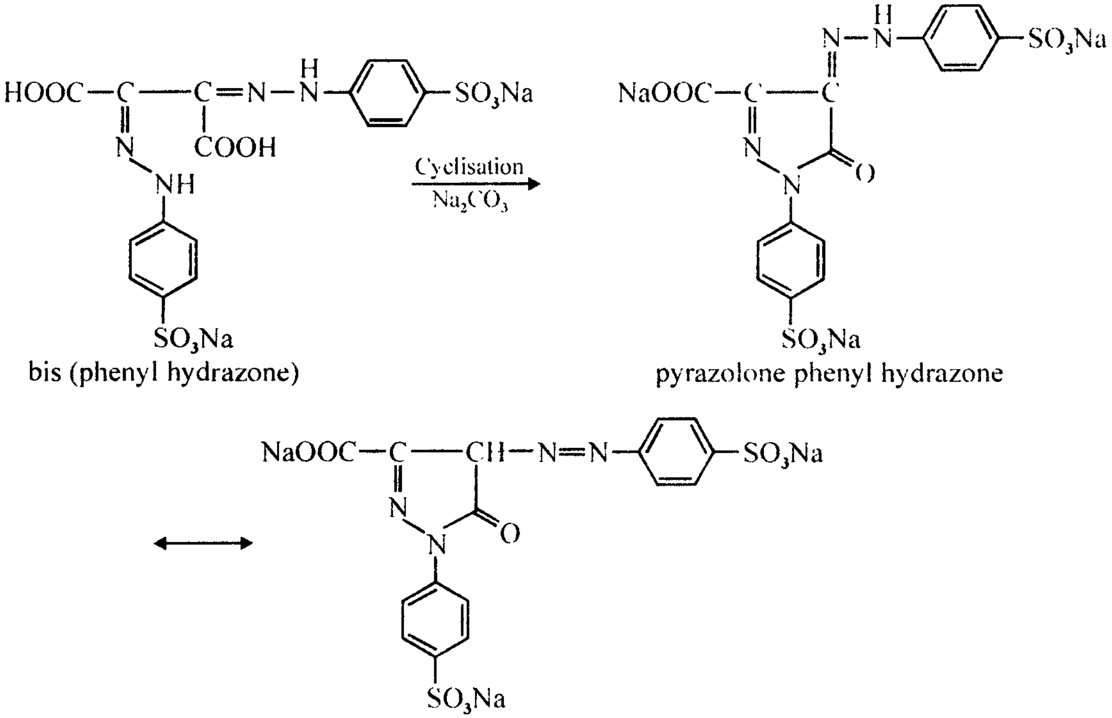
The method of preparation of the pyrazolone required for the synthesis of tartrazine is to condense phenyl hydrazine-para-sulphonic acid (2 moles) with dihydroxy tartaric acid (1 mole) in aqueous phase and boil the solution to get tartrazine. The dihydroxy tartaric acid reacts in the form of diketosuccinic acid which yields bis-(phenyl hydrazone) which cyclises and rearranges to the dye.



dihydroxy tartaric acid

diketo succinic acid (1 mole)

phenyl hydrazine-*p*-sulphonic acid (2 moles)

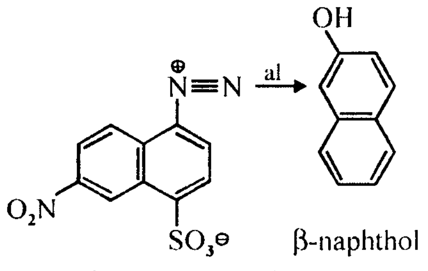


bis (phenyl hydrazone)

pyrazolone phenyl hydrazone

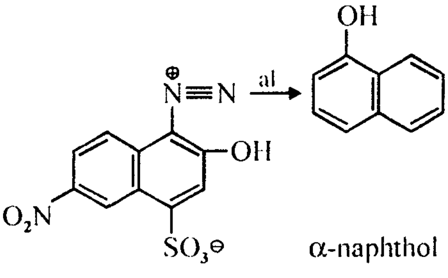
tartrazine

Monoazo Mordant Dyes : In the monoazo mordant dye series many important members of dyes are involved with various characteristic groupings mentioned under mordant dyes. Many examples could be given based on the azo salicylic acid and *o*, *o*′-dihydroxy azo groupings. Eriochrome black A, eriochrome black T and eriochrome red B have been the important members of dyes. Eriochrome black A and eriochrome black T have been obtained by the coupling of β-naphthol and α-naphthol respectively with 1-diazo-2-naphthol-6-nitro-4-sulphonic acid and eriochrome red B is prepared by the coupling of 1-phenyl-3-methyl-pyrazol-(5)-one with 1-diazo-2-naphthol-4-sulphonic acid.



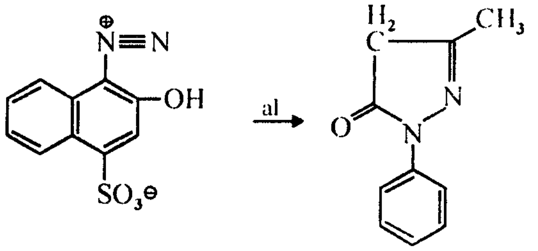
β-naphthol

1-diazo-2-naphthol 6-nitro-
4-sulphonic acid eriochrome black A



α-naphthol

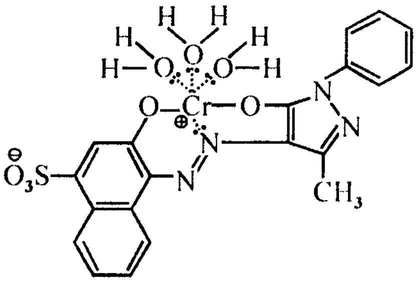
1-diazo-2-naphthol 6-nitro-
4-sulphonic acid eriochrome black T



1-diazo-2-naphthol-4-sulphonic acid eriochrome red B

1-phenyl-3-methyl-pyrazol-(5)-one

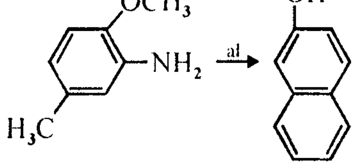
These dyes can be applied on cotton or wool in three ways, *viz.*, first the dye has been applied and then mordanted on cotton or wool, the dye and the mordant have been simultaneously applied on cotton or wool, the dye in the form of metal complex has been applied on cotton or wool. In any case, the metal complex obtained on the cotton or wool has better fastness properties than the dye itself. The chromium or copper complexes have the covalent and co-ordinate bonds. The structure of chromium complex of eriochrome red B called neolan red B is as an example.



neolan red B

Neolan red B is obtained as a red crystalline complex by the treatment of eriochrome red B with chromium chloride in alcohol. Eriochrome black A dyes wool dark red-brown as an acid dye, which is after chromed to a deep fast black, having excellent fastness to light. Eriochrome black T is prepared as described earlier, where the coupling on α-napthol occurs in 2-position instead of normal 4-position, dyes wool a reddish-black as an acid dye, which on after chroming provides a very fast bluish-black shade. The chromium and copper complexes in general can be prepared in two ways; one is to make the complex after the dye is obtained, as in the case of neolan red B and the second is to get the dye and the chromium complex together during coupling. Chromium complexes, have been invariably used for wool dyes and copper complexes have been invariably used for cotton dyes.

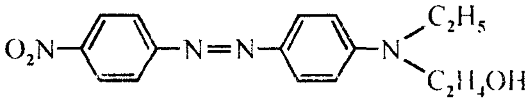
Monoazo Solvent Dyes : A few mono azo dyes find use as solvent dyes and they do not have any solubilising groups. One example of such series of dyes is the dye, sudan red R obtained by the diazotisation of cresidine (2-amino-1-methoxy-4-methyl benzene) and coupling with A-naphthol.



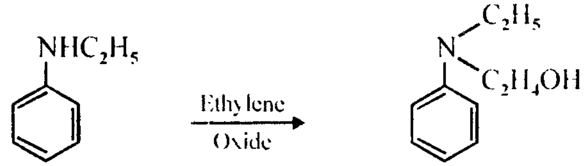
cresidine

β-naphthol

Monoazo Disperse Dyes : Various disperse dyes imparting yellow to blue shades on polyester and other hydrophobic fibres have been reported. An example of monoazo disperse dyes is celliton scarlet B which is prepared by acidic coupling of N-ethyl-N-(β-hydroxy ethyl) aniline with diazonium salt derived from para nitro aniline.



Celliton scarlet B



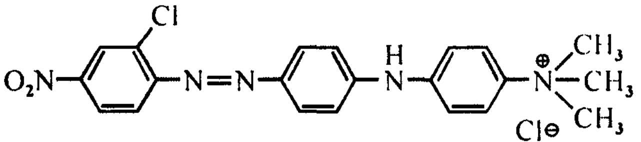
mono ethyl aniline
(1)

N-ethyl-N
(β-hydroxy ethyl) aniline
(2)

The intermediate (2) is obtained by condensing 1 mole of ethylene oxide with monoethyl aniline (1). Many other open chain alkylated anilines and cyclic tetrahydro quinolines find use by varying the diazonium component to get variety of shades in monoazo disperse dyes. Bis-(N-β-cyano ethyl) aniline and bis-(N-β-hydroxy ethyl) aniline are some examples of open chain alkylated anilines, whereas tetrahydro quinoline and tetrahydro benzoquinoline are considered to be the examples of cyclic alkylated anilines. As these dyes have small molecular size and groups which help in the formation of stable dispersions, they form an important group of disperse dyes.

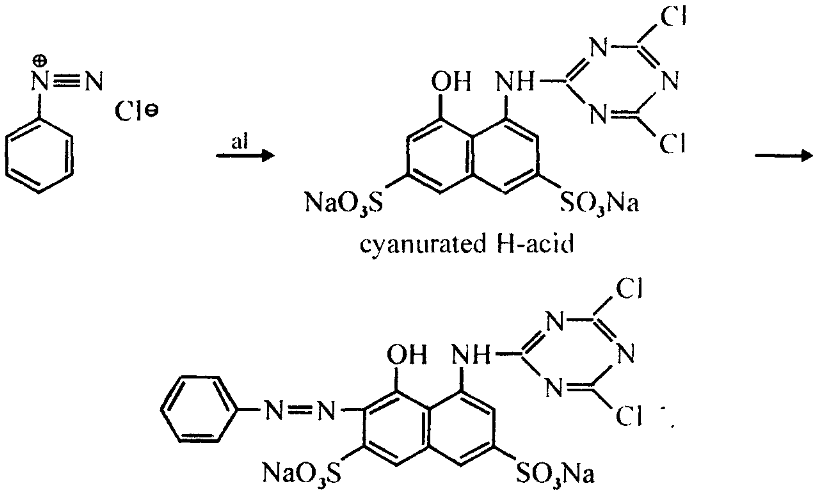
A small group of reactive disperse dyes used for polyamide (nylon) fibre have also been important.

Monoazo Cationic Dyes : They have been useful dyes for polyacrylonitrile fibre and have a positive charge by the virtue of the presence of a tertiary amino group. A scarlet dye prepared by the diazotisation of 2-chloro-4-nitro aniline and coupling under acidic conditions with 4-N, N-dimethyl amino diphenylamine, followed by the quarternisation with methyl chloride, has been a typical example.



a scarlet cationic dye

Monoazo Reactive Dyes : They are constituting a good number of members of reactive dyes. An example of monoazo reactive dye having dichlorotriazine ring as reactive system is already described under the discussion on chemical bonding between the reactive dyes and cotton. Reactive red B is synthesised by condensing H-acid with cyanuric chloride and coupling the cyanurated H-acid thus formed under mild alkaline conditions with phenyl diazonium salt.



cyanurated H-acid

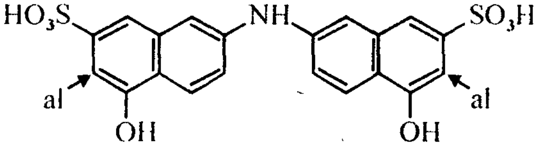
reactive Red B

Disazo or Bisazo Dyes

Many azo dyes belong to this group. Their methods of preparation are represented by the symbols used earlier. The coupling involved may be acidic or alkaline depending upon the individual components used.

1. $A \rightarrow Z \leftarrow A_1$
2. $D \begin{smallmatrix} \nearrow E \\ \searrow E_1 \end{smallmatrix}$
3. $A \rightarrow M \rightarrow E$
4. $A \rightarrow Z - L - Z \leftarrow A_1$

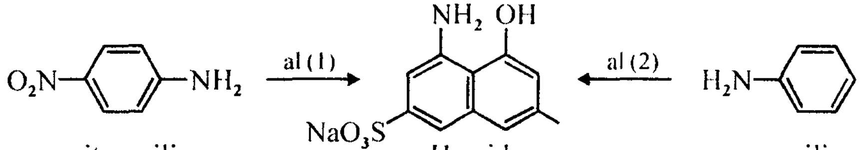
All the notations have been described in the general discussion of azo dyes. Z–L–Z represents a coupling component having dual coupling positions with linkages L like amino (–NH–) or urea (–NH–CO–NH) or other complex linkages, examples being di-J-acid and J-acid urea.



di-J-acid

Diazo Dyes of the Type : $A \rightarrow Z \leftarrow A_1$

Various coupling components (Z) such as resorcinol, metaphenylene diamine, H-acid, etc., are used for the manufacture of such dyes. One representative example of the dye of this type is naphthol blue black wherein A is para nitro-aniline, A_1 is aniline and Z is H-acid.



p-nitroaniline H-acid aniline

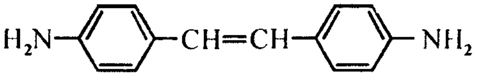
naphthol blue black

Disazo Dyes of Type : $D\begin{smallmatrix}\nearrow E\\ \searrow E_1\end{smallmatrix}$

Many diazonium components having two amino groups (D) are used. In such cases the process of getting doubly diazonium groups is known as tetrazotisation. Various aryldiamines (D) find use in this type of disazo dyes, examples being meta phenylene diamine, benzidine, *o*-toluidine and *o*-dianisidine. Due to the carcinogenic property of benzidine and its derivatives, etc., in the recent years, attempts have been made to replace them by safer diamines. 4, 4′-Diamino diphenyl urea having urea (NH–CO–NH) linkage and many other new diamines including those having heterocyclic ring linkages between two phenyl rings may be used for the preparation of this type of dyes.

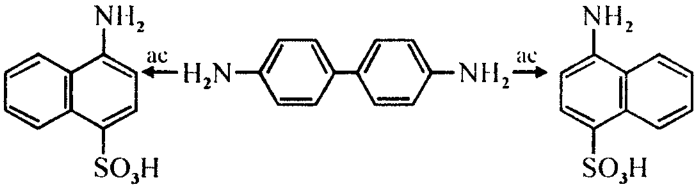
4, 4′-diamino diphenyl urea

4, 4′-Diamino stilbene derivatives also find use for the purpose and they are described under stilbene azo dyes.



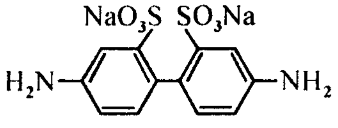
4, 4′-diamino stilbene

An example of this type of disazo dyes is congo red which in spite of its low fastness properties has been still to be one of the largest selling dyestuffs. The dye has been found to be sensitive to acids and turns blue-violet with acetic acid and blue with mineral acids. Congo red paper finds use for testing of acidity. Cango red, a direct dye, is formed by the tetrazotisation of benzidine and coupling with two moles of naphthionic acid under mild acidic conditions.



naphthionic acid benzidiae naphthionic acid

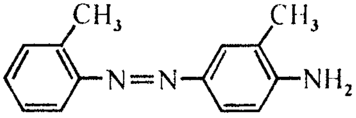
Acid, reactive and mordant dyes belonging to this type of disazo dyes have been derived from benzidine-2, 2′-disulphonic acid or 4, 4′-diamino stilbene-2, 2′-disulphonic acid, etc., with suitable coupling components.



benzidine-2, 2′-disulphonic acid

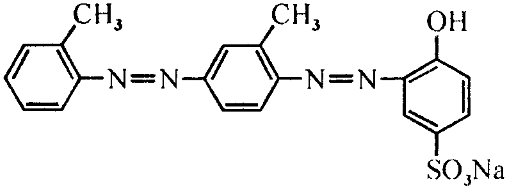
Disazo Dyes of the Type : A → M → E

In this case, the middle component M, has been an arylamino group which is capable of diazotisation and coupling with suitable end components E. M may be of two types. In the first type an arylamine used as M couples with diazonium salt of A, yielding a para amino azo benzene type of dye like fast garnet GBC which can further be diazotised and coupled with E. Examples of such M, middle components have been substituted anilines, like *o*-anisidine, *o*-toluidine *o*-toluidine *o*-chloroaniline and aniline etc., and 1-naphthylamine etc., all being capable of coupling in 4-positions and then undergo diazotisation. The second type of M possesses one phenolic grouping as coupling component by the virtue of this grouping, it undergoes coupling with A and an amino group which after the first coupling can get diazotised. Examples of such M, middle components have been J acid, gamma acid etc. One more type is also commonly involved and in this A → M this scheme is already completed as in the case of para aminoazo benzene, fast garnet GBC, etc., available as intermediates.



fast garnet GBC

An example of this type of dyes is the diazotisation of garnet GBC and coupling with NW acid, the dye is known as cloth red B.

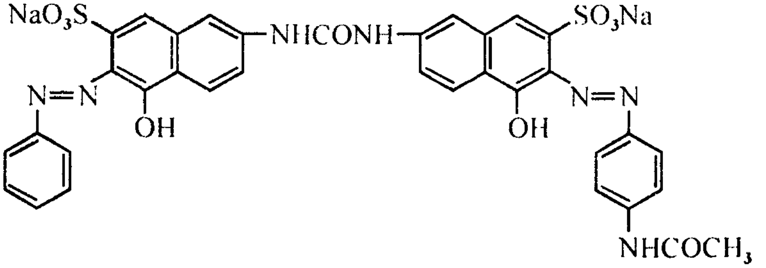


cloth red B

Disazo Dyes of the Type : $A \rightarrow Z - L - Z \leftarrow A_1$

Almost all members of this type of dyes belong to direct dyes class. L, the linking bridge can be made by using a condensing agent like phosgene ($COCl_2$) and cyanuric chloride.

An example of this type of disazo dye has been chlorazol scarlet 4 BS, where, A is aniline, Z–L–Z is J-acid-urea, and A_1 is *p*-amino acetanilide.



chlorazol scarlet 4 BS

In general, many direct dyes, acid dyes, food colours, mordant dyes, solvent dyes, disperse dyes, cationic dyes and reactive dyes belong to disazo dyes depending upon the specific structural requirements. However, for the sake of simplicity these classes by applications have not been described individually.

Trisazo Dyes

These dyes include a less number of commercially important members as compared to monoazo and disazo dyes, Among the various types of trisazo dyes which can be formed by combinations and permutations of diazonium components and coupling components, three types are important. They are as follows :

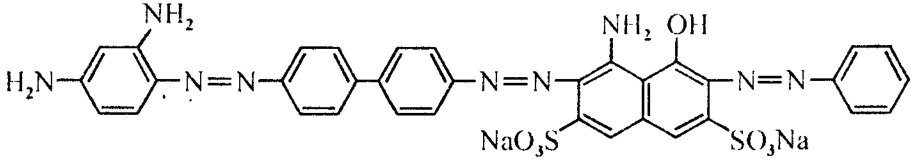
1. E ← D → Z ← A
2. $E \leftarrow D \rightarrow M \rightarrow E_1$
3. $A \rightarrow M \rightarrow M_1 \rightarrow E$

One example from each type is given as follows :

1. Trisazo Dyes of the Type : E ← D → Z ← A

A number of brown and black dyes are prepared by following this scheme. An important example has been direct black EW which is prepared by first acidic coupling of H-acid with benzidine, tetrazo, second alkaline coupling of the monoazo dye on H-acid part with phenyl diazonium salt and lastly, the third acidic coupling of the bis azo diazonium compound thus obtained to metaphenylene-diamine as shown in the following scheme :

$$[\text{Metaphenylene diamine}] \xleftarrow[\text{ac (3)}]{} [\text{Benzidine}] \xrightarrow[\text{ac (1)}]{} [\text{H-acid}] \xleftarrow[\text{ac (2)}]{} [\text{Aniline}]$$

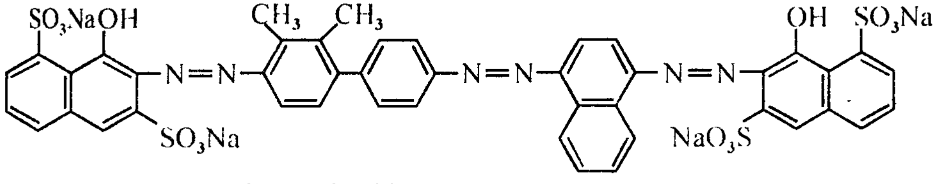


direct black EW

2. Trisazo Dyes of the Type : $E \leftarrow D \rightarrow M \rightarrow E_1$

A number of brown, blue, olive and black dyes are prepared by following the above scheme. An example of trisazo dyes of this type is benzo fast blue R which is prepared by first acidic coupling of 1-naphthylamine with *o*-toluidine tetrazo followed by the second simultaneous alkaline coupling of the terazotised monoazo dye to two moles of epsilon acid.

$$[\text{Epsilon acid}] \xleftarrow[\text{al (2)}]{} [o\text{-Toluidine}] \xrightarrow[\text{ac (1)}]{} [\text{1-Naphthyl amine}] \xrightarrow[\text{al (2)}]{} [\text{Epsilon acid}]$$

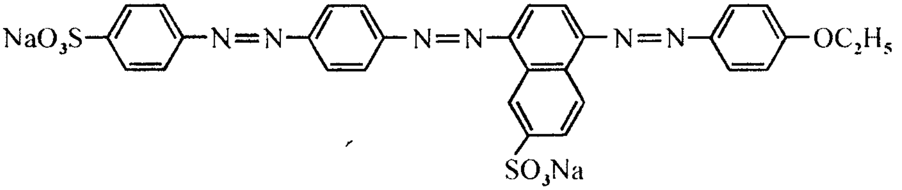


benzo fast blue R

3. Trisazo Dyes of the Type : A → M → M_1 → E

This type includes a good number of blue, green, brown and grey direct dyes having good fastness to light. An example is sirius supra brown RL which is obtained as shown below and then ethylating phenolic group.

$$[\text{Sulphanilic acid}] \xrightarrow[\text{ac (2)}]{} [\text{Aniline}] \xrightarrow[\text{ac (2)}]{} [\text{6-Cleve acid}] \xrightarrow[\text{al (3)}]{} [\text{Phenol}]$$



sirius supra brown RL

This and other dyes of this type have been bright, fast and give level dyeings on cotton. Only one difficulty in their preparation is that after the first and second acidic couplings, the disazo amino compound obtained is diazotised which sometimes yields a very weak diazonium salt and can couple with suitable coupling components with great difficulty. It is the usual practice to replace the usual alkaline bath for coupling by using pyridine-ammoniacal medium.

Trisazo dyes mainly comprise of direct dyes in application, a few dyes have also been suitable for dyeing of leather.

Polyazo Dyes

These dyes have four or more azo groupings in the dye molecule. Except only a few tetrakisazo dyes (having four azo groupings) they have been less important. These dyes belong to mainly direct dyes and leather dyes with red, brown and black shades.

Tetrakisazo dyes and polyazo dyes can be prepared by various combinations and permutations of the diazo components and coupling components. An example of a tetrakisazo dye is chrome leather black A which is useful for leather and is obtained by following the scheme.

$$A \rightarrow Z \leftarrow D \rightarrow Z_1 \leftarrow A_1$$

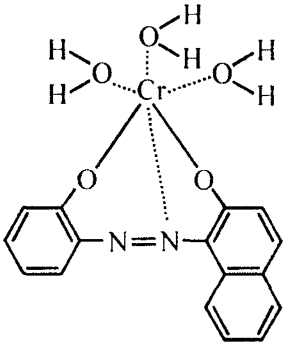
where, A and A_1 have been *p*-aminoacetanilide, Z has been H-acid, Z_1 has been *m*-phenylenediamine and D has been benzidine.

$$[p - \text{Amino acetanilide}] \xrightarrow{\text{al(3)}} [\text{H Acid}] \xleftarrow{\text{ac(1)}} [\text{Benzidine}] \xrightarrow{\text{ac(2)}}$$
$$[\text{Metaphenylene diamine}] \xrightarrow{\text{ac(4)}} [p - \text{Amino acetanilide}]$$

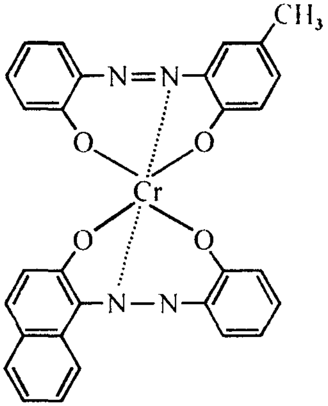
Mordant Azo Dyes

This class of dyes fall in groups such as 1, 1-metal-azo complexes, 1, 2-metal-azo complexes, etc.

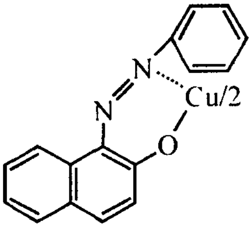
1, 1-Metal-azo complexes are those in which each metal atom forms covalent bonds with dihydroxy group or similar groups present in *O*, *O′*-positions to the azo group and forms a co-ordinate bond with the azo group of the dye. The representative structure is as follows :



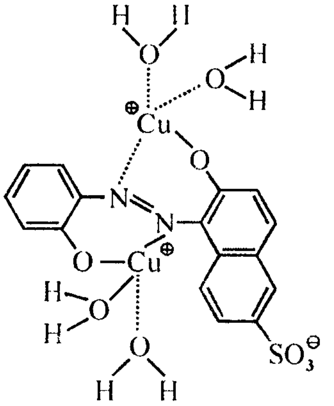
1, 2-Metal-azo complexes are obtained when 1, 1-metal azo complex undergoes combination with another molecule of the same or the other suitable dye to yield a complex in which the same metal atom forms covalent linkages with the four oxygen atoms of *o*, *o*-dihydroxygroups involved and forms co-ordinate linkages with the two azo groups of the two azo dye molecules. The representative structure is as follows :

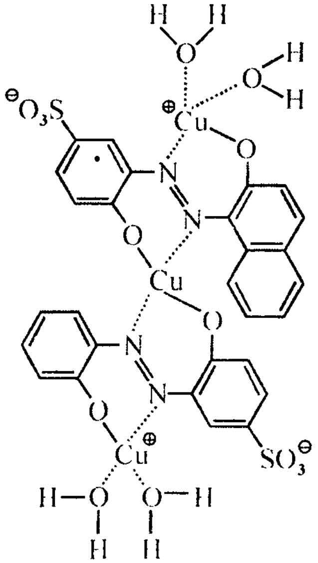


The metals like iron, manganese and zinc behave in the same manner while forming complexes. It becomes necessary to have *o*, *o′*-dihydroxy or similar two groups in *o*- and *o′*-positions to hold these metals. However, in the cases of copper, nickel and cobalt metals, they constitute stable complexes even with a single hydroxy or similar group present in the ortho position to azo group as represented in the following structure.

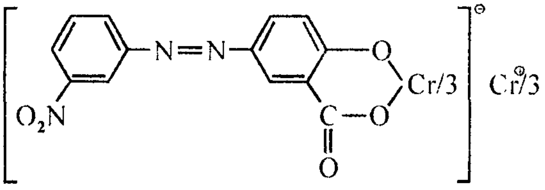


In copper-azo complexes, complexes having 3 copper atoms per axo group as well as 3 copper atoms per 2 azc groups are known. The structures given below illustrate these types of metal-dye complexes.



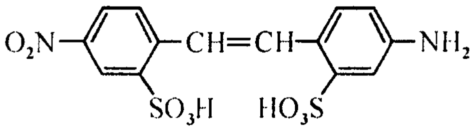


The azo dyes obtained from salicylic acid and similar intermediates are capable of forming metal-dye complexes by the virtue of the adjacent carboxylic acid and hydroxy groups, without involving the azo group in the complex formation as given below.



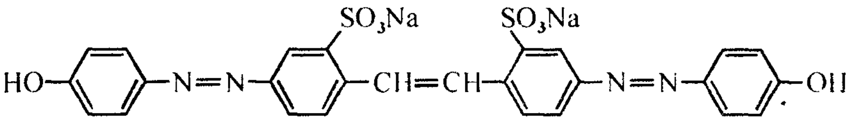
Stilbene Azo Dyes

Stilbene azo dyes having one or more azo groups are yellow to orange dyes having good fastness and substantivity for cotton. Most of the dyes of this class are derived from 4, 4′-diamino stilbene-2, 2′-disulphonic acid and the rest are derived from 4, 4′-dinitro and 4-amino-4′-nitro stilbene-2, 2′-disulphonic acids.



4-amino-4′-nitro stilbene-2 2′-disulphonic acid

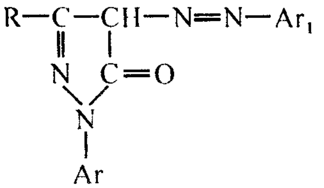
An important member of this class of azo dyes is chrysophenine G which is largely used as a direct cotton dye and has good fastness to light. Chrysophenine G is prepared by the tetrazotisation of 4, 4′-diamino stilbene-2, 2′-disulphonic acid coupling with two moles of phenol and subsequent ethylation of the product, brilliant yellow. The dye, brilliant yellow, however is only used as an indicator because of its sensitivity to alkali.



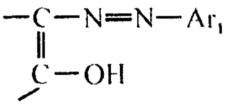
brilliant yellow

Although 4, 4′-diamino stilbene-2, 2′-disulphonic acid yields only symmetrical dyes by following tetrazotisation and coupling, 4-amino-4′-nitrostilbene-2, 2′-disulphonic acid yields unsymmetrical stilbene azo dyes by following diazotisation, coupling, reduction of nitro group with glucose, subsequent diazotisation of amino group thus formed and coupling with another suitable coupling component.

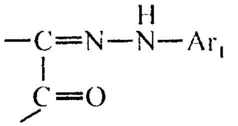
Pyrazolone Azo Dyes : The pyrazolone azo dyes possess the following general structure.



General structure of pyrazolone azo dyes.
R is alkyl, carboxylic acid group, Ar, Ar_1 are aryl groups.



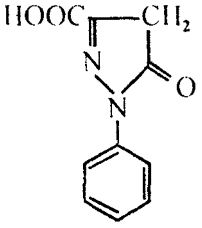
azo enol form



ketone hydrazone form

There are evidences which show that the pyrazolone azo dyes are also found in the corresponding azo enol form as well as ketone hydrazone form.

The key intermediates needed for the production of pyrazolone azo dyes have been 1-phenyl - 3-methyl-pyrazol-(5)-one, 1-phenyl-pyrazol-(5)-one-3-carboxylic acid and their derivatives, substituted in the phenyl ring such as 1-(*p*-sulphophenyl)-pyrazol-(5)-one-3-carboxylic acid which is a para-sulpho derivative of 1-phenyl-pyrazol-(5)-one-3-carboxylic acid.



1-phenyl-pyrazol-(5)-one-3-carboxylic acid

The pyrazolone azo dyes have been found to be important for yellow to red shades. They are used as direct dyes, acid dyes, metal complex dyes or pigments. Tartrazine finds use as a food colour. Two methods of preparation of tartrazine have been found in monoazo dyes derivatives. Eriochrome red B, a pyrazolone azo dye obtained from 1-phenyl 3-methyl-pyrazol-(5)-one has been already discussed under monoazo mordant dyes, the corresponding metal (chromium) complex is neolan red B. Most of the pyrazolone azo dyes are monoazo, though a good number of members belong to bisazo dyes.

10
CHAPTER

AZOIC DYES
(Ingrain Azo Dyes)

10.1. Introduction

Azoic Dyes are water insoluble azo colours which are formed on cellulose fibres from selected diazo and coupling components. These are prepared on the cellulose or cotton fibres in two districat stages :

(*i*) The fibre is treated with an alkaline solution of a coupling component.

(*ii*) This is then developed with a diazonium salt.

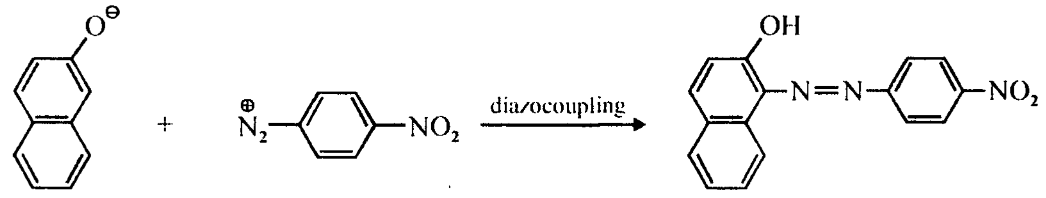
2-Naphthol was originally used as the coupling component. Later on it was replaced by anilides of 2-hydroxy-3-naphthoic acid (BON-acid). These new compounds had much greater substantivity to cotton and gave a range of bright shades. At present about 30 such coupling components and 50 different diazo components are marketed.

Azoic dyes give bright yellow, scarlet red, maroon and chocolate shades of excellent fastness. These dyes are very popular due to their cheapness and bright shades.

10.2. Some Examples of Azoic Dyes

We will now discuss the synthesis of some coupling and diazo components in azoic dyes.

1. **Para Red or Nitroaniline Red :** It is prepared by padding (dipping) the fibre with an alkaline solution of β-naphthol containing Turky red oil and then dipping in a solution of the diazotised primary aromatic amine.

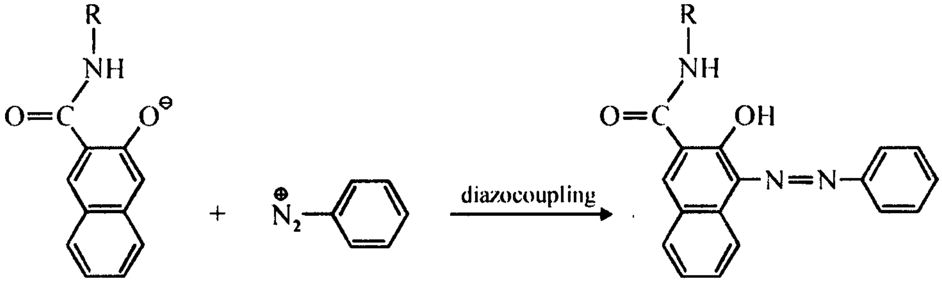


alkaline β-naphthol solution

p-nitrobenzenediazonium salt solution

Para Red or (nitroaniline red)

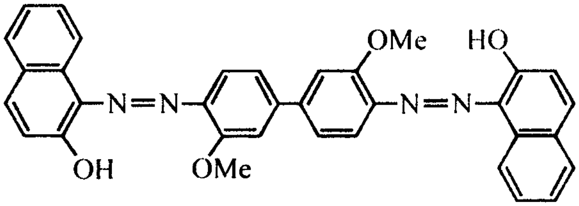
2. **Naphthol AS (R = Ph) :** Para red (nitraniline red) is an important azoic dye which has least affinity for the fibre. Hence a carbonamido group is introduced at 3-position in β-naphthol, *e.g.*, Naphthol AS (R = Ph).



Naphthol AS
(R = Ph)

Some other examples of azoic dyes are described as follows :

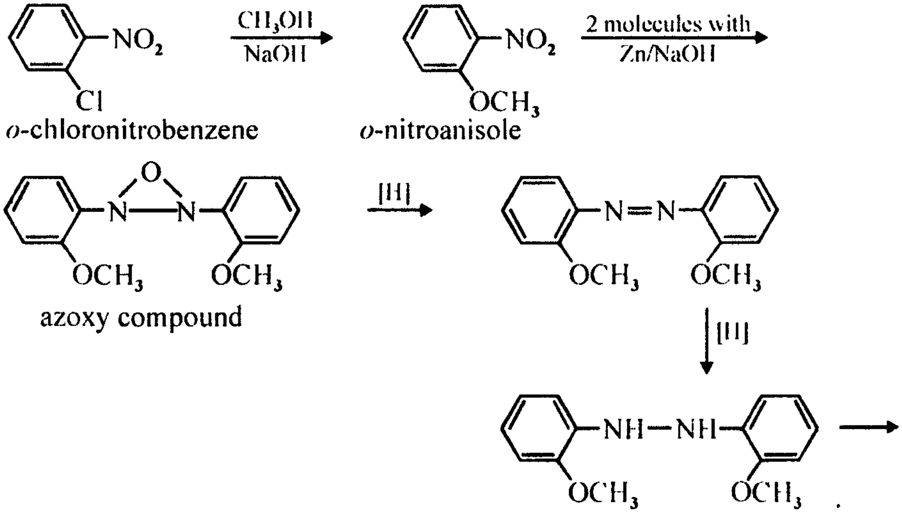
By changing the diazotised molecule and also R, the colour of the azoic dye can be varied, *e.g.*, 'nitroaniline orange' (β-naphthol with *m*-nitro benzene-diazonium), 'permanent red 2R' (β-naphthol with 2, 4-dinitrobenzene diazonium) and 'dianisine blue' (β-naphthol with bisdiazotised or tetrazotised dianisidine).



dianisine Blue

'Aniline black' is regarded as a special case of ingrain dyes, because the dye is produced within the fibre, either by oxidising the fibre padded with the aniline salt or by heating the fibre in a solution of aniline salt and oxidising agent, like potassium chlorate.

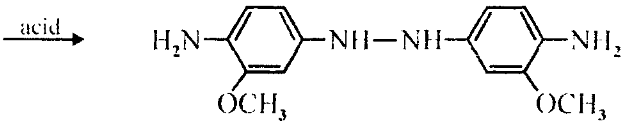
3. **Fast Blue B-base :** It is prepared by reducing *o*-nitro anisole with zinc dust and sodium hydroxide in water or in ethyl alcohol. The *o*-nitroanisole for this reaction is prepared by treating *o*-chloronitrobenzene with methanol at 70-95°C under pressure in the presence of sodium hydroxide.



o-chloronitrobenzene

o-nitroanisole

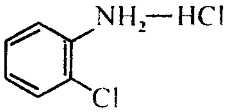
azoxy compound



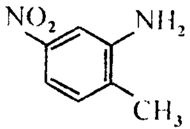
fast blue B
(3, 3′ dimethoxy benzidine)

It is an azoic diazo component. It can be diazotised and coupled with a phenol like naphthol AS to yield azoic dye on the fibre. However, it is mainly used to produce blue colour of moderate fastness on cellulose fibres.

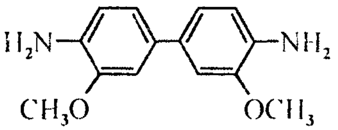
Other azoic diazo components are as follows :



fast yellow GC base



fast scarlet G base



fast blue B base

11
CHAPTER

DIPHENYLMETHANE DYES

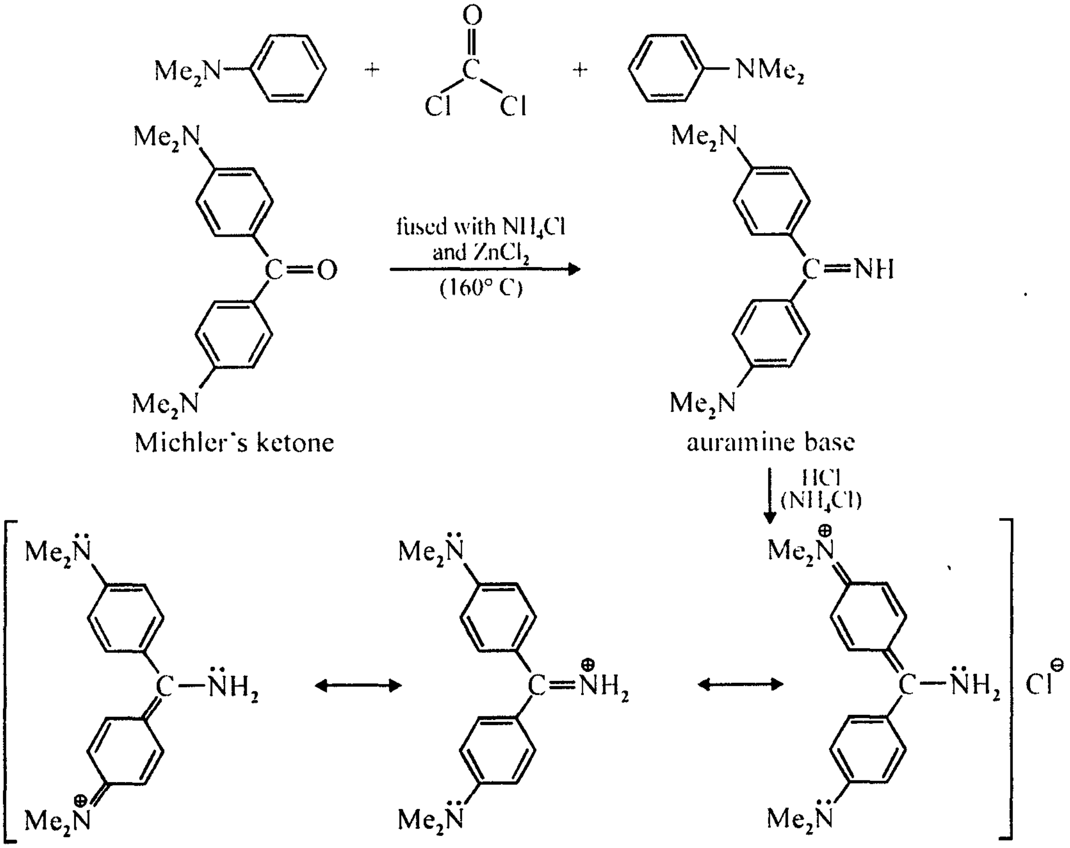
11.1. Introduction

The diphenyl methane dyes are characterised by the presences of a diphenylmethane nucleus. Only few dyes belonging to this class are commercially important.

11.2. Some Examples of Diphenylmethane Dyes

Some examples of these dyes are described as follows :

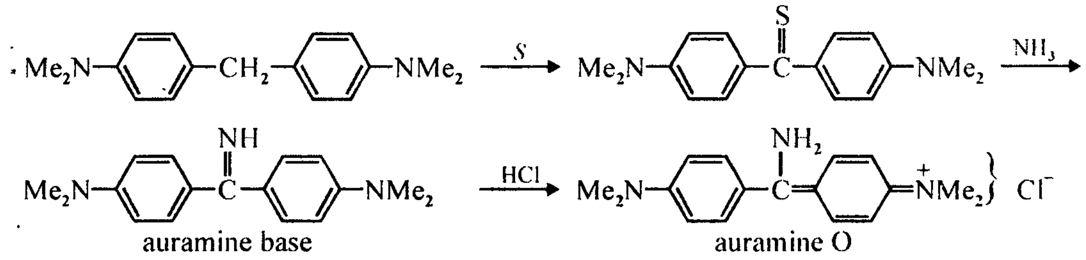
1. Auramine O : Kern and Karo prepared this dye by heating michler's ketone with ammonium chloride and zinc chloride at 150–160°C. The auramine base so obtained on treatment with HCl is converted into auramine O. The michler's ketone required for this synthesis is prepared by condensing N-dimethylaniline with phosgene.



Auramine O

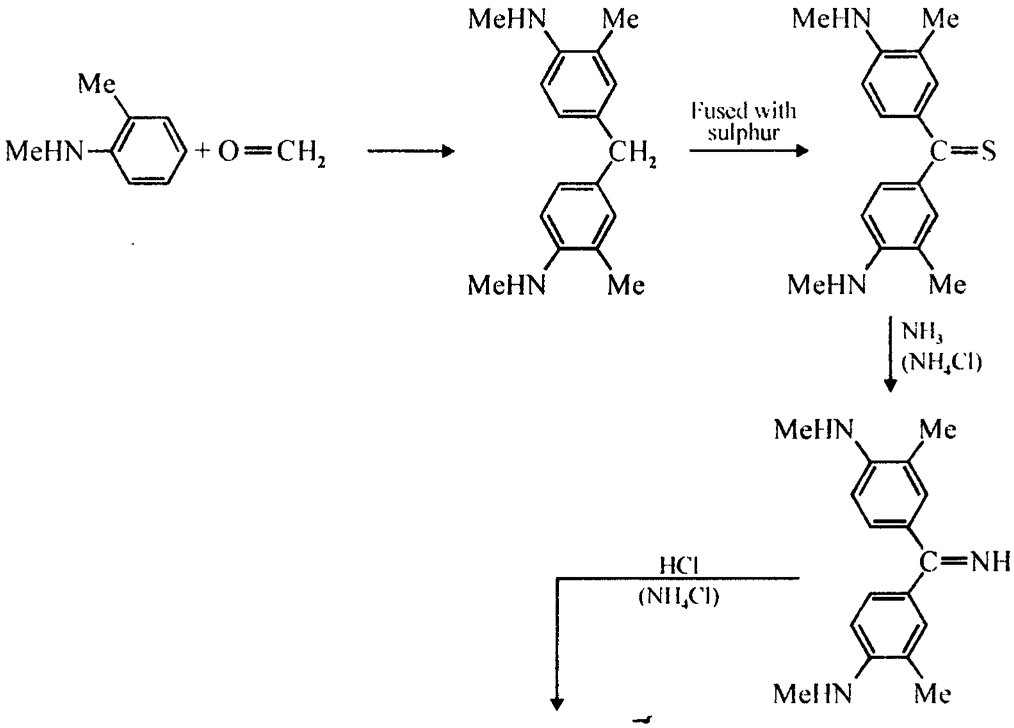
(11.1)

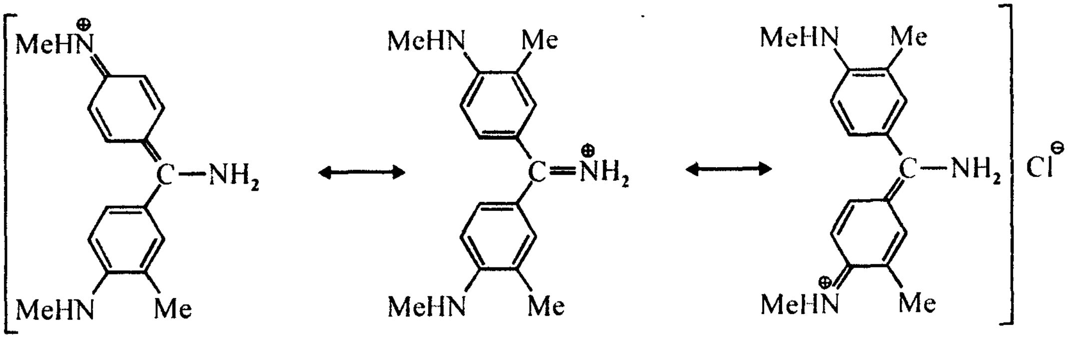
Now-a-days, it is prepared by heating 4, 4′-bis (dimethylamino-phenyl) methane with sulphur, ammonium chloride and large excess of sodium chloride in an atmosphere of ammonia at 175°C. The auramine base so produced is treated with hydrochloric acid to get auramine O. The sodium chloride is purely as a diluent.



It is marketed in the form hydrochloride. It is a cheap, brilliant yellow and extensively used dye for dyeing of paper, silk, leather and Jute. The yellow colour produced by it is not fast to light and is destroyed by boiling with water, and on treatment with hot acids and alkalis. However, it is still employed due to its cheaper cost than the other dyes of comparable colour.

2. Auramine G : It is a greenish yellow dye. It is prepared on the same lines as auramine O, but the starting material is *p, p′*-bis- (N- methylamino)-*m, m′*-dimethyl disphenylmethane, which is obtained by condensing N-methyl-*o*-toluidine with formaldehyde.





Auramine G

12
CHAPTER

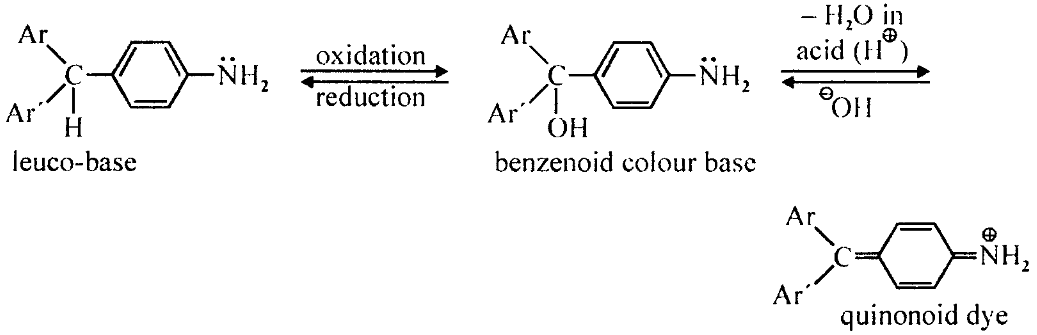
TRIPHENYLMETHANE DYES

12.1. Introduction

This group of dyes is one of the oldest known synthetic dyestuff groups, They are of brilliant colour due to resonance and cover a ranges of shades from red to blue, including violet and green. However, the colour fades rapidly in light and due to this reason they find less uses in textiles but are used for colouring papers, type writer ribbons and other articles where fastness to light is not of much significance.

These dyes have the quinonoid group as their chromophores. These dyes are obtained by the introduction of NH_2, NR_2 or OH groups into the para positions of the benzene ring of triphenyl methane. The compounds so obtained are colourless and are called *leuco-compounds*. These on oxidation are converted into the corresponding tertiary alcohols called *colour bases* which on treatment with acid are changed from the colourless benzenoid forms to the quinonoid dyes due to salt formation. The coloured salts on treatment with alkali are converted into the leuco-bases.

$$\underset{\text{(colourless)}}{\text{Leuco-base}} \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} \underset{\text{(colourless)}}{\overset{\text{colour-base}}{\boxed{\text{benzenoid}}}} \underset{\text{base}}{\overset{\text{acid}}{\rightleftharpoons}} \underset{\text{(coloured)}}{\overset{\text{dye}}{\boxed{\text{quinonoid}}}}$$



Some structures of this class of dyes involve an aryl group than phenyl and, therefore, in general this class can be called *triarylmethane dyes.*

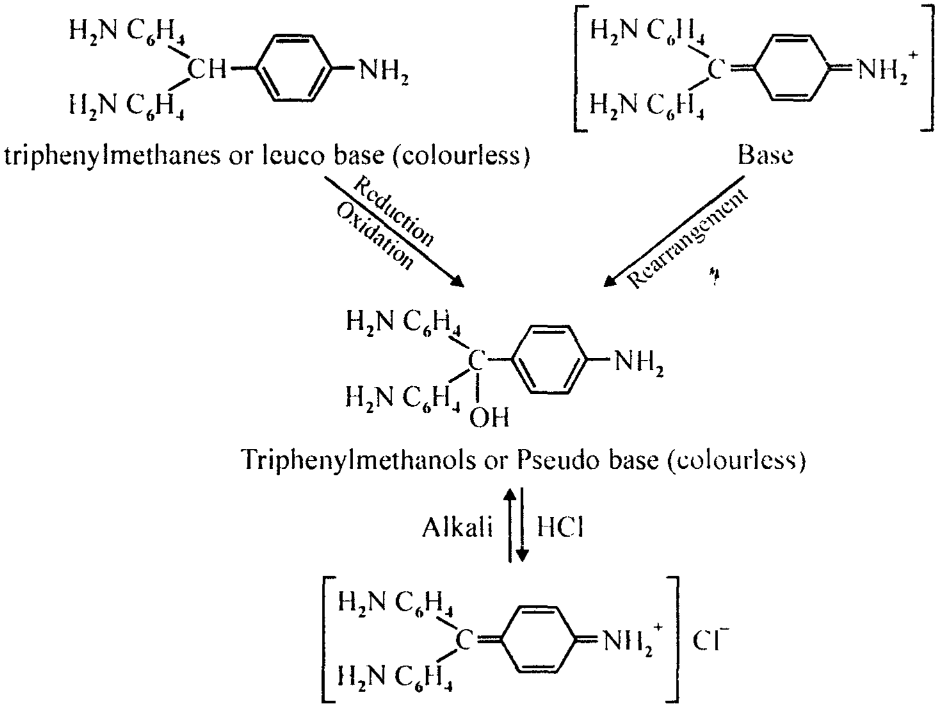
12.2. Classification

The triphenylmethane dyes have been further classified into the following types :

1. Aminotriphenylmethane dyes.
2. Hydroxytriphenylmethane dyes.

Let us discuss these one by one.

1. **Aminotriphenyl Methane Dyes** : These are the salts which are obtained by the action of mineral acids on certain di-or tri-amino substituted triphenylmethanols (colour bases). The colour bases are in turn prepared by the oxidation of the leuco bases (triphenylmethanes).

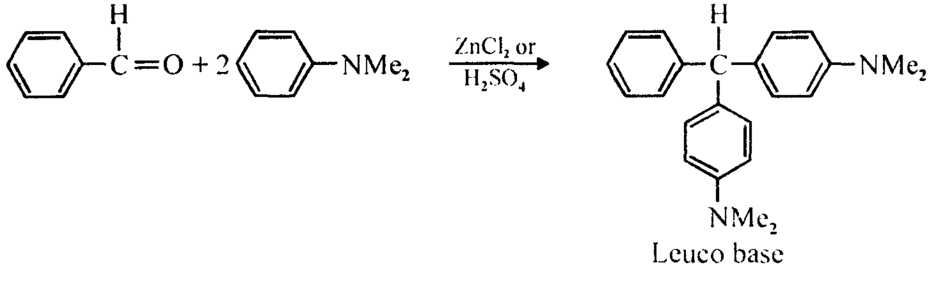


Dye (coloured)

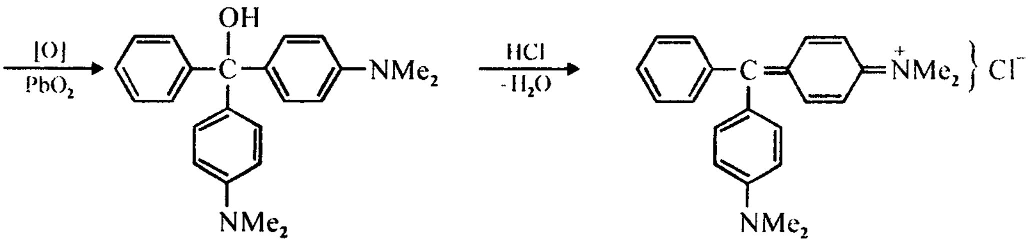
The intense colour of this group of dyes has been attributed to the resonance of unsymmetrical triphenylcarbonium ions. This resonance will be only possible if two or more of the benzene rings of the triphenyl carbonium ions have amino or substituted amino groups (generally in the *p*-position). The resonance energy stabilises the positive ion of the dye, thereby, favouring the formation of salt from the colour base.

We will now discuss the various important triphenylmethane dyes.

(*a*) **Malachite Green** : On a large scale is prepared by condensation of 2 moles of dimethylaniline with one mole of benzaldehyde at 100°C in the presence of zinc chloride or conc. sulphuric acid. The leuco-base produced is oxidised with lead dioxide in a solution of acetic acid having hydrochloric acid. The resulting colour base on acidification with excess of hydrochloric acid gives malachite green.

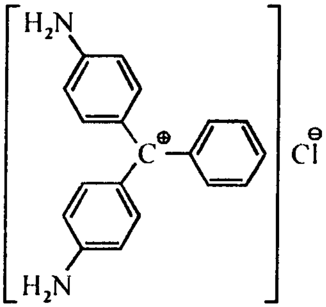


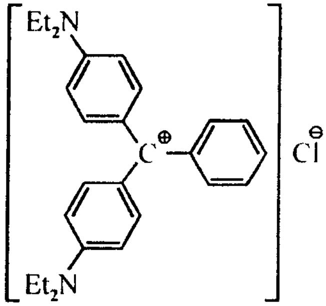
Leuco base


colour base
malachite green

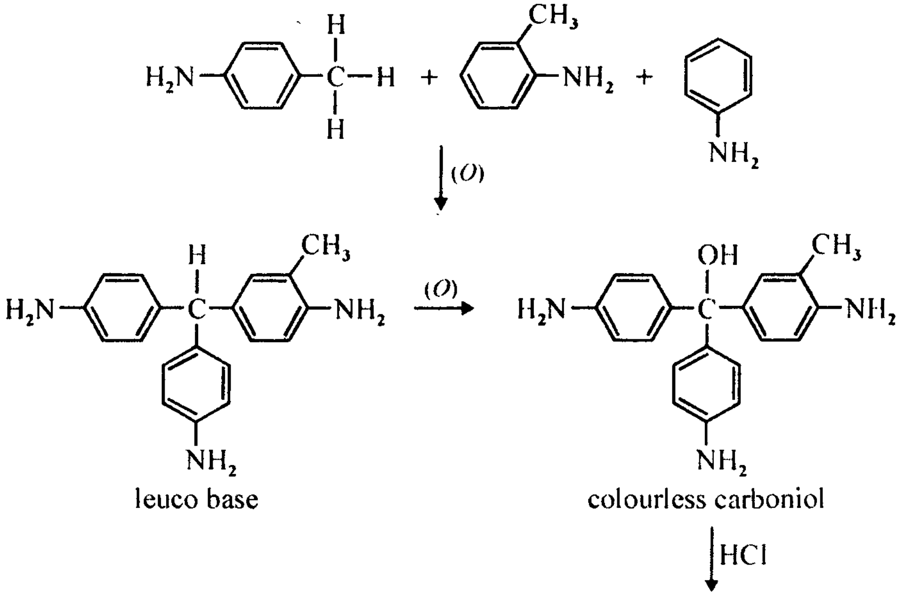
Malachite green dyes wool and silk directly, and cotton mordanted with tannin.

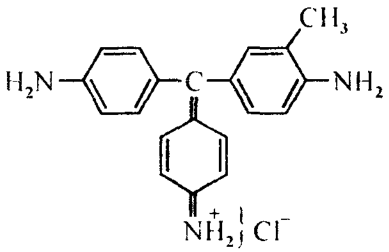
Doebner's Violet and Fast Green are the lower and higher homologues of Malachite Green respectively.


Doebner's Violet

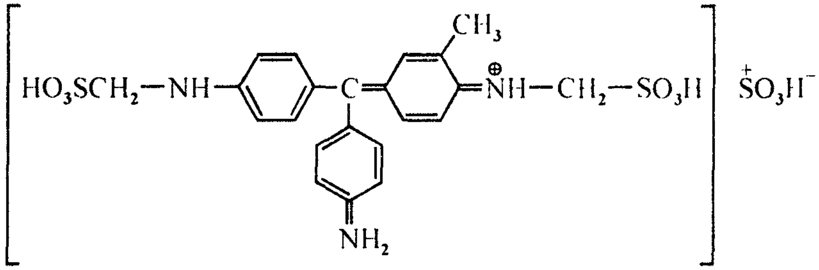

Fast Green or Brilliant Green

(*b*) **Rosaniline** (*Magneta or Fuchsine*) : It is prepared by oxidising an equimolecular mixture of aniline, *o*-and *p*-toluidines, and their hydrochlorides, with nitrobenzene in the presence of iron filings. The product so obtained is a mixture of rosaniline and pararosaniline in which the former is predominating.


leuco base
colourless carboniol

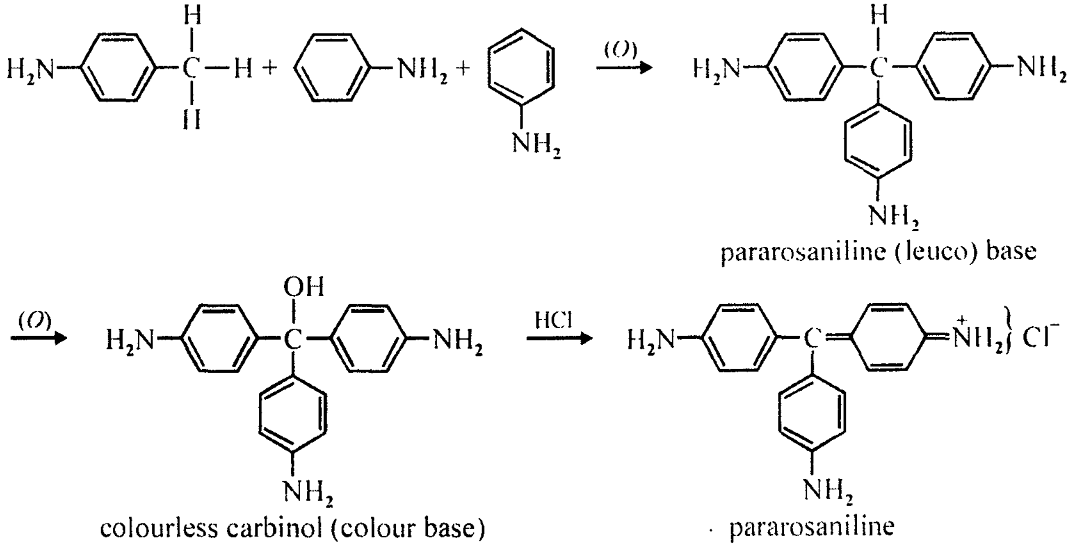


Rosaniline forms crystals which show a green metallic lustre. It dissolves in water, giving a deep red solution. This solution is decolourised by sulphur dioxide and is then called **schiff's reagent.** This reagent is used as a test for aldehydes. The restoration of the colour may be probably due to the formation of a dye with aldehyde (*e.g.*, formaldehye), having the following structure.

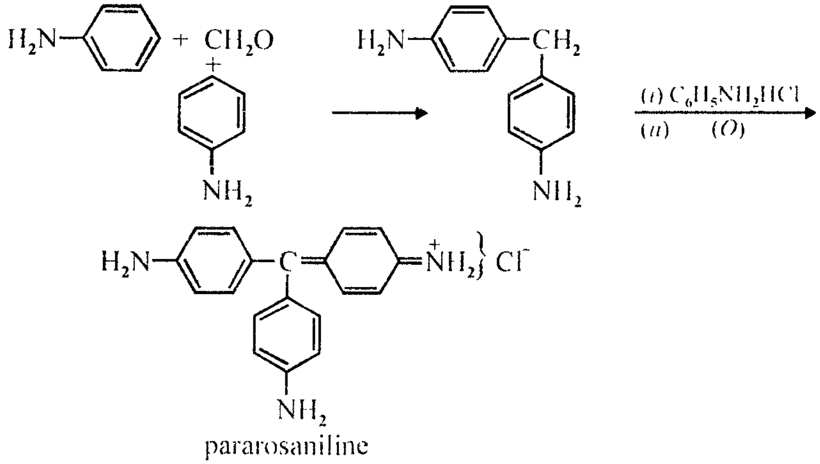


Rosaniline is used to dye wool and silk directly, producing a violet-red colour; however, cotton must be mordanted with tannin.

(*c*) **Pararosaniline** (*Para fuchsine*) : On a large scale it is generally prepared by oxidising a mixture of two moles of aniline and one mole of *p*-toluidine with arsenic acid or nitrobenzene. The resulting colour base on treatment with acid yields the dye.



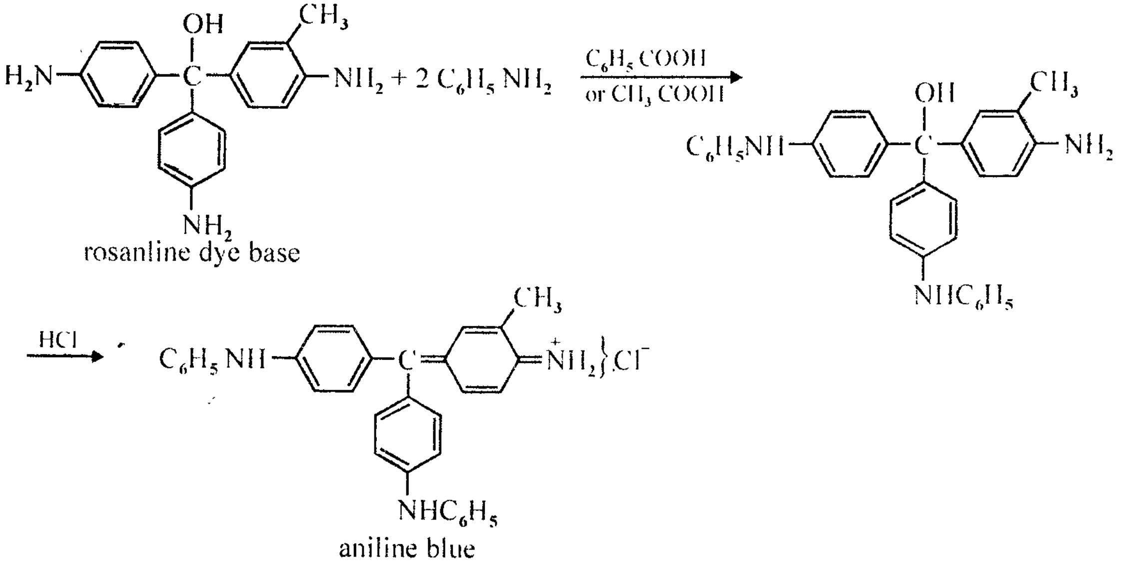
It is also possible to prepare pararosaniline by the following method :



Pararosaniline has the same properties as that of roesaniline. Like rosaniline, it dyes wool and silk directly, producing a violet-red colour; cotton must first be mordanted with tannin.

The N-phenylated sulphonic acid derivatives of pararosaniline are more important than the parent dyes. These are known as *ink blues* and are valuable acid dyes.

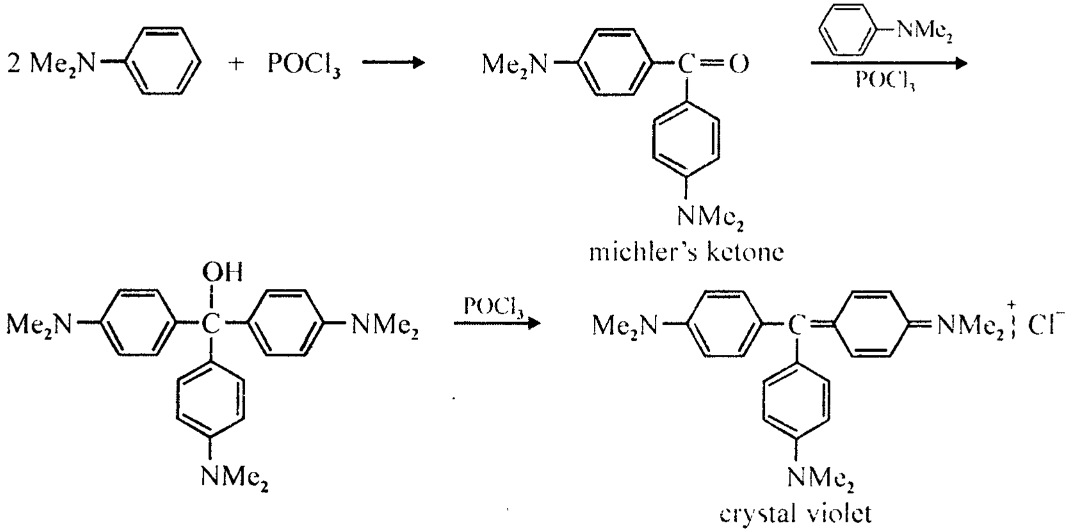
(*d*) **Aniline Blue** (*diphenylrosaniline*) : On a large, scale it may be obtained by heating rosaniline dye base with aniline in the presence of benzoic acid or acetic acid.

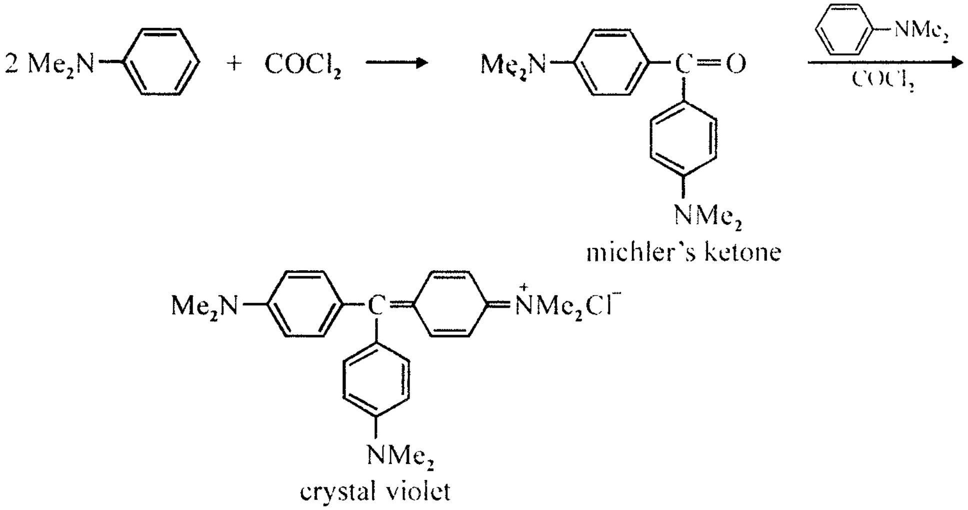


It is important to remember that the phenylation of the amino groups is prevented by the *o*-methyl group.

Aniline Blue and its sulphonic acid derivatives, *viz.*, 'alkali blue' (phenyl groups are para sulphonated) and 'soluble blue' (phenyl groups are trisulphonated), are used for dyeing wool and silk directly.

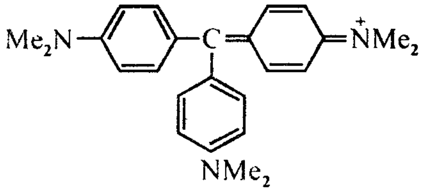
(*e*) **Crystal Violet** (*hexamethyl parafuchsine or hexamethyl-pararosaniline hydrochloride.* It may be obtained by heating michler's ketone with dimethylaniline in the presence of phosphoryl chloride or carbonyl chloride. If the latter compound is used, then crystal violet may be prepared directly by heating carbonyl chloride and dimethylaniline.



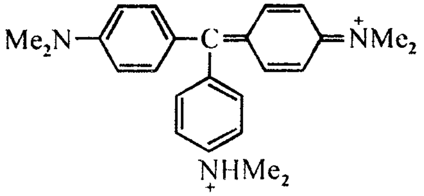


Its weak acid solution is violet, its strongly acid solution is green and its very strongly acid solution is yellow. The colour changes may be explained as follows :

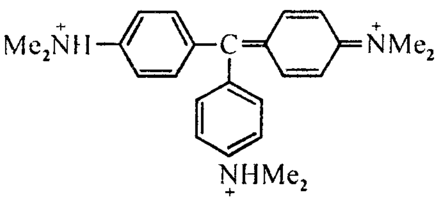
In weakly acid solution, the crystal violet has been found to exist as the singly charged ion (I). In this state, two-thirds of the charge will undergo oscillation in the horizontal direction. In strongly acid solution, it has been found to exist as the doubly charged ion (II). In this state, the whole unit of charge will undergo oscillation in the horizontal direction and, therefore, the colour deepens. It is important to remember that the vertical direction of oscillation gets inhibited due to the fixation of the lone pair by proton addition. In very strongly acid solution, it has been found to exist in form (III) having three charges. In this ion, relatively little resonance (with oscillation of charge) is possible and therefore the colour lightens.



(I)



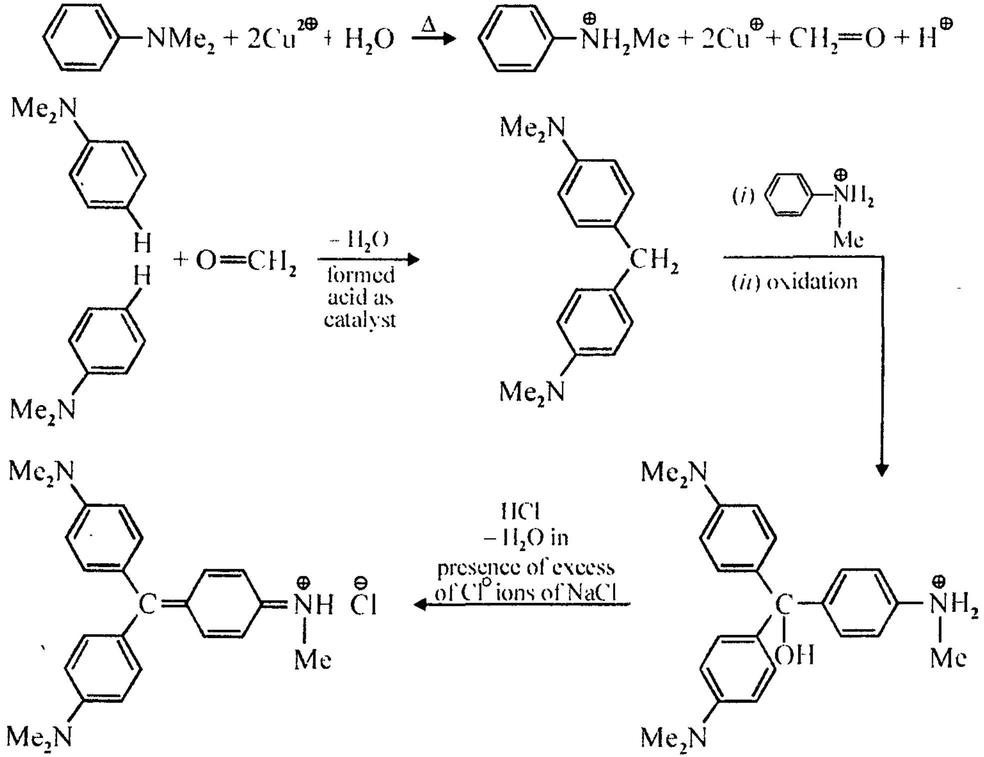
(II)



(III)

Crystal violet is used to dye silk, wool and tannin-mordanted cotton to bluish violet colour but the colour is not fast to light. Crystal violet is used in making indelible ink and pencils, in stamping pad, etc. It is used as an indicator in the determination of hydrogen-ion concentration of solution.

(f) **Methyl Violet** (*Pentamethyl parafuchsine or pentamethyl-pararosaniline chloride*) : On a large scale, it is prepared by the oxidation of dimethylaniline with air in the presence of a mixture of cupric sulphate and sodium chloride at 60°C for several hours. In this reaction, it seems that a molecule of dimethylaniline is first of all oxidised to a mixture of methylaniline and formaldehyde. Then this mixture undergoes condensation with two molecules of dimethylaniline in the usual manner to give methyl violet in the following way :



methyl violet

Methyl violet shows nearly the same properties as crystal violet. Since it has one less methyl group, hence it is more reddish than crystal violet.

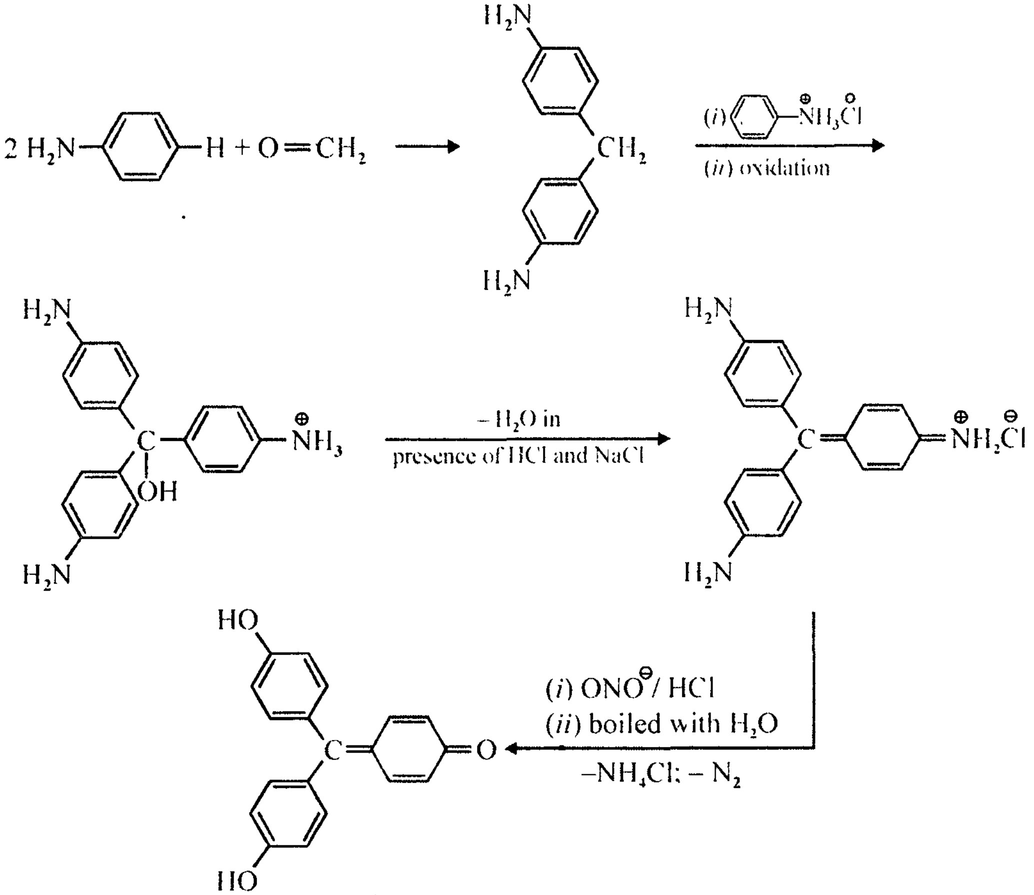
Methyl violet has been found to have the same properties as that of crystal violet. However, methyl violet contains one more methyl group that the crystal violet. Therefore, it is more reddish than the latter.

It is used for dyeing and printing. It is also extensively used in the manufacture of inks, copying pencils, type writer ribbons and other coloured

Gentain violet : It is obtained by mixing crystal violet and methyl violet. It is generally employed as an antiseptic for infected wounds and mucous membranes.

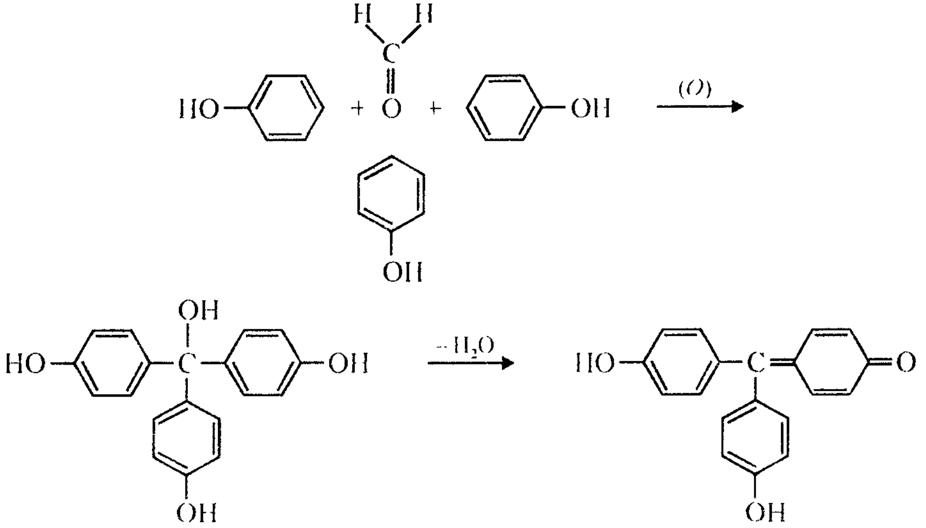
2. **Hydroxytriphenylmethane Dyes :** An example of these is *aurin* or *rosolic acid.* Other example is chrome violet.

(*a*) ***Aurin (Resolic Acid Dye) :*** Pararosaniline on complete diazotisation and subsequent hydrolysis by boiling with water changes into aurin. For the synthesis of pure pararosaniline, 2 molecules of aniline and 1 molecule of aniline hydrochloride are heated with formaldehyde in the presence of nitrobenzene, an oxidiser, in an iron bath.



Aurin

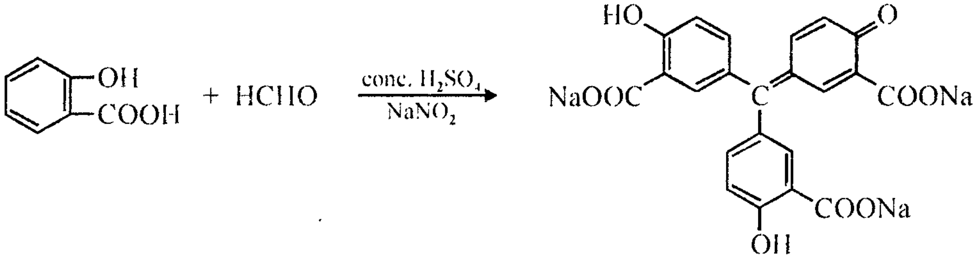
Kolbe and Schmidt (1861) prepared this dye by oxidising a mixture of phenol and formaldehyde or oxalic acid.



aurin

Aurin crystallises on yellowish-brown prisms which are soluble in alkalis to form intense red solution. It is used as an indicator and for dyeing paper.

(*b*) ***Chrome Violet :*** It is prepared by heating salicylic acid and formaldehyde in the presence of conc. sulphuric acid and an oxidising agent like $NaNO_2$.



chrome violet

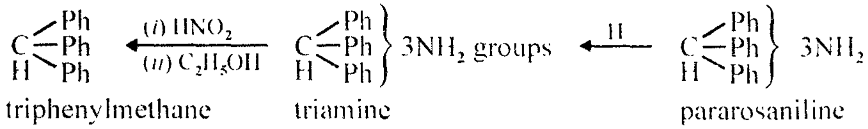
It is used as a mordant dye with reddish violet shade, though it lacks in light fastness.

Structure of Triphenylmethane Dyes Taking the Example of Pararosaniline

(*a*) As the colour of triphenylmethane dyes, *e.g.* pararosaniline and rosaniline, is in their salt form, they are first changed to pararosaniline base or pararosaniline proper.

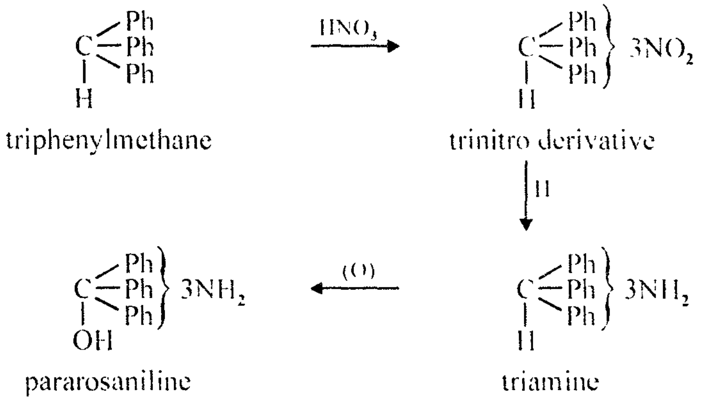
(*b*) From the usual tests it has been found that both pararosaniline and rosaniline possess three primary aromatic amino and one tertiary alcoholic groups.

(*c*) When reduced pararosaniline base yields leucoaniline which is a triamine, *i.e.*, having three primary amino groups. Leucoaniline on diazotisation following by boiling with ethyl alcohol gives triphenyl methane ($C_{10}H_{16}$).



(*d*) The presence of triphenyl-methane nucleus in pararosaniline base may be further proved by the following reactions :

When triphenylmethylmethane is nitrated with fuming nitric acid, it yields a trinitro-derivative which on reduction yields leucoaniline and this, on oxidation, yields pararosaniline base.

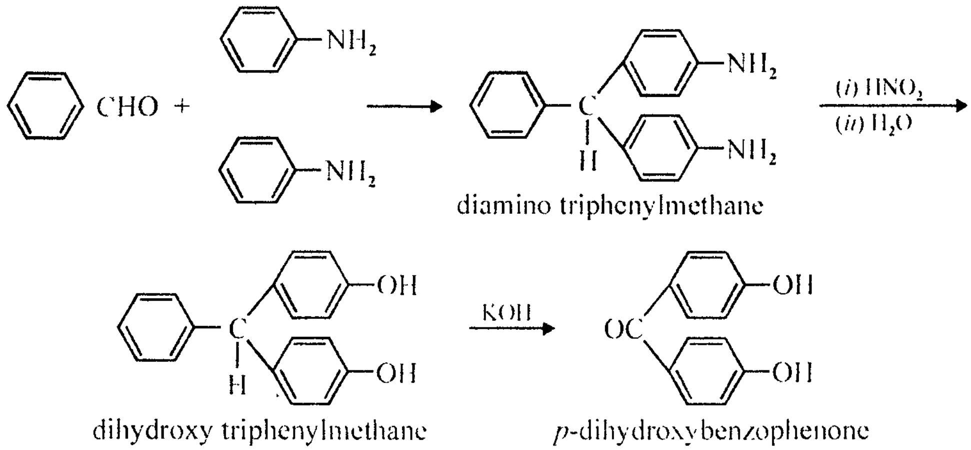


(*e*) From the foregoing facts (*ii*) to (*iv*), it may be concluded that pararosaniline is a triaminotriphenyl carbinol. Now the next problem is to assign the position of three aromatic amino groups This assigning has been done on the basis of following facts :

(*i*) As the synthesis of colour base involves two molecules of aniline and one molecule of *p*-toluidine, it reveals that the three amino groups are present in the colour base in the *p*-position with respect to the methane carbon atom of triphenylmethane.

(*ii*) From point (*d*), it may be seen that thriphenylmethane on niration gives a trinitro compound in which the three nitro groups must be presant in three different rings, *i.e.*, one each ring. The reason for this is that the nitro group is a deactivating group and thus as soon as it enters the benzene nucleus, it will retard the further substitution in that ring. Also, like the diphenylmethane substitutions the incoming groups in the triphenylmethane will enter the *p*-positions of the benzene nuclei and therefore the three amino groups in the *p*-position of the three benzene nuclei.

When benzaldehyde is condensed with two molecules of aniline in the presence of zinc chloride, it yields diaminotriphenylmethane. This on diazotisation followed by boiling with water yields dihydroxytriphenyl methane which on fusion with potassium hydroxide yields *p*, *p*′-dihydroxybenzophenone. The formation of this product reveals that the two amino groups in diaminotriphenylmethane are in the *p*-positions. But *p*-nitrobenzaldehyde on condensation with aniline followed by the reduction of the product yields leucopararosaniline. Therefore, the third amino group in latter compound and hence in the dye must also be present in the *p*-position to the methane carbon atom.



The position of the additional methyl groups of rosaniline is ascertained by its synthesis form *o*-toluidine which reveals that the methyl group is present in the *o*-position to the *p*-amino group. This is further ascertained by the synthesis of leuco rosaniline from aniline and 4-nitro-4-methal benezaldehyde followed by reduction.

13

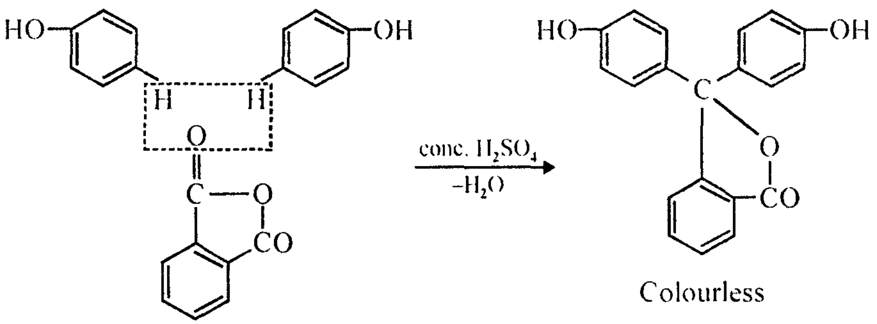
CHAPTER

PHTHALEINS

13.1. Introduction

These are dihydroxytriphenyl methane derivatives with a carboxyl or sulphonic acid group ortho to the central carbon atom in the third phenyl ring. These are used as indicators because they are sensitive to the action of alkali solutions. Phenolphthalein is the most important member of this group.

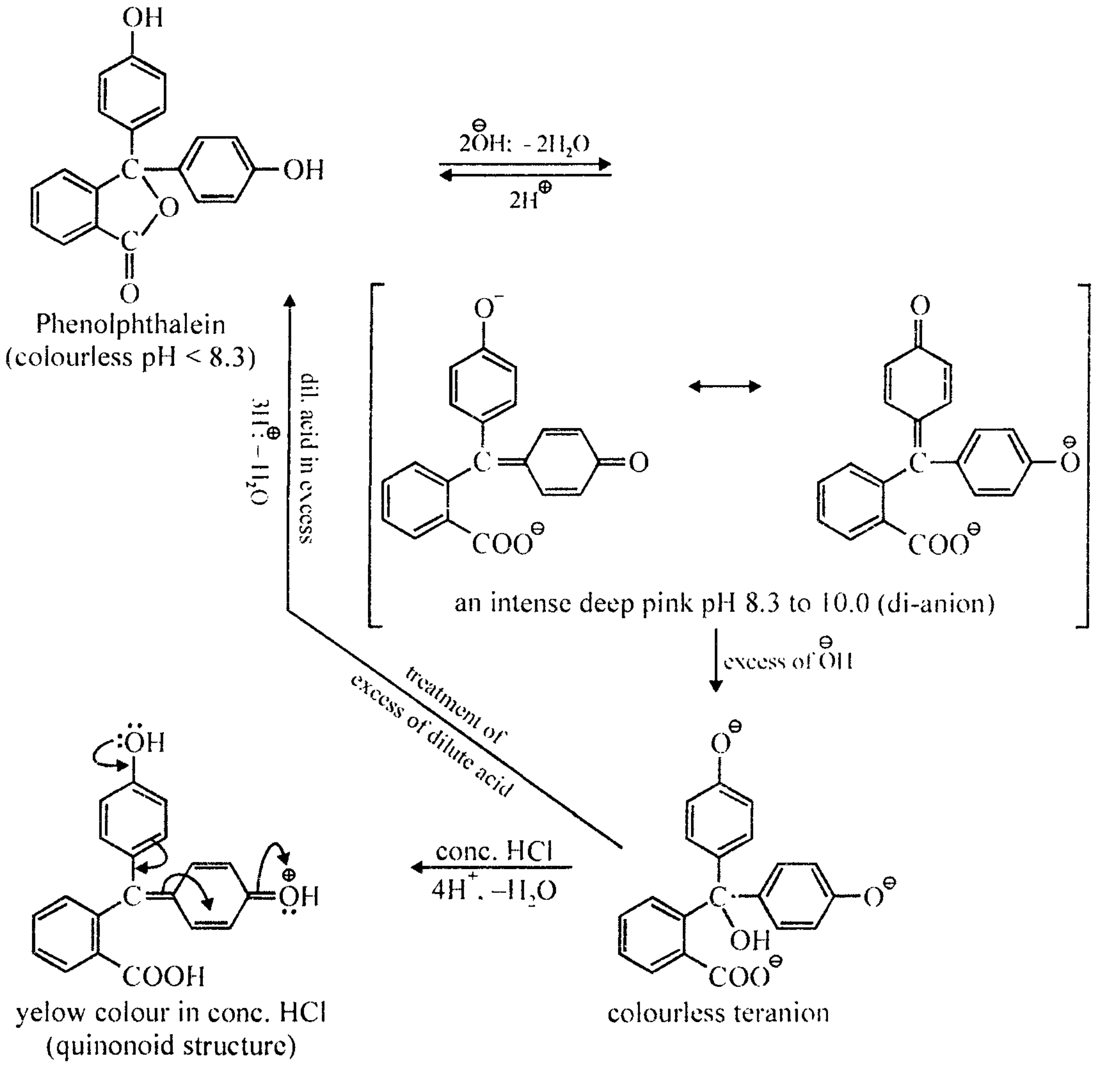
(*a*) **Phenolphthalein :** It is prepared by heating phthalic anhydride (1 molecule) with phenol (2 molecules) in the presence of conc. sulphuric acid as a condensing agent.



Colourless

It is a white crystalline solid insoluble in water but soluble in alkalis to form deep pink solution.

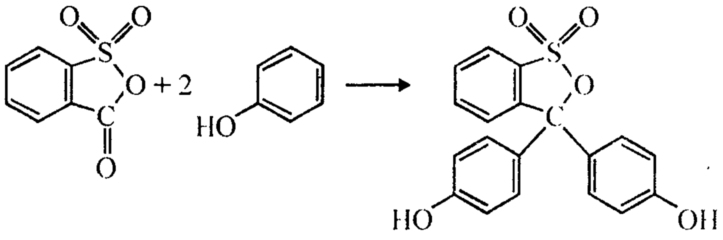
Phenolphthalein is a white crystalline benzenoid (m.p. 261°C), insoluble in water but soluble in alcohol. It is also soluble in alkalis where it gives a red colour due to the formation of its salt having quinonoid structure (dianion). On addition of a large excess of alkali, a colourless ter anion is formed white is again benzenoid. The coloured dianion may alkali, colourless ter anion formed which is again benzenoid. The coloured dianion may easily revert back to colourless benzenoid form in acid; because of this fact, phenolphthalein is used as an acid-base indicator. On addition of concentrated hydrochloric acid, the colourless teranion miraculously, gives yellow colour, while the dilute acids simply protonate the ter-anion. The following reactions explain the whole gamut.



If the excess of strong alkali is added to the pink solution, it becomes colourless again due to the loss of quinonoid structure and resonance.

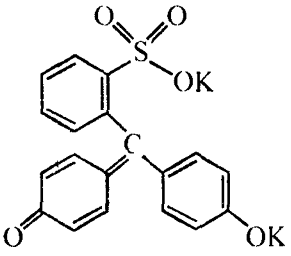
Its 1% solution in alcohol is used as an indicator in acid-alkali titrations. It is also used as a laxative in medicine.

(*b*) **Phenolsulphophthalein :** It is obtained by condensing one molecule of sulphobenzoic anhydride with two molecules of phenol in the presence of conc. sulphuric acid or zinc chloride.

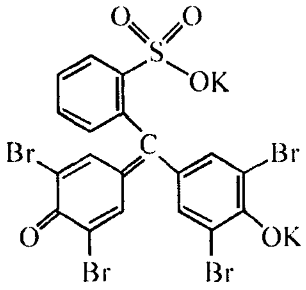


Phenolsulphophthalein

Some other examples of phthaleins are *phenol red* (dipotassium salt of phenolsulphophthalein and *bromophenol red* (tertrabromophenol sulphophthalein). Both these are used in the determination of the hydrogen ion concentrations of solutions.



Phenol red



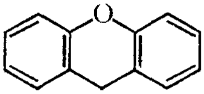
Bromophenol red

14
CHAPTER

XANTHENE DYES

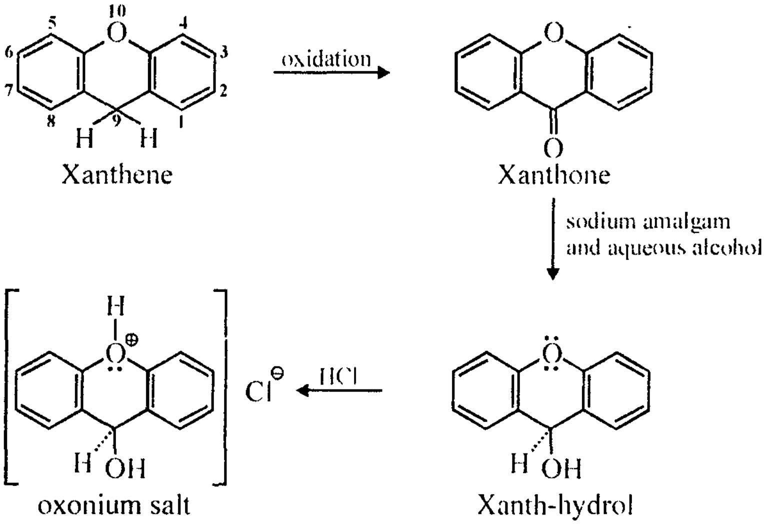
14.1. Introduction to Xanthene Dyes

These are derivatives of xanthene. This group gives rise to brilliant fluorescent dyes having red to yellow colour. Xanthene dyes obtained from xanthene by the introduction of auxochromes such as amino or hydroxyl group into positions 3 and 6, *i.e.*, the *para*-positions with respect to the carbon atom linking the two benzene nuclei :



xanthene or xanthen

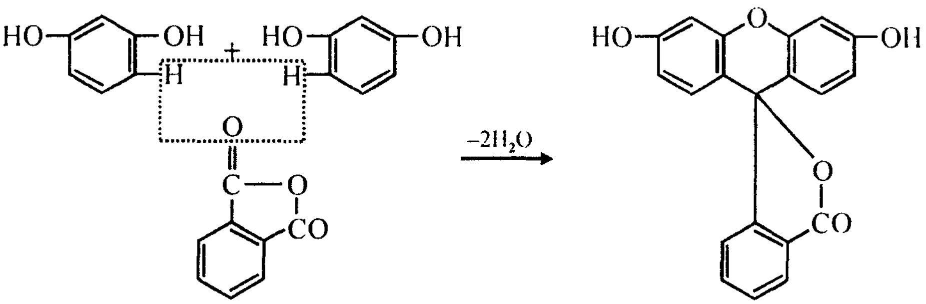
Xanthenes are prepared on the same lines as phthaleins, but these dyes have dibenzo-1, 4-pyran (xanthene nucleus). This dibenzo-1, 4-pyran, on oxidation, forms xanthone (9-keto-xanthene), which on reduction, changes into xanth-hydrol (9-hdroxyxanthene). Xanth-hydrols yield oxonium salts with mineral acids.



The introduction of auxochromes into 3 and 6 positions in the xanthene nucleus gives dyes of various shades.

Some important members of this group of dyes are described as follows :

(*a*) **Fluorescein :** It is prepared by heating phthalic anhydride and resorcinol (in concentrated sulphuric) at 200°C or at 120°C in presence of anhydrous oxalic acid. First of all, a phthalein is formed, which eliminates a second molecule of water by interaction of two phenolic groups to produce xanthene nucleus.

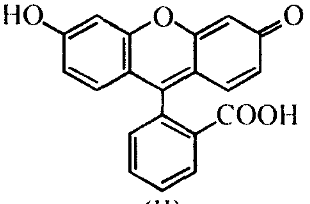


(I)

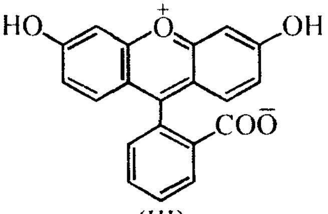
Fluorescein is an orange solid (*cf.* phenolphthalein; colourless), insoluble in water. Since fluorescein is coloured, hence it exists in *p*-quinonoid and *o*-quinonoid forms—the latter being in the form of dipolarion, predominates.

It dissolves in alkalis to a reddish brown solution, which on dilution exhibits a strong yellowish-green fluorescence (persists upto 4 × 10^6 times dilution).

As fluorescein is coloured, the structure (I), which is the non-quinonoid uncharged structure, is unsatisfactory, However, two quinonoid structures have been postulated in which the structure (II) is having the *p*-quinonoid structure while the structure (III) is having *o*-quinonoid structure (this contains tercovalent oxygen).



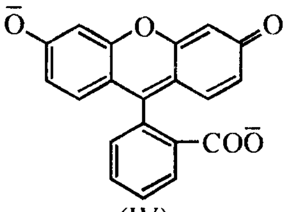
(II)



(III)

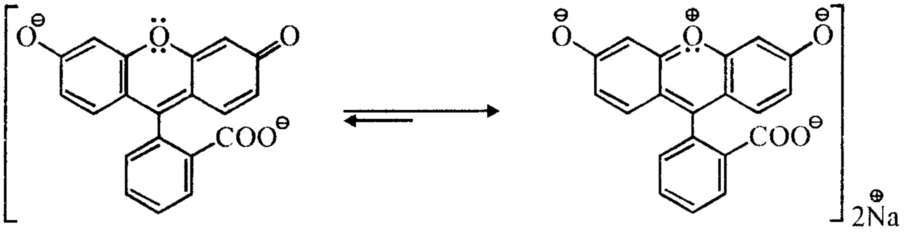
When Davies *et al.* (1954) recorded the infrared spectra of phenol, phenolphthalein, fluorescein and some of their alkali derivatives, they concluded that the structure (I) is preferred over other structures (II) and (III). The structure (II) is eliminated due to the absence of the characterised absorption of the carboxyl group. Similarly, the structure (III) is eliminated because the frequencies of the carboxylate ion in (III) are absent.

When fluorescein is dissolved in alkalis, it gives a reddish-brown solution which on dilution gives a strong yellowish-green fluorescence. The structure of flourescein anion is (IV).



(IV)

The sodium salt of fluorescein is known as *uranine*. Uranine is used to dye wool and silk yellow from an acid bath; the colours are fugitive.

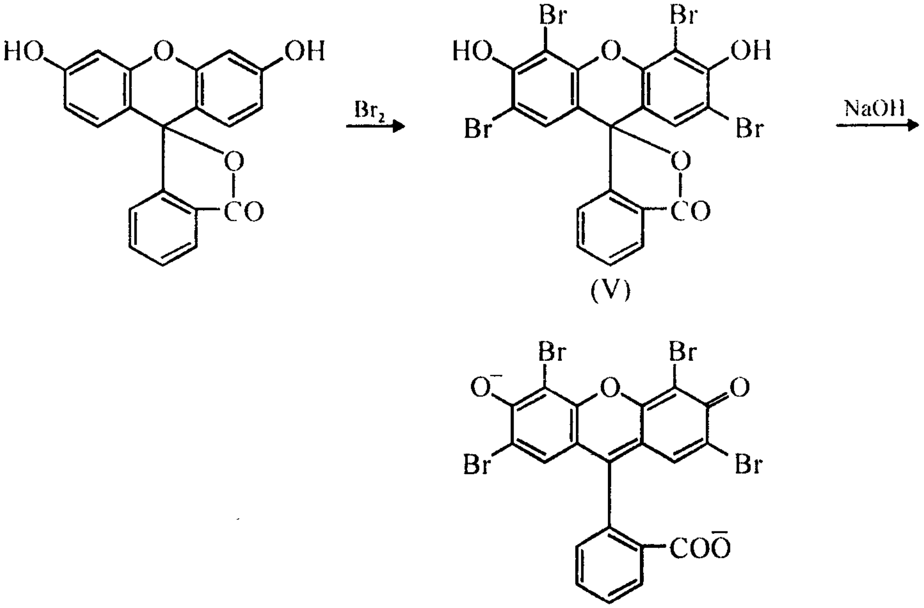


p-quinonoid (2-strs) *o*-quinonoid (2-strs)

Uranine

Fluorescein is used in tracing underground currents in sea and rivers as well as a marker during accidents.

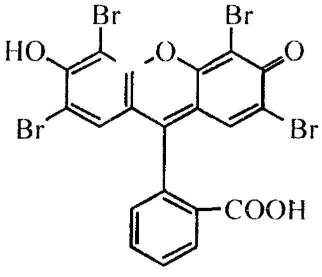
(*b*) **Eosin** : It is tetrabromofluorescein and is obtained by the action of bromine on fluorescein in glacial acetic acid solution.



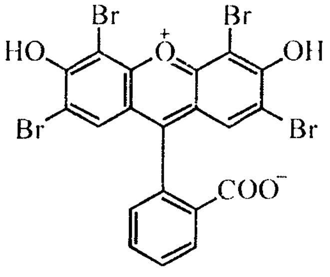
(V)

(VI)

As eosin is a red powder, its structure may not be (V) but may be (VII) or (VIII). The alkaline solution of eosin shows a yellow-green fluorescence which is attributed to the doubly charged structure (VI).



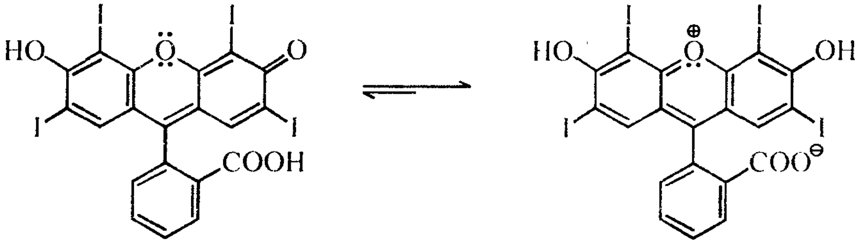
(VII)



(VIII)

Eosin is used to dye wool and silk a pure red, with a yellow fluorescence. It is also used as the lead like *vermilionette* for poster printing. Most red inks are dilute solutions of eosin.

(*c*) **Erythrosin :** It is tetraiodofluorescein and is prepared in a similar manner as eosin.



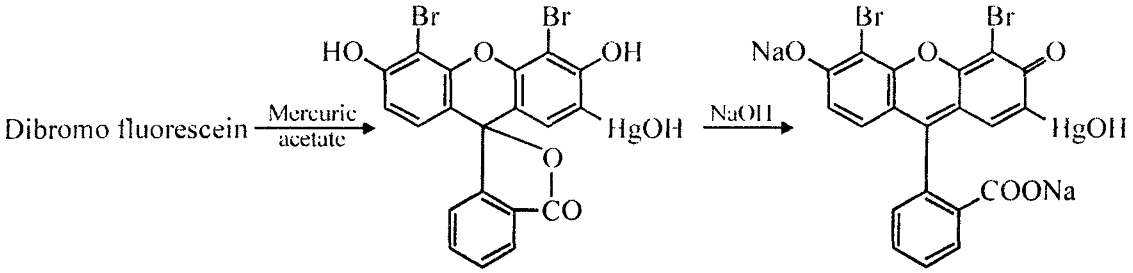
para quinonoid (2-strs) ortho quinonoid (2-strs)

Erythrosin
(dark red powder)

The alkaline solution of this dye exhibits yellowish-green fluorescence—attributed to their di-anions.

It is generally used as a food colouring matter. It is also used as a spectral sensitizer in photography.

(*d*) **Mercurochrome :** It is the disodium salt of dibromo-hydroxymercurifluorescein. It is prepared by heating dibromofluorescein with mercuric acetate or mercuric oxide in acetic acid and sodium hydroxide.



Mercurochrome

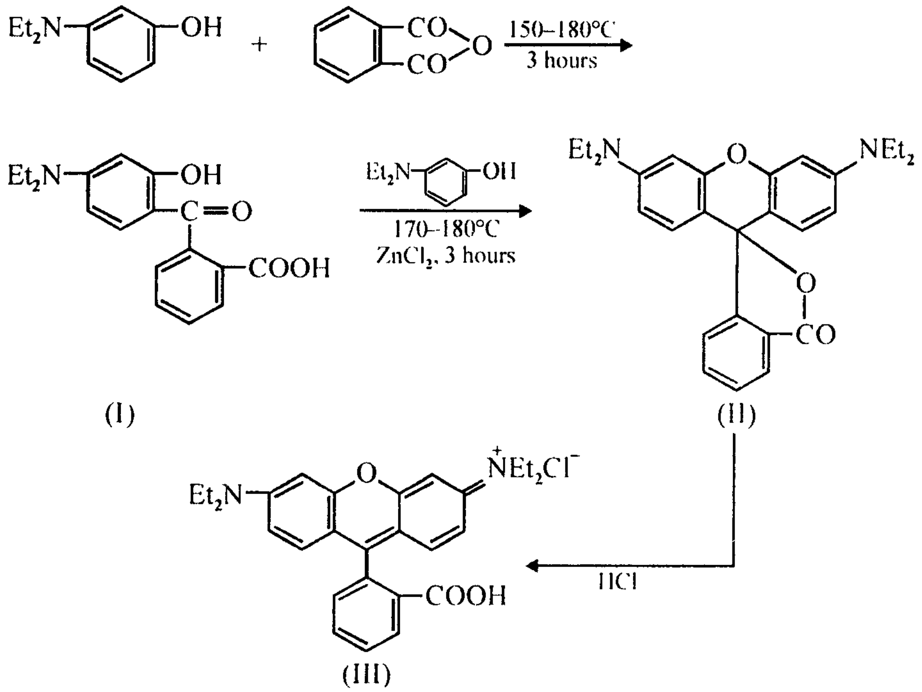
If forms green scales or granules. It dissolves in water forming a cherry-red solution. It is used as an antiseptic in 2-5% solution for the skin and in 1% solution for mucous membranes.

It has also found application as a biological stain. Unlike eosin, mercurochrome is extremely fast to light; preparations stained with this dye do not fade even when exposed to strong sunlight for very prolonged periods of time.

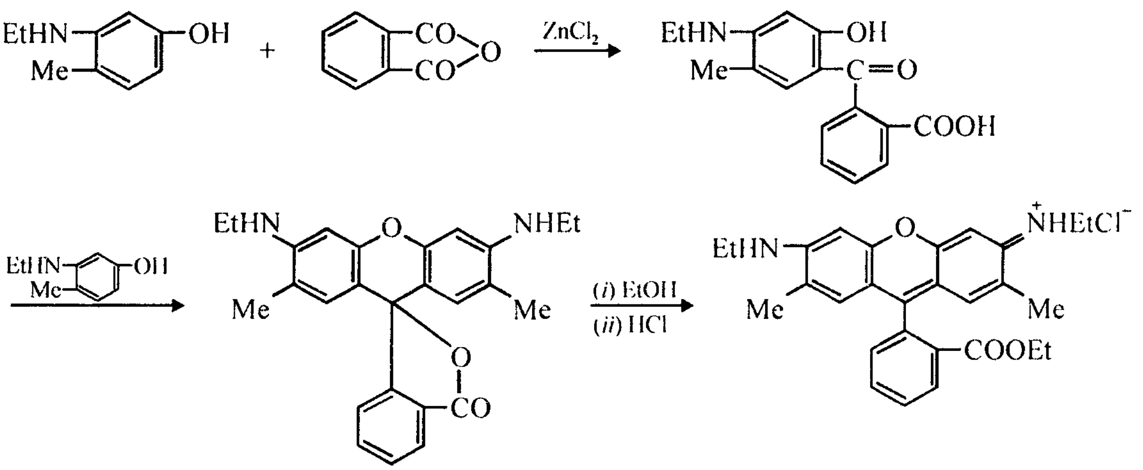
If mercurochrome is swallowed, it causes severe mercurial poisoning.

(*e*) **Rhodamines :** These are basic dyes belonging to xanthene class. Rhodamines range in shades from yellowish red to blue. Two most commonly used basic rhodamines are rhodamine B and rhodamine 6 G.

Rhodamine B is obtained by condensing *m*-diethylamino-phenol (1 molecule) with phthalic anhydride (1 molecule) at 150–180°C for 3 hours to yield the reaction product (I). Then the reaction product (I) is condensed with another molecule of *m*-diethylaminophenol in the presence of zinc chloride at 170–180°C for 3 hours to yield the dye base (II) which is converted into the dye (III) by treatment with dil. hydrochloric acid.



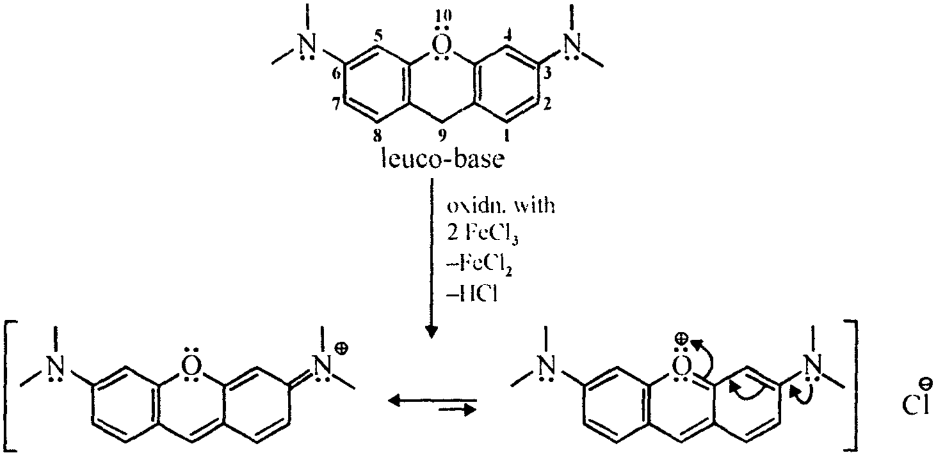
Rhodamine 6G is obtained by the condensation of N-monoethyl-*o*-toluidine with phthalic anhydride in the presence of the zinc chloride, the fusion product finally being esterified with ethanol and mineral acid.



Rhodamines are generally used to dye papers. They are used for the preparation of red and pink lakes used as pigments.

They are also used to dye the wool, silk and cotton mordanted with tannin where brilliant shades of fluorescent effects are required. However, these dyes are of secondary importance.

(*f*) **Pyronines :** A dibenzo-1, 4-pyran (xanthene), where 3- and 6-positions are replaced by amino or alkylated amino, gives a leuco-base for pyronine dyes. The leuco-base, on oxidation with ferric chloride, produces pyronine dyes of crimson red shades



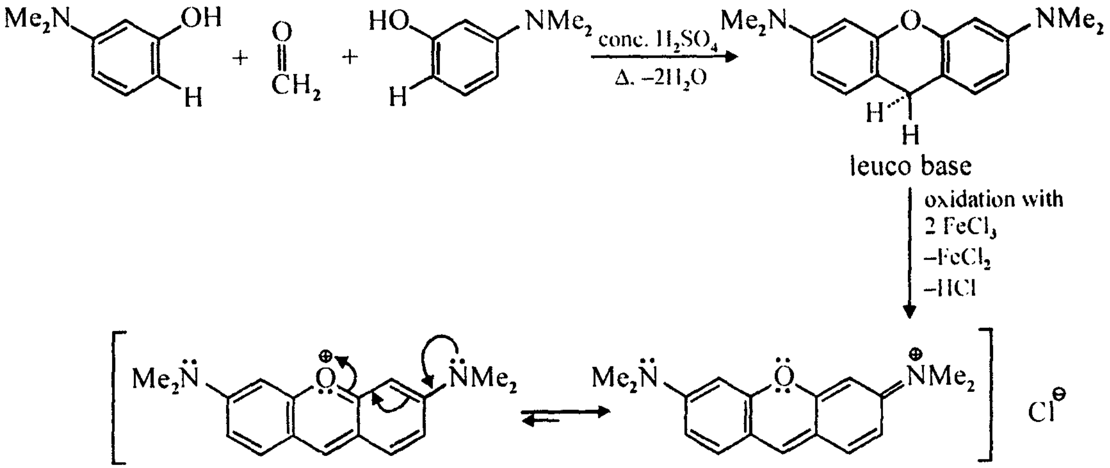
p-quinonoid (2-strs)

o-quinonoid (2-strs)

A Pyronine dye

All dyes of this group are cationic, where positivity lies predominantly on either of the two nitrogens; hence *p*-quinonoid prevails.

(*g*) **Pyronine G :** (*Pyronine Y*). It is obtained by condensing one molecule of formaldehyde with two molecules of dimethylaminophenol in the presence of zinc chloride or conc. H_2SO_4 followed by the oxidation of the leuco compound so obtained by ferric chloride.



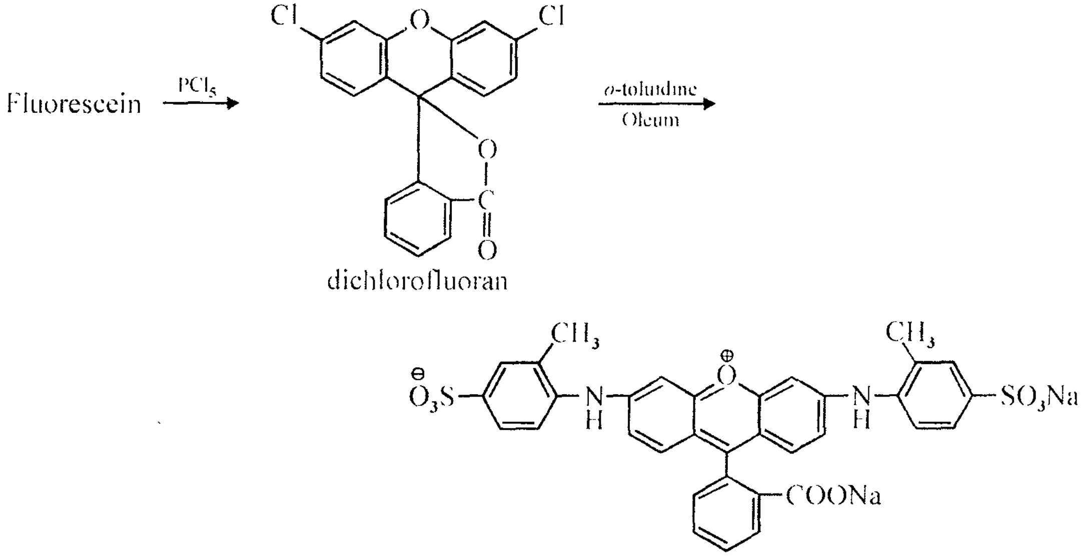
o-quinonoid (2-strs)

p-quinonoid (2-strs)

Pyronine G (carmine)

It is soluble in water giving intense red colour and yellow fluorescence. It is used to dye silk and tannin-mordanted cotton a crimson red. It is a very important biological stain, its principal use being in conjunction with methyl green for the differential staining of the two types of nucleic acids. It is used for the detection of mercury, silver and tin.

(*h*) **Acid Violet R** : Acid dyes of sulphorhodamine subclass can be synthesised from fluorescein to get acid violet dyes. Thus, for example, fluorescein, is converted to dichlorofluoran and subsequently condensed with *o*-toluidine and sulphonated with oleum to get acid sulphorhodamine dye, acid violet 4R.



dichlorofluoran

acid violet 4R

15

CHAPTER

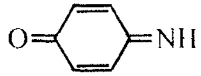
HETEROCYCLIC DYES

15.1. Introduction

These include dyes involving heterocyclic rings and are not grouped under other specific groups. They can be further divided as follows :

1. Quinoneimine Dyes

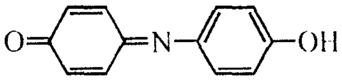
These dyes are obtained by replacing hydrogen atoms of the amino group of quinonemonoimine of dimine by hydroxy or amino substituted aryl groups.

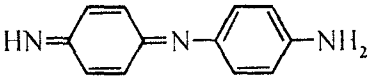

quinone imine


quinone dimine

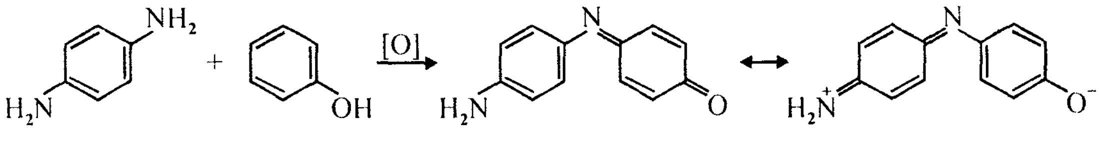
For example, indophenols and indamines derived from the above two compounds are employed as dyes.

Various indophenols and indamines come in this category of dyes. The groups like OH and C = O, have chemical analogy with NH_2 and C = NH respectively; hence an indophenol and an indamine are chemically alike.


an indophenol

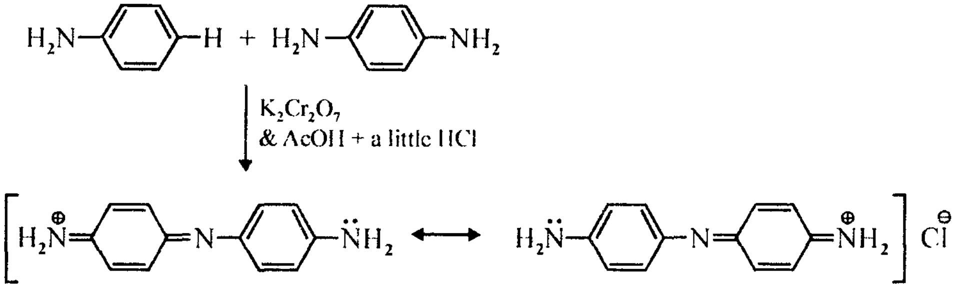

an indamine

(a) Indophenols : The simplest member of this group of dyes is indophenol blue. It is obtained by oxidising a mixture of *p*-phenylenediamine and phenol with an alkaline hypochlorite solution.



The indophenols are blue. These are very sensitive to acids and these are, therefore, not now used for textile coloration. However, these are applied in colour photography and also serve as intermediates for sulphur dyes.

(*b*) Indamines : The simplest member of this group of dyes is phenylene blue. It is obtained by oxidising a mixture of *p*-phenylenediamine and aniline with potassium dichromate in acetic acid.

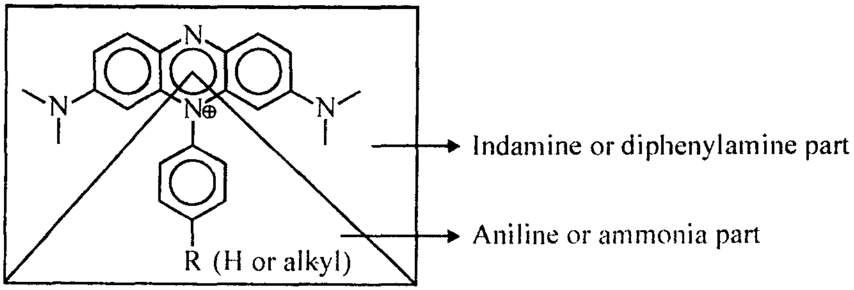


Phenylene Blue

These dyes are blue or green. Like indophenols these are very sensitive to acids and they are, therefore, not now used for textile coloration. However, they serve intermediates for the synthesis of azines, thiazines and oxazines.

2. Azine Dyes

These are the derivatives of phenazine which acts as chromophore. The amino and hydroxy-groups *para* to one of the ring nitrogens are the usual *auxochromes*. However, azine dyes having no auxochrome are known; an example is the obsolete dye flavinduline. The complex azines are inexpensive blues, violets, browns and blacks. The strong colour of the products is due to resonance stabilisation related to several contributing structures.



In most of the azine dyes, an indamine is allowed to react with aniline or para substituted aniline in presence of an oxidiser. Para quinonoid structure in these cationic dyes always prevails (cf. Fluorescein).

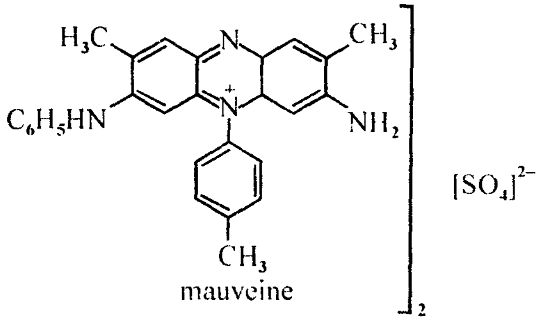
The azine dyes are not manufactured from phenazine but are obtained by condensation reactions.

The azine dyes are basic dyes which may be applied to wool, silk or tannin-mordant cotton. Many sulphonated azine dyes are acid dyes suitable for application to wool. silk or nylon.

Some azine dyes are described as follows :

(*a*) Mauve *(Mauveine, aniline purple or tyrian purple)* : It is the first commercial synthetic dye which was discovered by W.H. Perkin in 1856. This dye is no longer in commercial use.

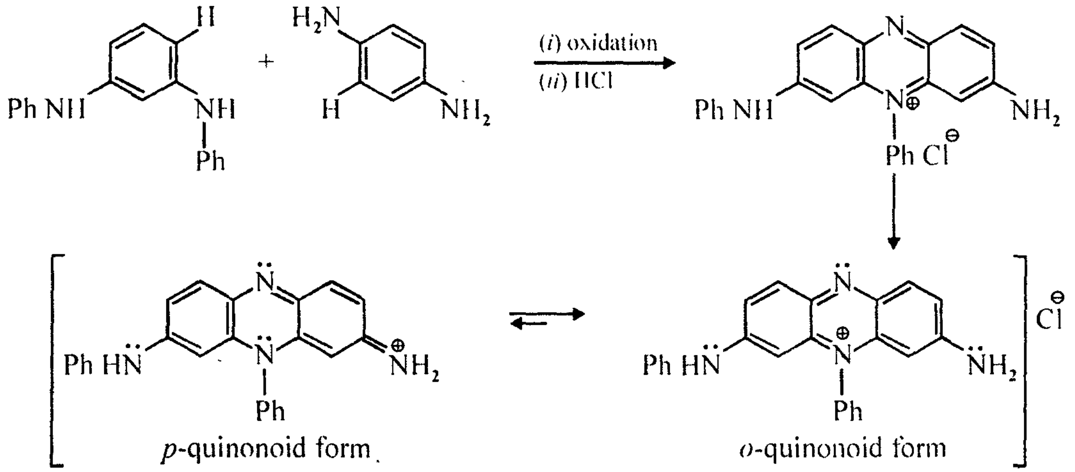
It is obtained by oxidation of impure aniline, *i.e.* aniline having *o*-toluidine and *p*-toluidine as impurities, with acidic dichromate solution (Perkin, 1856).



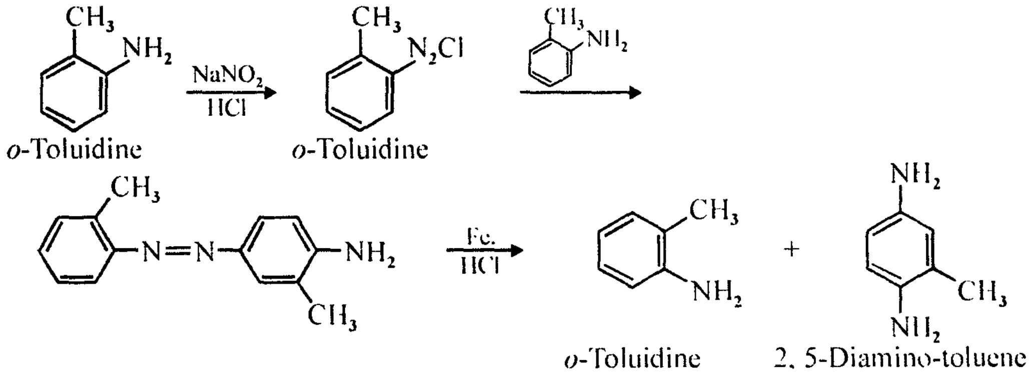
mauveine

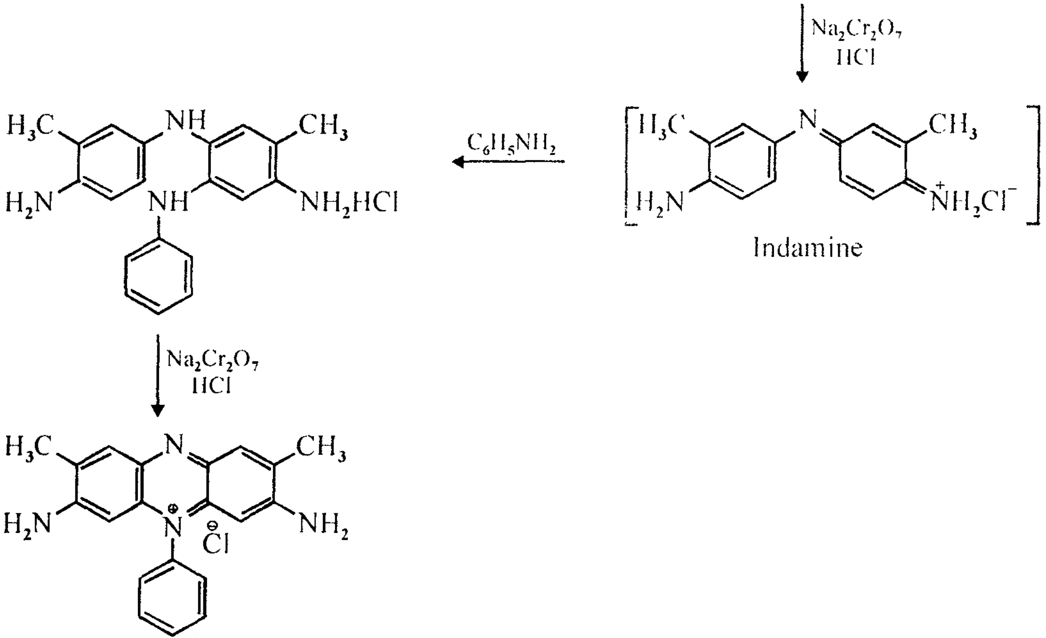
It is used to dye silk and tannin-mordanted cotton to reddish-violet colour.

Pseudo-mauveine can be synthesised by oxidising a mixture of N, N′-diphenyl-*m*-phenylenediamine and *p*-phenylenediamine with potassium dichromate in glacial acetic acid. The actual dye in its cationic form is separated by adding hydrochloric acid.



(***b***) **Safranine T** : It is obtained from *o*-toluidine which on diazotisation followed by coupling with another molecule of *o*-toluidine yields aminoazotoluene. This compound on reduction with iron and hydrochloric acid yields a mixture of *o*-toluidine and 2, 5-diaminotoluene. The mixture is next oxidised with sodium dichromate and hydrochloric acid. The indamine obtained is treated with aniline followed by oxidation to form the dye safranine T.

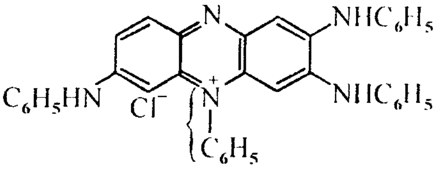




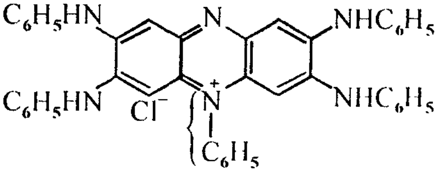
Satranine

It is used for dyeing tannin mordanted cotton, bast fibres, wool, silk, leather and paper. It has also various applications in textile printing. It gives a bright red but has poor fastness properties.

(*c*) **Indulines** : These are insoluble in water and are obtained by heating azo compounds, especially 4-aminoazobenzene, with aniline and aniline hydrochloride under pressure. The product is a mixture of azine bases of varying complexity, insoluble in water, but giving violet or blue solutions in ethanol. Examples of indulines are induline 3 B base and induline 6 B base.



induline 3B Base



induline 6B Base

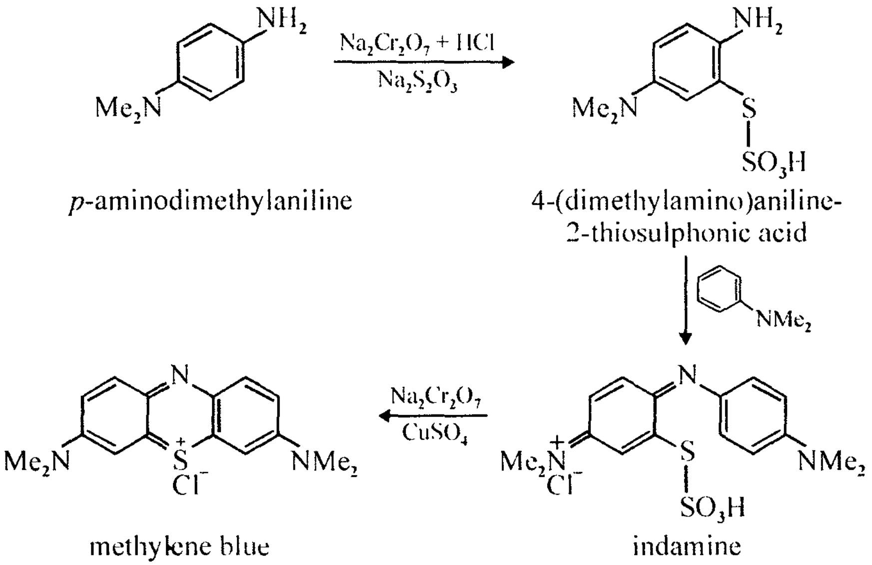
The dyes are used for colouring fats, printing inks, copying paper, typewriter ribbons and similar applications.

3. Thiazine Dyes

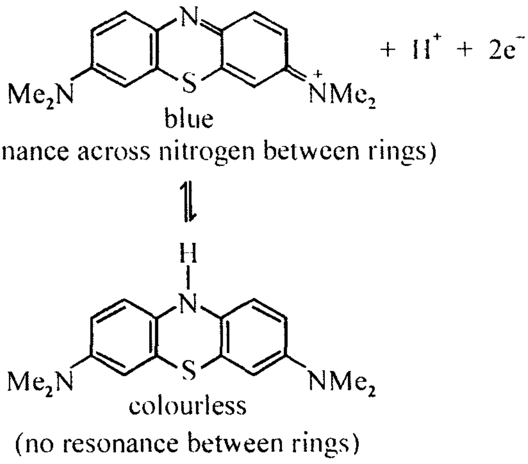
These dyes are analogues of the oxazines, an atom of sulphur replacing oxygen in the heterocyclic ring. These dyes have phenazonium nucleus as chromophore with amino groups para to the ring nitrogen as auxochromes. These dyes have a colour range from green to blue and have been used for colouring paper, tannin mordanted cotton and silk. Fastness to light is usually only fair.

Only five thiazine dyes are known to be still manufactured. The most important thiazine dye is methylene blue, discovered by Caro in 1876.

Methylene Blue : It is obtained by oxidising *p*-dimethylaniline with acid dichromate in the presence of sodium thiosulphate, followed by condensing the resulting 4-(dimethylamino) aniline-2-thiosulphonic acid with dimethyl aniline to form an indamine, and oxidising by dichromate and copper sulphate to yield methylene blue.



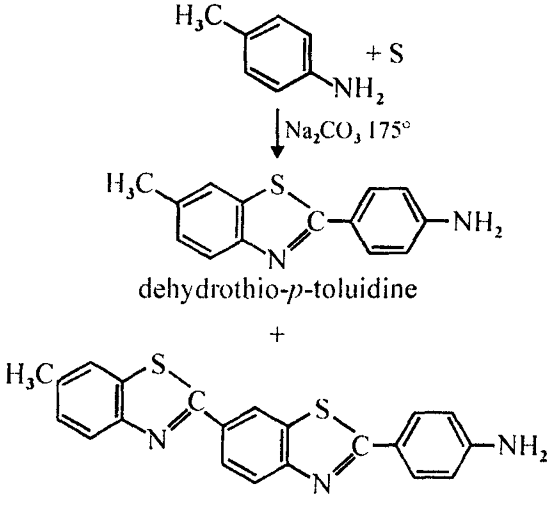
It is used in calico printing. It is used as an indicator and in medicine. Its zinc double chloride salt is used for dyeing tannin-mordanted cotton. The change in colour in methylene blue has been attributed to the following structural changes :



4. Thiazol Dyes

. This group of dyes has the thiazole ring system, the presence of this ring system, increases the substantivity for cellulosic fibres. The important examples of thiazole dyes are primuline and thioflavin T dyes obtained from dehydrothio-*p*-toluidine.

(*a*) Primuline : When *p*-toluidine is heated with sulphur, it leads to a mixture of primuline base and dehydrothio-*p*-toluidine. The latter is removed from the mixture solution by means of ethanol.

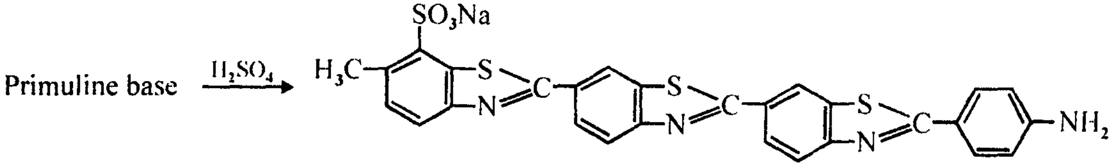


dehydrothio-*p*-toluidine

+

primuline base

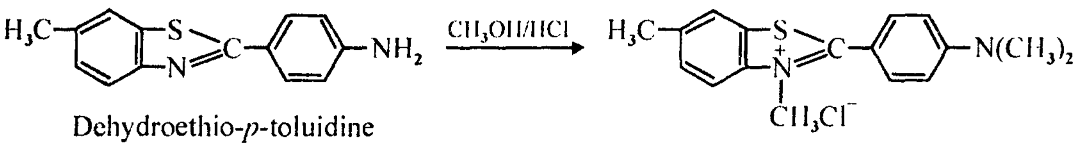
Primuline is made by sulphonating primuline base.



Primuline

This dye gives greenish yellow shades on cellulosic fibres but the direct shade is of no interest because of its low fastness properties. This dye may be diazotised on the fibre and coupled with 2-naphthol to a red shade. Similarly other shades are obtained with different coupling components.

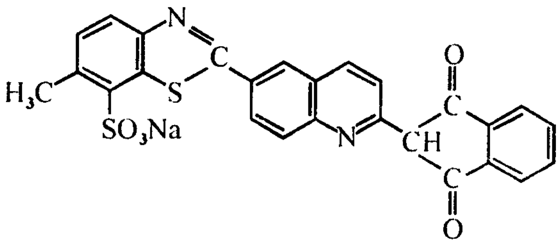
(*b*) Thioflavin T : Methylation of dehydrothio-*p*-toluidine (obtained as above) with methanol and hydrochloric acid gives thioflavin T.



Dehydroethio-*p*-toluidine

This dye is applied to cellulosic fibres but its fastness properties are poor.

(*c*) **Pontamine Brilliant Yellow 5 G :** It is obtained from dehydrothio-*p*-toluidine sulphonic acid by a reaction of the Skraup type with paraldehyde and condensation of the resulting quinaldine derivative with phthalic anhydride.



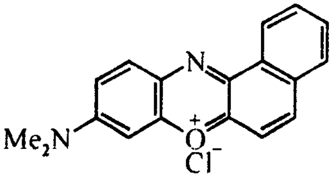
pontamine brilliant yellow 5 G

This dye is especially suitable for application to paper pulp and gives a good exhaustion over a wide pH range.

5. Oxazine Dyes

In these dyes the chromophore is the phenoxazonium group-while auxochromes are amino or hydroxy groups para to the ring nitrogen. These dyes range in shade from greenish to reddish blue. The various oxazine dyes are described as follows :

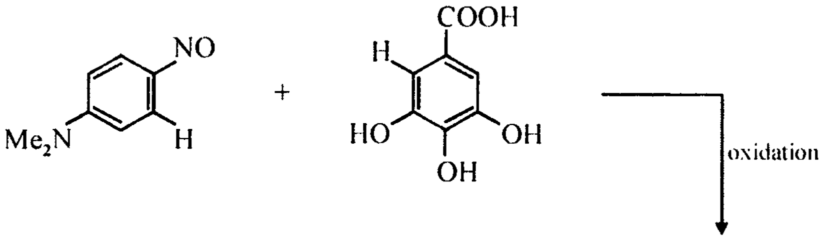
(*a*) **Meldola's Blue :** It was first oxazine dye which was prepared by Meldola in 1879. This dye is obtained by condensing *p*-nitrosodimethylaniline hydrochloride with β-naphthol in glacial acetic acid.

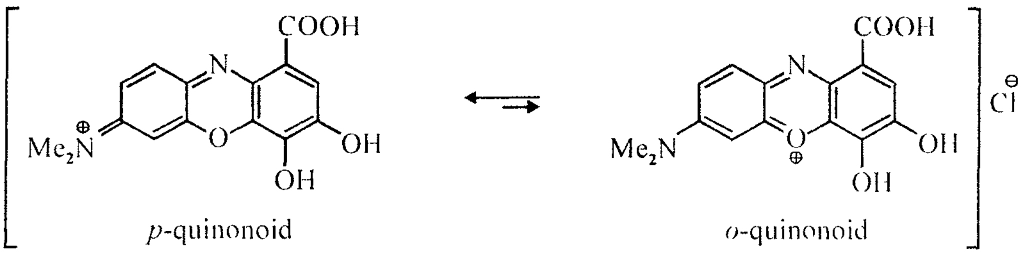


It is still manufactured on a considerable scale but the condensation is now usefully carried out in ethanol as solvent and the product is isolated as a zinc double chloride.

This dye is chiefly applied to leather.

(*b*) **Gallocyanine :** It was the first oxazine mordant dye which was discovered by Koechlin in 1881. It is obtained by condensation of *p*-nitrosodimethylaniline hydrochloride with gallic acid in methanol. It gives a bluish violet dye on a chromium mordant. Its quinonoid structures are as follows :





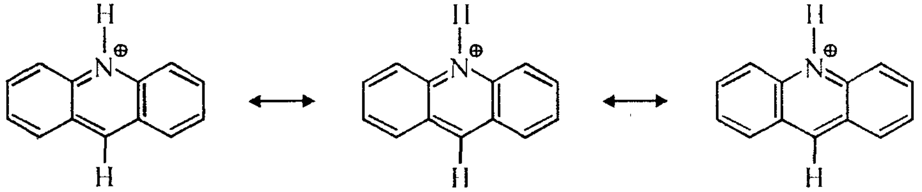
p-quinonoid

o-quinonoid

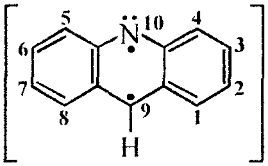
Gallocyanine

6. Acridine Dyes

These dyes are derivatives of the basic compound acridine. This structure provides the chromophore and an amino or alkylamino group is usually present in a *para* position with respect to the methane carbon atom. They are largely used on leather.



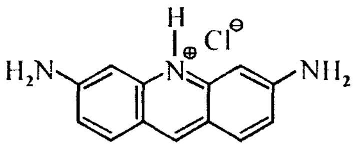
acridine nucleus



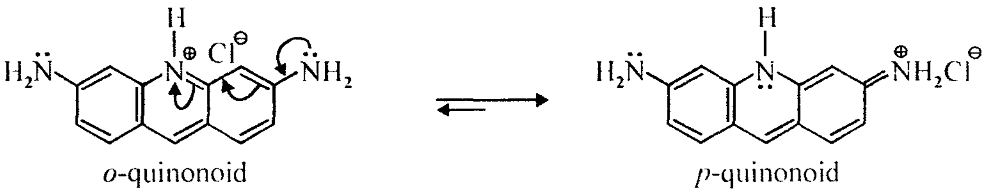
acridine as di-radical

Some important acridine dyes are described as follows :

(*a*) **3, 6-Diaminoacridine :** It is obtained by heating a mixture of *m*-phenylenediamine, glycerol, oxalic acid and zinc chloride and oxidising the leuco compound. It is the formaldehyde produced during heating which condenses with two molecules of *m*-phenylene diamine to get leuco-base.



3, 6-diaminoacridinium chloride
(yellow dye)

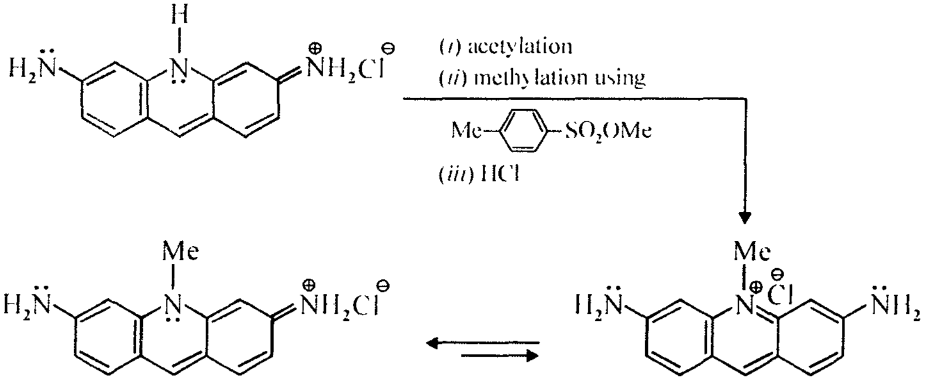


o-quinonoid

p-quinonoid

The corresponding sulphate is the antiseptic proflavin.

(*b*) Acriflavin : It is 3, 6-diamino-10-methyl-acridinium chloride. It is obtained by acetylating 3, 6-diaminoacridine, methylating the 10-N atom by means of methyl *p*-toluenesulphate and then hydrolysing the product with dilute hydrochloric acid.

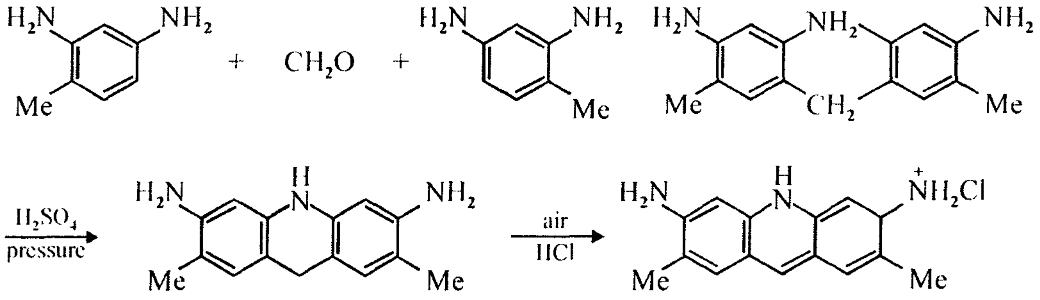


p-quinonoid *o*-quinonoid

Acriflavine (orange dye)

It possesses trypanocidal action, *i.e.*, it has the power to kill trypanosomes which are micro-organisms causing sleeping sickness and other diseases. It is also used as an antiseptic.

(*c*) Acridine Yellow G : It is one of the more important acridine dyes and is prepared from 2, 4-diaminotoluene and formaldehyde in the following manner :

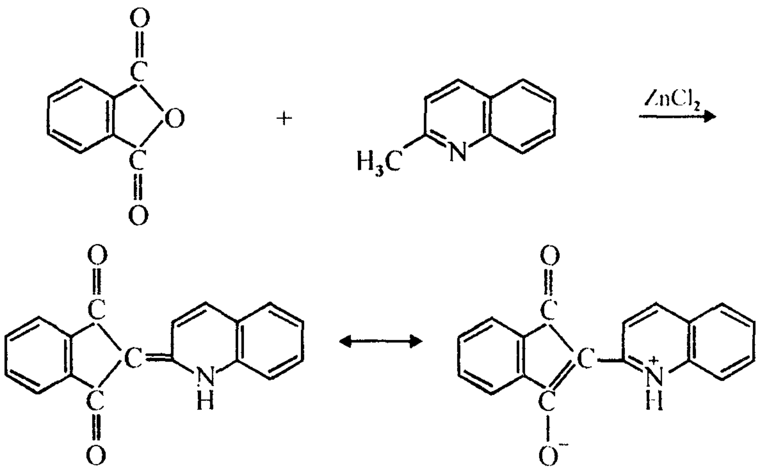


7. Quinoline Dyes

These dyes are characterised by the presence of quinoline nucleus in their structures. These are yellow, ranging from the reddish-yellow to the greenish-yellow. These are more important as photographic sensitisers due to their instability to light than as dyes for fibres.

One of the important quinoline dyes is described as follows :

Quinoline Yellow : It is prepared by the condensation of phthalic anhydride with quinaldine in the presence of zinc chloride.

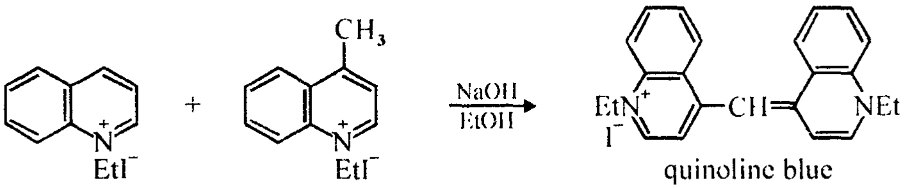


It is used as a dyestuff for fabrics.

8. Cyanine Dyes

These are the dyes in which the two quinoline nuclei are linked through the 4, 4′-positions by a = CH-group. The colour of the cyanine dyes is too fugitive. Therefore, these dyes are not used as dyes but used as photographic sensitisers because these make the photographic plates sensitive to yellow, orange, red or green region of the spectrum.

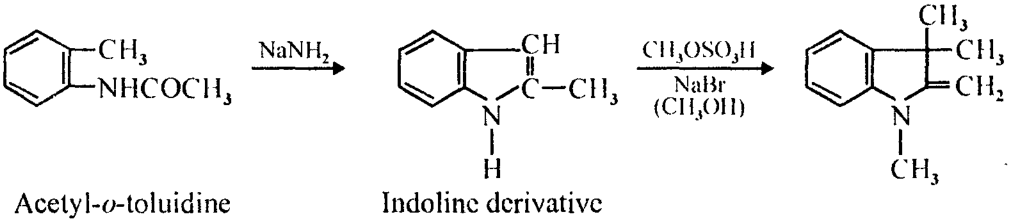
One of the most important cyanine dyes is **cyanine** or **quinoline blue.** It is prepared by heating a mixture of 1-ethylquinolinium iodide and 1-ethyl-4-methylquinolinium iodide in ethanolic sodium hydroxide solution.

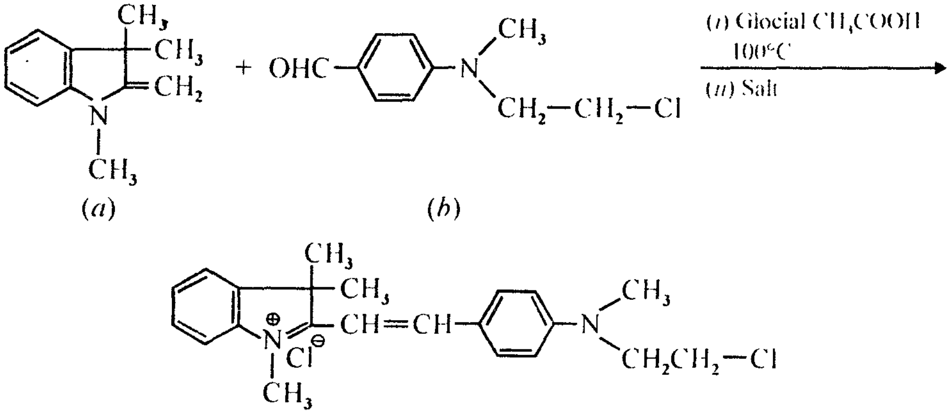


Other examples of cyanine does are a follows :

(*a*) **Astrazone Pink FG :** It belongs to polymethine or cyanine group of dyes because it contains methine (–CH=) linkages as part of their chromophoric system.

It is obtained by condensing 1, 3, 3-trimethyl-2-methylene indoline (Fischer's base) with *p*-[-2-chloroethyl) methyl amino] benzaldehyde (*b*) followed by treatment with hydrochloric acid. 1, 3, 3-trimethyl-2-methylene indoline (*a*) is obtained from acetyl derivative of *o*-toluidine.

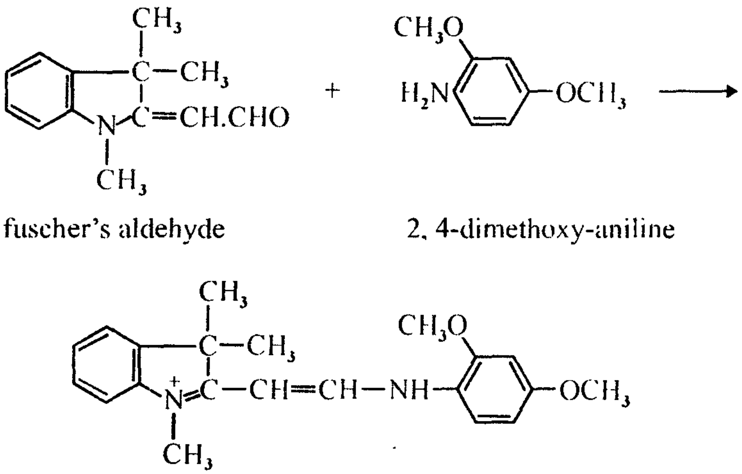




Astrazon pink FG

It is a bright, moderately fast, water soluble printing colour for cellulose acetate fibre. It is used as a basic (cationic) dye for polyacrylonitrile fibres (*i.e.*, orlon).

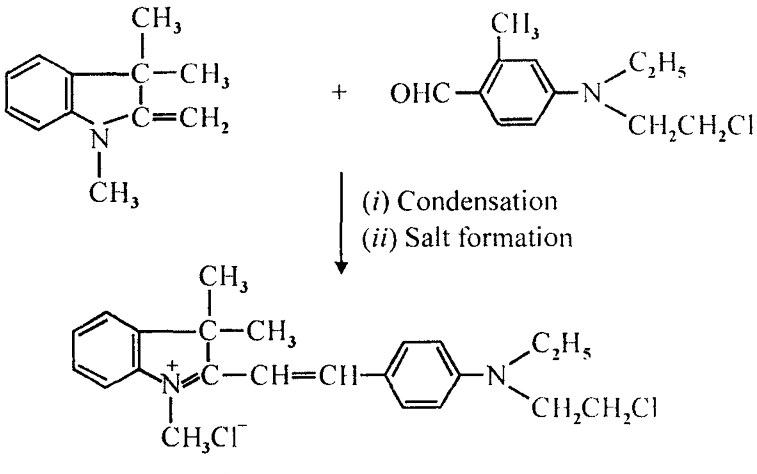
(b) Astrazone Yellow 3G : It is made by condensing 1, 3, 3-trimethylindolenine-w-aldehyde, *i.e.*, Fisher's aldehyde, with 2, 4-dimethoxyaniline, the product being converted into a salt (chloride).



astrazone yellow 3G

It is of very good fastness to wet treatment and has a light fastness on acetate of 4-5 and polyacrylonitrile of 6.

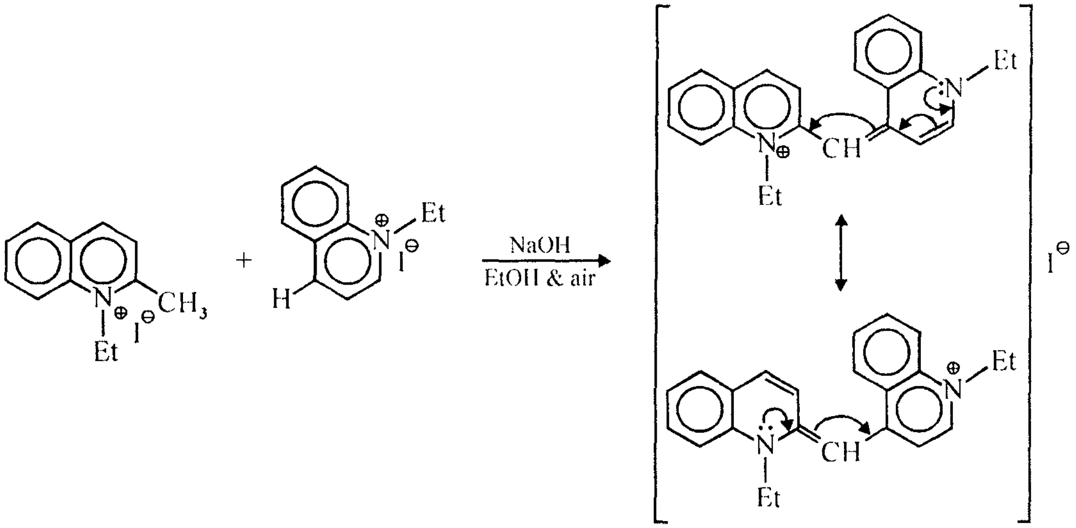
(c) Astrazone Red 6B : It is obtained by condensing 4-(N-β-chloroethyl-N-ethylamino)-2-methylbenzaldehyde with 1, 3, 3-trimethyl-2-methyleneindoline.



This dye has good general fastness but only moderate light fastnesses acetate (4) and polyacrylonitrile (4).

9. Isocyanine Dyes

In these dyes, the two quinoline nuclei are linked in the 2, $4'$-positions by a =CH–group. An important example of these dyes is ethyl red which is prepared by heating a mixture of quinoline and quinaldine ethiodides in ethanolic sodium hydroxide solution.

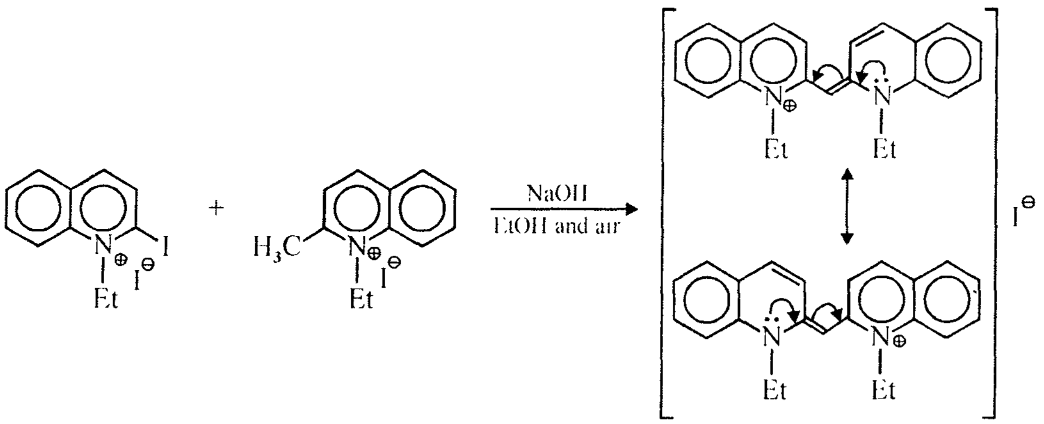


Ethyl Red

It sensitises the photographic plate from orange to ultraviolet region of the spectrum.

10. Pseudocyanine Dyes

When the two quinoline nuclei are linked in the 2, $2'$-positions by a = CH-group, pseudocyanine dyes are formed. These are obtained by heating a mixture of corresponding 2-iodoquinoline alkyl iodide and a quinaldine alkyl iodide in ethanolic potassium hydroxide solution.

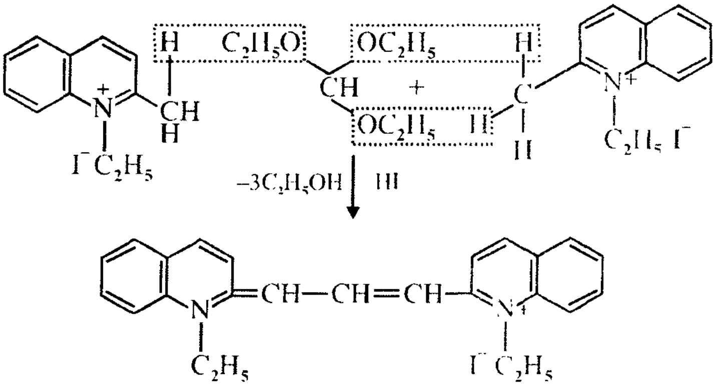


a pseudocyanine

These dyes sensitise the plates for the blue to green parts of the spectrum.

11. Carbocyanines

In these dyes, the two quinoline nuclei are linked in the 2, 2′-positions by a = CH–CH = CH–group. An important example of carbo cyanines is *sensitol red* or *pinacyanole*. Pinacyanole is obtained by heating a mixture of quinaldine ethiodide and ethyl orthoformate in pyridine.

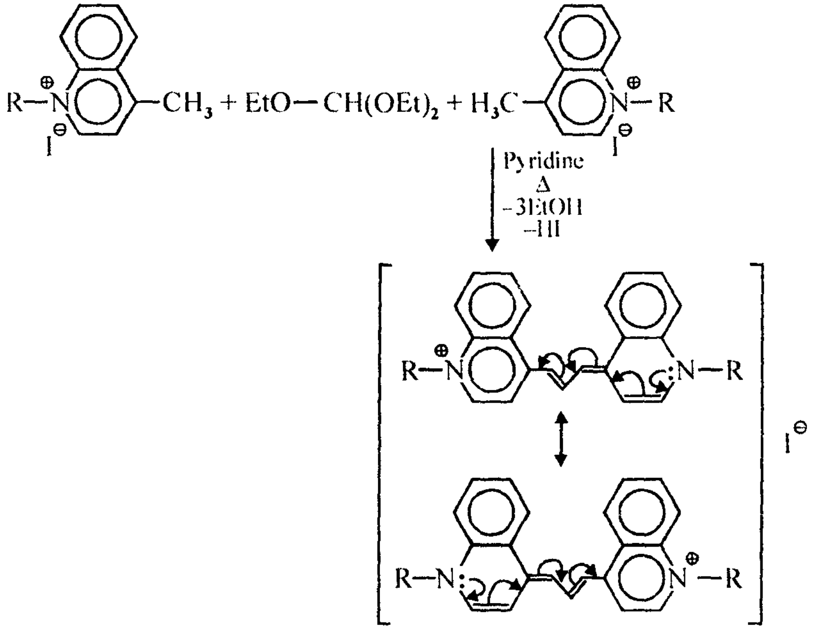


Sensitol red or Pinacyanola

Sensitol red sensitises the photographic plates from red to range region of the spectrum.

12. Krptocyanines or 4, 4′-trimethincyanines

They are prepared on the same lines as other carbocyanines, but here 1-alkyl lepidinium iodide is heated with ethyl orthoformate instead of 1-alkylquinaldinium iodide in pyridine.



a kryptocyanine

Krptocyanines sensitise the photographic plates, usually filmed by emulsions of silver chloride and bromide, to infra-red radiations.

16

CHAPTER

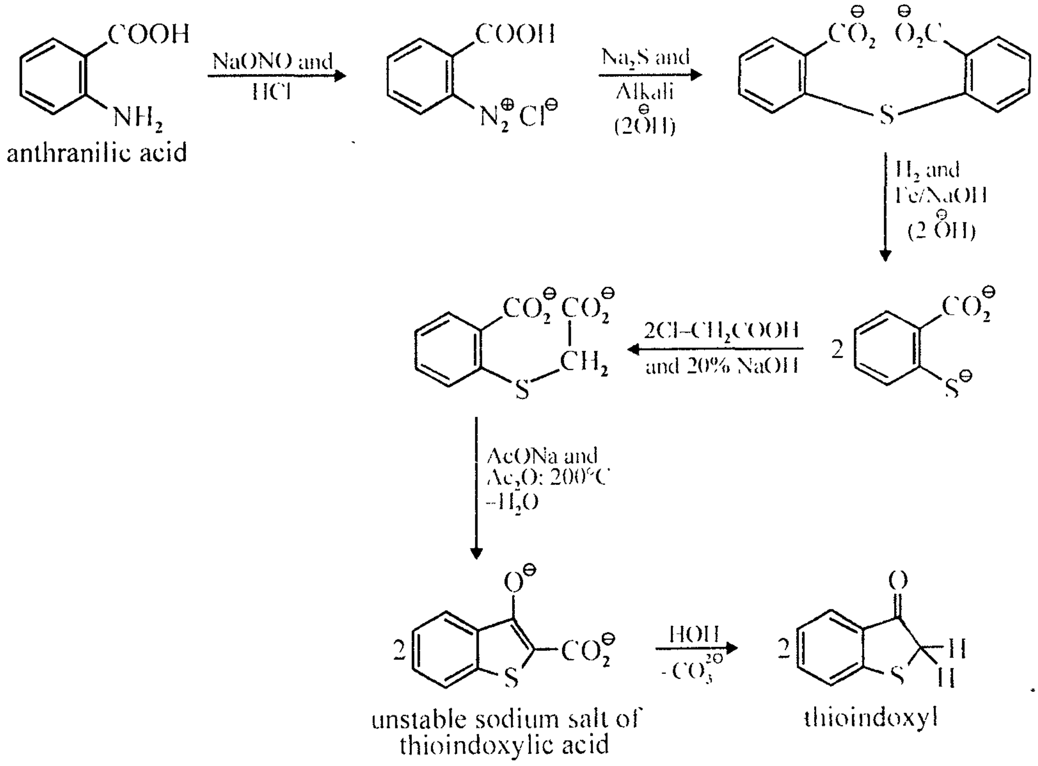
THIOINDIGOS AND INDIGOS

16.1. Thioindigoids

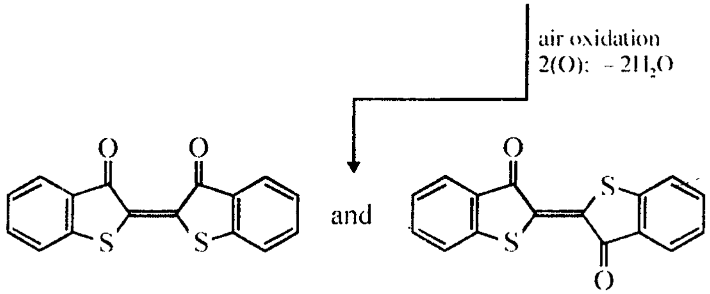
When one or both the NH groups of the indigo are replaced by sulphur atoms, the unsymmetrical and symmetrical thioindigos are obtained. These dyes produce brighter and faster shades to the fabrics. Some important thioindigos are described as follows :

(*a*) **Thioindigo :** It is obtained from anthranilic acid in the following manner :

Diazotised anthranilic acid is reacted with sodium bisulphide when 2, 2′-dithiodibenzoic acid is formed. This acid is reduced to *o*-mercaptobenzoic acid and then condensed with monochloroacetic acid when *o*-(carboxy-methyl-mercapto) benzoic acid is formed. This on heating with sodium hydroxide yields thioidoxyl (3 (2H)-thionaphthenone) which on oxidation yields thioindigo.



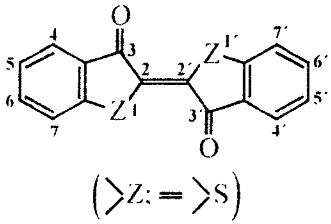
(16.1)



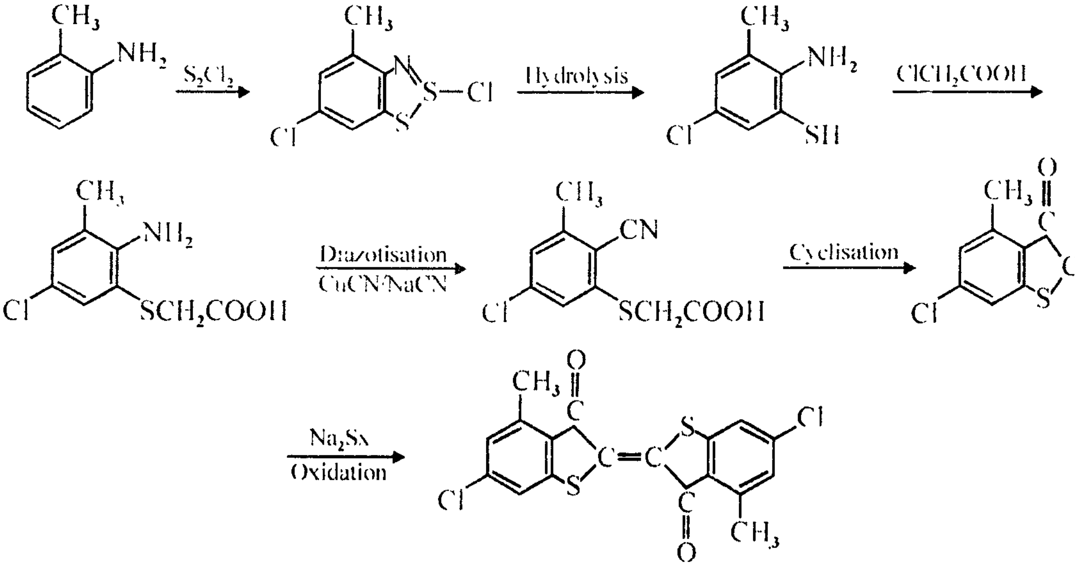
cis-Thioindigo
(minor)

trans-Thioindigo
(bluish red)

Unlike indigotin, it exists in solution in both the *cis*-and *trans*-forms because hydrogen bonding is very weak in sulphur compounds. It possesses a bluish red shade and is faster than indigo. Its 5. 5′-dibromo derivative gives brighter and faster shade.

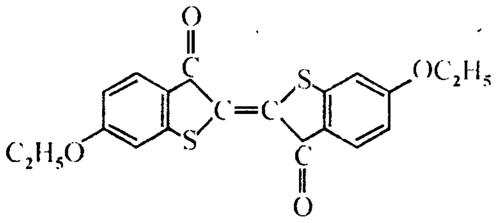


(*b*) **Indanthrene brilliant pink R** (***C.I. vat red 1, 73360***) : It is prepared from *o*-toluidine in the following manner :



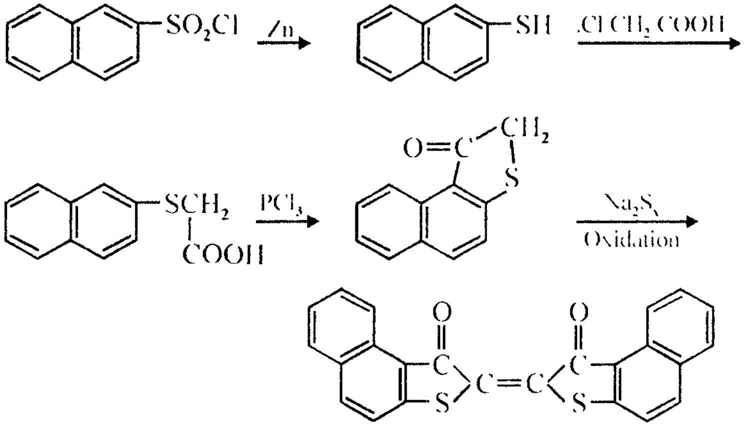
indanthrene brilliant pink R

(*c*) **Algol orange RF** (***C.I. vat orange 5, 73335***) : Like indanthrene brilliant pink, it may be prepared in a similar manner from *p*-phenetidine.



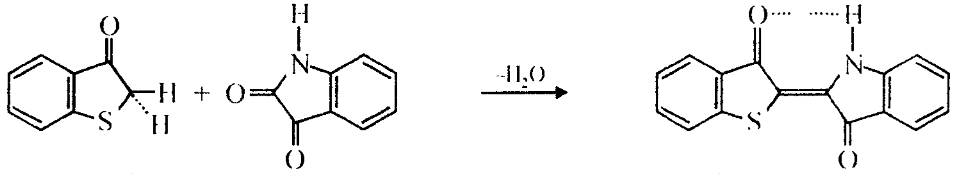
algol orange RF

(*d*) **Indanthrene brown RRD (*C.I. vat brown 5, 73410*)** : It is prepared in the following manner :



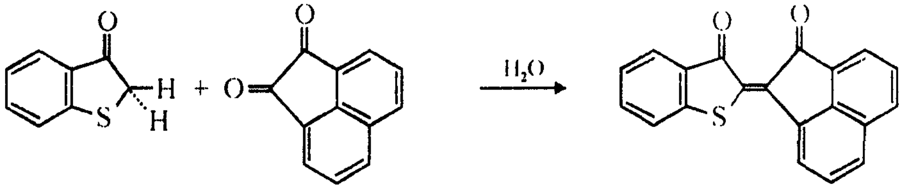
Indanthrene Brown RRD

(*e*) **Thioindigo scarlet R** : It is prepared by fusing together thioindoxyl and isatin.



thioindoxyl isatin Thioindigo Scarlet R

(*f*) **Ciba scarlet G (*C.I. vat red 45, 73860*)** : It is prepared by condensing thioindoxyl with acenaphthaquinone.

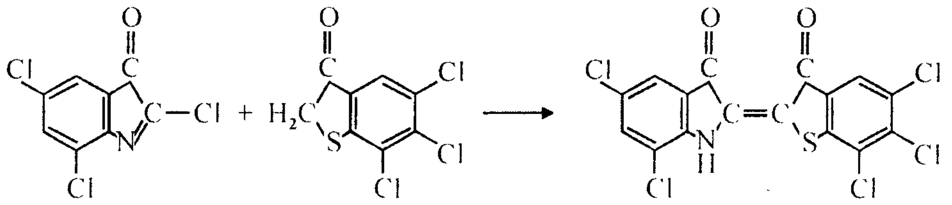


thioindoxyl acenaphthaquinone Ciba Scarlet G

Thioindigo vat dyes are applied to the animal or vegetable fibres in the same manner as indigo.

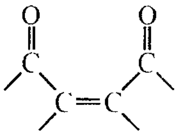
It is a fast dye useful for cotton. wool and silk. It gives very clear and bright scarlet shade.

(*g*) **Indanthrene printing violet BBF (*C.I. vat violet 5, 73545*)** : It is prepared by condensing 5, 7-dichloroisatin chloride with 5, 6, 7-trichlorothioindoxyl in chlorobenzene.

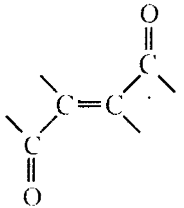


16.2. Indigoids

These dyes have the following structural parts as chromophores. They are also vat dyes and mostly used for cotton fibres.



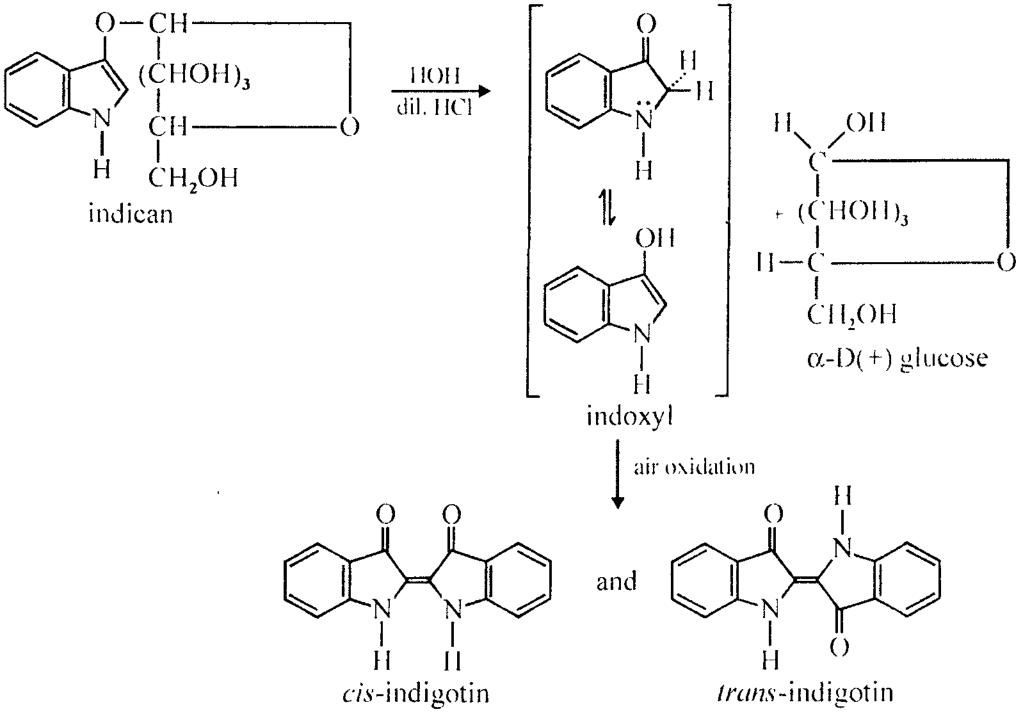
cis-carbonyls



trans-carbonyls

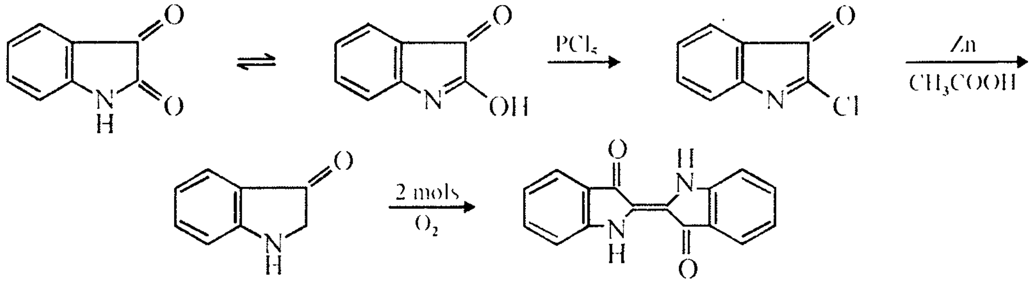
(*a*) **Indigo** : It is the oldest known dye. It occurs in the plants of *indigofera* group in the form of glucoside-the *indican*.

Indigo (or Indigotin) is the oldest and the most common indigoids. It was originally obtained from the plants of indigofera species, which were abundantly found in India. The indigofera plants contain indican, which on hydrolysis, produces indoxyl. Indoxyl, on air oxidation, gives Indigo.



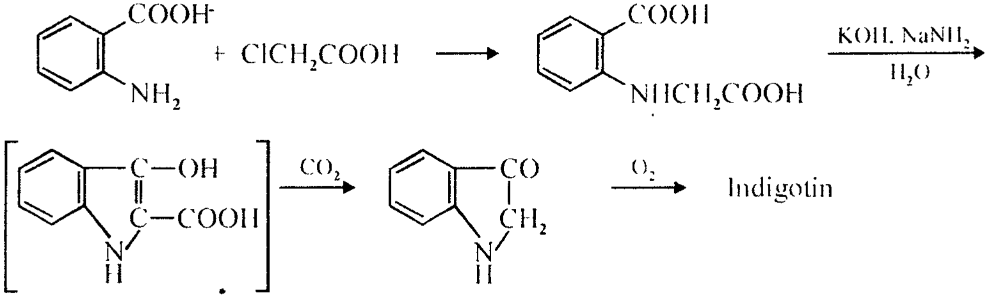
Indigo is also known as *Indigotin*. It is prepared by the following methods :

(*i*) Reduction of isatin chloride (obtained by the action of phosphorus pentachloride on isatin) with zinc dust in glacial acetic acid yields indoxyl which upon oxidation in air gives indigotin.



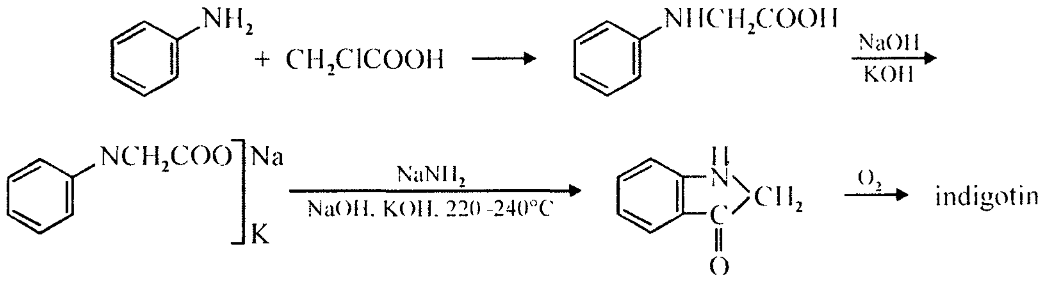
Indoxyl Indigotin

(*ii*) It is also synthesised from anthranilic acid. When this acid is made to react with chloroacetic acid, it yields the phenyl-glycine-*o*-carboxylic acid which undergoes ring closure and decarboxylation to indoxyl on fusion with a mixture of potassium hydroxide and sodamide. Atmospheric oxidation of indoxyl yields indigotin.

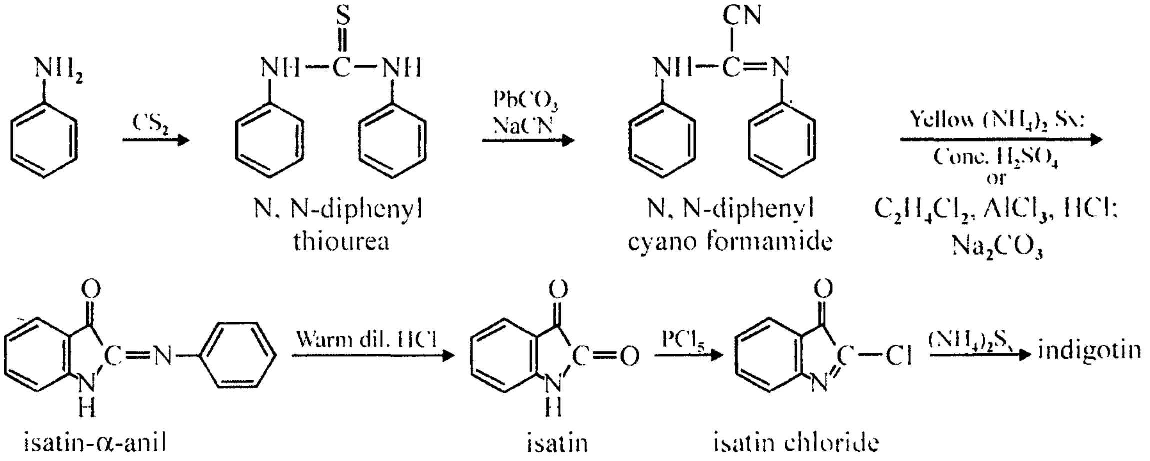


indoxylic acid indoxyl

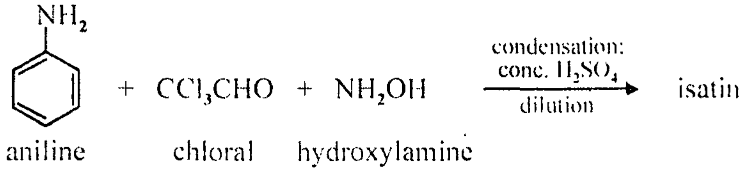
(*iii*) Another synthesis is from aniline. When aniline is heated with chloroacetic acid, it forms phenylglycine which upon treatment with sodium and potassium hydroxide is converted to a mixture of its sodium and potassium salts. Fusion of these salts with sodamide and a mixture of sodium and potassium hydroxide gives indoxyl which yields indigotin upon atmospheric oxidation.



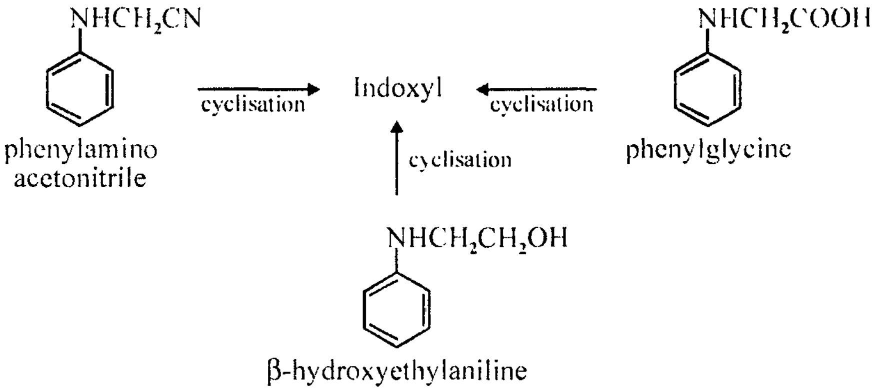
(*iv*) *Sandmeyer's Process* : In this process aniline is condensed with carbon disulphide to obtain thiocarbanilide (N, N-diphenylthiourea), which is heated with sodium cyanide and lead carbonate to yield N, N-diphenylcyanoformamide. This intermediate is converted to isatin-α-anil either by the treatment with yellow ammonium sulphide and then with concentrated sulphuric acid or by following Hoechst method which is using aluminium chloride, gaseous hydrochloric acid and a solvent such as ethylene dichloride and then hydrolysing with aqueous sodium carbonate solution. Isatin-α-anil thus formed gets hydrolysed with warm dilute hydrochloric acid to isatin. Isatin is converted to 2-chloro derivative isatin chloride by treating with phosphorus pentachloride and finally isatin chloride by treating with ammonium sulphide gives indigo.



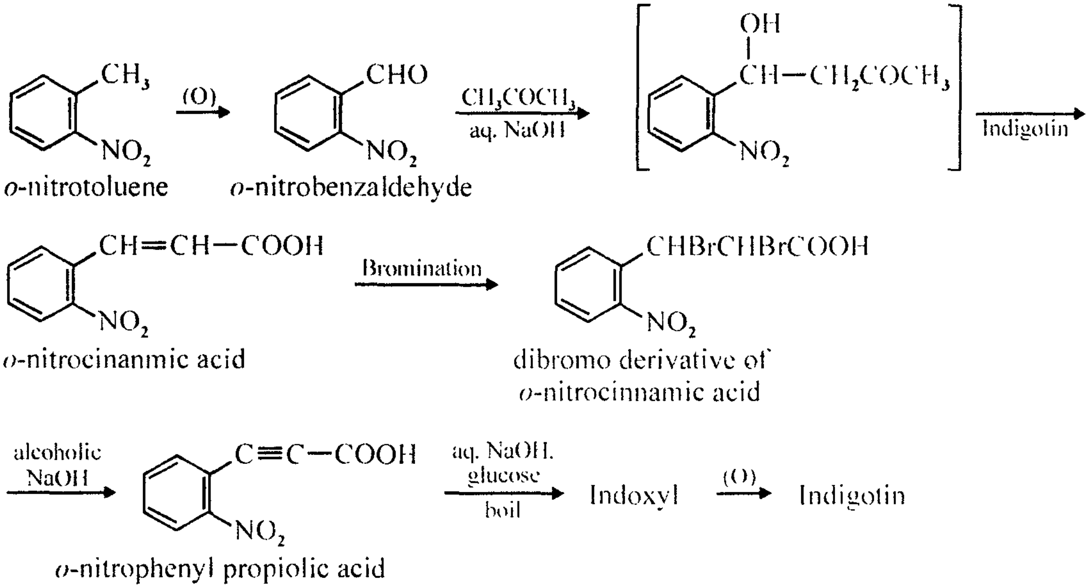
Isatin needed for indigo synthesis is also prepared from aniline by the condensation with chloral and hydroxylamine, subsequent dehydration with concentrated sulphuric acid and dilution.



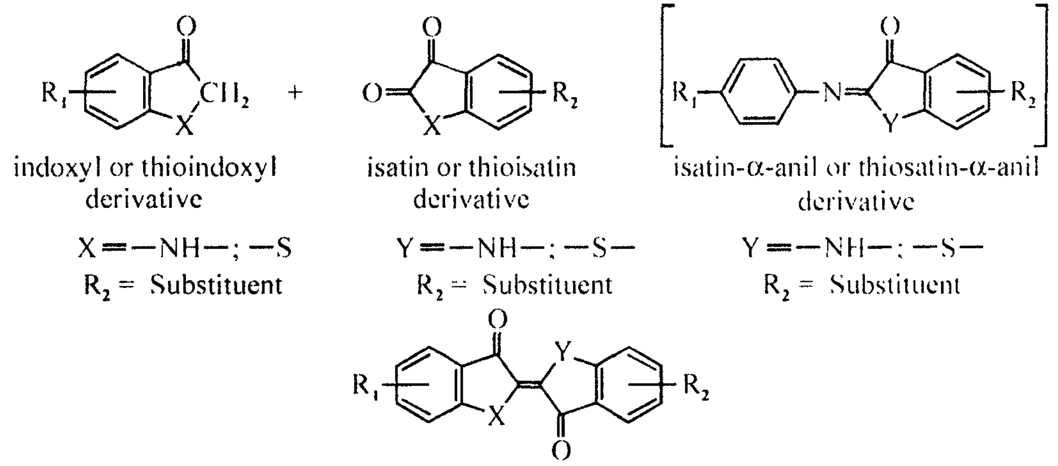
Other routes for indoxyl have been to cyclise phenylaminoacetonitrile as well as to cyclise phenylglycine or β-hydroxyethylaniline.



(v) Bayer synthesised indigo from *o*-nitrobenzaldehyde and *o*-nitrocinnamic acid. Thus, *o*-nitrobenzaldehyde obtained by the controlled oxidation of orthonitrotoluene is condensed with acetone in the presence of aqueous alkali to yield indigo. *o*-Nitrocinnamic acid is brominated to the dibromo derivative which on treatment with alcoholic potassium hydroxide yields acetylene derivative, *o*-nitrophenylpropiolic acid. This intermediate on treatment with aqueous sodium hydroxide and glucose at boil yields indoxyl which is oxidised to indigo.



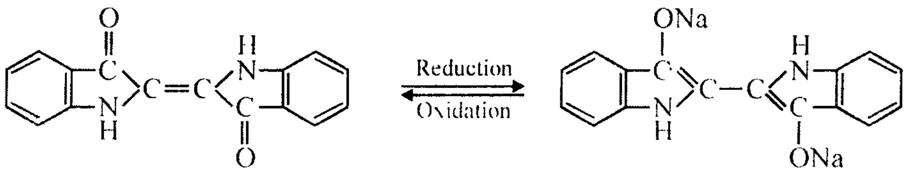
Among the general methods followed in the preparation of indigoid vat dyes, the methods involving the condensation of indoxyl derivative (or the corresponding thioindoxyl derivative) with either isatin derivative (or corresponding sulphur analogue) or isatin-α-anil derivative (or corresponding sulphur analogue) are important to obtain 2, 2′-bis-indigos.



2, 2′-bis-indigo

X = —NH—; —S —Y = —NH—; —S—; R₁. R₂ = substituents.

Indigotion is a dark blue coloured powder. It is insoluble in water. It may be reduced with alkaline sodium hyposulphite to a colourless form the indigotin-white, which is soluble in alkali. It is the alkaline solution which is applied to the fibre and then the fibre is exposed to air when the original blue colour of indigotin is regenerated in the cloth.

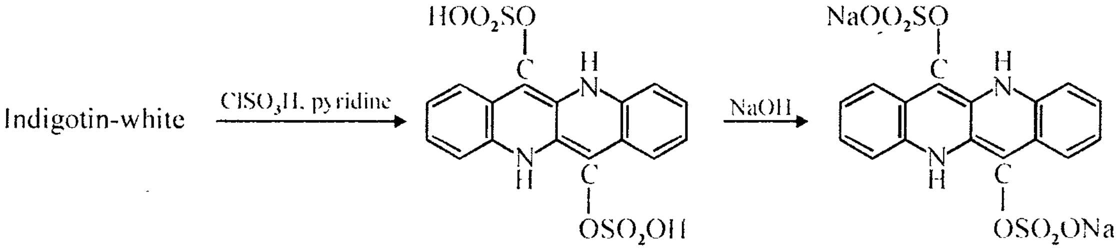


indigotin

indigotin-white (colourless)

(*b*) **Indigosol O (*C.I. solubilised blue 1,73002*)** : Indigotin-white is not stable. Therefore in ordinary dyeing, indigotin-white is first converted to its disulphonic ester (I) by treatment with chloro-sulphonic acid in the presence of pyridine. The alkaline solution of ester (I) is called the indigosol O (*II*).

When the indigosol O is applied to the fibre and is then subjected to oxidation with sodium nitrite in acid solution, the original blue dye is regenerated.

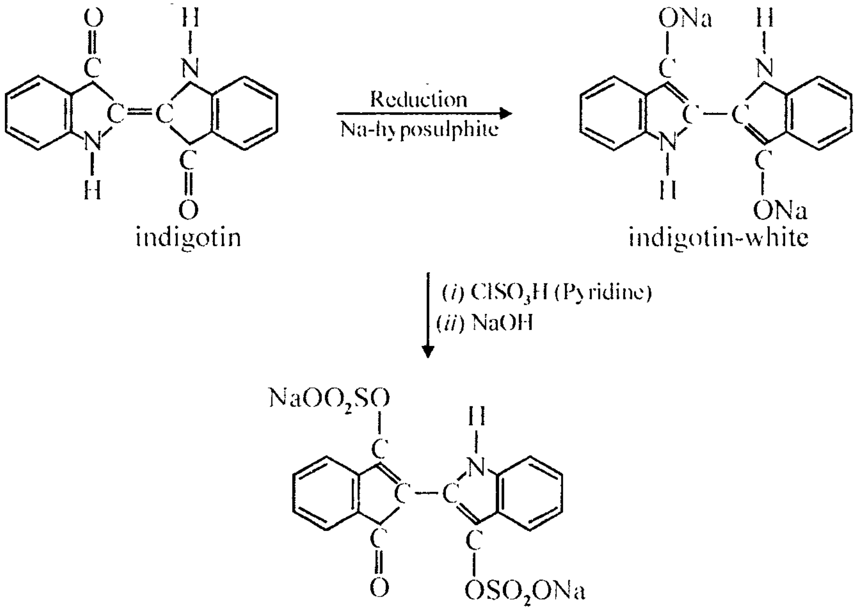


(I)

(II)

indigosol O

The above representation may be represented as follows :

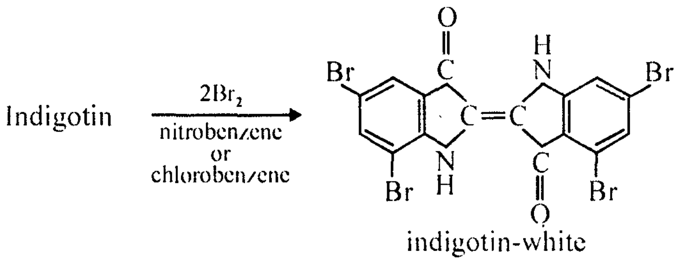


indigotin

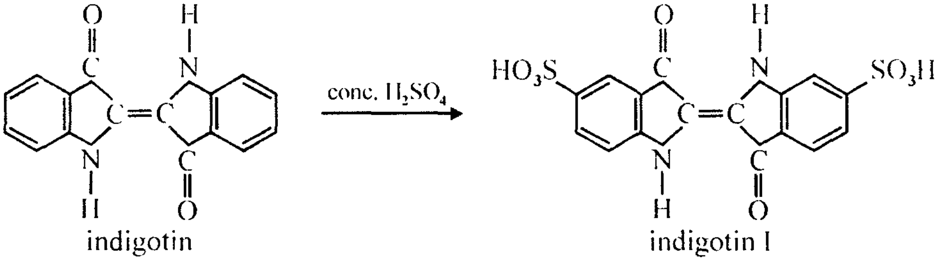
indigotin-white

indigosol O

(*c*) **Tetrabromoindigo ciba blue 2B (*C.I. vat blue 5, 73065*)** : It is obtained by bromination of indigotin in nitrobenzene or dichlorobenzene.



(*d*) **Indigotine I** (***Indigo carmine***) : It is obtained by sulphonation of indigo with concentrated sulphuric acid or oleum.



17

CHAPTER

ANTHRAQUINONE DYES

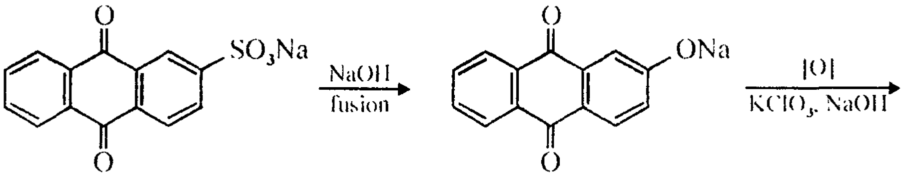
17.1. Introduction

Anthraquinone, the basic system of these dyes, has a faintly yellow colour, the edge of its long wave extends into the visible spectrum (λ_{max} 327 nm). It is not itself a dye. The introduction of relatively simple electron donors gives anthraquinone compounds which, according to the strength of the electron donors (OH < NH_2 < NR_2 < NHAr), absorb in any desired region of the visible spectrum. The position of the substituents in anthraquinone not only influences the absorption maximum but also some of the other properties. For example, anthraquinone derivatives that have hydroxyl or amino groups in the β-position generally exhibit better resistance to sublimation, better solubility and better affinity for textile substrates than α-substituted compounds.

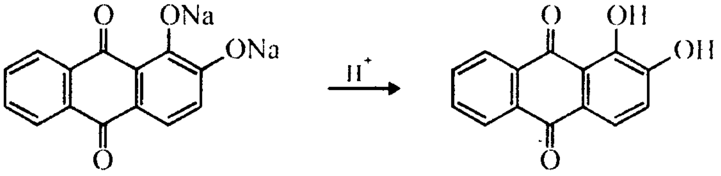
Dyes based on anthraquinone and related polycyclic aromatic quinones are of great importance. Many of the most light-fast acid, mordant, disperse, and vat dyes are of this kind. The chromophore is the quinonoid group > C = O.

(*a*) **Anthraquinone Mordant Dyes :** These contain groups such as hydroxyl or amino group, which can combine with metal ions so as to from insoluble compounds called *lakes*. The colour of the lake depends upon the mordant, *i.e.*, the metal used. Some of the important anthraquinone mordant dyes are as follows :

(*i*) ***Alizarin :*** It is 1, 2-dihydroxyanthraquinone. It is also known as mordant red 11. Previously it was obtained from the roots of the madder plant now-a-days it is obtained by heating, under pressure, *silver salt* (sodium anthraquinone-2-sulphonate, so called because of its silvery crystals), caustic soda, potassium chlorate and water in a steel autoclave at about 180°C. The resulting melt is blown into water and acidified to decompose the sodium alizarate, the precipitated alizarin is filtered, washed and used as a 20 per cent paste.



sodium anthraquinone-2-sulphonate
(silver salt)



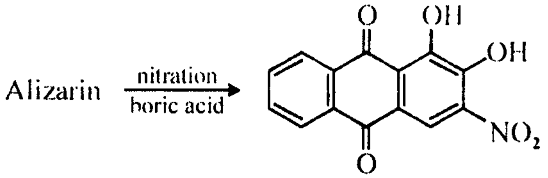
sodium alizarate alizarin

Alizarin is a red crystalline solid insoluble in water but soluble in alcohol and alkali. It is a mordant dye and combines with mordants, *i.e.*, metallic hydroxides, to form coloured insoluble compounds called *lakes*. The colour of the lake depends upon the mordant, *i.e.*, cation used. The colours of the lakes along with the respective mordants are given as follows :

Mordant used	*Colour of the lake*
Ca^{2+}, Ba^{2+}, Pb^{2+}	Bluish-red
Sr^{2+}	Red violet
Mg^{2+}, Sn^{4+}	Violet
Al^{3+}	Red
Cr^{3+}	Brownish-red
Fe^{2+}	Violet
Fe^{3+}	Brown black
Sn^{2+}	Red

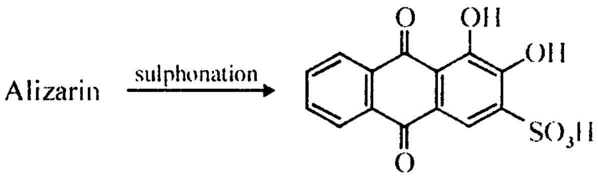
When alizarin is applied to wool with an aluminium mordant, it gives the well known turkey red. Alizarin, when converted to its calcium salt, forms a bluish-red powder useful as a pigment.

(*ii*) ***Alizarin Orange*** : It is obtained by nitrating alizarin in the presence of boric acid.



alizarin orange

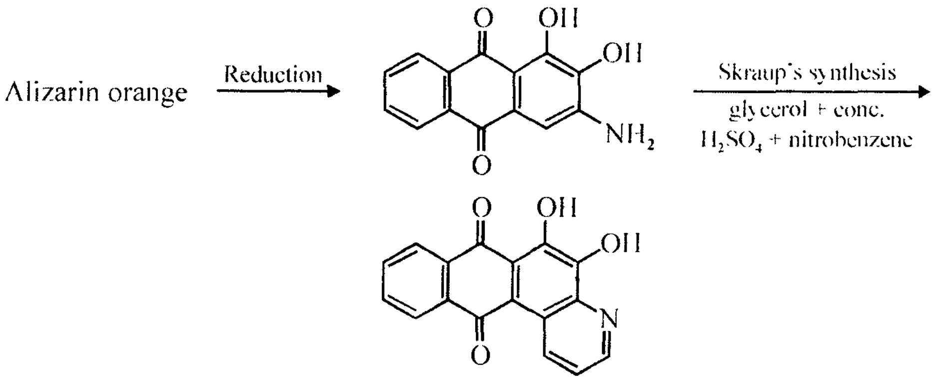
(*iii*) ***Alizarin Red S*** : *It* is obtained by the sulphonation of alizarin with fuming sulphuric acid.



alizarin red S

It is used for dyeing wool.

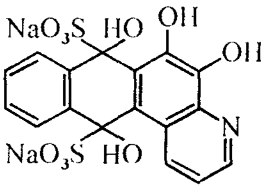
(*iv*) ***Alizarin Blue*** : It is obtained by reducing alizarin orange to 3-aminoalizarin followed by Skraup's synthesis of quinoline, *i.e.*, by heating with glycerol, conc. H_2SO_4 and nitrobenzene.



alizarin blue

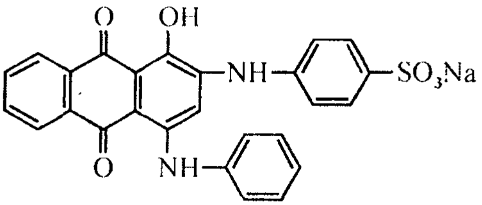
Alizarin blue dyes wool a blue colour when mordanted with chromium.

(*v*) ***Alizarin Blue S :*** It is the sodium bisulphite salt of alizarin blue. It is soluble in water. It when mordanted with chromium gives a reddish-blue lake.



alizarin blue S

(*vi*) ***Mordant Black 13 :*** It is made by condensing aniline with 1, 2, 4-trihydroxyanthraquinone and sulphonating the resulting base.

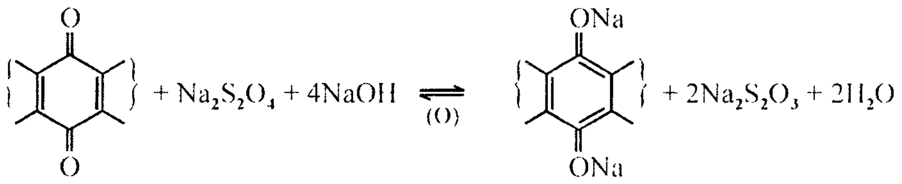


mordant black B

It is applied to wool with a chromium mordant and is quite fast to light and washing.

(*b*) **Anthraquinone Vat Dyes** : Most of the best vat dyes are derivatives of anthraquinone or related compounds. These essentially contain groupings such as $-CO-CH = CH-CO-$present as a quinonoid ring system or $-CO(CH = CH)_n\ CO-$where *n* is a suitable integral and $-(CH = CH)_n-$part is involved either through the fused heterocyclic or through the polycyclic systems. These have a high molecular weight and are insoluble in water. These are not volatile and are available in various brilliant colours and shades of exceptional fastness. These are mainly used for dyeing cotton, wool, nylon, silk, for calico-printing, etc. These are also used for colouring pulp, cements, photographic prints, etc.

In order to apply anthraquinone vat dyes to the fabrics, these are first of all converted into soluble form by treating them with a reducing agent (sodium hyposulphite) in alkaline medium. Then the cloth is immersed in the vat soluble dye solution, kept there for sometime and finally exposed to air. Oxygen of the air oxidises the alkaline solution on the cloth so as to produce the dyeing effect on the cloth. In some cases, the colour attained by the cloth is different from the colour of the vat.



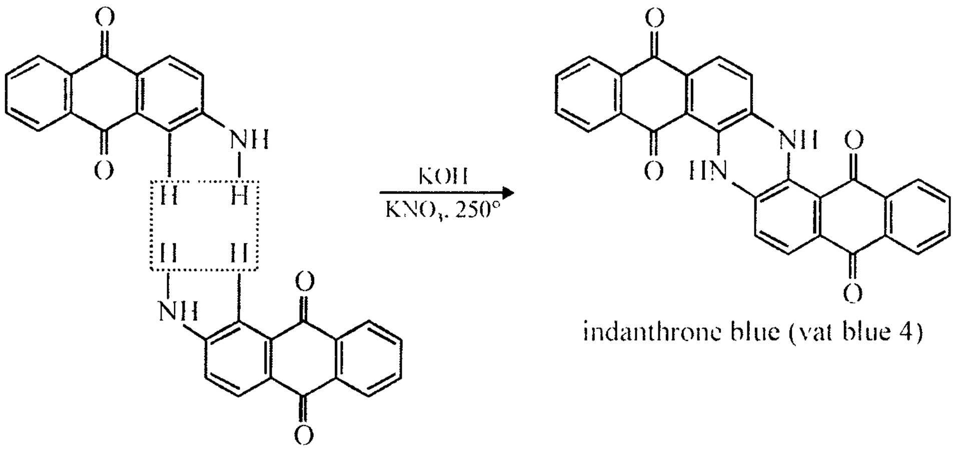
anthraquinone vat dye (insoluble)

sodium salt of an anthraquinol (soluble)

In 1924, Scottish Dyes Ltd. (now I.C.I. Ltd.) prepared stable solubilised anthraquinone vat dyes (*Soledon dyes*) by another method. In this method, the vat dye solution in pyridine is treated with chlorosulphonic acid in the presence of a metallic catalyst such as iron or copper when the pyridinium complex of the reduced form is obtained. This is then converted into the sodium salt of the half-sulphate ester of the leuco-vat dye. The soledone dyes are used in the dyeing and printing of cotton and viscose yarn.

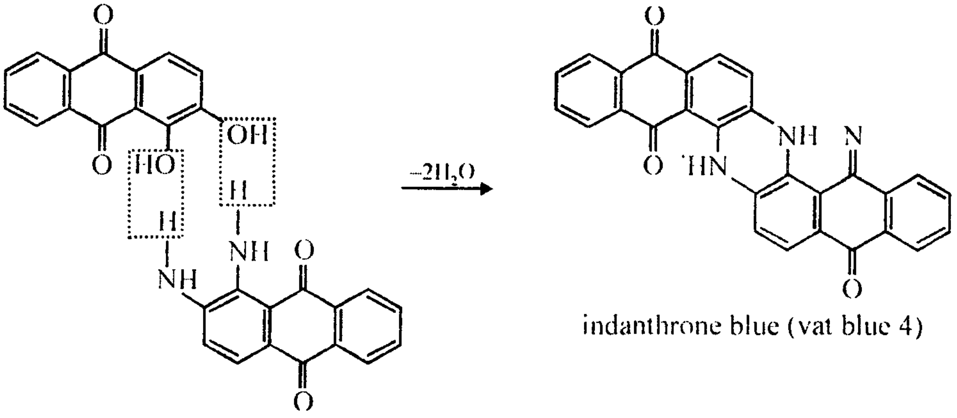
The important anthraquinone vat dyes are :

(*i*) ***Indanthrone Blue (Indanthrone, Indanthrene or Vat Blue 4)*** : It is manufactured by fusing 2-aminoanthraquinone with potassium hydroxide in the presence of potassium chlorate or potassium nitrate at 250°C.



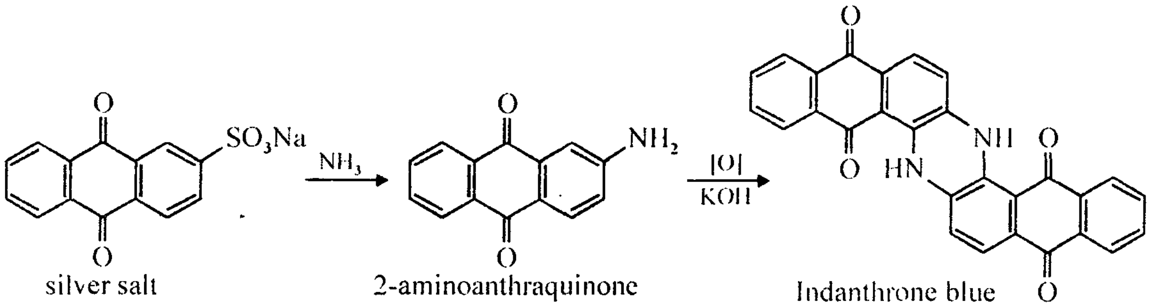
indanthrone blue (vat blue 4)

It may also be manufactured by heating alizarin with 1, 2-diaminoanthraquinone.



indanthrone blue (vat blue 4)

It may also be prepared as follows :



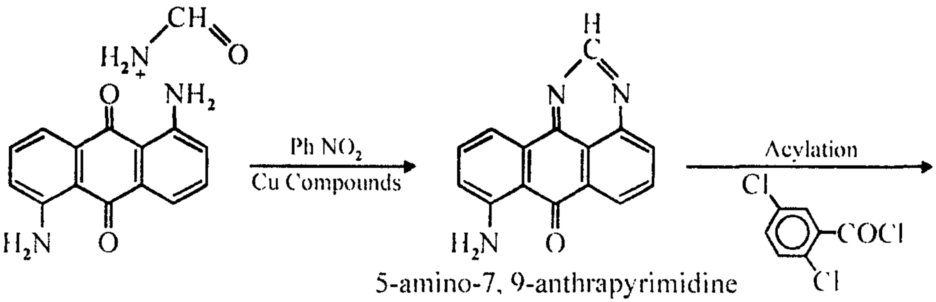
silver salt

2-aminoanthraquinone

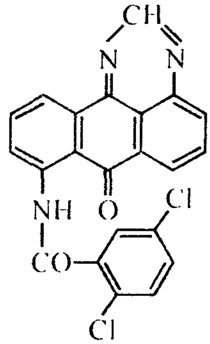
Indanthrone blue

Indanthrone blue is the best known of the anthraquinone vat dyes. The fastness to chlorine bleaching of indanthrone blue is improved by chlorination. A number of chlorinated indanthrones are in commercial use and make up the most important group of fast vat blues.

(*ii*) ***Indanthrone or Indanthrene Yellow 4 GK :*** It is prepared by condensing 2, 5-dichlorobenzoyl chloride with 1, 9-anthrapyrimidine. The latter compound is obtained by condensing 1, 5-diaminoanthraquinone with formamide in nitrobenzene solvent in the presence of copper compound.

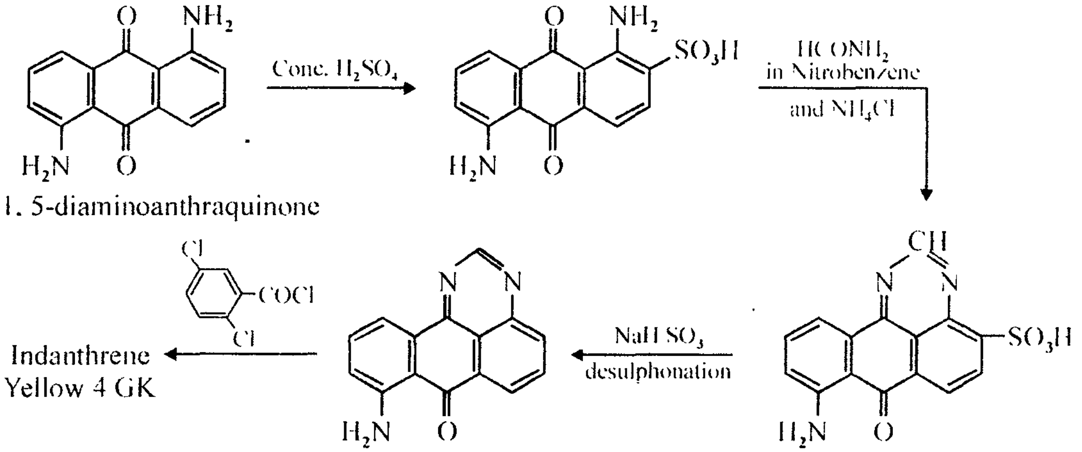


5-amino-7, 9-anthrapyrimidine



Indanthrene Yellow 4 GK

It is also prepared from 1, 5-diaminoanthraquinone which is sulphonated with conc. sulphuric acid to give 1, 5-diaminoanthraquinone-2-sulphonic acid. The latter compound on heating with formamide in nitro-benzene in the presence of NH_4Cl followed by desulphonation with $NaHSO_3$ yields 5-amino-1, 9-anthrapyrimidine. This is acylated with 2, 5-dichlorobenzoyl chloride when indanthrene yellow 4 GK is obtained.



It is used as a vat dye. However, it is no longer prepared.

Some substituted indanthrones which are used as dyes are as follows :

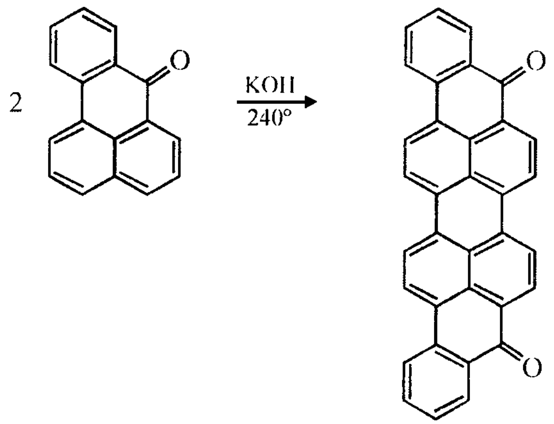
(*i*) 3-chloroindanthrone (indanthrene blue GCD).

(*ii*) 3, 3′-Dichloroindanthrone (indanthrene blue BCS or caledon blue RC).

(*iii*) N, N′-Dimethylindanthrone (indanthrene blue RK).

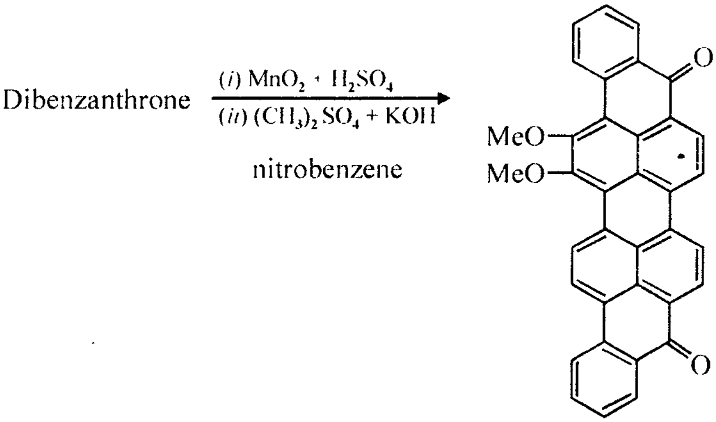
(*iv*) *Dyes from Benzathrone :* Several important vat dyes have been manufactured from benzathrone. Among these are dibenzathrone (vat blue 20) and caledon jade green (vat green 1 or violanthrone).

Dibenzathrone is manufactured by heating benzathrone with potassium hydroxide at about 240°C.



dibenzathrone

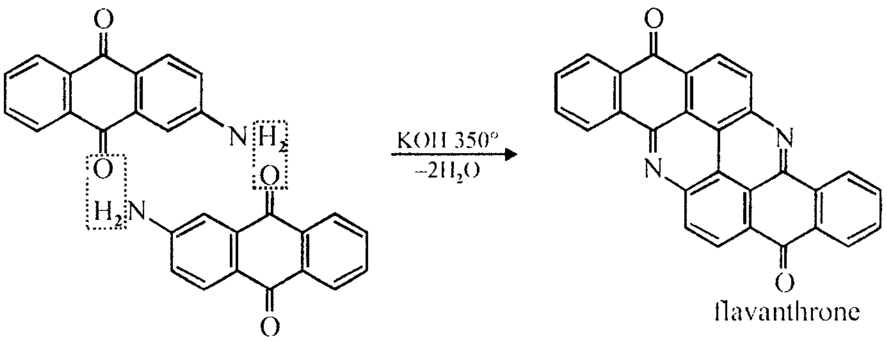
Dibenzathrone when oxidised with manganese dioxide and sulphuric acid followed by methylation with dimethyl sulphate in nitrobenzene and in the presence of alkali yields caledon jade green.



caledon jade green

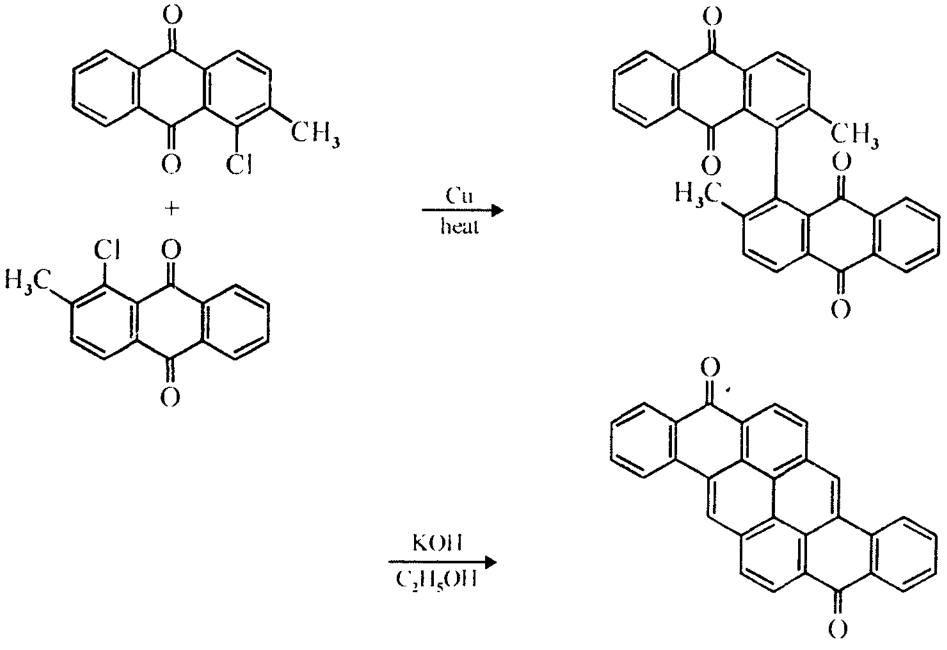
Caledon Jade green is one of the most attractive green vat dyes. It is very fast to light and washing. It is mainly used for dyeing and printing cotton.

(*iii*) ***Flavanthrone (Flavanthrene, indathrene yellow C. or Vat Yellow 1) :*** It is manufactured by fusing 2-amino anthraquinone with caustic potash at 350°C. Along with flavanthrone, a small amount of indanthrone blue is also produced.



flavanthrone

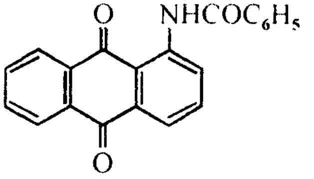
(*iv*) ***Pyranthrone (Pyranthrene, Indanthrene Golden Orange G or Vat Orange 9) :*** It is manufactured by heating 1-chloro-2-methyl anthraquinone with copper powder, followed by treatment with alcoholic KOH.



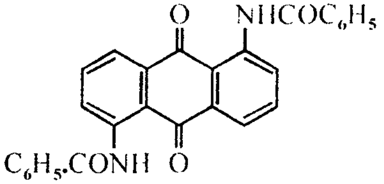
pyranthrone

It is a yellow dye and is very fast.

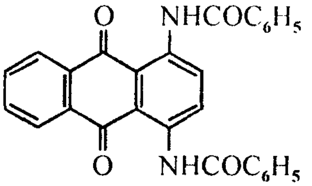
(*v*) ***Algol Dyes :*** (Acylaminoanthraquinones). Some important members of algol dyes are as follows :



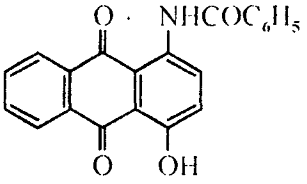
aglol yellow



caledon yellow 3G



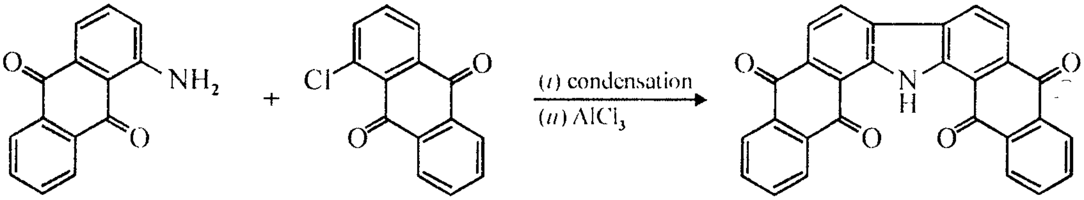
indanthrene red 5 G or
caledon red 5 G



algol rose R

Among the algol dyes, algol yellow is important. Chemically, it is 1-benzoyl-amino anthraquinone which is prepared by heating the corresponding amino compound with benzoic acid.

(*vi*) ***Anthraquinone Carbazoles :*** These are prepared by the cyclisation of a suitable dianthraquinoyl amine. For example, a yellow coloured dye is obtained by condensation of α-aminoanthraquinone with α-chloroanthraquinone followed by cyclisation with anhydrous $AlCl_3$.



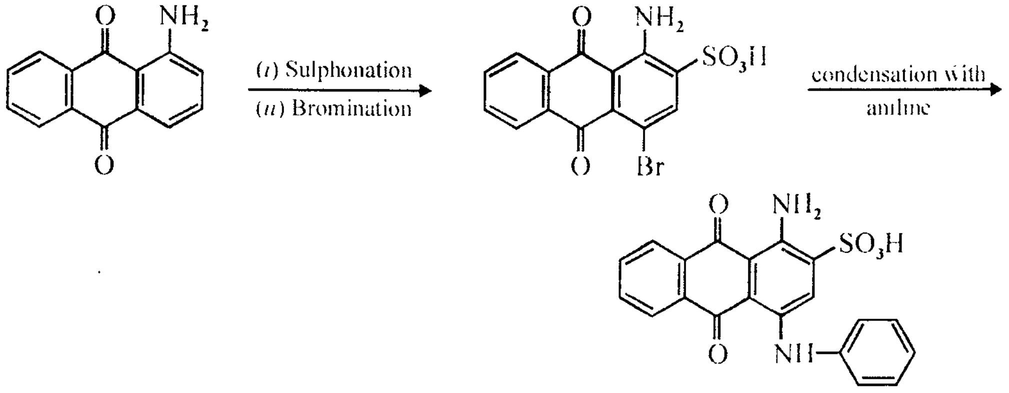
(yellow)

The cyclisation of dianthraquinoylamines having α-benzoyl-amino groups is done readily by treating with conc. sulphuric acid at 30-60°C.

Anthraquinone carbazoles are very fast to washing and alkali solution.

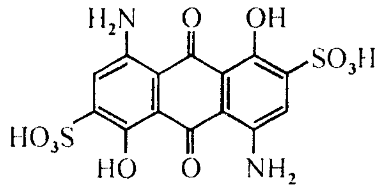
(*c*) Anthraquinone Acid Dyes : These dyes are water-soluble anthraquinone derivatives which are used for dyeing wool, silk, nylon, leather and paper. These have solubilising sodium sulphonate groups. These are among the fastest of those dyes which are applied to wool from a sulphuric acid dye bath. However, they are more expensive than those of the azo dyes.

An important example of anthraquinone acid dyes is solway ultrablue B (acid blue 25). It is prepared from 1-aminoanthraquinone which is sulphonated and brominated to give bromamine acid. Condensation with aniline then yields solway ultrablue B which is isolated as the sodium salt.

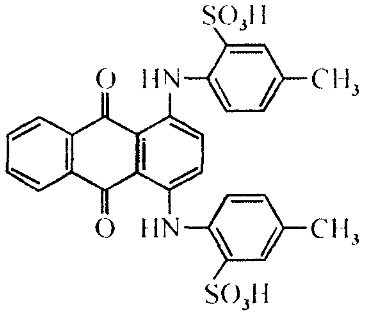


solway ultrablue B

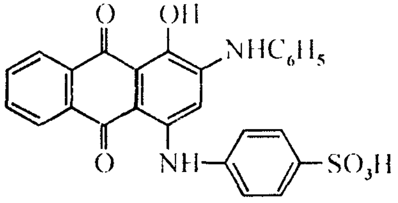
Other examples of anthraquinone acid dyes are as follows :



alizarin salphirol B (acid blue 45)

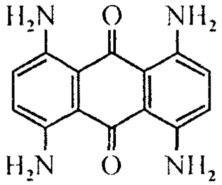


alizarin cyanine green

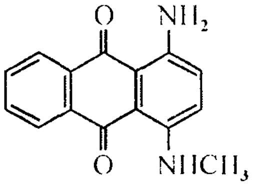


solway blue black BS

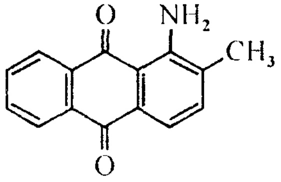
(*d*) **Anthraquinone Disperse Dyes :** These are simple insoluble derivatives of anthraquinone. These dyes are mainly used for dyeing of acetate polyester, polyamide and synthetic fibres. These dyes are faster to light. However, a serious disadvantage of most of these dyes is the fading and the shade change caused by gas fumes. This disadvantage has been overcome by substituting various groups like halogen, hydroxy, alkoxy, nitro and cyano groups in the anthraquinone nucleus. Some important examples of anthraquinone disperse dyes are given below :



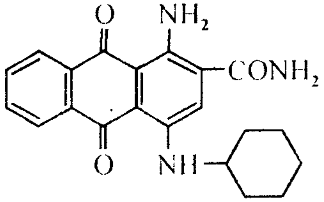
Duranol Brilliant Blue CB



Celliton Fast Violet 6B



Duranol Orange G



Celliton Fast Blue FFG

Anthraquinone disperse dyes are more expensive than the insoluble azo dyes.

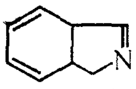
18

CHAPTER

PHTHALOCYANINES

18.1. Introduction

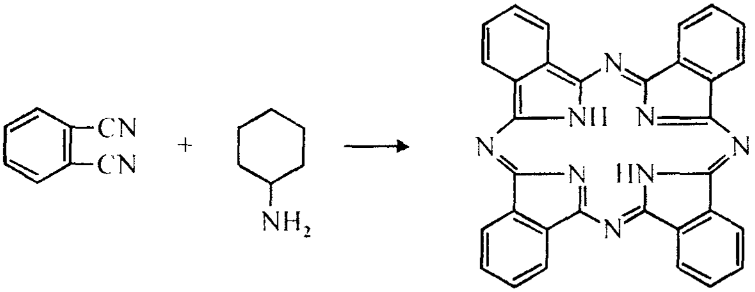
These constitute an important class of synthetic pigments and dyes. These are coloured blue to green. These may be regarded as the metal complexes of *iso*-indoles. These dyes contain tetraazo-porphine structure with or without the presence of a metal like copper, cobalt, nickel, iron, etc.



iso-indole

Phthalocyanines are very important compounds technically because they are very fast to light, heat, acid or alkalies. These are very useful for paints, printing inks, synthetic plastics, synthetic fibres, rubber, etc.

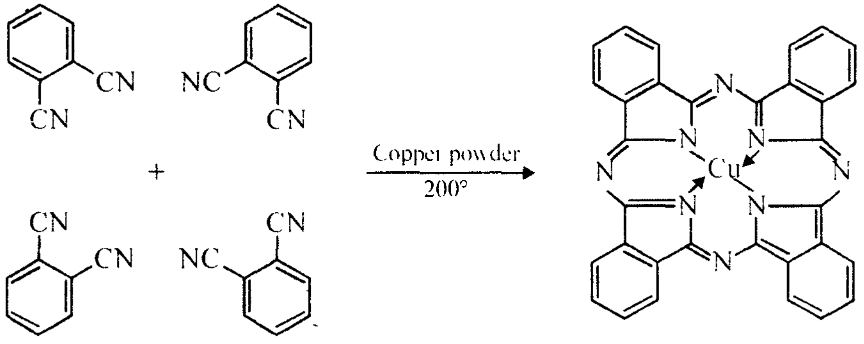
The parent compound of phthalocyanines is pigment blue 6, *i.e.*, *phthalocyanine.* It is prepared by the fusion of phthalonitrile with cyclohexyl amine in an inert solvent.



Phthalnitrile Cyclohexylamine Phthalocyanine

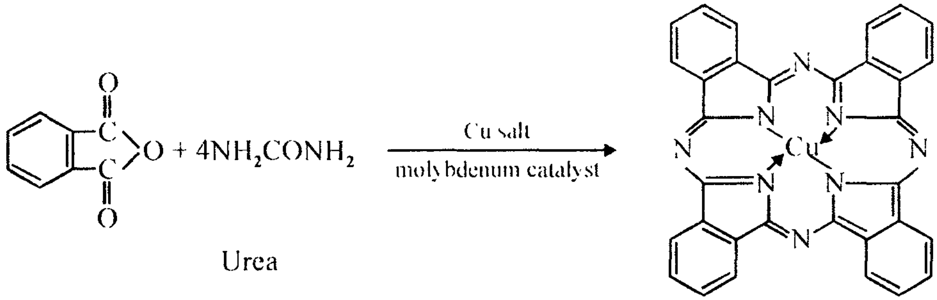
Pigment blue 16, *i.e.,* phthalocyanine is a greenish-blue pigment. It is stable to most of the solvents. However, it is affected by the acidic oxidising agents. It is mainly used for dyeing paper pulp and wall paper to which it gives deep blue or green shade with exceptional fastness.

Metal phthalocyanine derivatives may be obtained by replacing the two hydrogen atoms of phthalocyanine (I) by metals such as copper, nickel, iron and cobalt. It actual practice metal phthalocyanine derivatives are not made from phthalocyanine (I) but are synthesised directly. For example, copper phthalocyanine, *i.e.*, pigment blue 15 is made by the fusion of phthalonitrile with copper metal or a copper salt.



(I) Copper Phthalocyanine

Copper phthalocyanine is also prepared by the fusion of phthalic anthydride with urea and a copper salt in the presence of a molybdenum catalyst.



Urea

Phthalic anhydride Copper Phthalocyanine

Copper phthalocyanine is a deep blue pigment. It is very stable because it is not affected even by moltan alkali and by hot concentrated hydrochloric acid. It is distinguished by great brilliance, strength and stability and is used in every field in which coloured pigments are used.

Other metal phthalocyanines *e.g.*, magnesium, iron, lead, cobalt and nickel phthalocyanines, may be synthesised by the methods described as follows :

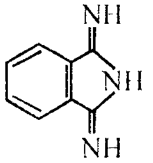
(*i*) These may be prepared by heating phthalic anhydride or phthalimide with urea and metallic salt in the presence of boric acid (catalyst).

(*ii*) These may be prepared by heating phthalocyanines or cyanoarylamides with the respective metals or metal salts.

(*iii*) These may also be prepared by passing ammonia into molten phthalic anhydride or phthalimide in the presence of the corresponding metallic salt.

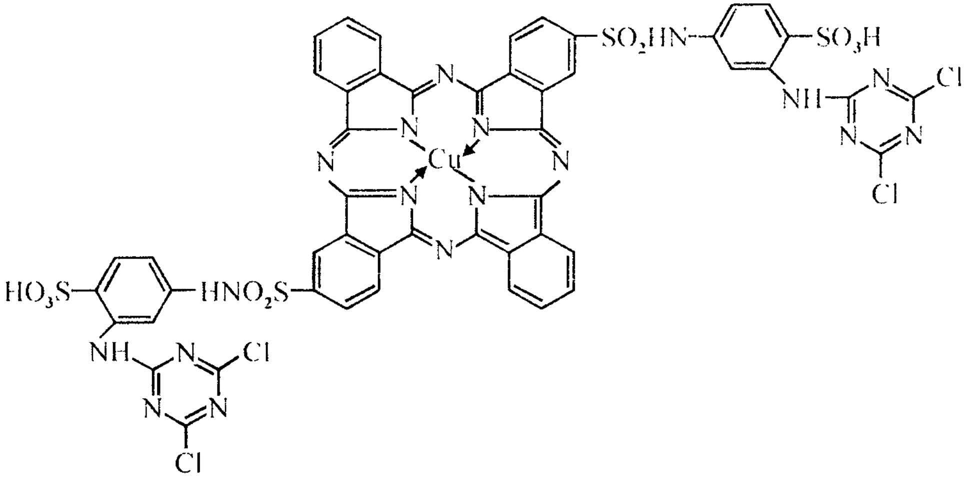
Metal phthalocyanines are insoluble in water. However, they are made soluble by sulphonation. For example, direct blue 86 is copper phthalocyanine which has been sulphonated to the extent of between two and three sulphonic acid groups per molecule. It produces very bright blue-green shades on cotton, viscose and paper. Another example is solvent blue 25 which is the reaction product of the tetrasulphonyl chloride of copper phthalocyanine with isohexylamine. It is a spirit-soluble dye which is useful for inks, lacquers and stains. Another example is vat blue 29 which is a partially sulphonated cobalt phthalocyanine. Reduction with sodium hydrosulphite in caustic soda solution converts it to a soluble form that can be applied to textiles and reoxidised to the pigment.

In the recent past, blue shades have been given to the fibres *insitu* by metal phthalocyanines. For example, a compound of the type I called *phthalogen* and a suitable copper or nickel salt is applied on a cotton fabric which is then heated gently to form the copper or nickel phthalocyanine on the fibre.



phthalogen (I)

Reactive dyes are also prepared from copper phthalocyanine by various methods. For example, the sulphochlorination of copper pathalocyanine, condensation with phenylenediamine-1-sulphonic acid and subsequent condensation with cyanuric chloride yields triazinyl reactive dyes of copper-phthalocyanine derivative.



A triazinyl reactive dye of copper phthalocyanine derivative.

19

CHAPTER

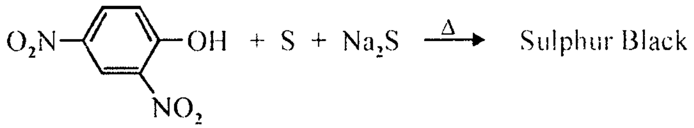
SULPHUR DYES

Introduction

These constitute a group of dyes of unknown constitution which can be applied to fibres when reduced with sodium sulphide. Most of them are insoluble in water before reduction. After reduction they are soluble and can be absorbed by fibres by fibres and than oxidised to an insoluble form with air. These dyes are popular because of their heavy shades, such as blue, green, black, brown, etc. of reasonable fastness to light and ordinary washing at a low cost. These dyes are second to the azo dyes in quantity produced.

Although structures cannot be written for the sulphur dyes, the methods for reproducing individual types are well established. These are manufactured by treating aromatic amines, phenols, amino-phenols, with sulphur and or sodium polysulphide at 150-200°C. Some important sulphur dyes are described as follows :

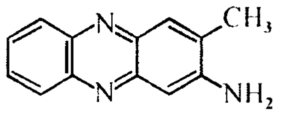
(*i*) Sulphur black I is manufactured by heating *m*-dinitrophenol with sodium polysulphide. The fused mass is dissolved in water and blown with air until all the dye has separated. It is then filtered, washed and dried.



intermediate for sulphur black I

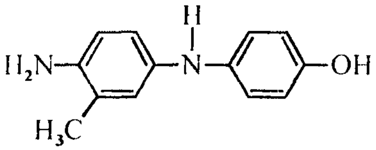
(*ii*) Brown sulphur dyes are obtained by fusing *m*-diamines (*e.g.*, *m*-toluenediamine) with sulphur. During this preparation, hydrogen sulphide gas is evolved.

(*iii*) Red shades are obtained by fusing sulphur with derivatives of azine, such as the compound below which produces sulphur red 6.

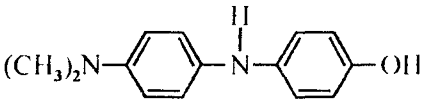


intermediate for sulphur red 6

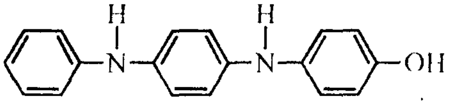
(*iv*) Blue sulphur dyes are manufactured by fusing diphenyl-amine derivatives with sodium polysulphide. For example, sulphur blue 7, sulphur blue 9 and sulphur blue 13 are manufactured from the intermediates given below :



Intermediate for sulphur blue 7

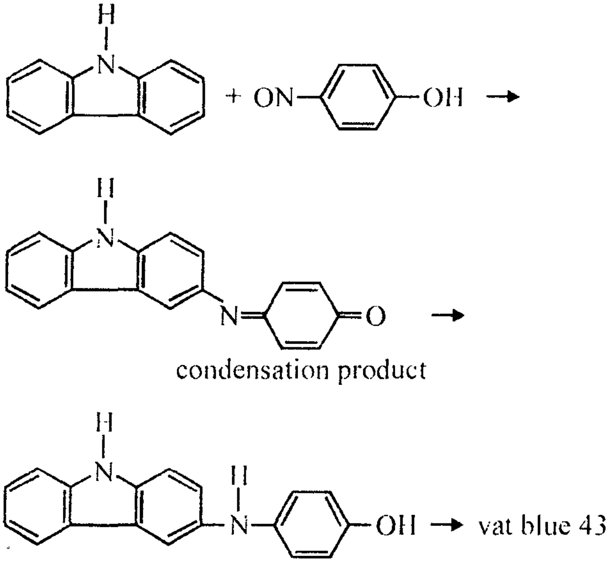


Intermediate for blue 9



intermediate for sulphur blue 13

(*v*) Vat blue 43 (hydron blue R) is also a kind of sulphur dye which unlike typical sulphur dyes may be reduced with sodium hydrosulphite without destruction. In order to manufacture this dye, carbazole is condensed with *p*-nitrosophenol in sulphuric acid to give an indophenol which is reduced and then fused with polysulphide.



Sulphur dyes are used principally for the dyeing of the cotton and then can be applied *via* the leuco compounds like vat dyes of the carbonyl series. Vatting is generally performed with sodium sulphide which reduces the polysulphide bonds to mercapto groups.

20
CHAPTER

REACTIVE DYES

Introduction

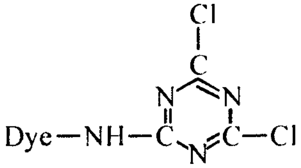
Rys and Zollinger defined a reactive dye as follows :

"It is a coloured compound which has a suitable group capable of forming a covalent bond between a carbon atom of the dye ion or molecule and an oxygen, nitrogen or sulphur atom of a hydroxy, an amido or a mercapto group respectively of the substrate".

The definition excludes mordant dyes and 1 : 1 chromium azo dye complexes which, in dyeing protein fibres, may form covalent bonds between metal ion and nucleophilic groups of the fibre.

The first reactive dye was introduced by I.C.I in 1956.

The reactive dyes contain dichlorotriazinyl group. These dyes were made by condensing a dye containing amino group with cyanuric chloride.

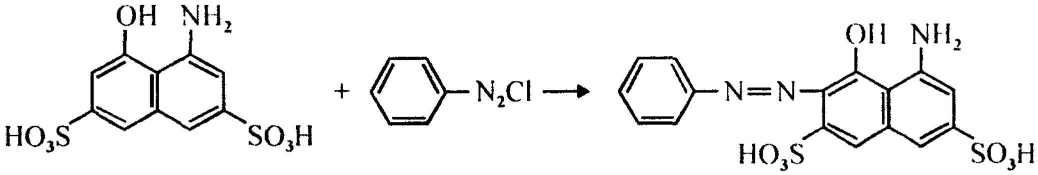


Cyanuric chloride is cheap and readily available. The reactivity of the chlorine atom in cyanuric chloride is due to the electron withdrawing properties of the nitrogen atoms.

The dyeing with reactive dyes is carried out at 70°-100°C under higher alkaline conditions. These dyes were sold as procion H brand and cibacron reactive dyes.

Some of the procion dyes are described as follows :

1. Procion Red Dye : it is obtained by coupling diazotised aniline with H acid. The resulting product is then condensed with cyanuric chloride in the presence of sodium carbonate at low temperature.



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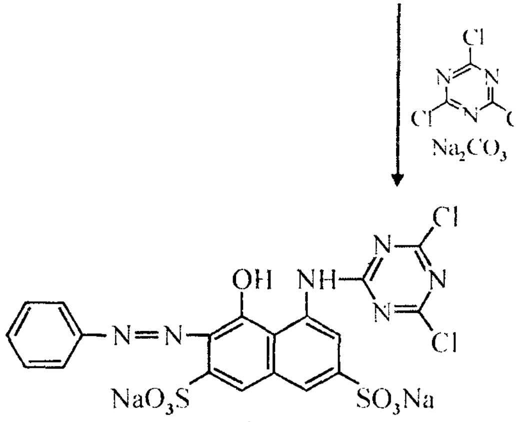
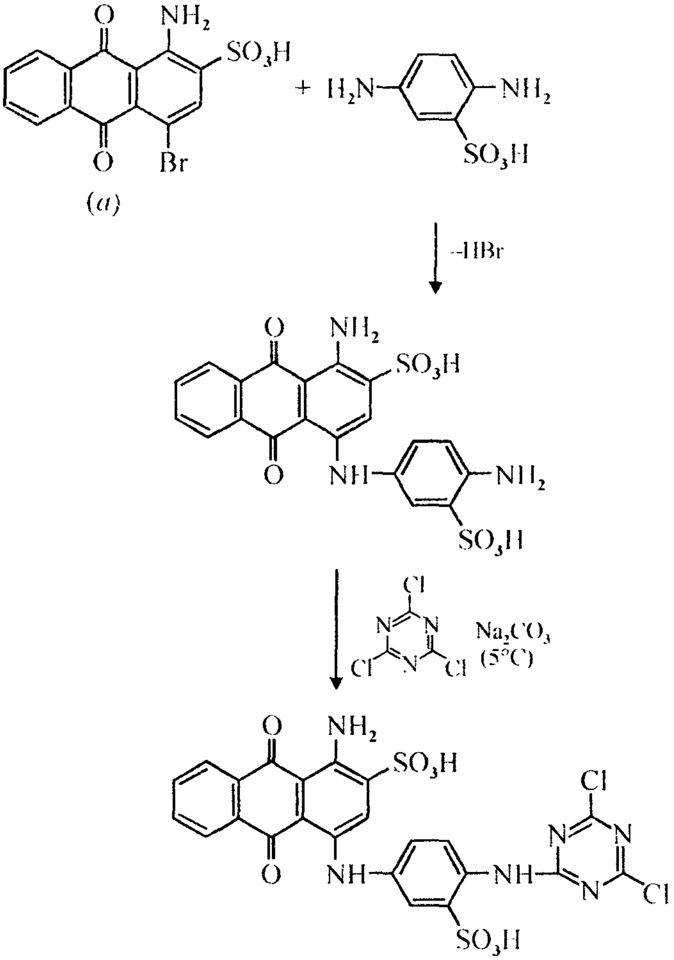
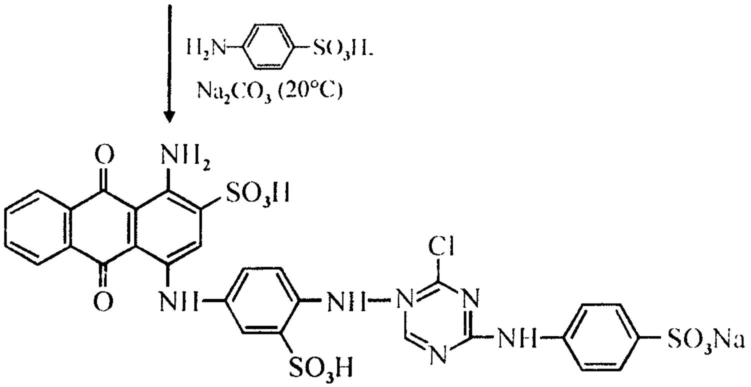


Procion Red dye

2. Procion Blue H.B. : It is obtained by condensing 1-amino-4-bromo-3-anthraquinone sulphonic acid (*a*) with 2-suilpho-*p*-phenylene diamine (*b*). The resulting product is next condensed with cyanuric chloride in presence of sodium carbonate at low temperature. It is now condensed with sulphanilic acid and ultimately converted into its sodium or potassium salt.

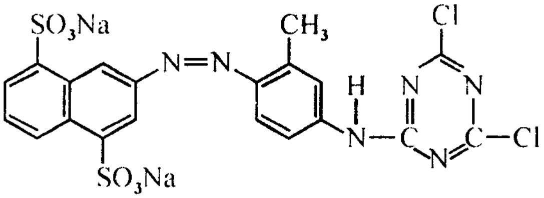




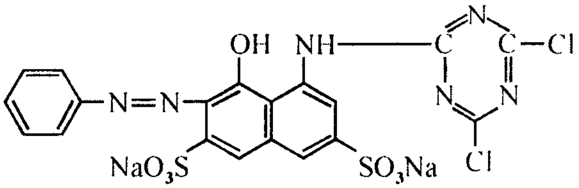
Procion Blue HB

It is used as a reactive dye. It gives a royal-blue shade.

3. Procion Yellow R

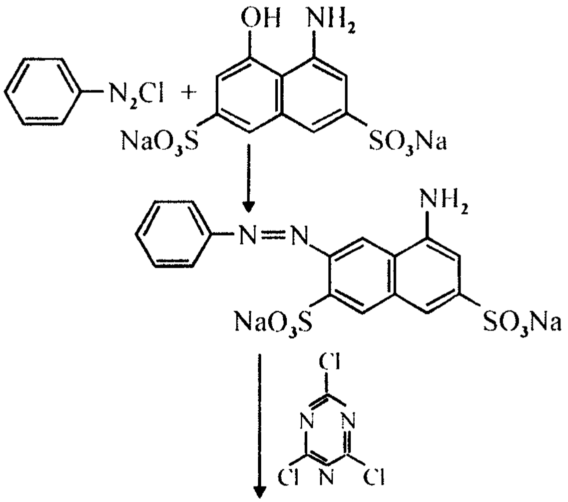


4. Procion Brilliant Red 5B



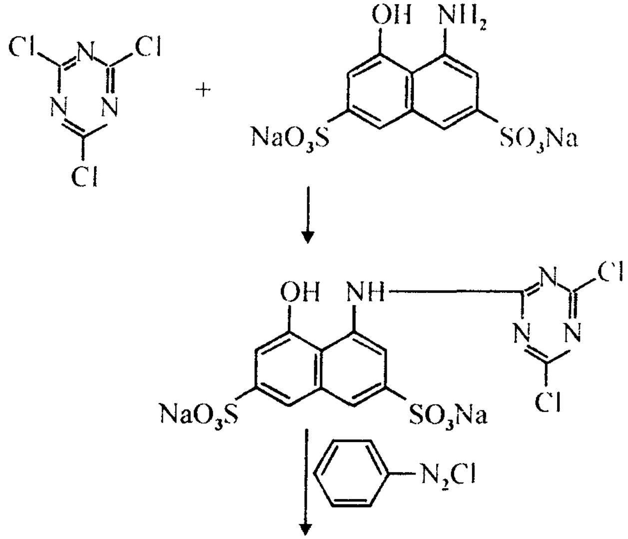
This dye is manufactured by the following two methods :

(*i*)



Pricion brilliant red 5B

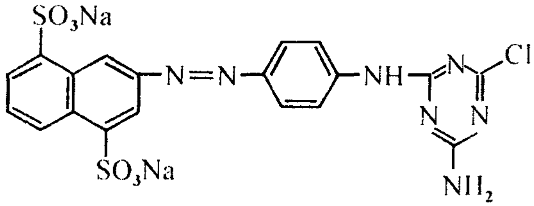
(*ii*)



procion brilliant red 5B

In both the above methods (*i*) and (*ii*), the temperature and pH of these reactions have to controlled in narrow ranges for retaining the reactivity of the dye.

5. Procion Yellow H AS (cibacron yellow R)



The monochlorotriazinyl dyes are much more stable in storage. Some of the factors which are important in the reactive dye system are as follows :

(*i*) It should align on the cellulose molecule in such a way so as to promote nucleophilic reaction.

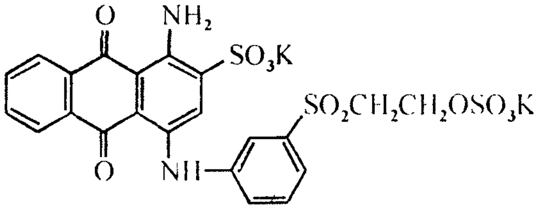
(*ii*) It should not be very costly.

(*iii*) It should possess low affinity for the fibre, high reactivity with cellulose and low reactivity with water.

(*iv*) The dye bond between fibre and reactive dye should be strong giving good fastness properties.

ICI has introduced supra dyes which have one additional monochlorothiazinyl group. These dyes have better fixation for fibres.

Many other reactive groups have been introduced into the reactive dye. In 1953, Farbwerke Hoechst introduced two Remalan dyes for wool silk and polyamies. In these dyes the reactive group is SO_2 -$(CH_2)_2$-SO_3H which gets hydrolysed to the vinyl sulphone (SO_2-CH = CH_2) in the presence of alkali and tends to form a covalent bond with amino ortho hydroxy group by addition reaction. In 1957, remazol dyes were introduced for cellulose. They yield vinyl sulphone group. The most important remazol dyes is remazol brilliant blue R.

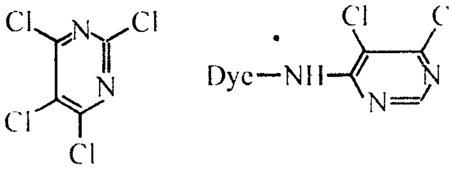


$$\text{Dye–SO}_2\text{CH}_2\text{CH}_2\text{OSO}_3\text{Na} + \text{NaOH} \longrightarrow \text{Dye–SO}_2\text{CH} = \text{CH}_2 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$$

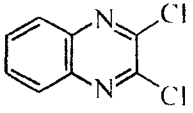
$$\text{Dye–SO}_2\text{–CH} = \text{CH}_2 + \text{cellulose} \longrightarrow \text{Dye–SO}_2\text{– CH}_2\text{.CH}_2\text{–O–cellulose}$$

6. Commercial Useful Reactive Dyes : Some commercial useful reactive dyes are as follows :

(*a*) ***Trichloropyrimidine Dyes :*** These are derived from tetra-chloropyrimidine. The chlorines present in positions 2, 4 and 6 are reactive whereas chlorine in position 5 is not reactive.

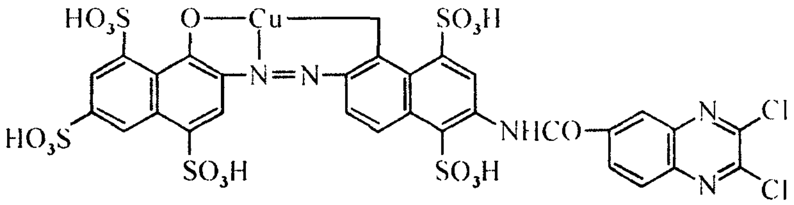


These dyes are marketed as *drimarines* and *reactones*. These are less sensitive to hydrolysis. Dyeing needs high temperature. The reaction with cellulose is similar to chlorotriazinyl system. 2, 6–Difluoropyrimidine deirvatives are also marketed as reactive dyes, *e.g.*, *drimalan*, verafix dye, etc.

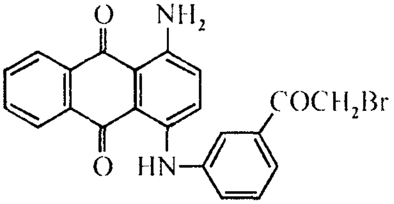


(*b*) ***Quinoxaline Dyes :*** Du Punt and Bayer have marketed these dyes having the following reactive group.

The acid chloride of quinoxaline is condensed with free amino group of an azo dye, *e.g.*



(*c*) ***Chloroacetyl and Bromoacetyl Dyes :*** These dyes are mainly used for wood dyeing. These dyes are known as *drimalam dyes* marketed by Sandoz and *cibalan dyes* marketed by CIBA.



21

CHAPTER

PIGMENTS

Introduction

These are insoluble powders of very fine particle size, *i.e.*, as small as 0.01 micron, which are used in paints, plastics, rubber, textiles, inks and other materials to impart colour, opaqueness and other desirable properties to the product.

Pigments are both natural and synthetic in origin; and organic and inorganic in composition. The oxides of iron, chromium, lead and other metals give a limited range of colour with good light fastness. However, many of these change colour with sulphur compounds found in urban atmosphere today, making them unsuitable. With the growth of dyestuff industry, a range of pigments giving bright colours of good fastness properties were discovered. A new chromophoric system of phthalocyanine pigment was introduced in 1935. This was followed by introduction of several new pigments.

The difference between dyes and pigments is their relative solubility; dyes are soluble while the pigments are essentially insoluble in the liquid media in which they are dispersed. (The table 21.1)

Organic pigments in general have lower hiding power but greater tinting strength than inorganic pigments.

Table 12.1 : Distinction Between Dyes and Pigments

Dyes	*Pigments*
1. Dyes are coloured substances which impart colour to substrate.	1. Pigments are descrete coloured particles which give colour to substrate.
2. Dyes are organic compounds or mixtures.	2. Pigments are organic or inorganic compounds.
3. Dyes are soluble in medium	3. Pigments are insoluble in medium.
4. Dyes are applied in solutions or in dispersions.	4. Pigments are used in suspensions.
5. The chemical constitution of dyes is important in the application.	5. The physical form, particle size of pigments is important in all applications.
6. Dyes are used for colouring textile materials, food stuffs, paper, leather etc.	6. Pigments are used for printing and used for colouring paints, varnishes.
7. *e.g.*, Tartrazine, Alizarin, Eosin.	7. *e.g.*, Indigo, Copper phthalocyanine.

Toner Pigments and Lakes : In the manufacture of organic pigments certain colouring materials become insoluble in the pure form whereas others require a metal or an inorganic base to precipitate them. The colouring materials which are insoluble in the pure form are known as *toner pigments* and those which require a base are referred to as **lakes.**

Use of Synthetic Organic Pigments : Pigments find application in aqueous and non-aqueous paints, printing inks, paper coating, leather finishing, plastic products, and other similar processes. The pigment may be used alone or incorporated with a while pigment such as zinc oxide, titanium dioxide or white lead as a means of controlling the opacity and the depth of shade required.

Most printing inks contain pigments and are used for the printing of metal-foil, tin-plate, card-board wrapping materials and so on. Pigments are extensively used in printing and textiles in combination with a resin binder. Pigments are incorporated in cellulose pulp to obtain coloured paper. Similarly, mass colouration of synthetic fibres, plastics and rubber is carried out. Pigments are also used in cosmetics, soap, wax chalks, crayons, artist's colours and so on.

In all applications, the physical form, shape and size of the pigment particles are of the highest importance. Great care is exercised in standardisation of manufacturing process of pigments to obtain correct crystalline structure and particle size of pigments.

Requirements of Organic Pigments : These are as follows :

(*i*) *Fastness to Light :* The most important criterion by which pigments are evaluated is fastness to light which depends on the medium in which the pigments are dispersed. In general, pigments are less fast to light in pale tints than in dark tints.

(*ii*) *Fastness to Heat* : A pigment should be stable to relatively high temperatures. This applies especially in surface coatings 'cured' or polymerised by heat and in thermosetting colouration. With inferior pigments, chemical decomposition may result from such heat treatment, or physical change from one modification to another may occur causing deterioration in hue and other properties.

(*iii*) *Insolubility in Solvents :* An ideal pigment should be insoluble in all media. However, this conditions is not completely fulfilled. Solubility in vehicle or solvent may bring about crystallisation of the pigment causing a change in the colour properties of the paint

(*iv*) *Fastness of Acid :* Pigments must be acid-fast if they are employed in acid media or if they are to be exposed to acid vapours.

(*v*) *Fastness to Alkalies :* Pigments must be alkali-fast if they are to be used in the manufacture of distempers or the coloration of plaster surfaces.

(*vi*) *Insolubility in Water :* Complete insolubility of pigment in water is rated as excellent. Where pigments have a slight degree of solubility in water or other liquid media they are said to show '*bleeding*'.

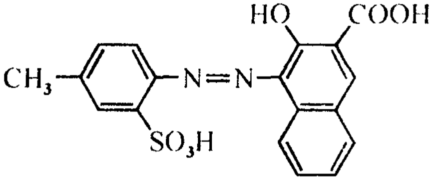
One particular pigment cannot fulfil all the above mentioned requirements. However, to satisfy all these a large number of organic pigments have been developed. These organic pigments belong to most of the different classes of dyestuffs.

Types of Pigments

Lakes of Acid or Anionic Dyes : These pigments are precipitated from solutions of anionic dyes of the type D^-X^+ (where X is generally a sodium atom) by double decomposition with the soluble salts of heavy metals such as calcium or barium, *e.g.*, pigment red 57.

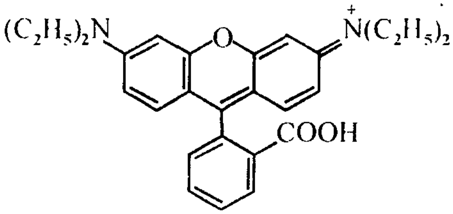
$$2\text{Dye–SO}_3\text{Na} + \text{BaCl}_2 \longrightarrow [\text{Dye–SO}_3^-]_2\text{Ba}^{2+} + 2\text{NaCl}$$

Such lakes are resistant to solvents but they are very sensitive to acids and alkalis.



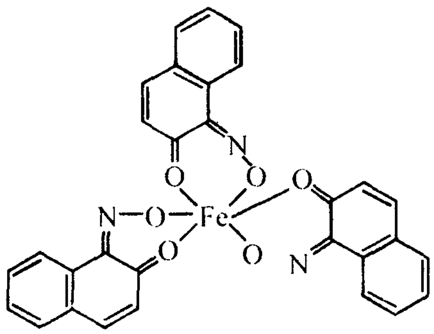
pigment violet 57

Lakes of Basic or Cationic Dyes : These pigments are precipitated from solutions of cationic dyes of the type D^+X^- (where D is a chromophoric system embodying one or more basic groups and X is a chlorine atom or similar salt forming group) by double decomposition with tannic acid or with certain inorganic polyacids. The best examples are the 'Fanal' or permanent pigments produced by BASF by precipitating a cationic dye with phosphotungstomolybdic acid (PTMA), *e.g.*, pigment violet 1. These lakes are generally superior in fastness properties to the parent dyes but they do not attain the all-round high standards of the modern pigments *i.e.*, phthalocyanines.

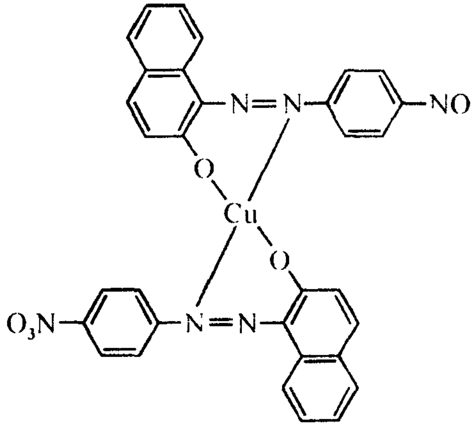


pigment violet 1

Metal Complexes : These pigments have excellent light fastness property but are inferior in other fastness properties. These are coordination or chelate compounds and require for their formation dye molecules which contain oxygen or nitrogen atom to donate electrons to the metal atom. One example is pigment green B (C.I pigment green 8, 10006) which is prepared from 1-nitroso-2-naphthol and ferric salt. Another example is C.I. pigment brown 2, 12071 which is the copper complex derived from the monoazo dye *p*-nitroaniline→2-naphthol.



(pigment Green B)

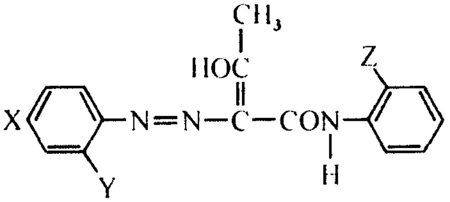


(pigment Green 8)

For many years, metal complexes of alizarin have been used as pigments. For example, the calcium/aluminium lake is bluish-red, chromium dull bluish-red and iron dull purple. These are all used either as such or formed on the fibre as in dyed-style printing.

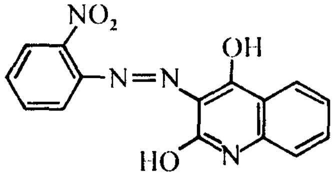
Neutral, Metal-Free Compounds : These are the most widely used groups of pigments. These include mainly monoazo and disazo dyes and also a few representatives from azine, indigo and anthraquinone classes. These are mostly dye molecules not containing solubilizing groups such as SO_3H or –COOH. These provide full range hues. These pigments have good fastness to acids and alkalies but have poor fastness to solvents and plasticizers. These are quite popular in India.

(*i*) ***Monoazo Pigments :*** An example is C.I. pigment yellow 1. 11680, Hansa Yellow G(4-amino-3-nitrotoluene-acetoacetanilide).



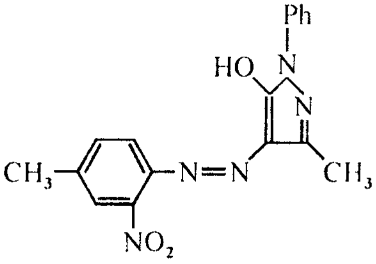
($X = CH_3$, $Y = NO_2$ and $Z = H$)

Another example is C.I. pigment yellow 7, 12780, 2-nitro-aniline-2, 4-dihydroxy quinoline. It is a bright, reddish-yellow-pigment.



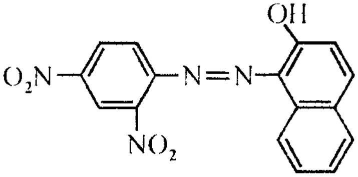
C.I. pigment yellow 7

An example of the large class of pyrazolone pigments is C.I. pigment orange 6, 12730, 4-amino-3-nitrotoluene → 3-methyl-1-phenyl-5-pyrazolone.



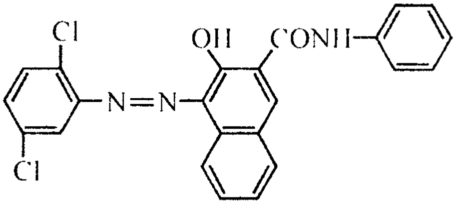
C.I. pigment orange 6

Another pigment derived from 2-naphthol is C.I. pigment orange 5, 12075, 2, 4-dinitroaniline-2-naphthol. It is widely used for its brightness and strength. However, its other fastness properties, particularly solvent and vehicle 'bleed' are inferior.

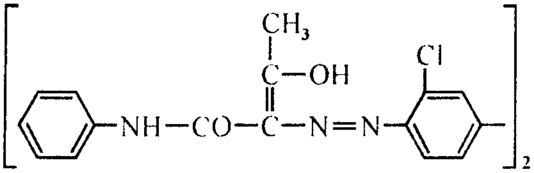


C.I. pigment orange 5

The pigments derived from components of the naphthol AS type show marked improvement in solvent and vehicle fastness as in C.I pigment red 2, 5-dichloroaniline → 3-hydroxy-2-naphthanilide.

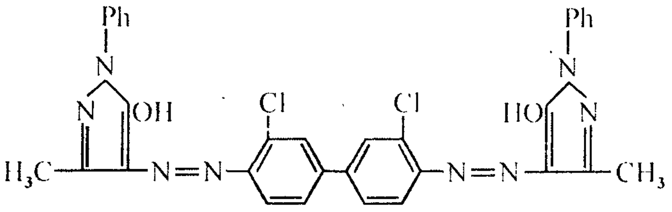


(*ii*) ***Disazo Pigments :*** These are widely used in the manufacture of printing inks and in the mass coloration of rubber. Typical examples are benzidine yellows which are well known for brilliance and high-tinctorial strength. An example is C.I. pigment yellow 12, 21090, 3, 3′-dichlorobenzidine ⇒ acetoacetanilide (2 moles).



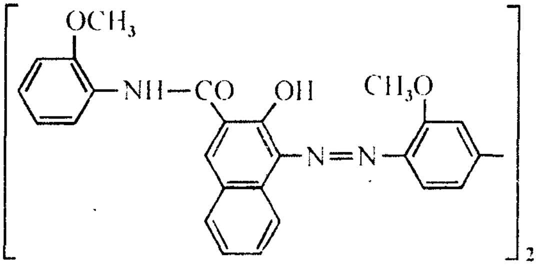
C.I. pigment yellow 12

Another example is C.I. pigment orange 13, 21100, permanent orange G. It uses a pyrazolone as coupling component.



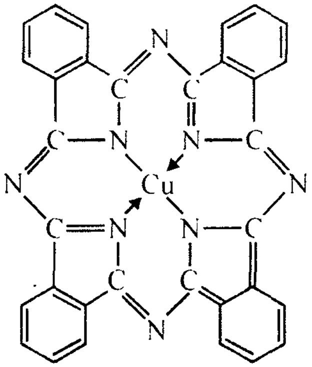
C.I. Pigment Orange 13

One more example is C.I. pigment blue 26, 21185, dianisidine blue. It is obtained from tetrazodianisidine and 3-hydroxynaphtho-*o*-anisidide.



There are some other pigments which belong to other class. C.I. pigment yellow 11 is obtained from 4-chloro-2-nitroaniline by condensation with formaldehyde with formaldehyde and is a nitro pigment. Azine pigment is obtained by oxidation of aniline in the presence of a catalyst such as copper or vanadium, *e.g.*, aniline black. Some vat dyes such as indanthrone are also used as pigments.

Modern High-Grade Pigments : In 1935, monastral blue was marketed by ICI. This was the first phthalocyanine pigment with high all round fastness properties. The structure determination was carried out by Linstead and coworkers who found a tetrabenzo-porphyrazino nucleus, a structure related to that of chlorophyll and also haemin, the red colouring matter of blood corpuscles.



Copper phthalocyanine

Copper phthalocyanine is prepared by several methods. One method involves the heating of phthalonitrile or a related compound such as *o*-cyanobenzamide or phthalamide with a cuprous salt. Another method called *urea process* for the preparation of copper phthalocyanine consists in heating together urea, phthalic anhydride. The yield of the method is increased by catalysts like boric acid, ammonium molybdate and ammonium phosphate.

Metal-free phthalocyanine may be prepared from sodium phthalocyanine by demetallization with a strong acid. It may also be obtained directly from phthalonitrile by heating, in an inert atmosphere, under pressure. It is a bright greenish-blue pigment.

Polychloro-copper phthalocyanine is a true green pigment. It is prepared by passing chlorine gas through a melt of copper phthalocyanine, aluminium chloride and sodium chloride at 200°C. A number of soluble dyes have been prepared from these pigments by introducing solubilising groups in the pigment.

Intensive research to obtain yellow, red and violet pigments having fastness properties similar to phthalocyanines has resulted in the production of modern high grade pigments.

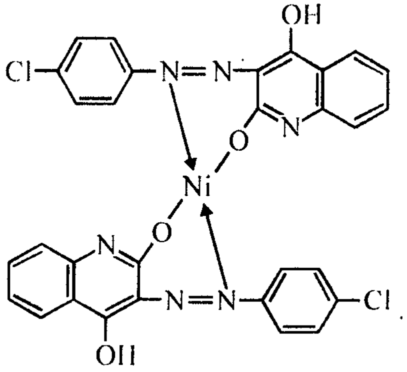
Modern high grade pigments belong to the various classes which are given in Table 21.2.

Azo Pigments : These are obtained by using more complex diazo and coupling components and in some cases by forming metal complexes. These show excellent fastness properties.

Table 21.2 : Modern High-Grade Pigments

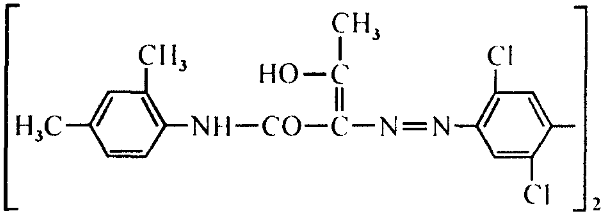
Class	*Colour change*
Azo coupling	Yellow
Azo condensation	Yellow, orange, red
Derivatives of 4, 5, 6, 7-tetrachloro-isoindolin 1-one	Greenish-yellow, orange, red brown
Anthraquinone	Yellow, orange, violet
Perinone, Perylene	Orange, red, violet
Quinacridone	Maroon, scarlet, red, magenta, violet
Dioxazine	Violet
Phthalocyanines	Blue, green

Nickel azo yellow (DuP) is the 1 : 2 nickel-dye complex which is obtained from the dye p-chloro-aniline → 2, 4-dihydroxy-quinoline.



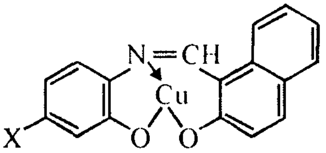
nickel azo yellow

Benzidine yellow Greenish (Hoechst) is prepared from 2, 5, 2′, 5′-tetrachlorobenzidine ⇒ acetoacet-m-xylidide (2 moles).



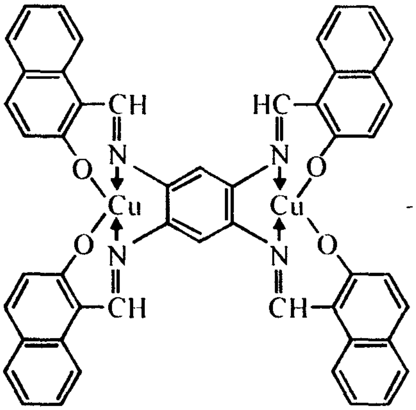
benzidine yellow greenish

Azomethine Pigments : Copper complexes of 2, 2′-dihydroxy azomethine dyes possess excellent light and heat fastness and are fast to cross-lacquering and migration. The structure of these pigments is as follows :



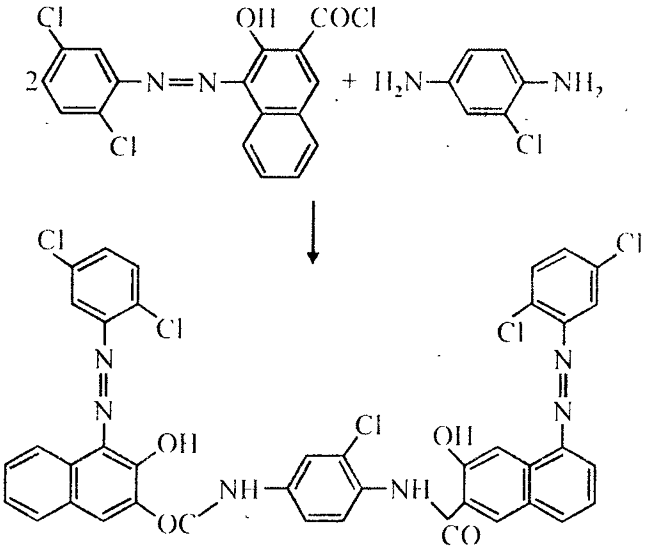
(X = H or Cl)

These pigments are obtained by condensing hydroxy-4-nitro-aminobenzene with 2-hydroxy-1-naphthaldehyde in DMF followed by conversion into the copper complex. In an analogous manner, BASF prepared a pigment (structure shown below) by condensing 1, 2, 4, 5-tetraminobenzene with 2-hydroxy-1-naphthaldehye. This pigment has high light fastness and high light fastness.



BASF, BP 1195 766

Azo Condensation Pigments : CIBA prepared these pigments by condensing 2-monoazo pigments. The following example illustrates the method.

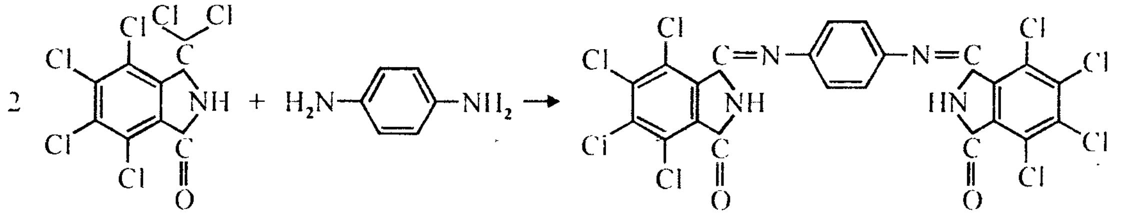


pigment red 344

Due to the insolubility of the pigment, it is very difficult to get a bisazo pigment by the normal method of diazotisation and coupling.

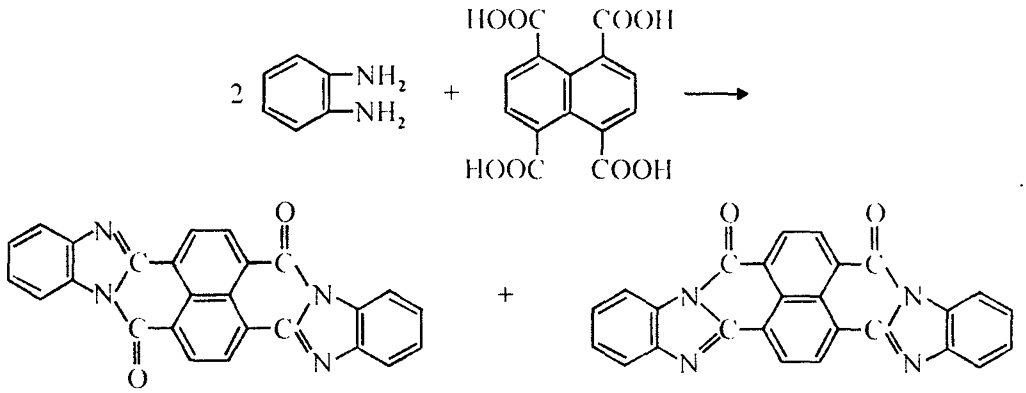
The constitution of many of these pigments is not known. However, a range of yellows, oranges, reds and browns of all round fastness properties are available. These pigments are used in mass-coloration of polymers and high grade lacquers for automobiles.

Tetrachloro-iso-indolin-1-one Pigments : In 1965, these pigments were introduced by Geigy. These pigments have a new chromophoric system. These are prepared by condensing a phthalimide derivative with *p*-phenylenediamine.



It is to be noted that the presence of all eight chlorine atoms in the pigment molecule is essential because their absence results in products unsatisfactory as pigments. By using other diamines, a full range of shades from greenish yellow-to orange, red, brown are obtained. Their fastness properties are very good.

Perinone and Perylene Pigments : Perinone pigments are derived from naphthlene-1, 4, 5, 8-tetracarboxylic acid and *o*-phenylenediamine.



C.I. vat orange 7

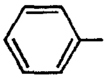
C.I. vat orange 7, 71105

C.I. vat red 15, 71100

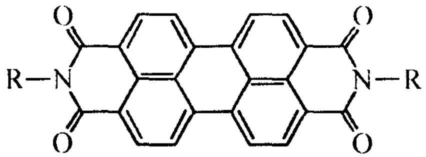
The orange has superior fastness to light, heat and solvents while the red is inferior by reason of solvent bleed and migration.

Hoechst developed the perylene pigments which are di-imides of perylene-3, 4, 9, 10-tetracarboxylic acid. Some examples of perylene pigments are :

perylene red	$R = CH_3O$
perylene maroon	$R = CH_3$
pigment red 123,	$R =$ *p*-substituted phenyl.



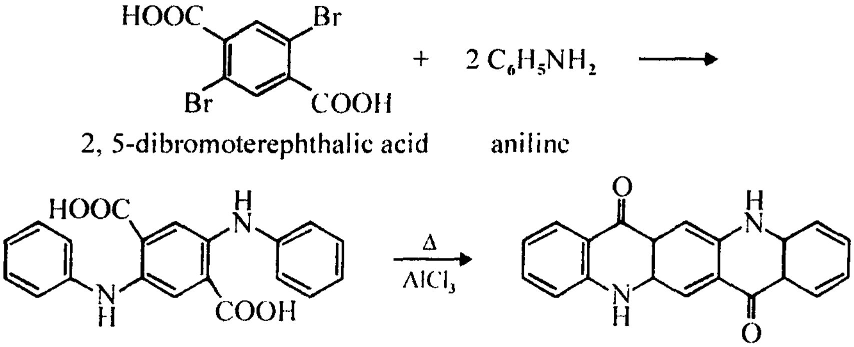
C.I. vat red 29, 71140



These pigments have light fastness ratings comparable with those of the phthalocyanines. Their excellent migration fastness makes them very suitable for the coloration of plastics. The high resistance to heat of C.I. pigment red 123 (R = *p*-substituted phenyl) makes it suitable for the melt-coloration of nylon (300°C).

Quinacridone Pigments : These were introduced by du Pont in 1958. The colour of the pigment depends on the different crystal modifications. γ-modification is red while β-modification is violet. The excellent fastness property may be due to hydrogen bonding between neighbouring molecules.

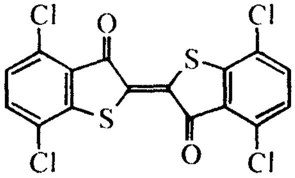
Quinacridone pigments may be synthesised from 2, 5-dibromo-terephthalic acid and aniline followed by ring closure which may be achieved by heating in oleum or aluminium chloride with or without a solvent.



2, 5-dibromoterephthalic acid aniline

2, 5-di(phenylamino) teraphthalic acid Quinacridone

Thioindigo Pigments : The best example of these pigments is the thioindigo bordeaux. It is reddish-violet and has light fastness comparable, even in light tints, with phthalocyanine pigments.

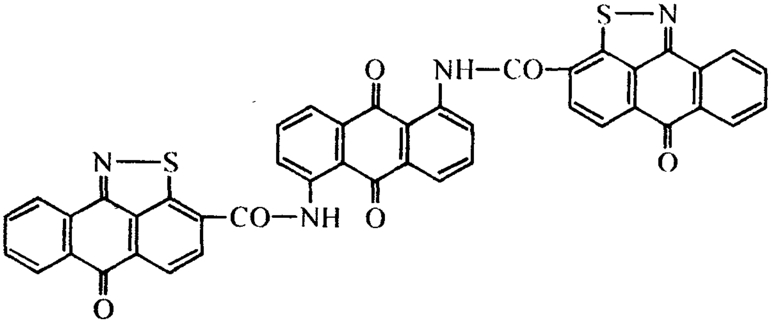


Thioindigo

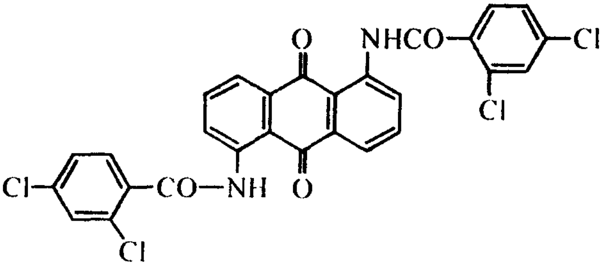
If the positions of any of the four chloride atoms are altered or one of the chlorine atoms is removed or one more chlorine atom is introduced, there occurs solvent bleeding in the products.

High-grade Anthraquinone Pigments : Several vat dyes are used as high grade pigments, *e.g.*, indanthrone, flavanthrone, halogenodibenzanthrone sulphonamide, etc.

Some recent anthraquinone pigments are :

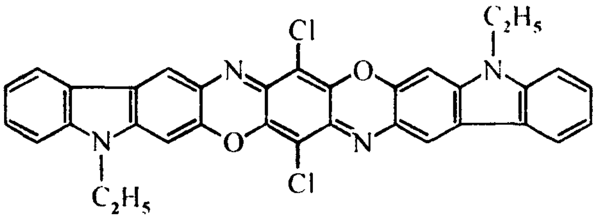


B.P. 998 704 (BASF)



B.P. 984 110 (CIBA)

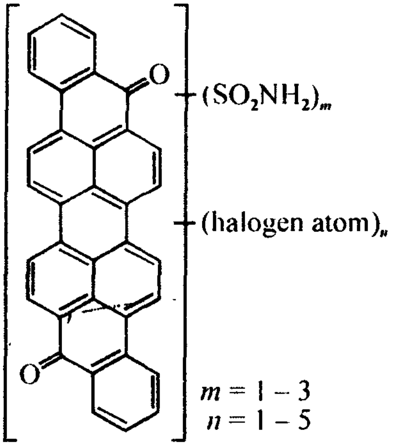
Dioxazine Pigments : In 1952 Hoechst introduced carbazole dioxazine violet.



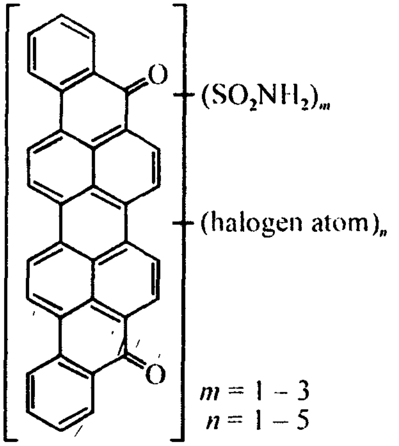
Carbazole Dioxazine Violet

It has high tinctorial strength and good light fastness. However, its fastness to solvents and plasticisers is inferior to other pigments.

Recently, it is claimed in a patent U.S.P. 3814724 by CGY that certain halogenated dibenzanthrone and isodibenzanthrone sulphonamides have excellent light and migration fastness. They are useful for shading copper phthalocyanines. They have greatly improved resistance to flocculation compared with the dioxazines.



halogenodibenzanthrone
sulphonamide



halogenoisodibenzanthrone
sulphonamide

22

CHAPTER

FLUORESCENT BRIGHTENING AGENTS

It is found that white textile articles attain yellow colour long before they are worn out. This undesirable effect can be overcome in the following different ways :

(*i*) In the **first method,** a chemical beaching agent such as a hypochlorite or peroxide may be used. However, one should use such substances carefully because they spoil the coloured goods and may damage the fibre.

(*ii*) In the **second method,** a small amount of blue colouring matter, *e.g.*, ultramarine, may be used. This absorbs yellow light and thus the yellowed fabric appears white. However, its actual function is to extend the region of the spectrum over which light is absorbed and, therefore, the treated article becomes pale-grey.

(*iii*) In the **third method,** fluorescent brightening agents may be used. *They are colourless compounds but they strongly absorb light of shorter wavelength in the ultraviolet region (330-380 nm) and fluoresce or re-emit lighter of longer wavelength in the visible region of the spectrum (430-490 nm) Thus, they produce a brightening or whitening effect which is useful in making yellow products appear whiter and whiter and white materials brighter.*

Fluorescent brightening agents have in fact largely replaced ultramarine and other blueing agents. The large quantities are consumed annually as ingredients in soap and washing powders. The principal textile application is on cotton, though fluorescent brightening agents suitable for wool, nylon and other synthetic fibres are of increasing importance.

Characteristic Properties of Fluorescent Brighteners

(*i*) A brightening agent molecule must possess a conjugated system.

(*ii*) It must be planar.

(*iii*) It must contain electron-donating groups such as–OH and–NH_2.

(*iv*) It must be substantive, non-toxic, compatible with detergent action under all likely conditions.

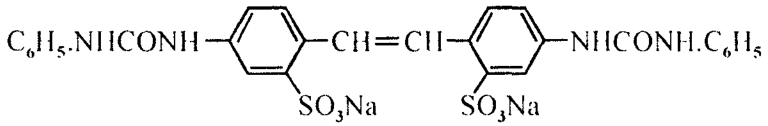
(*v*) On long exposure, it should not yield coloured decomposition products.

(*iv*) It must be sufficiently fast to light to remain effective for a reasonable period.

(*vii*) For maximum whitening effects, it must re-emit light of wavelength of 450 nm.

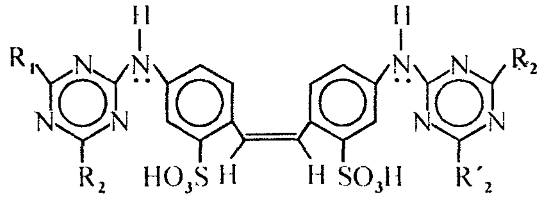
Classification of Fluorescent Brighteners : A number of molecules have the ability to fluoresce but relatively few have achieved commercial importance. Based on their chemical structures fluorescent brighteners can be classified as follows :

1. Stilbene Derivatives : Over 80% of the fluorescent brightening agents in use are stilbene derivatives. Blankophor R, one of the early brightening agents, was made by condensing phenyl isocyanate with 4, 4′-diaminostilbene-2, 2′-disulphonic acid.



blankophor R

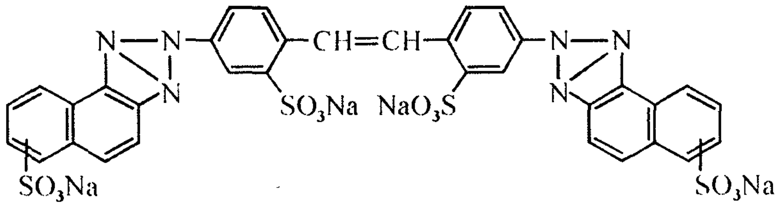
Most of the modern fluorescent brightening agents contain substituted triazinyl ring system and have the following general structure :



Tinopal BV

In the above formula if $R_1 = R_2 = NH_2$, tinopal BV is obtained. It is prepared by condensing disodium salt of 4, 4′-diaminostilbene-2 2′-disulphonic acid with cyanuric chloride at 0°-5°C followed by treatment with ammonia. The pH has to be maintained at 6.5–7.0 otherwise –Cl group is replaced by –OH. In other compounds R_1 may by aniline, methoxyphenylamino or sulphophenylamino groups and R_2 methylamino, ethylamino or hydroxyethylamino groups. The main effect of substituents is in modifying the solubility and substantivity of the product. Almost all these compounds are unstable to hypochlorite bleach.

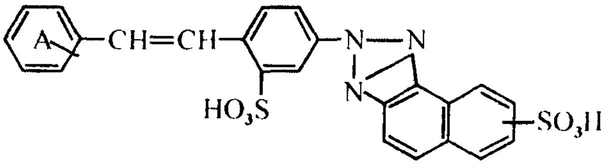
Stilbene Triazoles : Several other products have been claimed to be brightening agents. One of these is bistriazole which is obtained by oxidising the disazo dye, 4, 4′-diaminostilbene-2, 2′-disulphonic acid → naphthylaminesulphonic acid (2 moles) with hypochlorite.



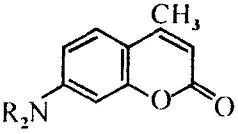
bistriazole

Bistrizole has a greenish fluorescence. It is useful in shading products. It is very stable to hypochlorite.

Blue fluorescence and hypochlorite stability are displayed in the unsymmetrical product described in B.P. 717889 (Gy) in which ring may contain a substituent like CH_3–, CH_3O–, –Cl or –SO_3H.

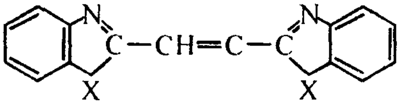


2. Coumarin Derivatives : Compounds of the type of the structure given below are suitable for nylon and wool. These are used from aqueous solution either as acid salts or where one R is alkyl and the other H, as the aldehydebisulphite (methane-w-sulphonate) compound.



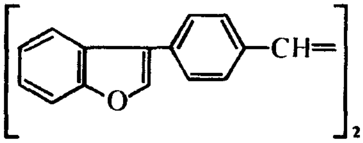
(where R is alkyl)

3. Benzthiazoles, Benzoxazoles and Benziminazoles : CIBA claimed that the compounds having the structure given below have good fastness to chlorine, *e.g.*, uvitex RS.

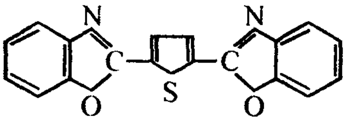


CIBA also investigated compounds of general formula (shown below) where X may be S, O, NH or NR (*e.g.*, R = $-CH_2-CH_2OH$). Such compounds have been found to possess good fastness to hypochlorite, a substantivity for nylon. Quaternary derivatives of this series have been found to possess improved substantivity for nylon, polyester and cellulose acetate.

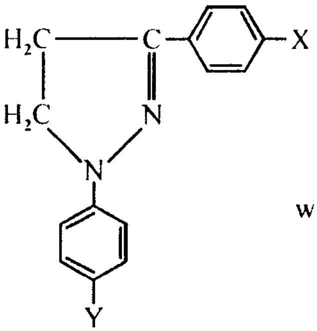
CIBA also reported that the compounds having the structure shown below are useful for the mass coloration of polyester and nylons.



CIBA also synthesised the compound of the structure given below. This compound is stated to be suitable for plastics and hydrophobic fibres.

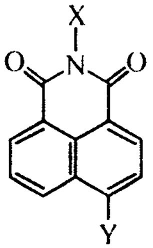


4. Diarylpyrazolines : These compounds having the structure shown below are effective brighteners. These can be applied with detergents in the form of a dispersion or in solution when sulphonated.



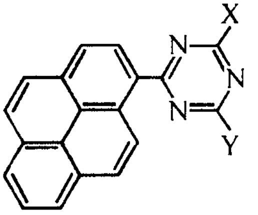
where X = H, Cl
Y = H, $COOCH_3$,
SO_2NH_2 or SO_3H

5. Naphthalimide Derivatives : BASF claim in B.P. 741798 that compounds of the type having the structure given below are suitable fluorescent brightening agents for synthetic materials such as polyesters and polyamides. They may also be added to the detergents.



where X = alkyl or aryl
Y = alkoxyl, $NHCOCH_3$
$NHCONH_2$ or
$NHCONHC_6H_5$

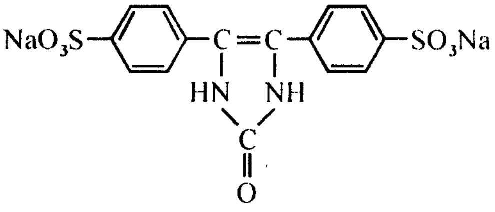
6. Pyrene Derivatives : Triazinyl derivatives of pyrene having that structure given below have been found to be highly effective brighteners for synthetic fibres.



X = substituted amino, alkoxy,
substituted alkoxy,
alkylthio
or substituted alkylthio.
Y = X or Cl.

These may be applied either from aqueous dispersion or incorporated during fibre manufacture. These may also be added to the detergents.

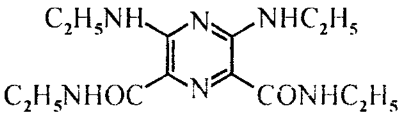
7. Miscellaneous Chemical Classes : One of the early brighteners was blankophor WT which was obtained by the condensation of benzoin with urea followed by the disulphonation of the product.



blankophor WT

It is mainly applied to wool.

There are many pyrazine derivatives which are suitable as brighteners for wool and synthetic fibres of various types.



23

CHAPTER

NON-TEXTILE USES OF DYESTUFFS

Introduction

The main application of dyes is for colouring textiles. However, dyes are also used for colouring a number of other substrates such as leather, paper, food-stuffs, drug, polymers, cosmetics, printing inks, lacquers, varnishes, paints, oils, soaps, plastics; etc. These are also used in photography for sensitizing and desensitizing photographic plates and as indicators in analytical work. Dyes are also useful as staining agents in bacteriological work.

The chromophoric and auxochromic groups in the dyes used for dyeing these substrates have been found to be similar to those used for textile fibres. However, their choice should be such that resultant dyed substrate must be quite satisfactory.

The various non-textile uses of dyestuffs are as follows :

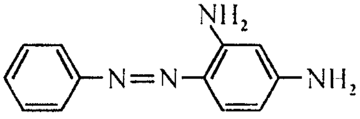
1. Leather Dyes : Natural leather is a protein substance and can be dyed with acid dyes, among others. Finished leather can also be dyed with pigments, the choice of the colour type depending on the nature of finish.

When basic dyes are used for dyeing leather, they give powerful, rich and full shades on leather. Although these dyes produce surface dyeing, they withstand perspiration. However, the main drawback of these dyes is that they are not fast to light and when deep shades are dyed, a reddening of the shades takes place.

Whenever light shades on dye are desired, acid dyes are used in the presence of formic acid.

The dyes used for leather may not have the fastness properties but the dye used should not be highly sensitive to variations in the leather and, thus there should be uniform dyeing. In some leather dyes, alkyl sulphonic groups are present in one of the components and they improve the penetration.

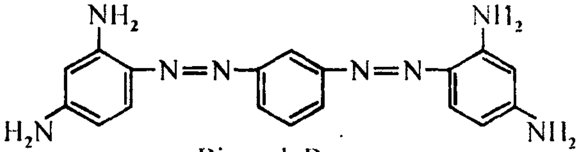
The chemical class of dyes used is mostly azo dyes. However some acridine and aniline dyes are also used *e.g.*, chrysoidine Y is basic mono azo dye used for dyeing leather.



chrysoidine Y

Some of the dyes used for dyeing leather are as follow :

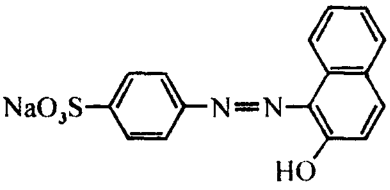
Bismark Brown is basic diazo dye.



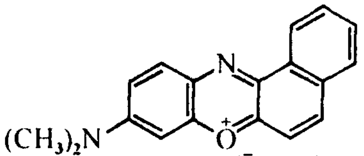
Bismark Brown

Basic dyes produce deep and rich shades. They are resistant to perspiration so leather dyed with these dyes are used for making gloves and clothings.

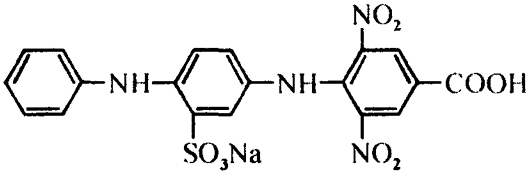
Orange II is acid mono azo dye used for dyeing leather.



Orange II

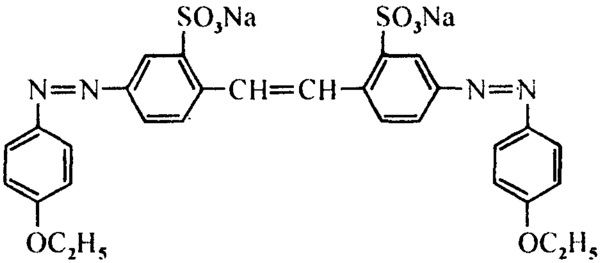


Cl^- Meldala's blue



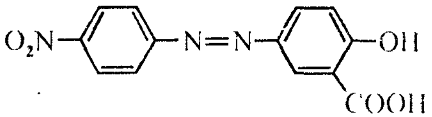
Amido Naphthal Brown 3G

Some direct dyes are used for dyeing chrome leather and semichrome leather whenever level shades are required.



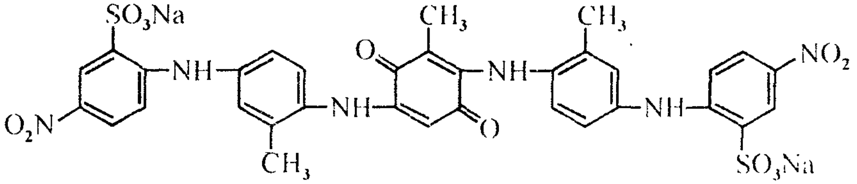
yellow dye

Mordant dyes are becoming popular with glove tanners and are dyed by the metachrome method. An example of these orange dye.



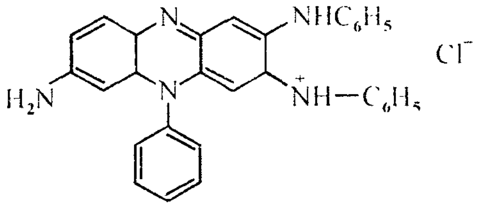
orange dye

The *p*-quinone nitro dyes have the property of deep penetration and they give fast to light brown colour to leathers. An example of these dyes is acid leather brown EGB.



acid leather brown EGB

Nigrosines are bluish-black to black dyes. These are water-soluble dyes which are used chiefly for the dyeing of the leather. These are prepared by the oxidation of aniline hydrochloride with nitrobenzene in the presence of ferric chloride at 160°-180°C. Nigrosines are also useful in the preparation of boot polishes.

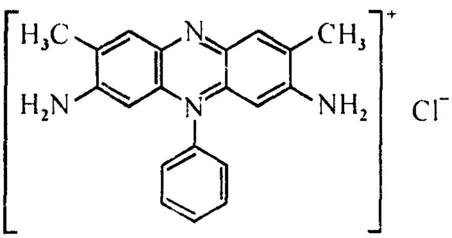


Nigrosine C (New)

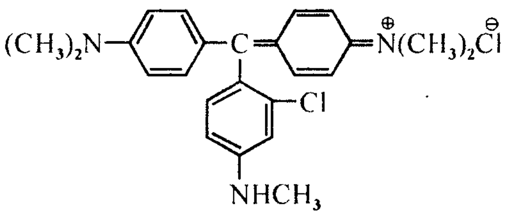
Metal complexes are also useful for leather dyeing. An example of these is igenal brown IRBF (IG). It is the copper complex of the monoazo dye. It is prepared by heating the dye in aqueous solution with copper sulphate and ammonia. It has good levelling and penetrating power on vegetable-tanned and chrome-leather. Chromium complexes are also used for dyeing leather.

2. Paper Dyes : Paper is a non-woven material made up primarily from cellulose of varying degrees of refining. Dyes are adsorbed on the pulp by their affinity for the cellulose.

Paper is coloured either by dyeing or be pigmentation. Direct dyes are most commonly used. The dyes used for dyeing leather are also used for dyeing paper. Examples of these are :

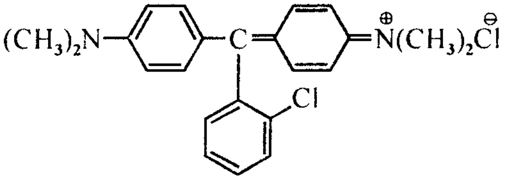


The coloured materials used for pigmentation must be finely divided. Most of the carbon papers contain elemental carbon in finely divided form and wax with small amount of oil-soluble dye to counteract the reddish tone of the carbon black. In some cases a basic dye methyl violet 10 BNS is employed.



methyl violet 10 BNS

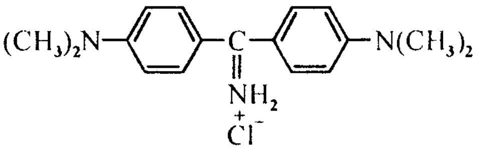
Safranine T



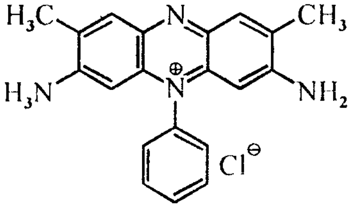
Basic Blue dye

Vat dyes are very suitable for colouring paper pulp because of their fastness to alkalies.

Examples of Basic Dyes

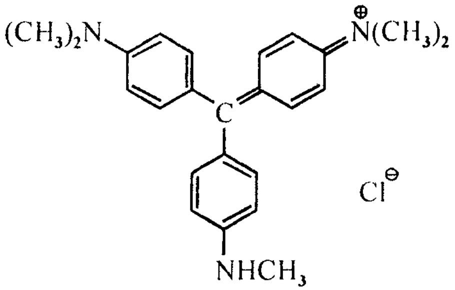


Auramine O



Safranine T

Carbon papers are made by coating the paper with a composition containing waxes, oils and oil soluble dyes. Most of the carbon papers contain carbon black and a small amount of a blue dye soluble in oil. The blue dye is used to counteract the slight-reddish tone of carbon black.



Methyl Violet 10 BNS

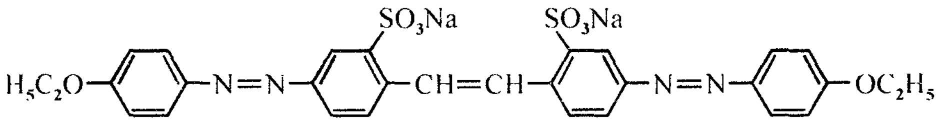
The paper may be coloured in the pulp or by dipping or by impregnation. Acid dyes are used for internal colouring of paper but such papers will bleed in water. Coloured papers and paper boards are manufactured for a multiplicity of end uses, which in turn demand certain degrees of fastness *e.g.* light, alkali, acid, chlorine, ink eradicators, and wet rubbing.

A coloured sheet used in plastic laminates requires the utmost in fastness to light since this may be exposed to light over quite extended periods of time.

Fastness to alkali is of importance for paper subjected to gluing or pasting operations where adhesives may be alkaline. Papers used for packaging alkaline materials such as soap must not change shade on storage.

Fastness to acid is important in writing papers where acid inks may be used, acidic glues and adhesives may be encountered also.

Napkin papers, paper towels, facial tissues, and papers employed for packaging wet materials should be fast to bleeding in water. *e.g.*, chrysophenine G, a direct dye.



Chrysophenine G

3. Food Colours : Food is mainly used for nutrition. However, it may be made more acceptable by colouration.

Originally, the substances used for colouration of food were naturally colouring matters like chlorophyll, cochineal, saffron and turmeric. However, they are still used to a great extent. These days synthetic dyes find extensive use due to the following reasons :

(*i*) They offer a variety of shades.

(*ii*) They are cheap.

(*iii*) They can be handled easily.

The criteria for selecting a synthetic dye for dyeing food are as follows :

(*i*) They should be stable to light and heat.

(*ii*) They should not interact with other ingredients.

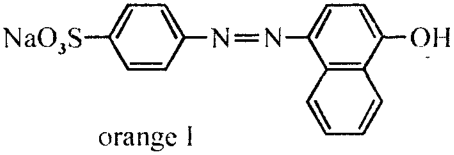
(*iii*) They should not interfere the taste and flavour of the food.

(*iv*) They must be made free from harmful constituents such as lead and arsenic.

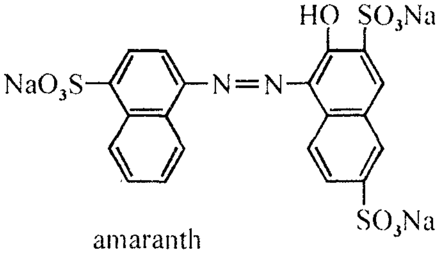
(*v*) They must be totally harmless to human beings.

In order to achieve the above properties, the food colours are to be certified and permitted. These are certified on the basis of their complete analysis. Thus, there is legislative control for restricting the use of food colours to certain permitted items which have been found to be harmless after rigorous examination.

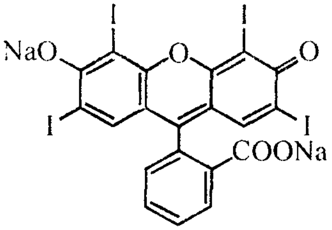
The dyes used for colouring food are orange I, tartazine, amaranth, erythrosine, naphthol yellow, crystal red F, fast red E, victoria scarlet 3R, etc.



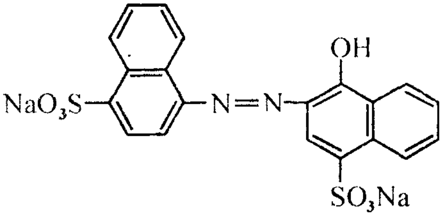
orange I



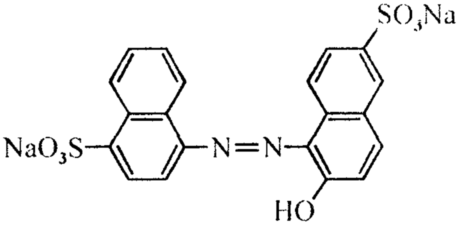
amaranth



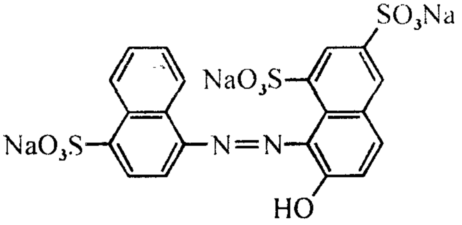
erythrosine



crystal red F

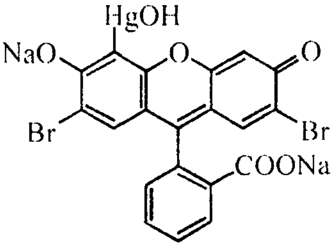


Fast red E



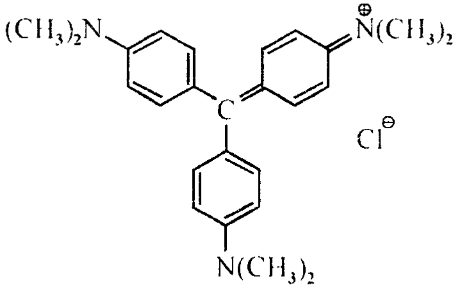
victoria scarlet 3 R

Certain dyes are used as medicine, Mercurochrome a derivative of fluorescein is used as antiseptic.

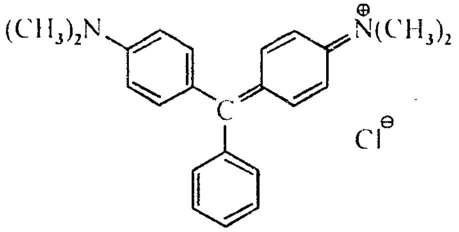


Mercurochrome (Merbromin)

Crystal violet and malachite green are effective against skin eczemas, ulcers and burns.



Crystal Violet

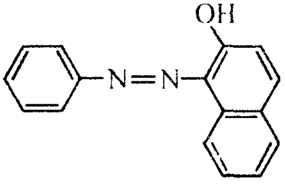


Malachite Green

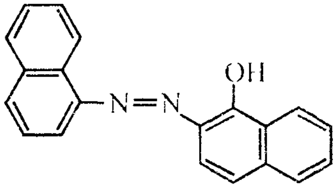
Acriflavin, prontosil and neoprontosil are used in the treatment of trypanosomiasis (sleeping sickness).

Phenothiazine is used as urinary antiseptic. Phenolphthalein is used as mild laxative. Ethoxazene, Pyridium and Neotropin are used as antiseptics for genitourinary infections.

4. Solvent Dyes : These dyes are not soluble in water but soluble in organic solvents. These dyes are derived from azo, anthraquinone, phthalocyanine and xanthene dyes. These dyes find uses in varnishes, polish, printing inks, blue pen inks, polymers, fats, oils, waxes, etc.



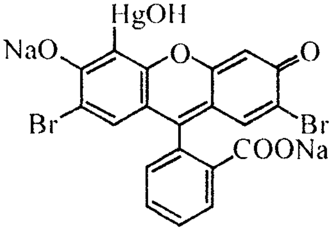
sudan orange R



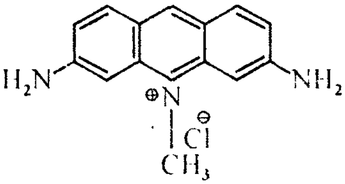
brown dye

5. Wood Dyes : These are applied to wood in water, alcohol or other solvents. These are used for staining wood in various shades for matching the same with other parts of building. When the wood is painted with or soaked in the dye solution, the solvent evaporates.

6. Medicinal Dyes : The application of dyes in pathology was first of all discovered by Ehrlich who found that the staining of nerve calls by methylene blue is selective. Later on, several dyes were found to stain and paralyse specific micro-organisms. These discoveries gave a clue to the use of dyes as antibacterial and chemotherapeutic agents. However, their use in chemotherapy has considerably diminished because more effective drugs like penicillin, streptomycin, sulphanilamides have been discovered. Mercurochrome and acriflavine still find use as antiseptics in medicine. Other dyes having limited application as bactericides are brilliant green, crystal violet, malachite green, methyl violet gention violet.

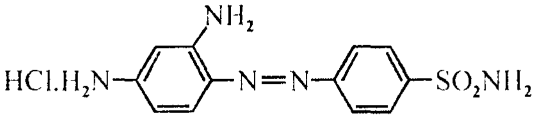


mercurochrome

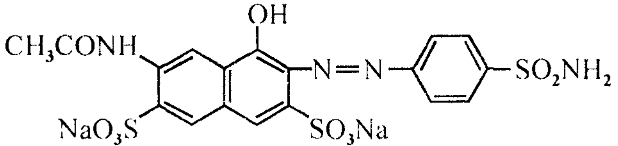


acriflavine

Pyridium was once used as ordinary antiseptic but the drug is excreted in an inert form and colours the urine red. Scarlet red is used as 4-8 per cent ointment. It promotes growth of epithelium over ulcers. Prontosil and neoprontosil are also azo dyes. These are used in the treatment of *trypanosomiasis* (sleeping sickness).



prontosil

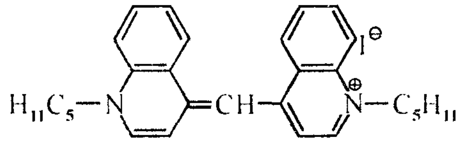


neoprontosil

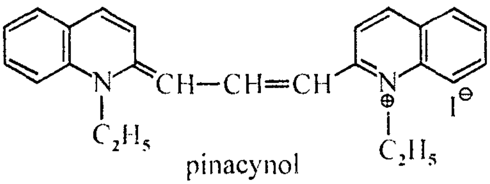
Acroflavine and proflavine are acridine dyes. Their solutions are effective germicides against gram positive micro-organisms in an alkaline medium. These compounds are said to be 20 times as powerful as $HgCl_2$ and several hundred times more efficient than phenol.

7. Photography : An ordinary photographic plate or film is sensitive only to violet and blue in the visible region and to ultraviolet light. It is found that if certain dyes are added to the photographic emulsion, it is interested to note that the coated plate becomes sensitive to the whole visible spectrum and also sensitive to the near infrared. The dyes added to the photographic emulsion are known as *photographic sensitizers*. All dyes cannot act as photographic sensitizers. If the complete effect is to be achieved, the sensitizer added should be highly pure and must be employed in very diluted form. The discovery of colour photography could be attributed to the synthesis of efficient sensitizing dyes.

Cyanine is one of the oldest synthetic dyes but its sensitizing properties were discovered many years later. However, its use as a protographic sensitiser is limited because it causes fogging of the plates. The sensitizing property of a cyanine dye can be enhanced by adding ammonium or alkali aurous thiocyanate to the emulsion. Carbocyanine and isocyanines have been found to be much more effective sensitizers in colour photography. Aqueous solutions of certain acid dyes are employed for hand colouring and retouching of black and white photographs.



cyanine



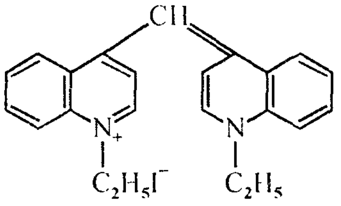
pinacynol

Super sensitizing is very important is colour photography. It is achieved by employing mixtures of dyes and by compounds which do not have senstitizing activity by themselves.

Cyanine Dyes (Polymethine Dyes)

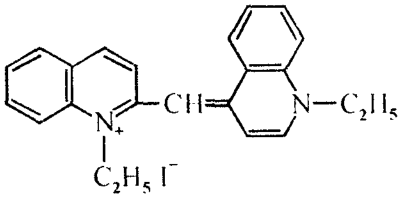
These dyes are extensively used as photographic sensitizers and desensitizers. The cyanine dyes have two quinoline nuclei linked through uneven number of methine groups (–CH=). They are sub-classified on the basis of number of methine groups and the position of linkage. They sensitize the photographic film to different colours.

(*i*) **Cyanine Dyes :** The two quinoline nuclei are linked through 4, 4′ position by a methine group (–CH=). They sensitise the photographic film to yellow, orange, red or green regions.



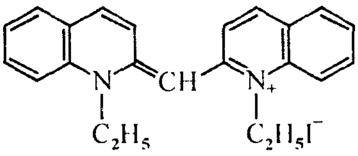
Cyanine

(*ii*) **Isocyanine Dyes :** In this case two quinoline rings are linked through 2, 4′ position by a methine group (–CH=)

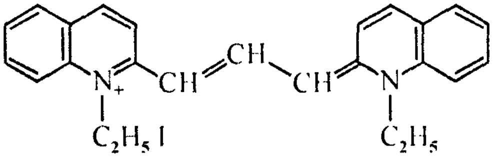


Ethyl Red

(*iii*) **Pseudo Eyanine Dyes :** Contain two quinoline rings attached through 2, 2′ positions by a methine group (–CH=). These dyes sensitize the films to blue and green colours.

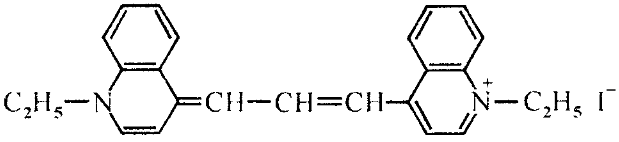


(*iv*) **Carbocyanines :** These dyes have the quinoline rings lined through 2,2′ positions by three methine groups (–CH = CH–CH=). Pinacyanol sensitizes the film to red colour.



Pinacyanol

(*v*) **Kryptocyanines :** The quinoline units are linked through 4, 4′ positions through three methine groups (–CH = CH–CH=). The film is sensitized to green by this dye.



Kryptocyanines

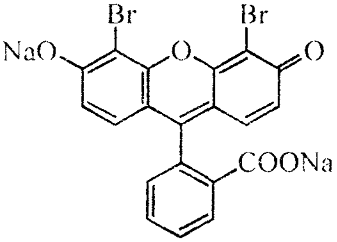
8. Dyes Used in Cosmetics : A number of dyes are used in the preparations of various beauty aids such as face powders, lipstics, nail polishes, hair darkening formulations etc.

The dyes and pigments used in cosmetics require to have certain properties.

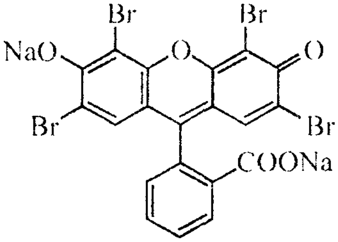
1. They should have brightness and attractiveness.
2. They should have resistance to perspiration.
3. They should be non-toxic.
4. They should be water soluble or oil soluble.
5. They should not affect skin.

Face powders and lipsticks are coloured with organic or mineral pigments.

The dyes used for nail and lipstic are derivatives of fluorescein. Dibromoderivative of fluorescein *i.e.*, Eosin dispersed in oil is used as nail polish while tetrabromo derivative of fluorescein gives coloured lakes with transition metal salts which are oil soluble and are used in lipstics.

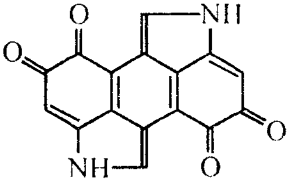


Eosine

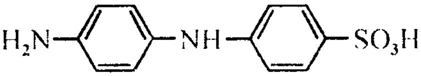


Tetrabromo fluorescein

Melanin and p-aminodiphenyl sulphonic acid are used as black dye in hair dye formulation.



Melanin



p-aminodiphenyl amino sulphonic acid

9. Indicators and Reagents : In analytical chemistry, a number of dyes find valid applications which are as follow :

(*i*) *As pH indicators*, in volumetric analysis *e.g.*, phenolphthalein, methyl orange, methyl red, congo red, etc.

(*ii*) *As oxidation-reduction indicators*, in volumetric analysis *e.g.*, methylene blue, indigo carmine, etc.

(*iii*) *As adsorption indicators* in volumetric analysis in the titration of halides with silver nitrate, etc., dichlorofluorescein, eosin, etc.

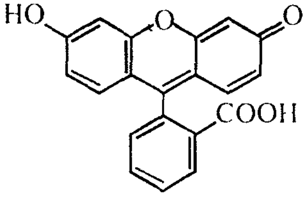
(*iv*) *As precipitants* for the determination of metals listed as below :

Dyes	*Detection of metals*
Naphthol Yellow	CO, Hg, K, Rb
Orange IV	Zn, Mg,
Benzo Fast Yellow 5 GL	Cr, Cu, Sc, Ni
Direct Green B	Cu
Eriochrome Blue Black B	Co
Diamond Black F	Many metals
Safrarine	Sb, Hg, Ag
Naphthazarin	Al, Be, Mg
Methylene Blue	Many metals and anions

Certain dyes are known which change colour at specific temperatures. Such dyes are used in observing the variations in temperature in different parts of machinery.

10. Flourescent Dyes : In our daily life, luminescence is desired. For this purpose, fluorescent dyes are used for dyeing and printing theatrical fabrics, carpets in cinemas and other purposes. Certain fluorescent dyes, which are activated by ultraviolet light but do not have after-glow, are used for night marking of streets and direction signs.

An example of fluorescent dyes is fluorescein. This emits an intense green fluorescence. This is mainly used for the detection of leaks in drains. During the war, airmen are provided with a pack of fluorescein. If they are forced down into sea, the dye is released into the water and this produces a green patch which can be seen from a great distance. Thus, the rescue operations can then be easily guided.



fluorescein

11. Coloured Smokes : During the wartime, coloured smokes are produced for giving signals. These are produced by igniting a mixture of the pigment, potassium chlorate and sugar. The pigment used must have the properties like colour, volatility and thermal stability. The pigments used in producing coloured smokes are 1, 5 and 1, 3 bis *m*-toluidino anthraquinone (violet), 2-bromo-l-amino-4-toluidino anthraquinone (blue), 1-amino-4-hydroxy anthraquinone (wine red) and 1, 2, 4-trihydroxy anthraquinone (brown).

12. Camouflage Colours : During war times, precautionary steps are required to prevent the detection of targets by infrared photography. For this purpose, the dispersions of the phthalocyanines and of the pigment green (iron complex of 1-nitroso-2-naphthol) are used.

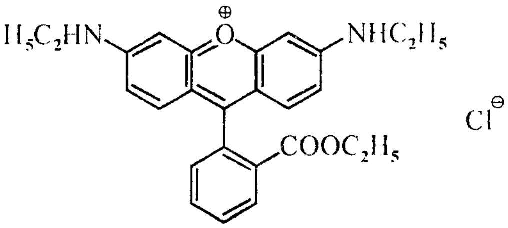
Recent Application of Dyes

1. Dyes for Lasers

Definition of 'Laser'. The word laser is actually an acronym which stands for Light Amplification by stimulated Emission of Radiation. Lasers are used for a variety of applications in medicine *e.g.*, for eye surgery therapy, for Carpel Tunnel Syndrome and for photocoaquation. Laser light is monochromatic, directional and coherent, while ordinary white light is a combination of many colours of light, emitted in many directions away from the source. Lasers consists of a lasting medium which is either gaseous or liquid or solid. Sometimes semiconducting material is also used as laser medium Organic dyes, from Rhodamine or coumarin or polymethine class are also used as dye lasers which may be in liquid solution or in suspension form. They are tunable over a broad range of wavelengths. Dyelasers, in which complex organic dyes in solution are the lasing material can be tuned to produce light of any chosen wavelength over a range of a sizable fraction of the visible spectrum.

One of the major sources of chemical hazards from lasers is from the organic dyes used in dyelasers. Most dyes used as dyelasers are fluoresent organic dyes from rhodamine class are considered to be mutagenic or carcinogenic while other dyes from polymethine class are toxic.

Rhodamine CG is used as dyelaser.



Rhodamine 6 G

Bio-Medical Applications of Dyes

1. Methylene blue, a thiazine dye is useful as a vital stain, since it deeply colours parts of the living tissues. such as peripheral nervous system, leaving other parts unstained.

   Methylene Blue is one of the most common stains used in bacteriological technique for examination of pathogenic organisms such as tuberculosis and cholera bacilli.

2. Malachite green free from zinc is used as bacteriological and histological stain.
3. Phenolphthalein, a triphenylmethane dye is a mild tasteless purgative while disodium salts of tetraiodophenolphthalein and phenoltetraodo phthalein are used for X-ray examination of gall bladder. Disodium phenoltetrabromophthalein disulphate is used in the examination of liver function.
4. The opacity of 3-iodo and 4-iodoalizarin is used in X-ray visualisation.

5. Erythrosine A and erythrosine B are used as microscopical stains.
6. Ethoxazene, pyridium and neotropin are mono azo dyes which are useful staining media for tumors.
7. Riboflavin (vitamin B_2) is a fluorescent yellow, water soluble pigment.
8. Nile Blue 2B is an oxazine dye used as a stain and inhibits the growth of cancer cells.

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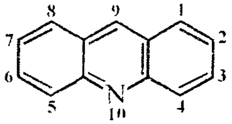
CHAPTER

ACRIDINE DYES

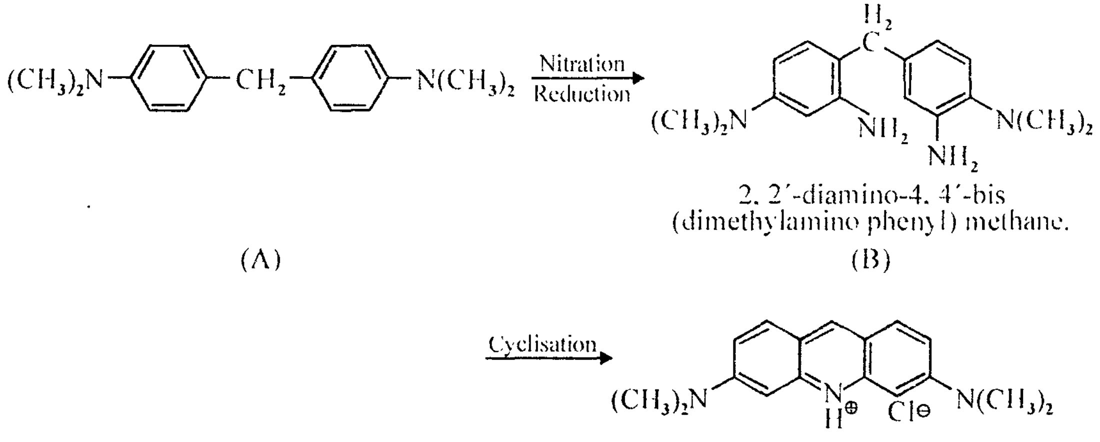
Introduction

Acridine dyes have basically acridine skeleton. Most of these dyes have amino or substituted amino groups in 3 and 6 positions or only in 6 position.



Like xanthene dyes, the acridine dyes can be divided into two subgroups corresponding to diphenylmethane and triphenylmethane derivatives. In the latter case the third phenyl ring is present in 9 position.

Among the acridine dyes, acridine orange NO is important. It is prepared from 4,4′-bis (dimethylaminophenyl) methane (A) by nitration and subsequent reduction with zinc and hydrochloric acid to yield 2, 2′-(diamino)-4, 4′-bis (dimethylaminophenyl) methane (B) which then gets cyclised. The cyclisation of (B) is done either by heating the reduction mixture to boil and isolating the dye as zinc chloride double salt or by heating (B) with aqueous sulphuric acid at 140°C under pressure and salting out the dye by the treatment of common salt in the presence of copper sulphate and air at 80°C.



(A)

2, 2′-diamino-4, 4′-bis (dimethylamino phenyl) methane.

(B)

acridine orange NO

Acridine orange NO is used to dye silk orange with a green fluorescent. However, it has poor fastness properties. Acridine orange NO is used for leather dyeing and in ink manufacture.

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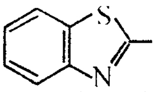
CHAPTER

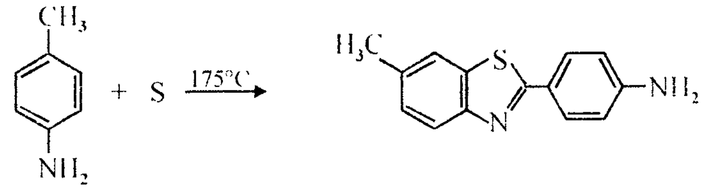
THIAZOLE DYES

Introduction

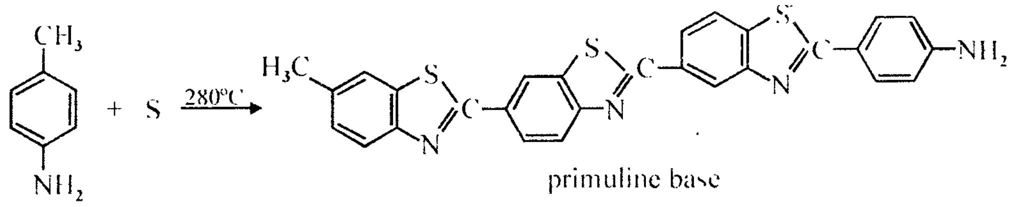

benzothiazole

In these dyes, thiazole or benzothiazole ring system is present. These dyes are characterised by the substantivity of the dyes and hence made use of in azo direct dyes. Thiazole ring system is also found in certain cyanine dyes and anthraquinone dyes.

Two important intermediates involved in the synthesis of azo direct dyes of this class are dehydrothio-*p*-toluidine and primuline base. They are obtained by heating *p*-toluidine and sulphur in appropriate proportions at 175°C and 280°C respectively.



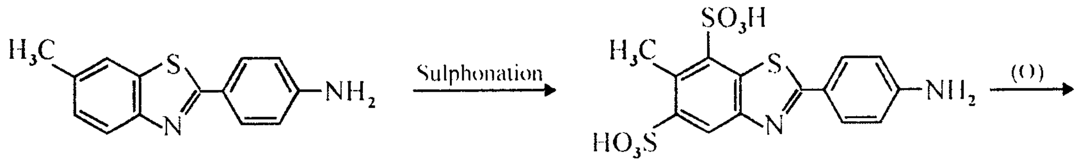
p-toluidine dehydrothio-*p*-toluidine



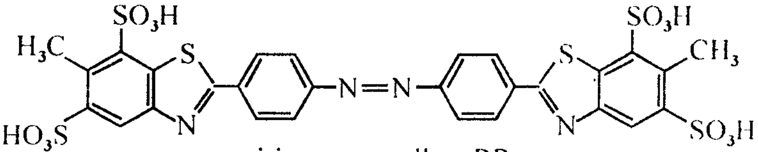
primuline base

Dehydrothio-*p*-toluidine and primuline base find use after sulphonation in the preparation of azo direct dyes. Some examples of this are as follows :

1. Sirius Supra Yellow RR : It is prepared by the oxidation of dehydrothio-*p*-toluidine-5, 7-disulphonic acid with hypochlorite in alkaline solution.

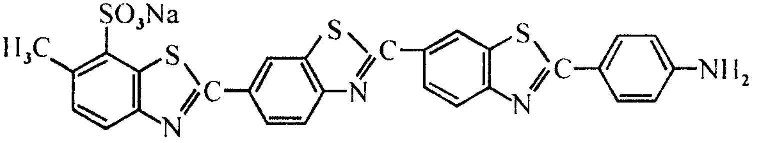


dehydrothioparatoluidine-5, 7-disulphonic acid



sirius supra yellow RR

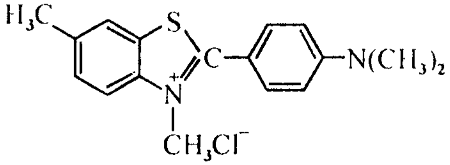
2. Primuline (C.I. Direct Yellow 59, 49000) : It is prepared by sulphonating primuline base.



primuline

This dye is used to dye cotton yellowish green. The dye may be diazotised on the fibre and coupled with 2-naphthol to a red shade. Similarly other shades may be obtained with different coupling components.

3. Thioflavine T (C.I. Basic Yellow 1, 49005) : It is a basic dye which is prepared by methylating dehydrothio-*p*-toluidine with methanol and hydrochloric acid at about 170°C under pressure.



thioflavine T

This dye is used to dye wool and silk directly. It is also used to dye cotton by tannin mordanting or by converting it into phosphotungstomolybdic lake.

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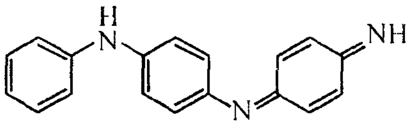
CHAPTER

INGRAIN DYES

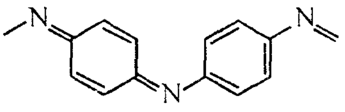
Introduction

These dyes include *oxidation colours* and *phthalogens*. As these dyes are produced on the fibre, they are similar to azoic colour as far as their application is concerned.

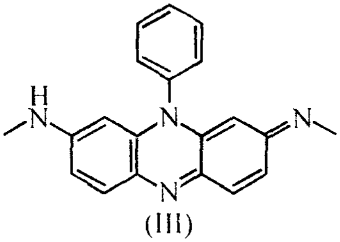
1. Oxidation Colours : An important member of this class is aniline and aniline hydrochloride and subsequently carrying out oxidation with a suitable reagent like dichromate or chlorate in the presence of a catalyst like copper salt. The colour so formed on cotton possesses good fastness and because of the cheapness it finds extensive use in commercial practice. The structural units present in aniline black are as follows :



(I)

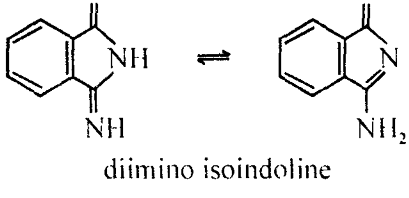


(II)



(III)

2. Phthalogens : Phthalogens are the precursors for phthalocyanines which are produced on cotton by dyeing and printing. The intermediate diiminoisoindoline is mixed with certain additives like copper salts and an organic solvent and the mixture is printed or padded on to cotton, on drying or steaming, the metal phthalocynanine gets formed *in situ*.



diimino isoindoline

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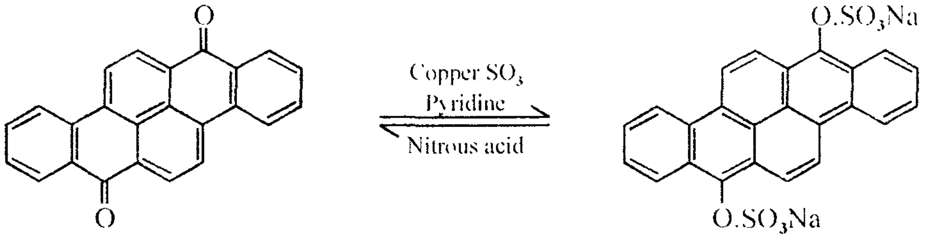
CHAPTER

SOLUBILISED VAT DYES

These dyes are derived from vat dyes or their intermediates in which the two keto groups in the quinonoid system $-CO-CH = CH-CO-$ or similar systems $-CO-(CH = CH)_n-CO-$ as explained under vat dyes get converted to stable leuco sulphuric esters like $-C\ (OSO_3Na) = CH-CH = C\ (OSO_3Na)$. The synthesis of solubilised vat dyes from the corresponding vat dye or a vat dye intermediate is done by treatment with sulphur trioxide in anhydrous pyridine having a metal such as copper, iron or zinc, and subsequently converting it into the sodium salt to the leuco sulphuric ester. The solubilised vat dye is applied on cotton and the parent vat dye gets regenerated on cotton by using an acid oxidising agent like nitrous acid. For example, indigosol golden yellow IGK is obtained from indanthrene golden yellow GK, the indigosol is applied on cotton and then gets oxidised on cotton to the parent dyes (I).



indanthrene golden yellow GK
(I)

indigosol golden yellow IGK

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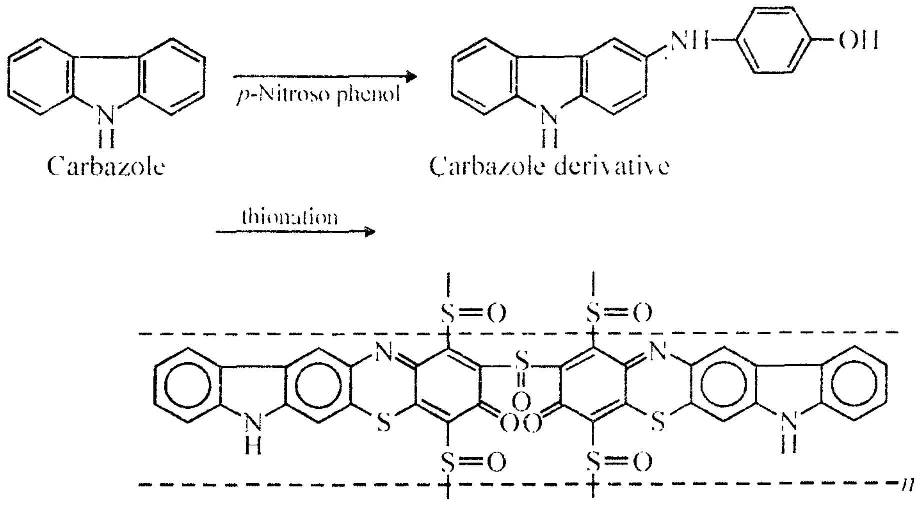
CHAPTER

SULPHURISED VAT DYES

Introduction

This group includes complex sulphur linkages having characteristic groupings by the virtue of which, the dyes can be vatted, because these groupings have quinonoid type of structures. The dye is applied on cotton as a vat dye and then regenerated on fibre by oxidation. Hydron blue R is an important example of this class which is obtained by the thionation of carbazole derivative. Unsubstituted carbazole is made to react with *p*-nitrosophenol in concentrated sulphuric acid at -20 to -25°C and the product obtained is reduced to obtain the carbazole derivative which is refluxed for 24 hours with sodium poly-suphide and sodium nitrite in butanol and the solvent butanol is distilled off to yield the dye.



hydron blue R

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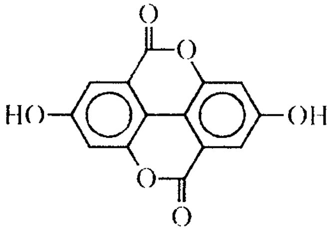
CHAPTER

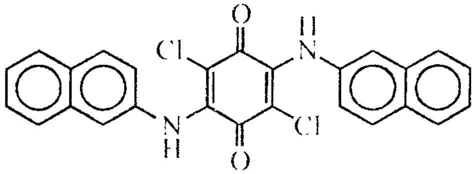
LACTONE, AMINO KETONE AND HYDROXY KETONE DYES

Introduction

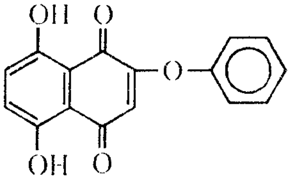
These dyes do not have any commercial uses but they are only important from their structural point of view. The respective examples of lactone, amino ketone and hydroxy ketones are resoflavine W, helindon brown CR and alizarin dark green W respectively. These are now obsolete as dyes.



resoflavine W



helindon brown



alizarin dark green W

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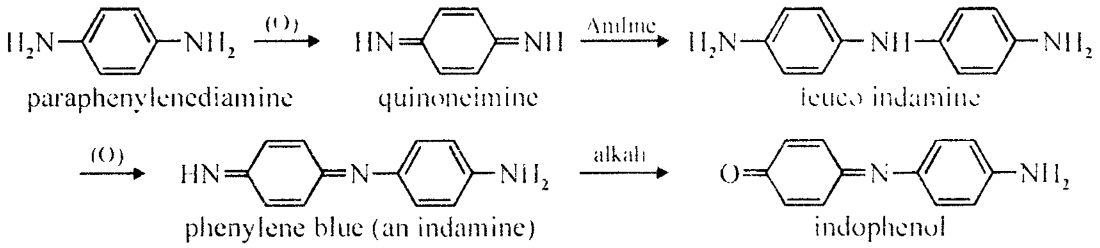
CHAPTER

INDAMINES AND INDOPHENOLS

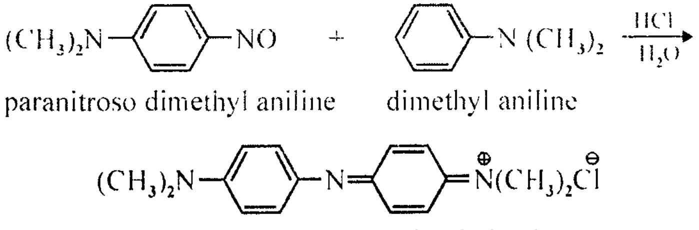
Indamine and indophenol structures together are known as quinoneimines. These include blue and green compounds and are obsolete as dyes. However, they find use as intermediates for azine, oxazine, thiazine, sulphur and sulphurised vat dyes.

There are two methods of preparation for indamines such as (*i*) and (*ii*) as well as for indophenols such as (*iii*) and (*iv*). Indamines are obtained by oxidising a mixture of one mole of an arylparadiamine like paraphenylene diamine having least one primary amine groups and one mole of an arylamine like aniline having vacant para position. In the second method, a nitroso compound is made to condense with a tertiary amine. Indophenols are obtained by analogous methods and also by the action of alkali on indamines. Toluylene blue is an example of indamines.

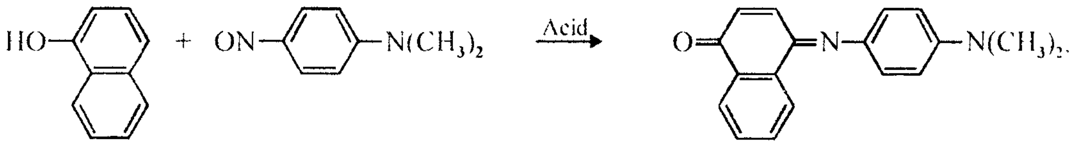
(*i*)



(*ii*)

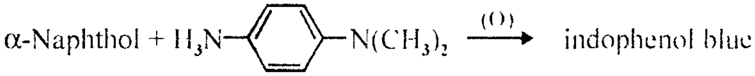


(*iii*)



α-naphthol　　para nitroso dimethylaniline　　indophenol blue (an indophenol)

(*iv*)



paraamino dimethyl aniline

For indamines and indophenols, see Chapter 15, *i.e.*, Heterocyclic Dyes.

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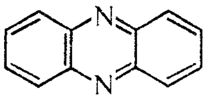
CHAPTER

AZINES

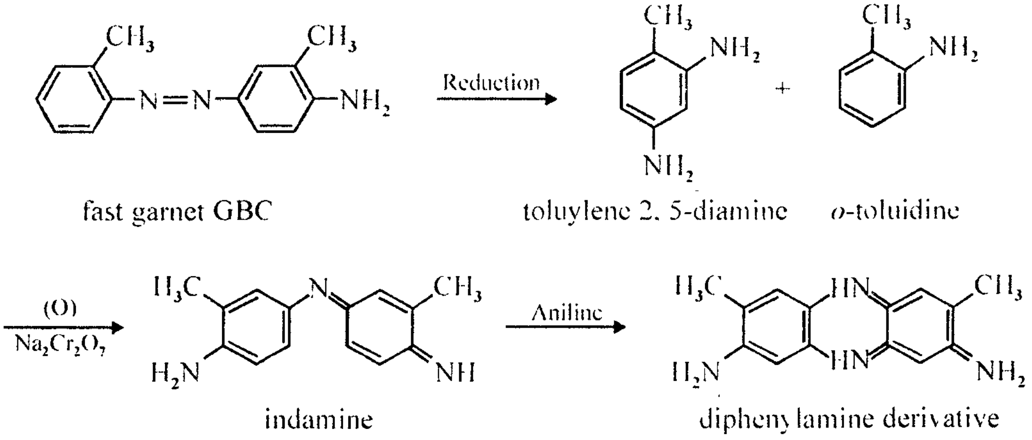
Introduction

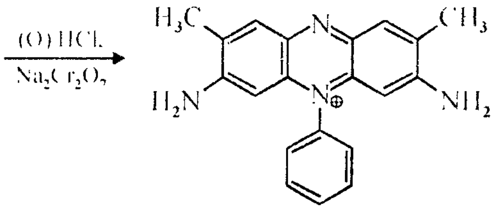
Azine class in one of the oldest known class of dyes and the first synthetic dye, Mauveine, belongs to this class. The azine ring structure is found in safranines like safranine T, indulines, nigrosines, oxidation colours like aniline black and also in anthraquinone derivatives.



azine ring structure

Safranine T is an important member of the class and used as a red paper dye. It is prepared from *o*-toluidine. Ortho toluidine has been converted to fast garnet GBC by diazotisation of one mole and coupling in conditions with another mole of ortho toluidine. This is then reduced with a suitable reducing agent like iron and hydrochloric acid to obtain *o*-toluidine and toluylene-2, 5-diamine, the filtered solution of the mixture of these arylamines, and then gets oxidised with dichromate solution at 10°C to yield indamine, which gets subsequently treated with one mole of aniline with the formation of a diphenylamine derivative, neutralised, to remove the precipitate of chromium sludge and oxidised with acidic sodium dichromate solution at 80°C to yield the dye, safranine T.





safranine T

Indulines are blue dyes which are prepared from azo compounds like aminoazo benzene by heating with aniline and aniline hydrochloride at 180°C.

Nigrosines are black dyes which are obtained from nitro compounds such as nitrobenzene or nitrophenols by heating with aniline and aniline hydrochloride in the presence of iron or ferric chloride. Aniline Black has been described in oxidation colour under ingrain dyes.

Note : Also, see chapter 15, *i.e.*, Heterocyclic Dyes.

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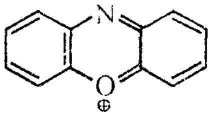
CHAPTER

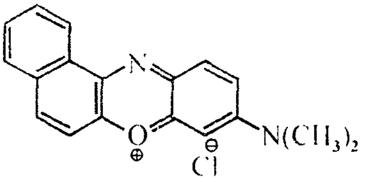
OXAZINES

Introduction

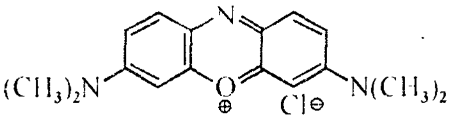
Oxazine class of dyes have characteristic oxazine ring system This class of dyes includes basic, chrome mordant and direct dyes as well as dioxazine pigments. The shades obtained are generally blue. Oxazines are obtained by the condensation of para nitroso-dialkyl anilines like paranitroso dimethylaniline with a suitable phenol in alcoholic solution in the presence of zinc chloride. Thus, capri blue GN is obtained by the condensation of metadiethylaminophenol and paranitroso dimethylaniline. Capri blues are basic dyes. They possess brilliant shades, good fastness to light and moderate fastness to washing.



oxazine ring system

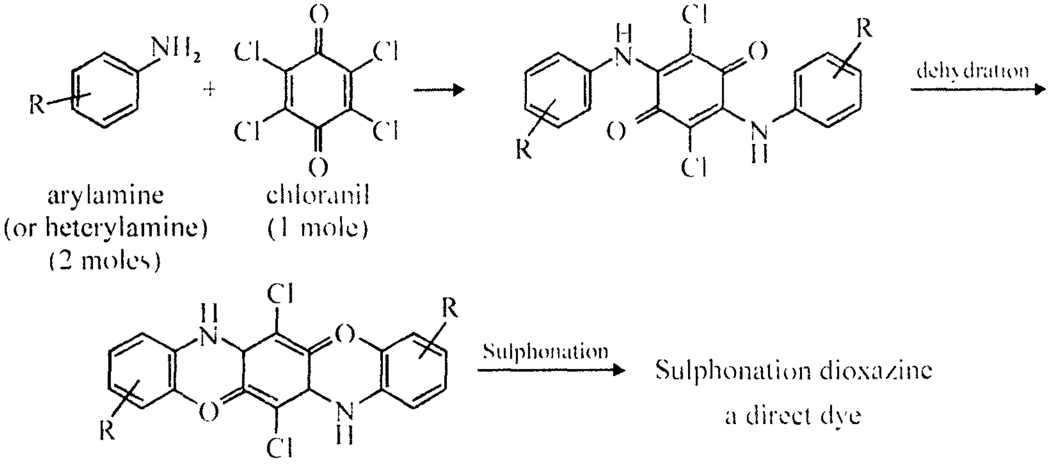


meldola's blue



capri blue GN

Medola's blue and many other dyes of this class are obtained by following the general procedure using variety of phenols. Dioxazine pigments and light fast direct dyes have dioxazine ring system which is generally built up by the condesation of an arylamine or heterocyclic amine with chloranil.



arylamine (or heterylamine) (2 moles)

chloranil (1 mole)

dioxazine pigment

Note : Also, see chapter 15, *i.e.*, Heterocyclic Dyes.

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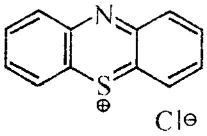
CHAPTER

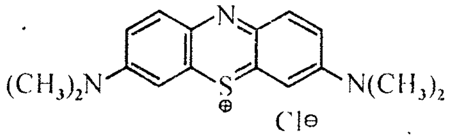
THIAZINES

Introduction

Thiazine ring system has been the characteristic structure of this class of dyes. Methylene blue has been an important member of this group.

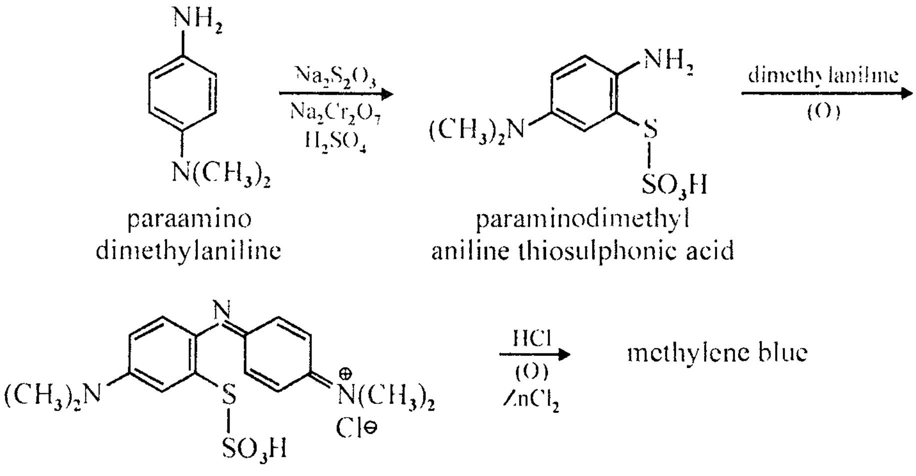


thiazine ring system



methylene blue

Methylene blue is obtained from N, N-dimethylaniline by nitrosation and reduction to obtain paraaminodimethylaniline which gets converted to thiosulphonic acid by treating with aqueous sodium thiosulphate, sodium dichromate and sulphuric acid. To this a further mole of dimethylaniline is then added under oxidising conditions to obtain indaminethiosulphonic acid which on further oxidation in the presence of an acid such as hydrochloric acid and zinc chloride in the presence of an acid such as hydrochloric acid and zinc chloride yields methylene blue. In its manufacture from dimethylaniline no intermediate has been isolated. Methylene blue finds use as a basic dye and leather dye, and zinc free dye possesses medicinal uses.



paraamino dimethylaniline

paraminodimethyl aniline thiosulphonic acid

indamine thiosulphonic acid

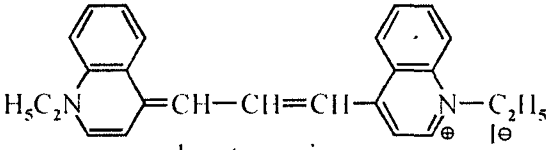
CHAPTER 34

CYANINE DYES

Introduction

In cyanine dyes there are two nitrogen containing ring systems, in one of these the nitrogen is quaternary while in another, it is tertiary; these two nitrogen atoms have been linked by a conjugated chain of an uneven number of carbon atoms, like –CH = and –CH = CH–CH =, etc., or similar chains having nitrogen atoms such as = CH–N = N– etc., The heterocyclic nitrogen having systems such as quinoline, pyridine indole, benzothiazole, etc., find use in their synthesis.

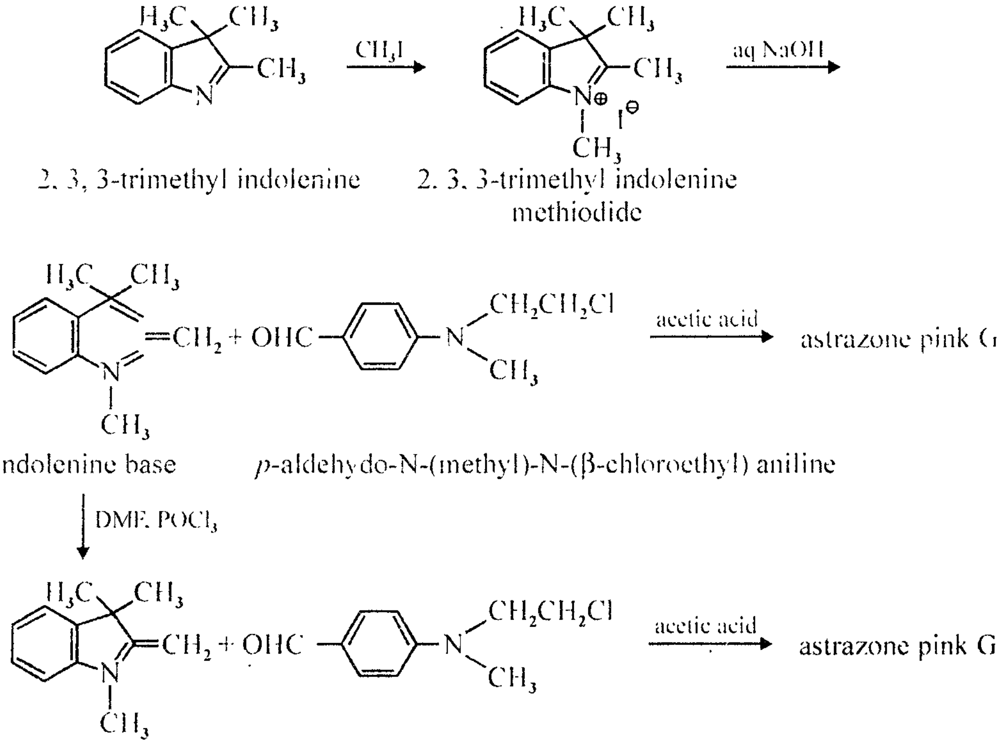
There are different classes of cyanine dyes which mainly depend upon the positions of heterocyclic systems attached to each other and the number and type of linkages of carbon chain or similar chain between two nitrogen atoms. For simplicity, an example has been described below. Kryptocyanine is a cyanine dye which is derived from quinoline derivatives. both the heterocylic nitrogen systems being quinoline. It belongs to a subclass carbocyanine because the two rings have been joined by the linkage. –CH = CH–CH=, and as the positions of attachment are 4, 4′, (the ring systems are linked through their 4 positions) this carbocyanine dye is also included in kryptocyanines



kryptocyanine

Most of the cyanine dyes find use in photography as photographic sensitisers and desensitisers, because they favour sensitisation or desensitisation in a particular region of visible and infrared spectrum.

As most of the cyanine dyes do not have fastness to acids and other agencies such as light, they have very limited application for textiles. A few members of cyanine dyes are also known as polymethine dyes. They are useful basic or cationic dyes for textile purpose. Most of these dyes are obtained from heterocyclic nitrogen system indole with peculiar structures. These dyes are also called astrazon colours. Astrafloxine FF and astrazon pink FG have been the two examples of the series. The key intermediate needed for their synthesis has been the indolenine base which gets condensed with the appropriate aldehyde or the indolenine-ω-aldehyde which gets condensed with the appropriate amine or active methyl group of a suitable compound. The indolenine base is prepared by the action of alkali on 2, 3, 3-trimethylindolenine methiodide which is obtained by the quarternisation of 2, 3, 3-trimethyl indolenine with methyl iodide. The indolenine-ω-aldehyde is obtained from the indolenine base by direct formylation with dimethyl formamide and phosphorus oxychloride. The synthesis of astrazon pink FG is described below.



2, 3, 3-trimethyl indolenine

2, 3, 3-trimethyl indolenine methiodide

indolenine base

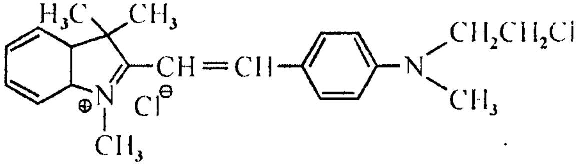
p-aldehydo-N-(methyl)-N-(β-chloroethyl) aniline

indolenine-ω-aldehyde

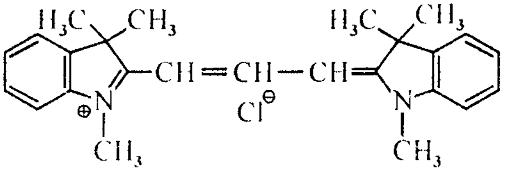
N-(methyl-N-(β-chloroethyl) aniline

(I)

The N-(methyl)-N-(β-chloroethyl) aniline needed for the synthesis is obtained from N-methylaniline by condensation with ethylene oxide to obtain N-methyl-N-(β-hydroxyethyl) aniline which is subsequently treated with phosphorous trichlororide or phosphorous oxychloride. The corresponding aldehyde is prepared by the formylation of I with dimethyl formamide and phosphorous oxychloride. Astraphloxine FF is obtained by condensing two moles of 2, 3, 3-dimethylindoleninemethosulphate with ethylorthoformate in pyridine at boil and isolating the dye as chloride.



astrazone pink FG



astraphloxine FF

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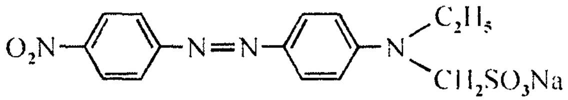
CHAPTER

DYES FOR SYNTHETIC FIBRES

Disperse Dyes

Disperse dyes include water insoluble dyes which could be applied on synthetic fibres. The first disperse dyes were reported for cellulose acetate rayon by British Celanese Corpn. in 1920. None of the other classes of dyes had been good for dyeing cellulose acetate.

Some dyes were reported which did not possess the solubilizing groups like SO_3Na. These had been found to dye the cellulose acetate from a water dispersion. Green and Sanders in 1923 prepared temporarily solubilized dyes having $-N-CH_2SO_3Na$ groups. These dyes were sold as ionamines *e.g.*, ionamine orange CB.



This dye got hydrolysed in the dye-bath giving a finely divided insoluble dye which got dissolved in the fibre yielding a solid-solid solution. These dyes lost the solubilising CH_2SO_3Na group on hydrolysis. Several ionamine dyes had been marketed.

These dyes were later replaced by acetate dyes which were aqueous disperse ions of insoluble dyes in a finely divided state (1 to 4 μ) and could be able to dye the fibre from aqueous dispersion.

Several dyes manufacturs produced these dyes which were named disperse dyes by C.M. Whittaker in 1953. These dyes had been dispersed by several techniques such as precipitation, milling with surface active agent, or milling with special kind of sand or glass. The disperse dyes should possess a slight solubility in water for proper dyeing. Dispersing agents are added to the dye to disallow aggregation but to enhance solubility. Several kinds of dispersing agents like alkyl sulphates, alkylaryl sulphonates. Fatty alcohol or amine + ethylene oxide condensation products, naphthalene sulphonic acid+ formaldehyde condensation products, lignin sulphonate, etc. have been used with disperse dyes.

Some of these dyes get sublimed during ironing. Hence a sublimation fastness rating has to be introduced. Some of these dyes with NH_2, N-alkyl group are influenced by traces of nitrogen oxides in the city atmosphere resulting in change of shade. Fastness to burnt gas fumes provides rating of this capacity.

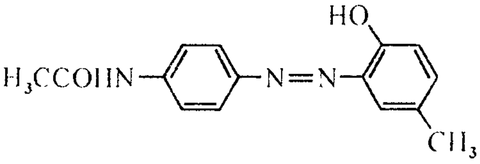
With the introduction of polyester fibres in 1950 there occurs the rapid development in this field to make dyes suitable for polyester fibers and several modifications have been carried out.

The dyeing could be carried out at about 100°C in presence of emulsified aromatic compounds like biphenyl, *o*-phenylphenol, di and tri chlorobenzene etc. The dyeing could be carried out to 130° in pressure vessels. Some new methods evolved are thermofixation, solvent dyeing and transfer printing. The chemical constitution of many of the new disperse dyes is unknown. However, most of the disperse dyes belong to azo and anthraquine one class which will be described in the following pages.

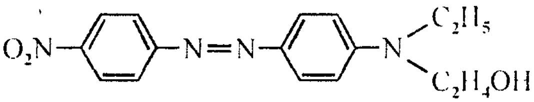
Azo Dyes

The monoazo disperse dyes have been reported to give almost a complete range of shades. These dyes are largely used for cellulose acetate (CA) and polyester (PE) fibers and their blends with cotton, polyamides (PA), polyacrylonitriles (PAN) and cellulose triacetate (CTA).

The CA dyes were mostly dyed red and yellow shades. They possess simple structures *e.g.* cibacet yellow GBA, C.I. disperse yellow 3, 11855.

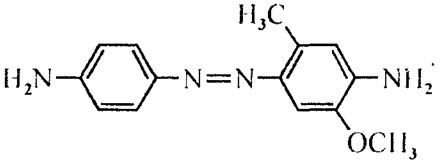


C.I. disperse red 1, 11110 possesses following structure :

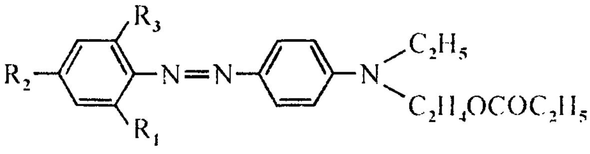


This dye is having light fastness 5 but possesses poor sublimation fastness. Its chloro derivative possesses higher light fastness.

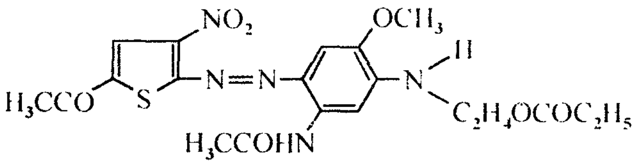
Cibacet diazo black B disperse black 2, 11255 is having following structure. It is applied to CA, then diazotised on the fibre coupled with 2, 3 hydroxy naphthoate to yield a good black :



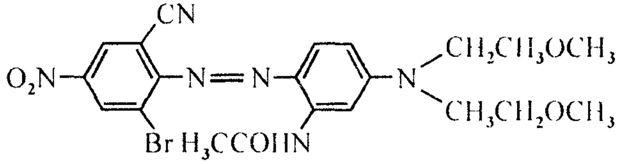
Many of these dyes are obtained from 4-aminophenylazobenzene substituted in various positions. The substitution of Br, Cl, NO_2 and CN provides bathochromic shift *i.e.*, the colour of dye moves from red to blue end of spectrum. It is possible to intensify colours by substitution on the nucleus as well as on the nitrogen. In the following example substitution of R_1, R_2 and R_3 by electron withdrawing groups causes batho-chromic shift :



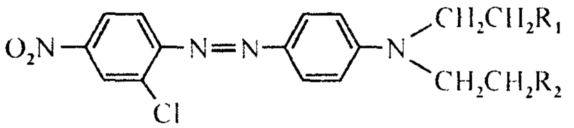
The dye BP 1351382 has been a bluish green dye for PE. Its structure is as follows :



Another example of blue dye for PE is RP 1370034 whose structure is as follows :



For polyester fibres most of the cellulose acetate dyes could not be used due to poor fastness to sublimation. As the PE dyes are fixed at high temperatures, these dyes get sublimed to a large extent. Structural variations are being made to make more complex dye molecules having improved fastness for PE fibres. The following example provides the structure of a dye molecule and effect of some substituents fastness properties :

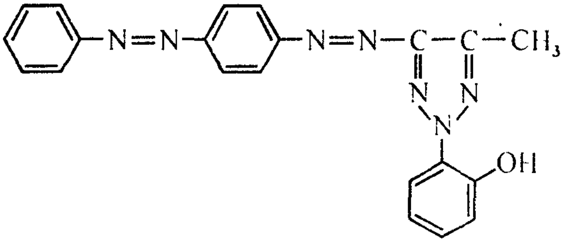


R_1 =	H	H	OH	$OCOCH_3$	CN
R_2 =	OH	H	CN	CN	CN
Light fastness	3	3.5	4.5	7	7
Thermo fixation fastness	2.5	1.5	4	4	4.5

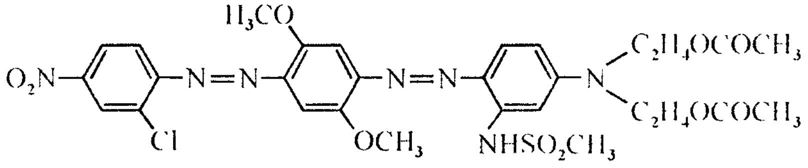
The cyanoethyl group tends to improve both light and thermo fixation fastness properties. The sublimation fastness has been improved by introducing acetylamino group in 3-position of coupling component.

Disazo Dyes

The disazo dyes find use is dyeing CTA and PE fibres. The following examples are from patents BP 1171803 Orange PE, and B.P. 1805326 Navy, P.E.



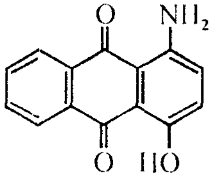
B.P. 1171803 Orange PE



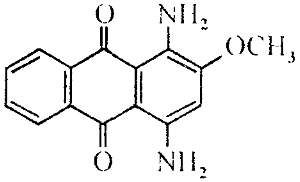
B.P. 1,805326 Navy PE.

Anthraquinone Disperse Dyes

This group largely provides blue and violet dyes. The earliest known dye was Duranol Red 2B, C.I. Disperse Red 1560710. Another dye has been celliton Fast Pink FF 3B, C.I. Disperse Red 11.

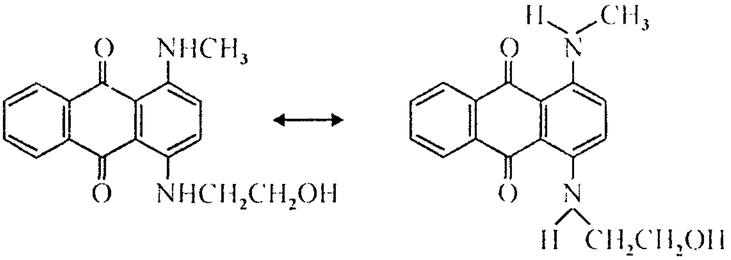


Duranol Red 2B

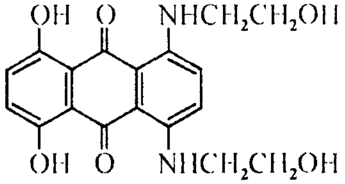


Celliton Fast Pink FF 3B

The 1, 4-diaminoanthraquinone dyes provide red shades on CA. By the introduction of electron withdrawing groups it becomes possible to improve fastness by inhibition of nitrosation or diazotisation of amino group by nitrogen oxides. Cibacet Brilliant Blue BG C.I. Disperse Blue 361505 has been an important dye for CA which is prepared from leucoquinizarin by condensing with a mixture of methyl amine and 2-hydroxy ethylamine.

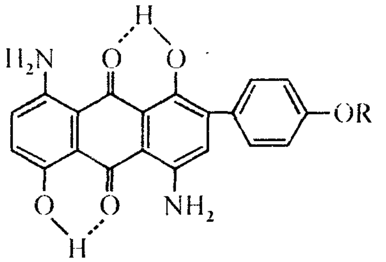


The structure of Setacyl Turquoise Blue G.C.I. Disperse Blue 762500 is as follows :

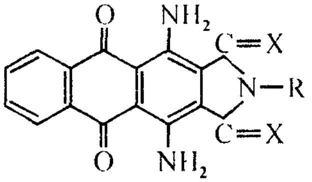


1, 3, 5, 8-tetra-anthraquinone is also a CA dye Disperse Blue 160710. This 4-amino dye on partial methylation with methanol and sulphuric acid provides Celliton Blue Extra C.I. Disperse Blue 31.

Many other anthraquinone dyes for PE fibers have been developed. For example, F.P. 1345377.

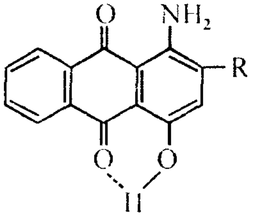


R = H, alkyl
or $COCH_3$

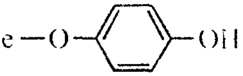


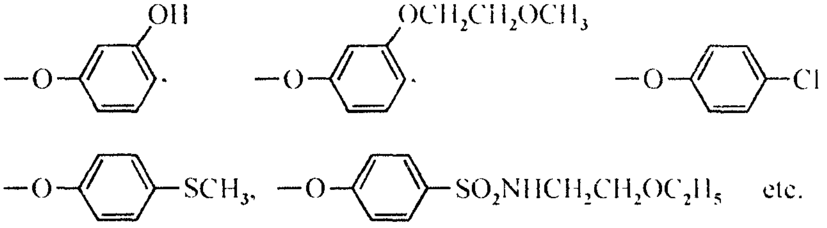
X=O or NH
R=alkyl, alkylaryl hydroxy alkyl
or cyanoalkyl group

By introducing phenoxy and other derivatives in 2-position of 1-amino 4-hydroxy-anthraquinone, it becomes possible to improve thermofixation fastness.



R could be

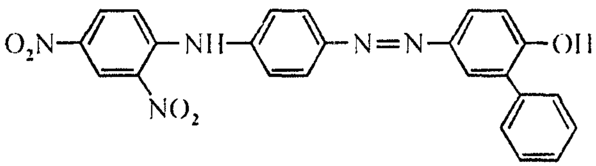




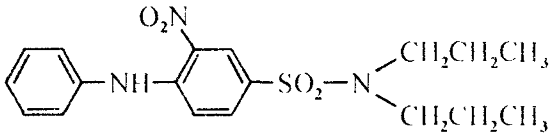
etc.

Miscellaneous Disperse Dyes

Nitro dyes find use on CA and PE fibres. The structure of Serilene golden yellow RFS is as follows :

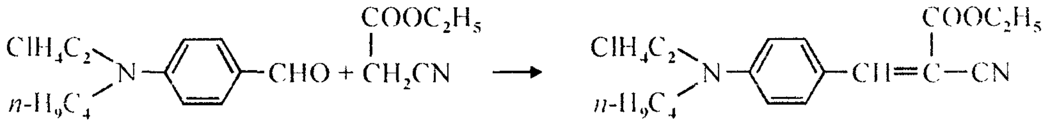


The following structure gives a nitro dye for PE having good fastness properties according to BP 998918.

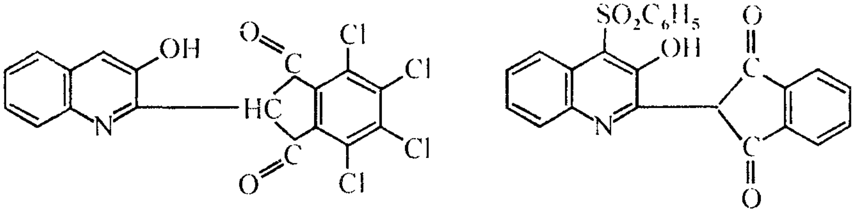


Methine or Styryl Dyes

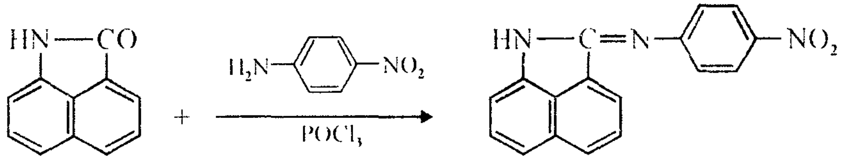
Methine dyes provide yellow shades *e.g.*, Celliton Fast Yellow 76, C.I. Disperse Yellow 31, 48000. It has excellent fastness properties. It is obtained by condensing 4-(N-*n*-butyl-N-chloroethyl amino)-benzaldehyde with ethylcyanoacetate.



Quinphthalone Dyes : These are used for PE providing yellow shades.

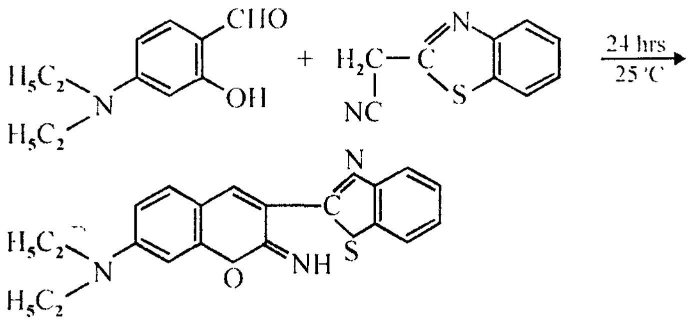


Naphthostyril dyes provide yellow oranges shades. They are obtained from naphtho-styril by condensing with aniline derivatives *e.g.*,



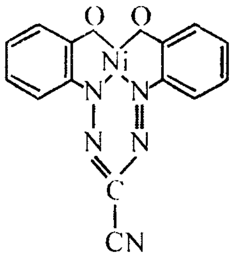
Coumarin Dyes

These dyes are used for polyester fibres and give fluorescent yellow shade. A dye is obtained by condensing N, N-diethylamino-2-hydroxy-benzaldehyde and 2-cyanomethyl benzothiazole in a mixture of acetic acid and dimethy formamide.



Formazin Dyes

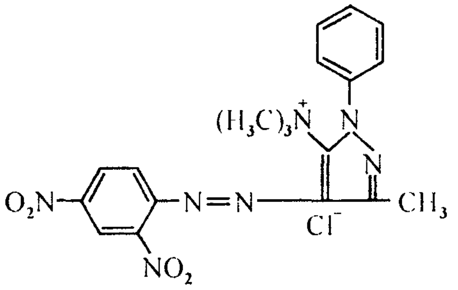
These give blue disperse dyes which are suitable for nylon.



Benzene ring has substituents such as $NHCOCH_3$, SO_2 R, SO_2NR^1 R^2 etc.

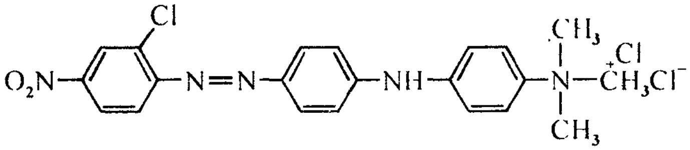
Cationic Dyes for Synthetic Fibres

These dyes are used specially for acrylonitrile fibres. These are marketed under several trade names such as Basacryl, Astrazone etc. These dyes possess azo, anthraquinone or triarylmethane or cyanine as the chromophoric system. Most of the basic dyes can act as cationic dyes. Some of the basic dyes possess good fastness properties for polyacrylonitrile (PAN) fibres. The constitution of the earlier marketed Astrazone dyes are known but the constitution of many of the new cationic dyes are not known with certainty.

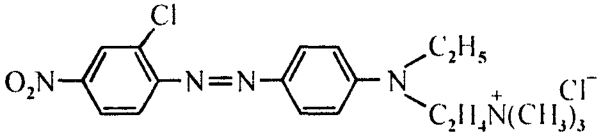


This dye is used to give reddish yellow shade on PAN.

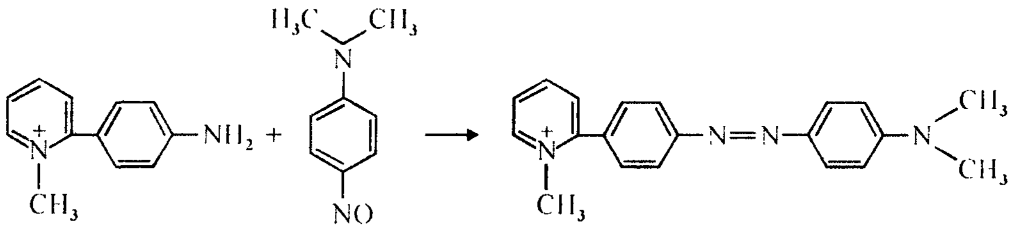
A red cationic dye is prepared from 2-chloro-4-nitroaniline and 4-N, N dimethylamine diphenylamine followed by methylation.



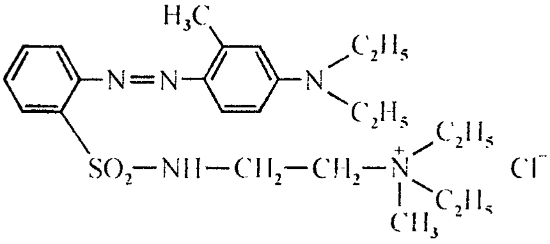
The structure of Astrazone Pink FG. C.I. Basic Red 18 11085 is as follows :



Sometimes cationic azo dyes can also be prepared by condensing an amine with a nitroso compound *e.g.*,



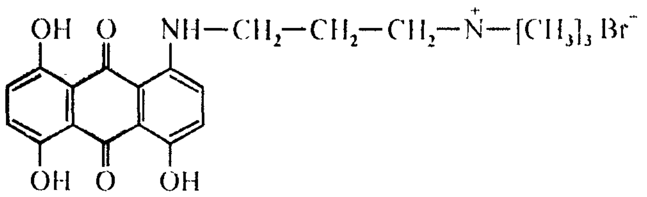
This dye consists of a cation as part of the chromophoric system and such dyes are known as delocalised cationic dyes. Other dyes possess a separated chromophoric system which is isolated by an alkylene link and are known as pendant cationic dyes. These dyes possess duller shades but better fastness on PAN fibres. An example of a pendant dye is as follows :



The third category of cationic dyes have been amine salts which possess an unquaternised amino groups which gets quaternised during dyeing in acidic condition.

Anthraquinone Based Dyes

An example of anthraquinone based cationic pendant dye is as follows :

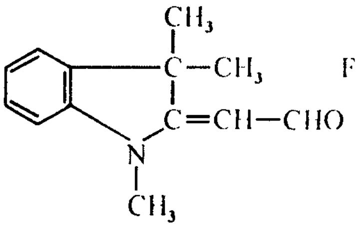


It is obtained by condensing leuco 1, 4, 5, 8-tetrahydroxy anthraquinone with 1-amino-3-dimethyl aminopropane followed by reaction with methyl bromide.

Cyanine Dyes (Methine and Polymethine Dyes)

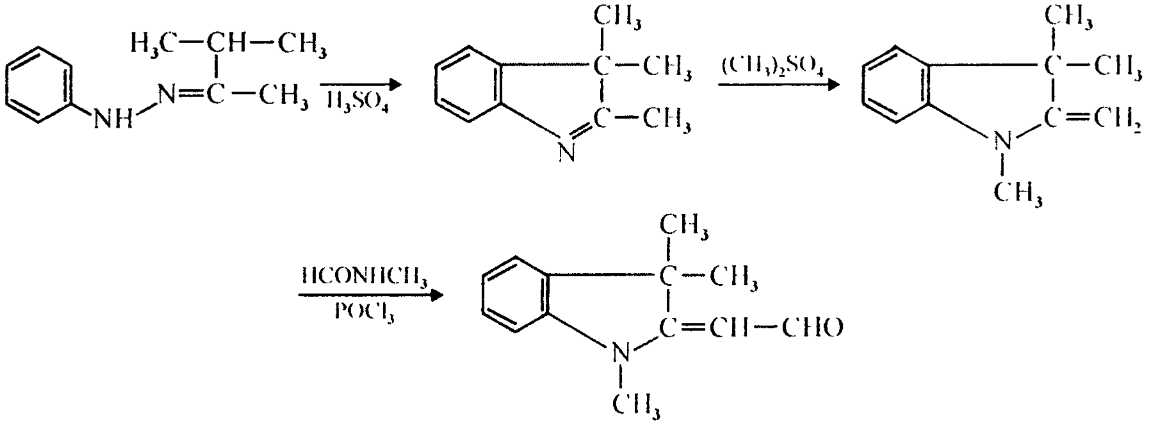
This group of dyes is termed as cyanine dyes. The molecules of dyes have a methine $-CH=$ or a chain of conjugated methine groups. The terminal groups and the number of conjugated methine groups ascertain the colour and properties of the dyes. A number of these dyes find use as photographic sensitisers in colour photography. Some of these dyes also find use as cationic dyes.

The cationic dyes of this class have at least one of the terminal groups as a quaternary nitrogen group. Several cationic dyes have been synthesised from Fischer's aldehyde which possesses the following structure.



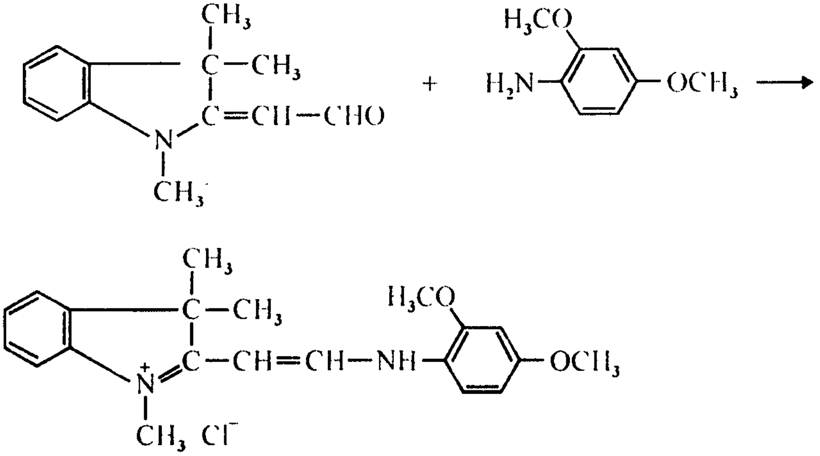
Fischer's aldehyde

The Fischer's aldehyde is obtained by Fischer's Indole synthesis starting from the phenylhydrazone of isopropylmethyl ketone. The indole obtained has been first methylated and then formylated with N-methylformamide and phosphorus oxychloride.

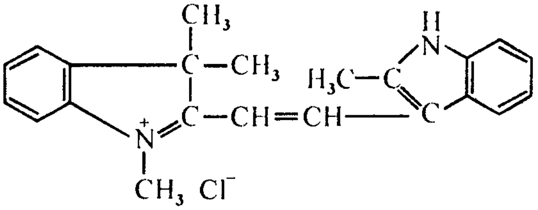


Some of the cationic dyes of this type marketed in India have been as fallows :

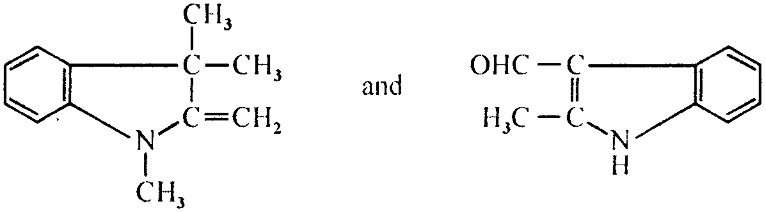
Astrazone Yellow, 3GL C.I. Basic Yellow 11 48055 possesses good fastness properties on cellulose acetate and PAN fibres. It is obtained by condensing Fischer's aldehyde with 2, 4-dimethoxyaniline.



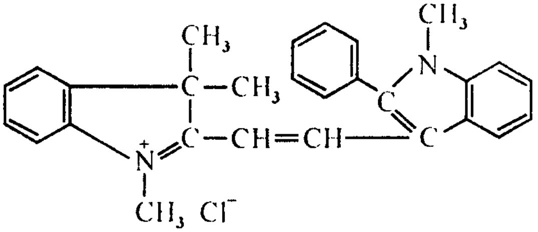
Other yellow dyes have been Astrazone Yellow 7 GLL. C.I. Basic Yellow 21 and Astrazone Golden Yellow GL C.I. Basic Yellow 28 whose constitutions are not known with certainty. The structure of Astrazone Orange G.C.I. Basic Orange 21 480 35 is as follows :



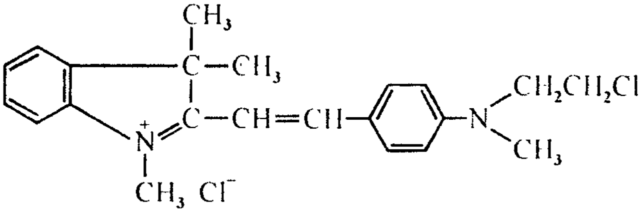
This dye is prepared by condensation and sal formation from the following compounds :



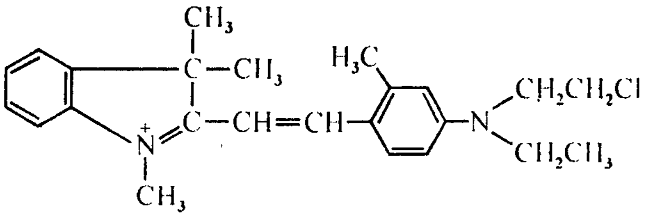
The structure of Astrazone Orange R.CC.I. Basic Orange 22 48040 is as follows :



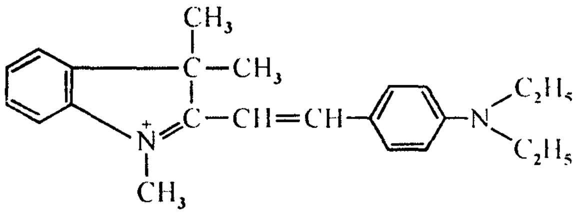
Astrazone Pink FG C.I. Basic-Red 13 48015 obtained by condensing Fischer's indole (1, 3, 3-trimethyl-2′-methylene indoline) with 4 (N-methyl-*n*-β chloroethyl) benzaldehyde and has the structure :



Astrazone Red 6B C.I. Bagic Violet 7 48020 is obtained by condensing 1, 3, 3-trimethyl-2-methylene indoline with 4-(methyl-N-chloroethyl)-2-methylbenzaldehyde. This dye has the following structure :

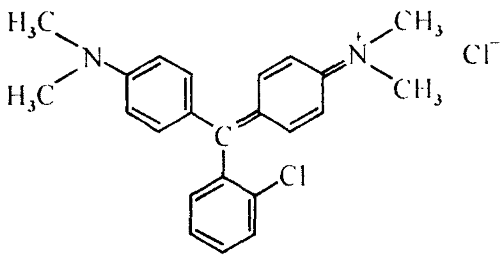


The structure of Astrazone Red Violet 3R C.I. Basic Violet 16 48013 is as follows :

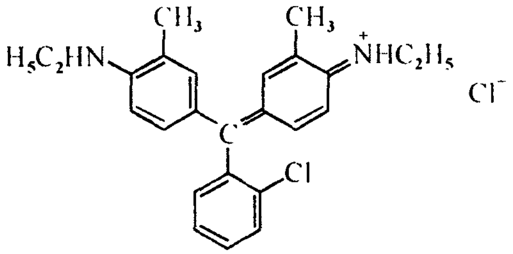


Triarylmethane Cationic Dyes

Two of the dyes belonging to this class have been Astrazone Blue G or Rhoduline 6G C.I. Basic Blue 1,42025 which possesses the following structure :

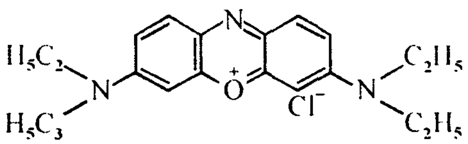


The structure of Astrazone Blue B. C.I. Basic Blue 5 42140 is as follows :

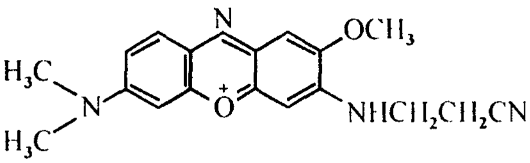


Oxazine Cationic Dyes

An oxazine dye for PAN fibres has been Astrazone Blue BG C.I. Basic Blue 3 51004 whose structure is as follows :

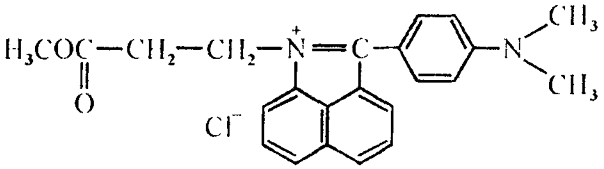


It is obtained by condensing *m*-diethyl aminophenol with *p*-nitroso-diethylaniline. Many oxazine derivatives are found in patent literature as cationic dyes *e.g.*, BP 1339300.



Naphthostyrile Cationic Dyes

The dyes of this type are prepared by condensing naphthostyril with.N-substituted aromatic amines with $ZnCl_2$ or PCl_3. These are blue dyes having good fastness. One example from BP 1353983 is as follows :



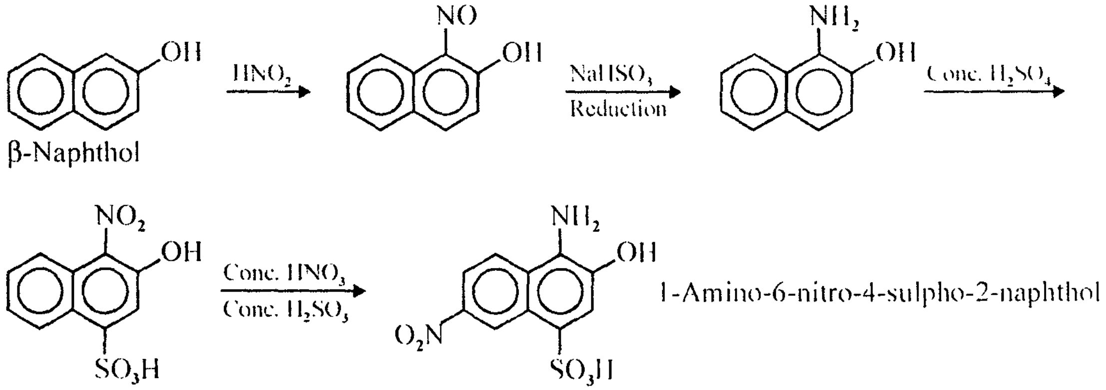
36

CHAPTER

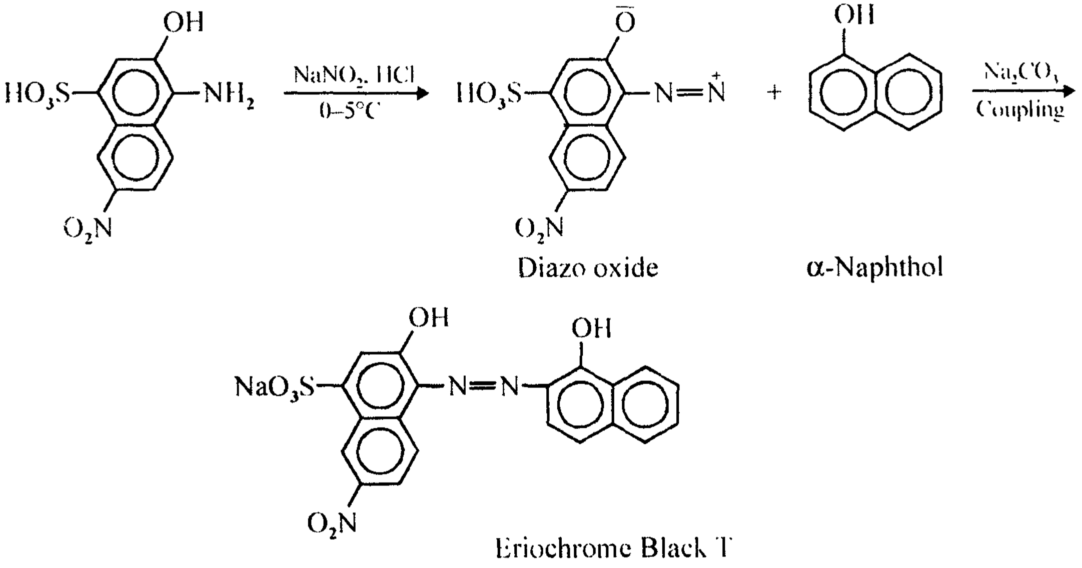
SYNTHESIS OF SOME SPECIFIC DYES

1. Eriochrome Black T

Step : (*i*)



Step (*ii*) (*Coupling*)

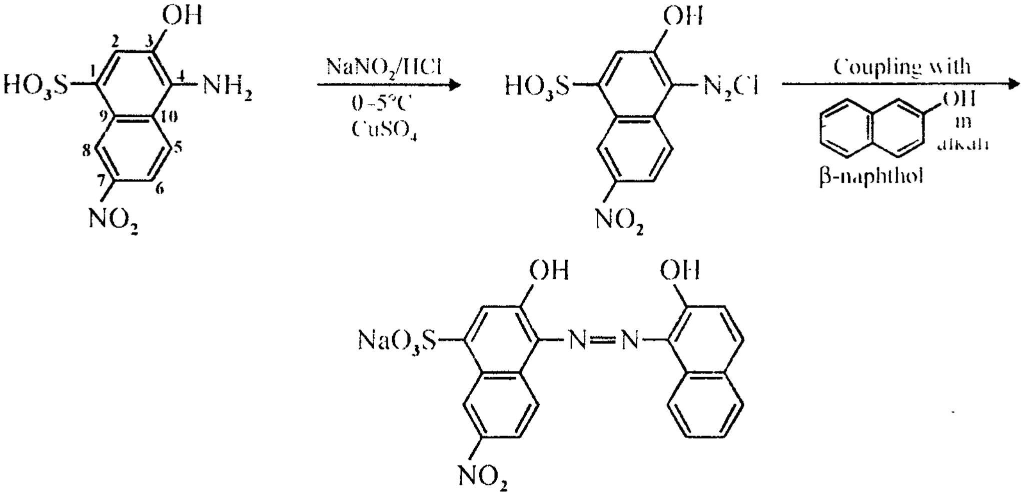


β-Naphthol is first of all converted into nitroso derivative and then reduced to get 1-amino-2-naphthol. Now it is sulphonated and nitrated to get 1-amino-6-nitro-4-sulpho-2-naphthol. This amine is diazotised and coupled with α-napthol in alkaline medium to give Eriochrome Black-T.

It is a chrome azo dye. The fibres are made to treat with solution of chromium salts, followed by the dye to deepen the colour. Eriochrome black T is used as an indicator for complexometric titrations using EDTA.

2. Eriochrome Black A

Its preparation is similar to Eriochrome black T. Diazotization of 4-amino-7-nitro-3 naptho-1 sulfonic acid in presence of a small quantity of $CuSO_4$ is followed by coupling the product obtained with naphthol.



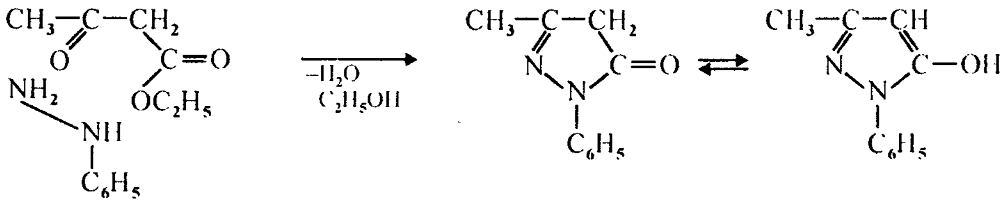
Eriochrome Black A

It is an azochrome dye which can be applied to wool by the modified method.

3. Eriochrome Red B

(i) Preparation of Pyrazolone derivative

Aceto acetic ester

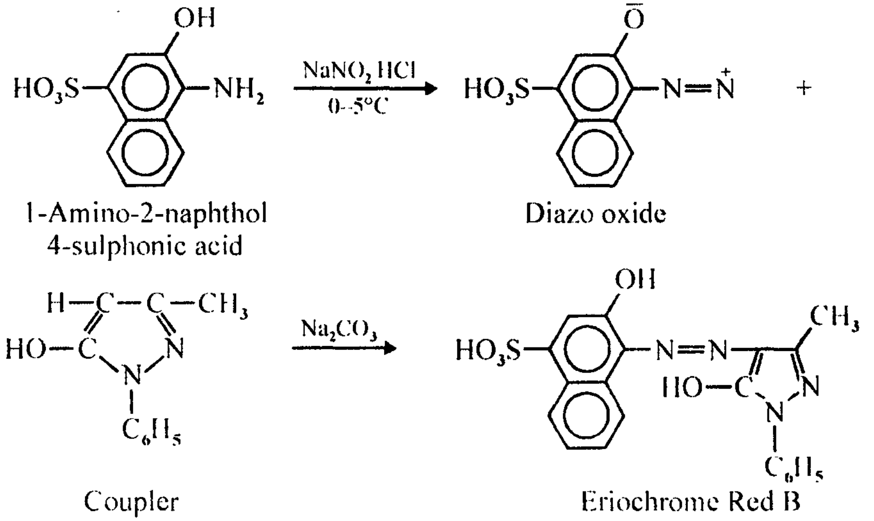


(Keto) (Enol)

Phenylthydrazine

3-Methyl-1-phenyl-5-pyrazolone

(*ii*) *Diazotisation and Coupling*


1-Amino-2-naphthol 4-sulphonic acid

Diazo oxide

Coupler

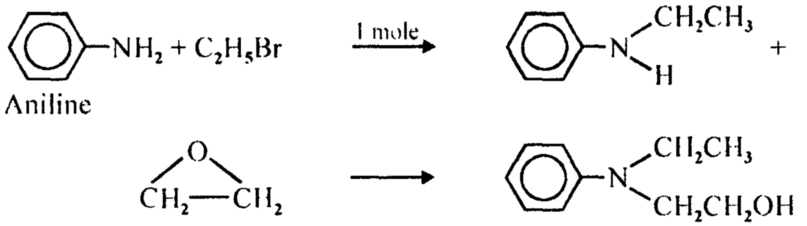
Eriochrome Red B

Aceto acetic ester is first of all made to condense with phenylhydrazine to obtain a pyrazolone derivative which is the coupler. 1-Amino-2-naphthol-4-sulphonic acid is diazotised and coupled with the pyrazolone derivative.

It also find use as a chrome azo dye and has better fastness to light and washing.

4. Celliton Scarlet B

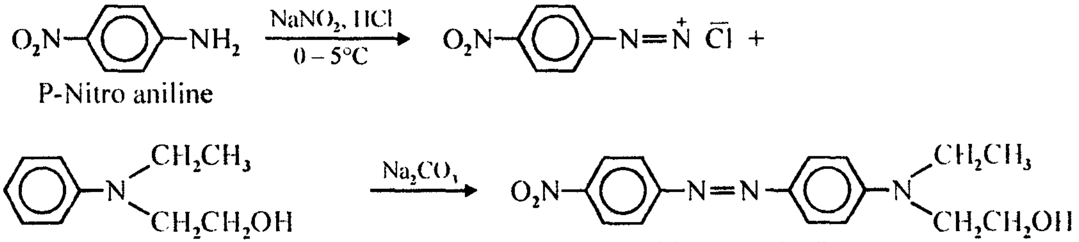
(*i*) *Preparation of Coupler*


Aniline

Ethylene Oxide

N-Ethyl-N-(2-hydroxy) ethylaniline

(*ii*) *Diazotisation and Coupling*


P-Nitro aniline

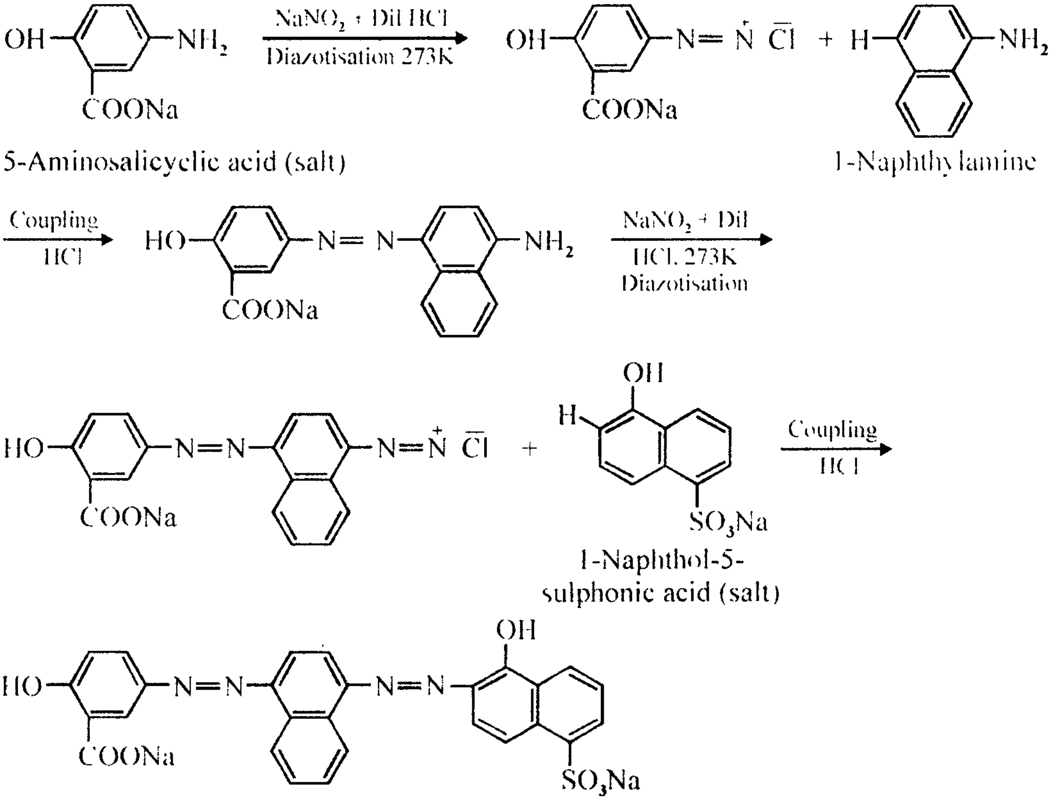
Celliton Scarlet B

Aniline is condensed with ethyl bromide (1 mole) followed by ethylene oxide to get the ethanol amine derivative, which is used as the coupler. Then *p*-nitroaniline is coupled with the ethanol amine derivative to get celliton scarlet-B.

This is a disperse azo dye. The hydroxyethyl group ($-CH_2CH_2OH$) is the solubilizing group. Their dispersions are used to dye hydrophobic fibres like cellulose acetate, nylon etc.

5. Diamond Black-F

5-Amino salicylic acid is diazotised and coupled with 1-naphthyl amine in mild medium. The resulting amino azo compound is again diazotised and coupled with 1-naphthol-5-sulphonic acid (sometimes 1-naphthol-4 sulphonic acid is also used).



5-Aminosalicyclic acid (salt)

1-Naphthylamine

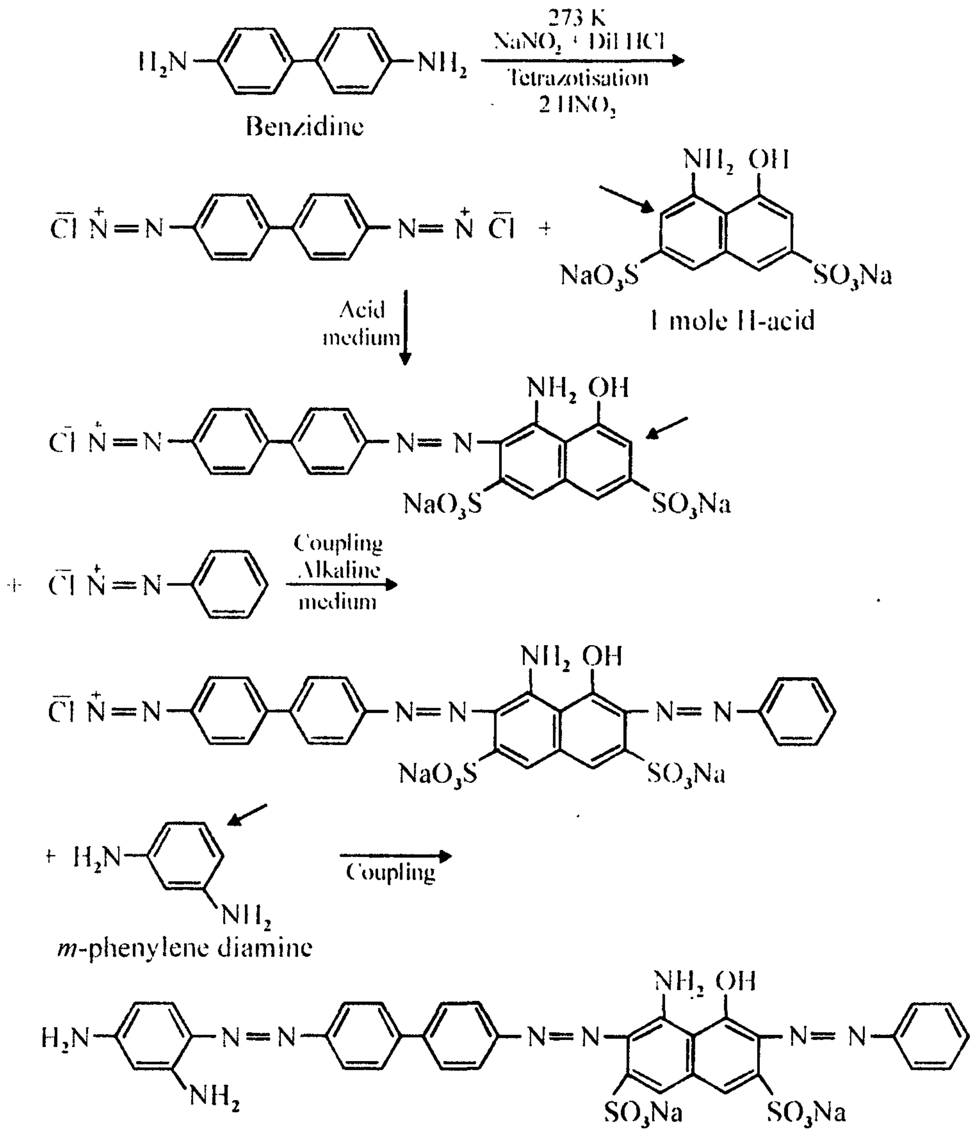
1-Naphthol-5-sulphonic acid (salt)

Diamond Black F

This is a disazo mordant dye which forms complex with chromium. The fabric is mordanted by boiling with sodium dichromate in presence of a reducing agent. This dye has good fastness to light and washing.

6. Direct Deep Black

Benzidine is tetrazotised and coupled with one mole of H-acid (1 amino-8-naphthol-3, 6 disulphonic acid in acid medium). The product is used as a coupler in the next step when it is coupled with one mole of benzene diazonium chloride in alkaline medium. Finally, this product is coupled with *m*-phenylene diamine when the second diazonium group of benzidine reacts, to give direct deep black.

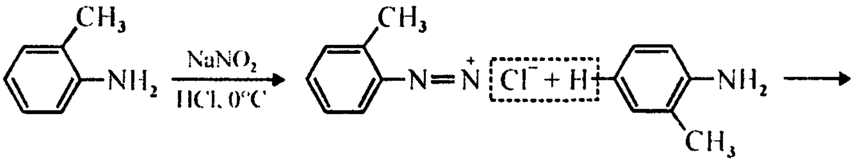


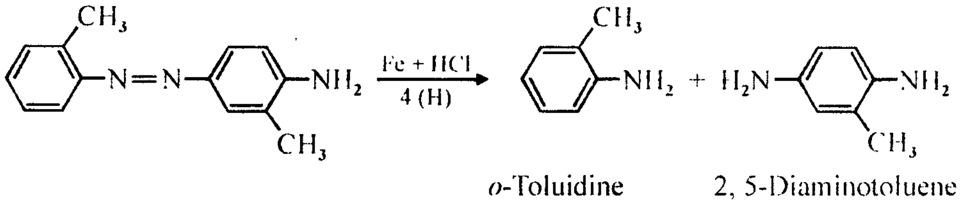
Direct deep black

This is a trisazodye which is a very widely used black dye.

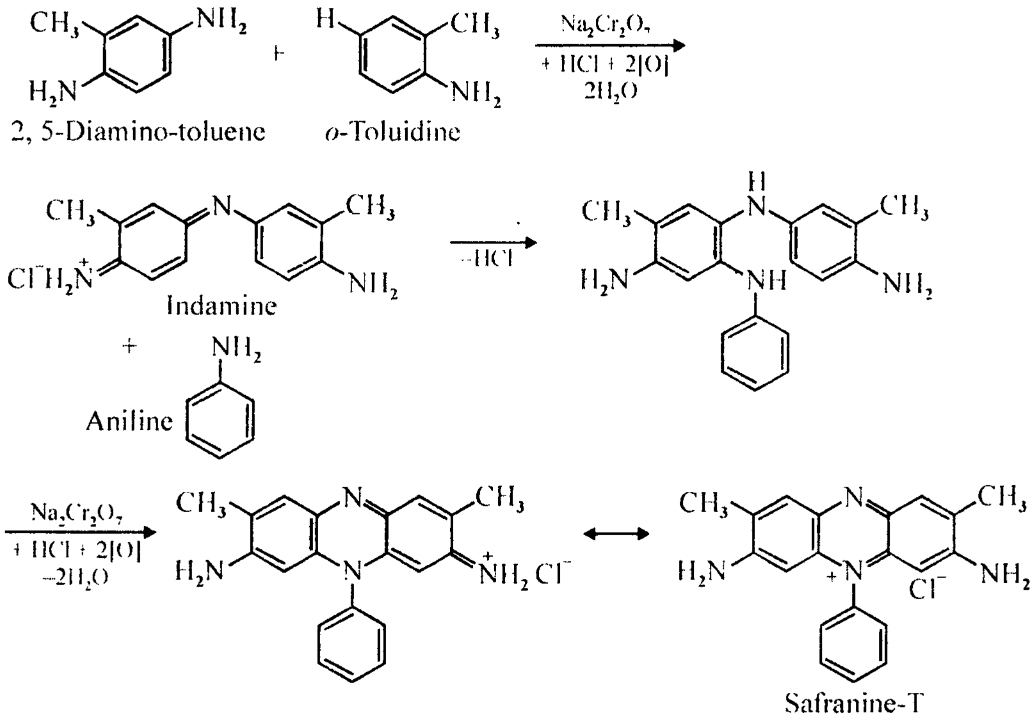
7. Safranine-T

(i) *Formation of 2, 5-Diaminotoluene*





(ii) Conversion into Safranine-T



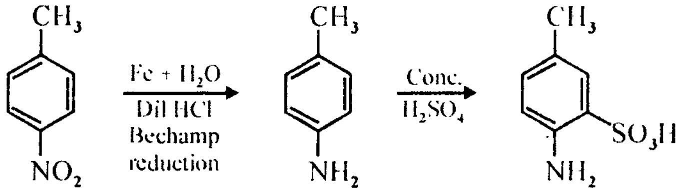
o-Toluidine is made to diazotise and couple with *o*-toluidine. The azo compound on reduction with iron and acid yields back *o*-toluidine and 2,5-diaminotoluene. These products are condensed and oxidized with sodium dichromate in acidic medium. The resulting indamine is condensed with aniline and the product is again oxidized with sodium dichromate to give safranine-T.

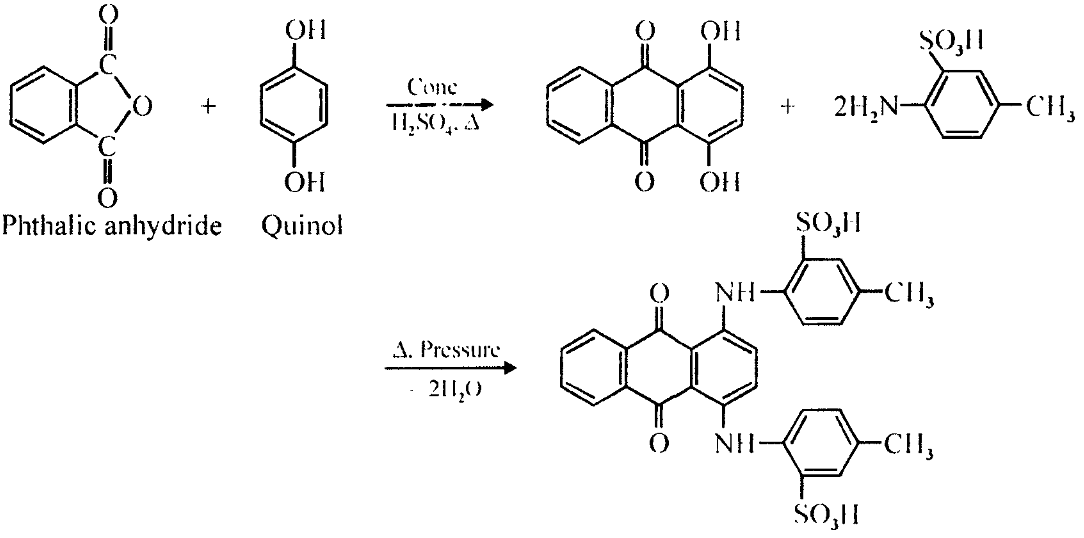
It is a basic dye belonging to phenazine group dyes. Mauveine belonging to this group, is the first synthetic dye prepared by Perkin. This red dye is especially used for dyeing of paper. It is also used for dyeing of wool, silk and also cotton mordanted with tannin.

8. Cyanin Green G

The *p*-nitro toluene is made to reduce by steam and iron filings (Bechamp reduction). The product, *p*-toluidine, is sulphonated to yield 4-amino-toluene-3-sulphonic acid.

Phthalic anhydride is condensed with quniol in presence of concentrated sulphuric acid. The resulting quinizarin is condensed with 2 moles of 4-amino toluene-3-sulphonic acid under pressure to get alizarin cyanin green G.



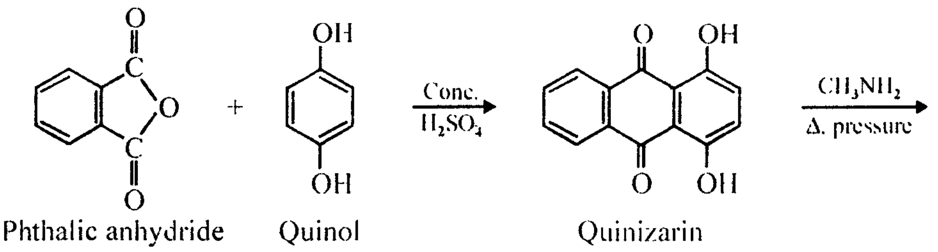


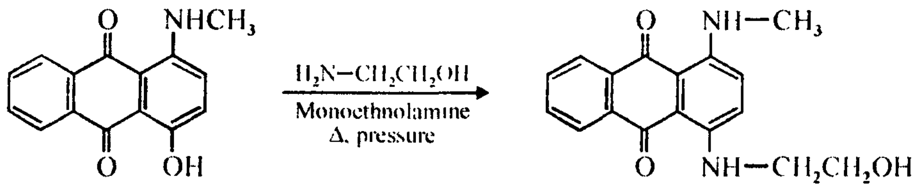
Alizarine cyanine green G

This is a water soluble anthraquinone acid dye, due to the presence of solubilizing sodium sulphonate group. It has very good fastness when applied to wool in acid medium.

9. Dispersol Blue

Phthalic anhydride is made to fuse with quinol in the presence of concentrated sulphuric acid to get quinizarin. This is condensed first with methyl amine under pressure and then with mono ethanol amine under pressure to get dispersol blue.



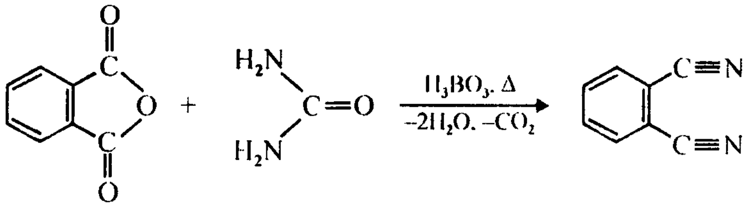


Dispersol blue

This is an anthraquinone disperse dye. Ethanolamine is the group which helps the formation of dispersion of the dye.

10. Copper Phthalocyanine (Monastral fast blue)

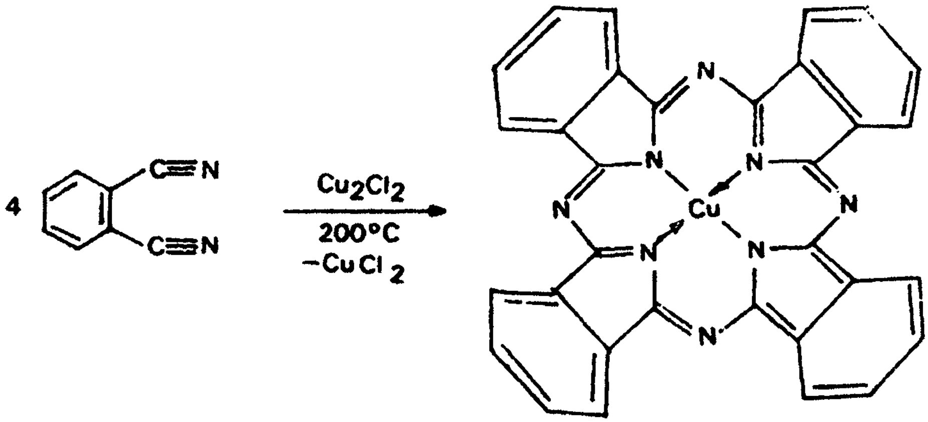
Step (*i*) Formation of phthalonitrile



Phthalic anhydride Urea Phthalonitrile

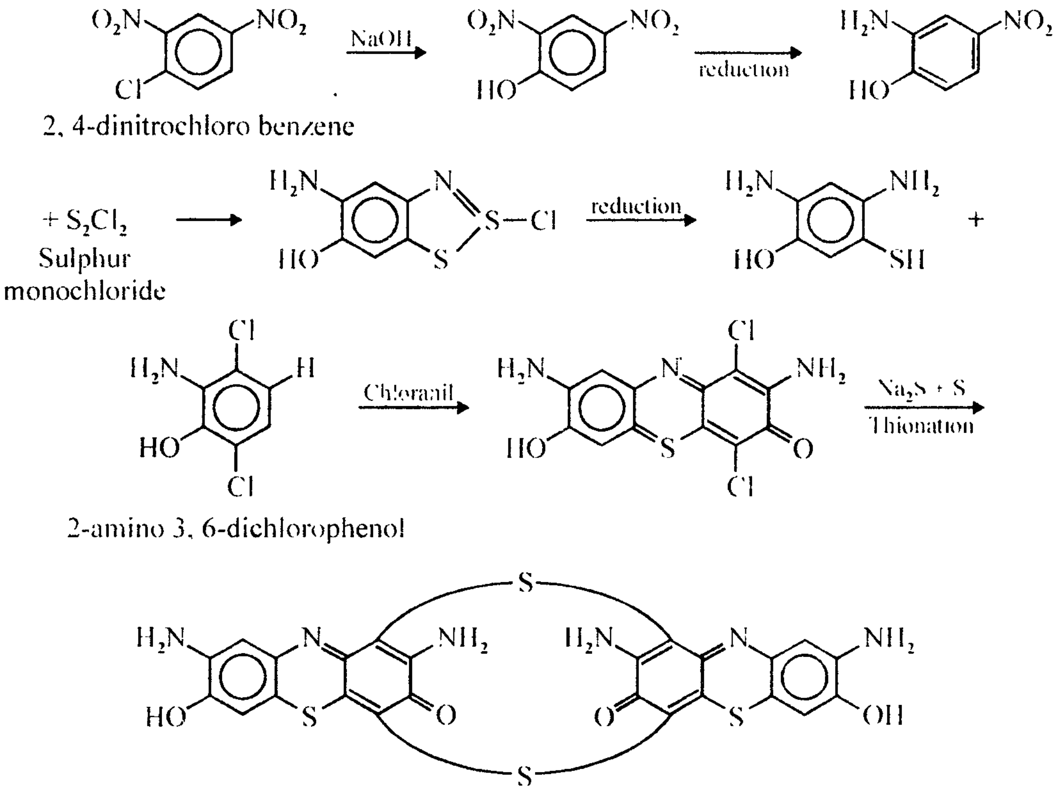
Step (*ii*) Conversion into phthalocyanine :

Phthalic anhydride is made to heat with urea and cuprous chloride in the presence of boric acid as catalyst. Phthalic anhydride first reacts with urea to form phthalonitrile. Then it is condensed with cuprous chloride to form the complex, copper phthalocyanine.



This is a deep blue coloured pigment which is insoluble in water and resistant to temperature. It possesses extremely good fastness properties. The sulphonated derivative is soluble and it can be used as direct dye.

11. Sulphur Black T



Sulphur Black T

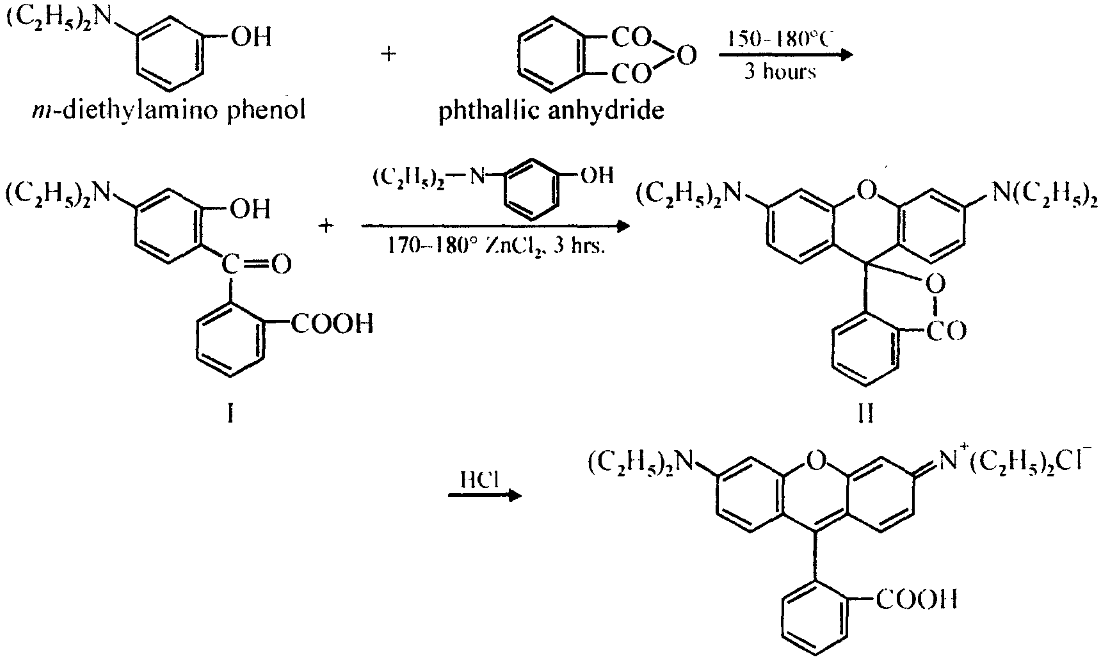
Sulphur dyes get solubilized by reduction and the cellulosic fabric is impregnated with this solution. Then the dye is regenerated by atmospheric oxidation.

$$\underset{\text{Sulphur dye}}{\text{Ar—S—S—Ar}} \quad \underset{(O)}{\overset{Na_2S.\,2[H]}{\rightleftharpoons}} \quad \underset{\text{Solubilized dye}}{\text{Ar—SH}}$$

Sulphur dyes yield dark shades and they are cheap. They have good fastness towards light and washing. However their drawback is that they are affected by chlorine. They cannot be used for dyeing wool and silk as they are damaged by sodium sulphide. Sulphur black-T is used for dyeing umbrella cloth.

12. Rhodamine B

The *m*-diethylamino phenol (1 molecule) is made to condense with phthalic anhydride (1 molecule) at 150–180°C. Reaction is continued for three hours. The reaction product (I) obtained is made to condense with another molecule of *m*-diehylamino phenol in the presence of zinc chloride at 170 to 180°C for three hours. The dye base (II) product obtained is treated with dilute hydrochloric acid, and thus, the dye III Rhodamine B formed.



m-diethylamino phenol

phthallic anhydride

I

II

III Rhodamine B

Rhodamines are basic dyes belonging to xanthene series. Rhodamines range in shades from yellowish red to blue. Rhodamine B is most commonly used basic dye for papers, wool, silk and cotton mordanted with tannin *e.g.*, where brilliant shades of fluorescent effects are needed. These dyes are of secondary importance.

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CHAPTER

IMPORTANT QUESTIONS

Q.1. How does a dye differ from a coloured compound?

Ans. A dye differs from a coloured compound in this respect. A dye can be applied to another substrate say fibre, paper, leather, etc., and impart colour to it. The applied colour will be retained by the substrate. A coloured compound such as copper sulphate is not a dye for the reason that this colour is not imparted to substrate and is not retained by it. Whereas Indigo or Congo Red, the typical coloured organic compounds under certain conditions can be applied to say cotton fibre and the colour will be retained by the fibre. Thus, the latter is a dye whereas the former is only a coloured chemical. Further, all dyestuffs need not be coloured substances as most of the optical brighteners are white in colour.

Q.2. An object appears to be black or white or coloured when white light falls on it. How do you explain this?

Ans. When visible light falls on a substance, depending, upon the substance, some of it is absorbed, and some reflected. White surfaces reflect all the light whereas black surfaces absorb light over the entire range of visible light. In the case of dye, however, there is a selective absorption in visible region and reflection the rest of this region. There is a definite relationship between the colour absorbed and colour visualised with respect to a given range of wavelength. This is shown in table.

The structural configuration in a molecule determines the part of the visible region the dye will absorb. Certain groups present in the dye molecule respond to the specific oscillation frequency because of induced vibrations of electrons. The colour absorbed and colour visualised are complementary to each other *i.e.*, if the two are mixed, the resultant will always be white.

Colour Absorbed and Colour Visualised with Respect to Wavelength Regions

Wavelength Å	*Colour absorbed*	*Colour visualised*
4000-4350	Violet	Yellow-Green
4350-4800	Blue	Yellow
4800-4900	Green-Blue	Orange
4900-5000	Blue-Green	Red
5000-5600	Green	Purple
5600-5800	Yellow-green	Violet
5800-5950	Yellow	Blue
5950-6050	Orange	Green-Blue
6050-7500	Red	Blue-Green

Q.3. (*a*) What are pigments?

(*b*) What are uses of pigments?

(*c*) What are types of pigments?

Ans. (*a*) Pigments are coloured organic compounds (solids) which are completely insoluble in water or usual organic solvents. The pigments may be organic or inorganic derivatives. The organic metal complexes of iron, copper, cobalt *etc.*; are used as pigments. Zinc oxide (ZnO) and titanium dioxide (TiO_2) are white pigments, whereas carbon black is an example of black pigment.

The pigments also contain same chromophores and auxochromes as in dyes. The characteristic which distinguishes pigment, form dye, is its insolubility. Thus the dye is soluble in water or organic solvents whereas pigments are completely insoluble. The same coloured substance can be used as the dye as well pigment. If solubilizing gropus like $-SO_3H$, $-CH_2-SO_2.ONa$, etc. are introduced in a pigment, it becomes a dye. The difference also lies in the mode of application. The dye is applied in the form of its solution (dyeing process). But pigment is applied as a paste or dispersion during the printing process.

The physical properties are very important while preparing the pigment. The most important physical property is the particle size and its uniformity. It affects the tone and brightness of the pigment. Many additives are added to the pigments to improve affinity to substrate. The actual composition depends on the end use of the pigment.

Characteristics of Pigments

1. The colour of the pigment depends not only on the chemical structure but also on the physical properties. Thus the tone and brightness depends on physical form, shape and size of the pigment particles.
2. Pigment should be completely insoluble. Even if it is slightly soluble, the pigment crystallises on the substrate causing change of shade. The printed design should remain sharp without spreading.
3. The pigment should be stable and must be resistant external to agencies like light, heat etc., during preparation and application. Fastness to heat becomes important when it is used in glass, ceramics, enamels etc.
4. The pigments are applied in the form of pastes or dispersions. The reproducibility of the shade and brightness depends on consistency of the composition and uniformity of the shape and size of the pigment particles.
5. The pigments must be resistant to the acid if it is used in acidic medium. The pigments used for distempers or in plasters should have resistance to alkalies.
6. The pigments should have good hiding (covering) power and tinctorial properties. These properties become important in case of paints. This also depends on the shape and size of the pigment particles

(*b*) Uses of Pigments

1. The pigments are most commonly used for printing designs or textile fabrics. The pigment is ground with dispersing agent to get a paste of uniform concentration and suitable consistency. The over milling results in loss of brightness. The resin binders are added. which help to fix the pigment to fabric. Finally, thickners like carboxymethyl cellulose (CMC) and stabilizers like rangolite (*Na* suphoxylate formaldehyde) are added and the kerosene emulsion is used for printing.
2. The paints are surface coating agents which impart colour to a surface and protect it from corrosion. The paint is an emulsion of pigment in a drying oil like linseed oil. The covering power and opaqueness are important for the paint. The white pigment like zinc oxide or titanium dioxide are added to the paint to control the capacity and the depth of the shade.
3. The printing inks are made up of dispersion of pigments and used in the form of a paste. It is used to print on paper, metal foil, plastic *etc*. Temperature resistant paints are used for ceramic printing.
4. The mass colouration of plastic and rubber is carried out by mixing the pigment with molten plastic or rubber. The pigments can also be mixed with cellulose pulp and beaten for making coloured paper.
5. The pigments also find use in making distempers, crayons, artists colour etc. The soap, wax, *etc*. are also coloured by pigments.

(*c*) Types of Pigments

The pigments are mainly of two types :

(*i*) ***Lakes*** **:** They are soluble organic dyes which are precipitated on an inorganic substrate. The inorganic substances are colourless compounds like hydrated alumina or barium sulphate. Lake can also be the insoluble metal complex of an organic dye. The lakes have higher brightness and better transparency when used in oil paint.

(*ii*) ***Toners*** **:** They are the salts of the dyes which are precipitated without using any substrate. They were initially used for toning printing inks and hence they are called toners. The toners have better colour strength compared to lakes.

Q.4. Distinguish between : Dyes and Pigments.

Ans. (*i*) Dyes and Pigments :

Dyes	*Pigments*
1. Dyes are mainly organic.	Pigments are organic as well as inorganic.
2. Dyes are always used in solution.	Pigments are always insoluble materials which are used directly.
3. Dyes are classified into numerous groups according to the structures.	Pigments are classified into limited groups according to the structural features.
4. Dyes are durable and fast.	Pigments are not as durable as dyes.
5. Dyes are used directly as solution.	Pigments are usually mixed with other materials, like in paints, varnishes, etc.

Q.5. Classify the following dyes on the basis of chemical structure of dye–(*i*) Picric Acid, (*ii*) Crystal Violet, (*iii*) Eriohrome Black T, (*iv*) Alizarin, (*v*) Methylene Blue, (*vi*) Procion Blue, (*vii*) Astrazon Pink FG.

Ans.

(*i*) Picric Acid → Nitro dye.
(*ii*) Crystal Violet → Aminotriphenyl methane dye.
(*iii*) Eriochrome Black T → Monoazo acid dye.
(*iv*) Alizarin → Anthraquinone mordant dye.
(*v*) Methylene Blue → Thiazine dye.
(*vi*) Procion Blue HB → Reactive anthraquinone
(*vii*) Astrazon Pink FG → Polymethine.

Q.6. How would you carry out diazotisation of amino phenols?

Ans. Aminophenols are readily oxidised by nitrous acid to the corresponding quinones. Hence, in such cases, a special procedure has been adopted. In place of HCl, $CuSO_4$ is used. Aminophenols can be diazotised at 20°C by first adding $CuSO_4$ solution and then 30% $NaNO_2$ solution with vigorous stirring, the temperature rising to 30°C. The diazo oxide may be used as its sodium salt by the addition of sodium chloride or as free sulphonic acid by the addition of acid.

Q.7. (*a*) Describe the different use of dyes other than dyeing textile fibres. (*b*) Write a note on optical brighteners.

Ans. (*a*) Besides textile fabrics which consume a good portion of dyes, other substrates are also coloured by dyestuffs. These are polymers (other than textiles) foodstuffs, leather, paper, etc. In order to achieve satisfactory resultant colour, it is necessary to choose and select appropriate class of dyes suitable for the substrate. The dyeing conditions required for these substrates may or may not be similar to those of dyeing textile fabrics and brightness, fastness and attractive look needed may need to be ascertained before a choice is made of the dye.

In the case of polymers, selecting a dye may be dependent on the nature of side chain groups present in the polymer. If hydrophobic groups are present disperse dyes could be made use of. If hydrophilic groups are present, dyeing can be carried out with direct, acid and basic dyes; sometimes mass colouration is employed where the substrate and dye are intimately mixed and processed.

In the case of foodstuffs, food colours are employed. Since many of the dyes are toxic, it is necessary to choose dyes which are totally harmless to human beings. They generally belong to direct, acid and basic type. Typical example of dyes used in food is tartrazine.

Dyeing of leather is another important application of dyes. The dyes finding application in this field belong to acid dyes, metal complex dyes and a few basic dyes categories.

Basic dyes find application in paper industry though other classes of dyes are also employed depending upon the end uses. Black and white and colour photography are also dependent upon the use of dyes.

(*b*) **Optical Brighteners :** In order to achieve an overall whitening effect optical brighteners are used for textile fabrics and other substrates. They can be classed as white dyes. The optical brighteners contain various characteristic groups or systems responsible for fluoroscence effect. Some of the systems which find commercial application are as follows :

(*i*) Stilbene derivatives, (*ii*) Triozolo derivatives, (*iii*) Coumarian derivatives, (*iv*) Benzasoles derivatives, (*v*) Naphthalimide derivatives and pyrazline derivatives.

The structural features of an optical brightener is so made that it absorbs in the ultraviolet region of spectrum in the range 3300–3800Å and it is in the region of 4300–4900Å in the blue region of spectrum. The whiteness seen on fabrics is the result of addition effect of emitted blue light and normal white light reflected from the surface.

Q.8. Explain the following terms as used in dyestuff chemistry : (*i*) Toners, (*ii*) Lakes.

Ans. (*i*) **Toners :** These are chemical compounds which are used to change the colour of the fabrics before applying the main dye itself. This is specially applied for synthetic fibres where disperse dyes are used.

(*ii*) **Lakes :** These are chelate compounds formed between the metal and dye. They are formed when the dye is applied by mordant dyeing where the metal hydroxides are usually used as mordants.

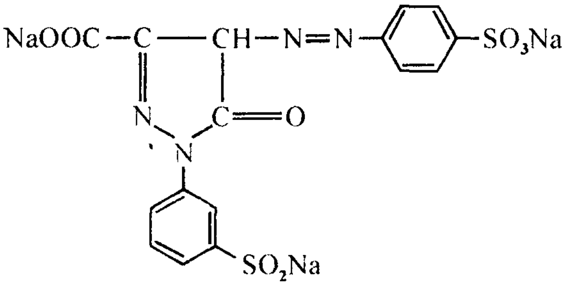
Q.9. Explain fastness properties of dyes.

Ans. The extent to which the dye on the fabric is able to withstand the action of light, heat, washing, perspiration, etc., gives an indication of its fastness. Each fastness, *i.e.* fastness with one agent is given on a scale 1, 2, 3 etc. For example, light fastness is graded 1 to 8, and heat fastness 1 to 5, where 1 indicates the lowest rating for fastness in both cases, and 8 as the highest rating for light fastness and 5 for heat fastness. For a given dye to be commercially sold it should have at least minimum rating in each field. However, in case of the phenyl methane dyes, though they have low light fastness, they are still used because it is possible to obtain brilliant shades on fabrics.

Q.10. Write short notes on the following : (*a*) Dyes for paper and leather, (*b*) Food colours.

Ans. (*a*) Dyes for Paper and Leather : Generally, basic class of dyes find application for colouring paper, but other classes of dyes can also be used depending upon the end uses. In the case of preparation of copypapers where there is no need to have carbon paper, basically colour forming precursors are applied to paper which are converted into parent colours by hard pressing. In photography also certain colour forming components are suitably coupled with aromatic diamines capable of getting oxidised and these are used along with the silver halide. Even in development of black and white pictures, use is made of certain diazonium components along with coupling components to develop the picture from the silver halide *e.g.* of dyes used in paper–Safranine T, Auromine. The dyestuffs employed in leather industry belong to acid class, metal complex class and basic class. Polyazo and azo types of dyes find application in dyeing leather *e.g.* Chrome leather Black A.

(*b*) **Food Colours :** Dyes used for colouring foodstuffs are called as food colours. Though many of the dyes can be used for colouring food stuffs, they are not all useful as food colours since many of them are toxic to humans. Thus the dyestuffs used in food have to be of very low toxicity and totally harmless to human beings. The class of dyes that are generally used are from direct, acid and basic class of dyes. Tartrazine is one of commonly employed food colours.



Q.11. Write the role of mordants in dyeing.

Ans. In dyeing of fabrics, certain metallic salts such as salts of chromium, aluminium, copper, cobalt, nickel, iron and tin are used as mordants. In the case of mordant dyes, there are certain groups present in dye molecule which help to hold the metal residue by formation of covalent and coordinate bonds by chelation. The mordants themselves are capable of forming covalent and co-ordinate bonds not only with dye molecule but also with the fabric, thus improving fastness of the same dye structure used without mordanting. There are three ways how mordant dyeing is done. The dye can be applied first and subsequently the mordant can be used. The dye and mordant can be applied simultaneously and the dye can be premordanted to get a metal dye which can be then applied to fabric as such. Dyestuffs containing *0-0′* dihyxroxy, *0-0′*dihyroxy azo, azo-*0′* –hydroxy-nitroso groups form mordant complex and hence can be used in mordant dyes.

Q.12. Classify the following dyes on the basis of chemical structure of dye.

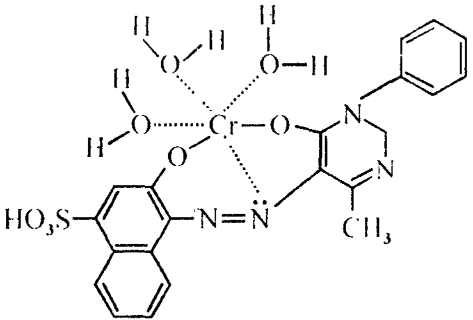
(*i*) Picric Acid, (*ii*) Congo Red, (*iii*) Crystal Violet, (*iv*) Tinopal BV (*v*) Methylene Blue.

Ans.

	Dyes	*Classification*
(*i*)	Picric Acid	Nitro dye
(*ii*)	Congo Red	Diazo direct type
(*iii*)	Crystal Violet	Triphenylmethane class
(*iv*)	Tinopal BV	Stilbene
(*v*)	Methylene Blue	Thiazine class

Q.13. What is chrome dyeing?

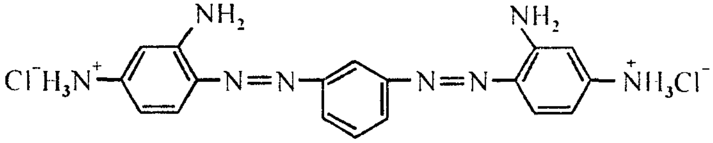
Ans. It is similar to mordant dyeing. Chromium and copper complexes possess both covalent and coordinate bonds that the made use of for binding the dye to the fabric. Neolon Red B for example is a red crystalline solid obtained by the treatment of Eriochrome Red B with chromium chloride in alcohol. This chromium complex is then applied to fabric wool generally where it imparts light fastness to the fabric. Similarly, Eriochrome Black A gives a dark brown colour to wool on dyeing which when treated with chromium salt gives a deep fast black colour which has excellent light fastness property. Similarly, Eriochrome Black T with chromium salts gives a fast bluish black shade.



Neolon Red B

Q.14. Discuss the dyes used in leather.

Ans. Leather being of animal origin. mainly consists of collagenous protein and hence acidic and basic dyes used for dyeing wool silk can also be employed for dyeing leather. Basic dyes produce a rich variety of shades, and though they are not light fast, they withstand perspiration and are held strongly on the leather surface. Acid dyes in the presence of formic acid are used to dye leather in light shades. The main criteria for dyeing leather is that the dye should not be very sensitive to variations in leather and should dye leather uniformaly well. Bismark Brown. Meldole Blue, Acid leather brown, etc. are some of the dyes used for dyeing leather.

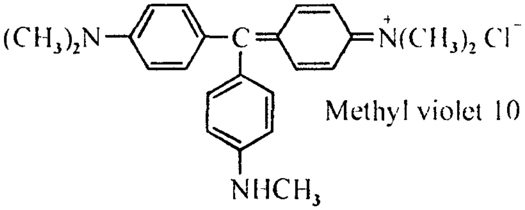


Bismark Brown

Q.15. Which dyes are used for paper, food and photography?

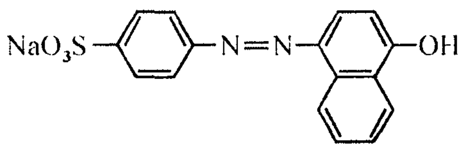
Ans. (*a*) **Dyes used for Paper :** Paper is cellulose and hence direct dyes can be very well used for dyeing paper. Basic dyes are also employed such as basic blue dye.

Safranine T is used in paper dyeing. Basic dye Methyl Violet 10 BNS is used in the making of carbon paper.

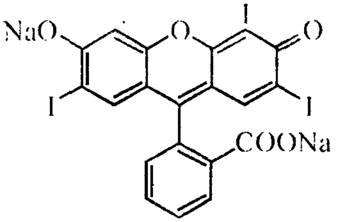


Methyl violet 10 BNS

(*b*) **Dyes used for Food :** Though many classes of dyes can impart colour to food products. dyes that can be used are limited to low toxicity and do not add to state of flavour in an offending way. They should be totally harmless to human beings. Again, a high degree of purity is also essential, since impurities present may have undesirable properties and thereby create problems by continuous use over a period. Hence, food colours are subjected to vigorous control to ensure that the population not in any way affects. The dyes generally used in foods and drugs are Orange I, Tartrazine, Amarnath, Erythrosine, Naphthaol Yellow S, Crystal Red F, Fast Red E.

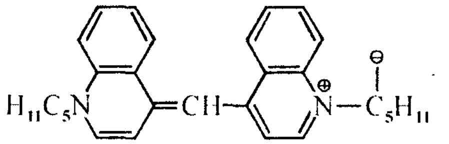


Orange -I

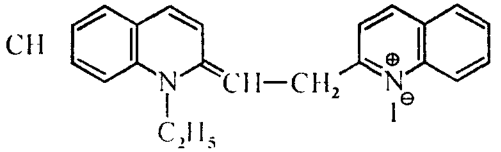


Erythrosine

(*c*) **Dyes Used in Photography** : The blue and violet region of light have effect upon the usual gelatin silver bromide emulsion but addition of certain dyes such as carbocyanines and isocyanines have been found to make the photographic emulsion sensitives to whole range of visible spectrum.



Cyanine



Pinacymol

Q.16. What are the requirements for optical brighteners? What are their requirements?

Ans. For a compound to be optical brightener, the following points are to be taken into account.

(*i*) A brightening agent should be substantive, non-toxic and compatible with detergent action under all likely conditions.

(*ii*) It should be sufficiently fast to light and the effect should remain for reasonable period.

(*iii*) The molecule should not contain chromophoric system. Its structure should be similar to those of reactive dyes.

(*iv*) The molecule should have linear and coplanar configuration.

(*v*) Coloured decomposition products should not be formed on prolonged exposure.

Q.17. What are the requirements of organic pigments? Give two examples of organic pigments with their structure.

Ans. For a substance to be an organic pigment, the following criteria are applied :

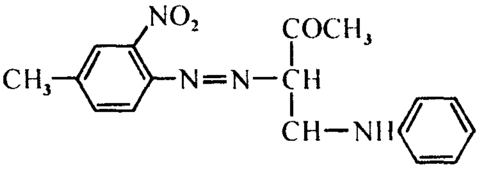
(*i*) Factors on which pigments are evaluated and depend upon are fastness to light, heat, water, solvent, action of acidic and basic compounds, action of other chemicals. For a pigment to be useful, it should be fast to light. This depends upon the pigment and the medium in which it is dispersed. Pigments are less fast in pale tints, than in the dark tints. Fastness to heat becomes an important factor where the pigment is exposed to higher temperature as in the case of baking enamels, moulded plastics, etc. As most of the pigments are exposed to atmosphere, action of water, gases in air have effects upon the pigment, its colour and its durability. Where acidic or alkali medium are present, the pigment should be able to withstand the effect due to them.

(*ii*) The pigment should be insoluble in all media. This condition, though not strictly applicable, is necessary since solubility of pigment may give rise to other problems such as crystallisation of pigment and change in the colour properties of pigment.

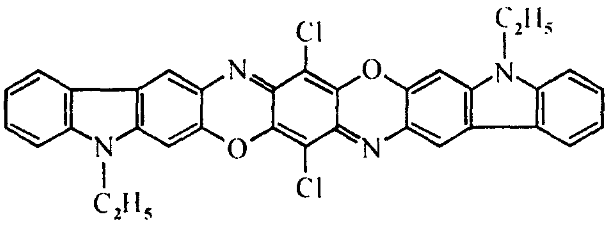
(*iii*) In all applications, the physical form, shape, size of pigment particles are very important. The pigment colour-will also depend upon the medium in which it is dispersed, hence the medium also should be such that it just helps to act as a carrier for the pigment in an efficient manner. The shape and size of the particles determine the binding power of the pigment and hence pigment should have such size and shape to give maximum binding power. Though all these conditions would not be met by a single pigment, hence a number of pigments have been developed to satisfy the particular condition which plays a crucial role in its application and use.

Examples of Organic Pigments

Hansa Yellow G is used in paints and printing inks and has the following structure.

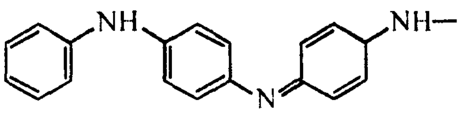


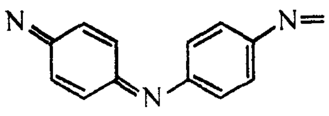
Carbazole dioxazine is another example of high grade pigment giving a blue to violet shade.

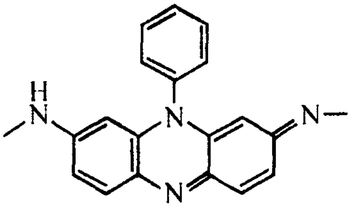


Q.18. Discuss oxidation colours.

Ans. Aniline Black is an example of oxidation colour ingrain dye. It is obtained on fibre cotton by treatment with aniline and aniline hydrochloride and subsequent oxidation with dichromate or perchlorate in the presence of copper salt. The colour obtained has good fastness and properties and as it is cheap it is extensively used. There are three types of structures associated as shown below :







Q.19. What are the differences between primaries and intermediates?

Ans.

	Primary	*Intermediates*
1.	Primary are basic raw material which are obtained from the natural sources.	Intermediates are the pure organic substances which are obtained from the primaries.
2.	The aromatic primaries are obtained from coal tar distillation products as different fractions depending upon the fractional distillation temperature.	The intermediates are obtained from the aromatic primaries by means of unit processes like nitration, sulphonation, halogenation etc.
3.	The examples of primaries are benzene, naphthalene, phenol, anthracene, cresol, etc.	The examples of intermediates are nitrobenzene, aniline and its derivatives, sulphuric acid, amides, etc.
4.	The primaries are not very pure in form.	Intermediates are comparatively in pure form.
5.	The dyes are not directly obtained from primaries.	Dyes can be directly prepared from intermediates.

Q.20. Suggest the types of dyes applicable to them.

Ans. (*i*) **Cotton :** The dyes which are used are direct dyes, basic dyes with the help of mordants, vat dyes, like indigo and anthequinone type sulphur dyes.

(*ii*) **Silk :** It is protein fibers : so the dyes used are acidic and basic dyes directly. All types of direct dyes.

(*iii*) **Polyester Fibres :** Mainly disperse dyes are used for the synthetic fibres.

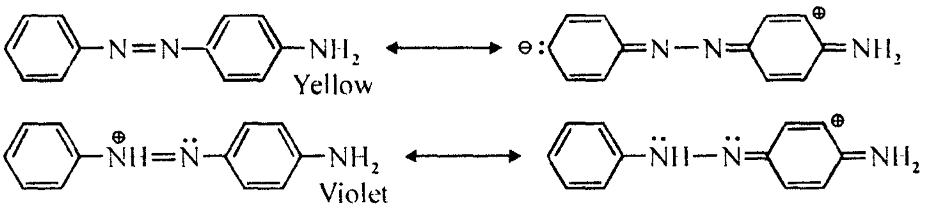
Q.21. Write short note on substantive dyes.

Ans. These are also called as direct dyes. Dyes having affinity for cellulose fibres which do not require any mordant are termed as substantive dyes. These dyes are salts of colour acids and are generally azo dyes. Direct dyes are sometimes known as salt dyes since common salt is added to dyebath. These substantive dyes are substances of high m.p. showing colloidal properties and fixed on fibers by hydrogen bonding. The substantive cotton dyes are surpassed in brilliance by the basic dyes and in fastness by mordant dyes. Direct cotton dyes with excellent light fastness, which are either copper complexes or dioxane are now available. However, direct cotton dyes such as Congo Red with poor fastness properties continue to be used in very large quantities on account of the low cost of the dyes and the simplicity of the dyeing process. They dye wool silk from a neutral bath. Some of the examples of substantive dyes are Congo Red, Direct Black EW, etc.

Q. 22. Explain why *p*-amino azobenzene is yellow in colour but in acidic medium it becomes violet.

Ans. In *p*-amino azobenzene only one charged structure contributes to the resonance hybrid. But when it gets protonated in acidic medium, both the structures contributing to the resonance hybrid are charged. Thus, the absorption band is shifted to longer wavelength and the colour gets deepened.

This is an example where the coordination with proton produces a greater bathochromic shift than is caused by addition of an auxochrome.



Q.23. Explain why Malachite Green is more deeply coloured than crystal violet.

Ans. In crystal violet, the cation of which all three benzene rings participate in resonance, polarizability in equal in all directions in the plane of the molecule but there is only one principal absorption peak λ_{max} 5900Å. In the unsymmetrical malachite green there are two axes of polarizability differing in degree, lying at right angles, and two absorption peaks occur (λ_{max} 4230 Å and 6250 Å). The magnitude of the charge on each nitrogen atom in crystal violet is less than that in alachite green and thus colour will be lighter as compared to Malachite Green.

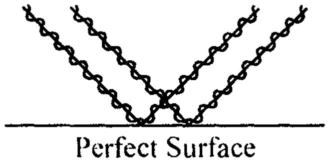
Q.24. Write short note on fluorescent brightening agents?

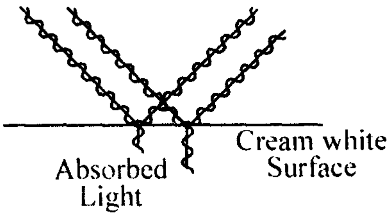
Ans. These are chemical compound used to mask the yellow or brownish tint in the fabric. They are colourless compounds which are also called optical bleaches or white dyes.

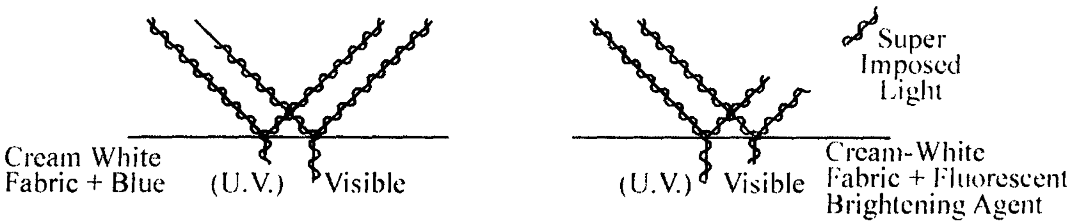
We know that the yellow impurities in the cloth absorb blue colour. The reflected light is depleted of the blue component and hence the fabric has yellow tint. The fluorescent brightening agent which is added does not absorb visible light as it is colourless. Hence it reflects all the visible radiation which is incident on it. The fluorescent agent absorbs the U.V. light present in the incident light. This excites the electrons in the pigment to higher energy states. But when these electrons come to the ground state, absorbed energy is re-emitted as visible light. This continues as long as the exciting radiation falls on the pigment. A part of the energy of U.V. radiation is used up and hence re-emitted light has slightly less energy. Therefore, this emitted light will have longer wavelength. The absorption of U.V. light and re-emission of visible light of longer wavelength is called flourescence. The flourescence converts a part of invisible U.V. light into visible light.

The light re-emitted by florescent agent has longer wavelength and corresponds to the blue region. Thus the fluorescent light having greater proportion of blue light is superimposed on the reflected light which is deficient in blue light. The balance of colours is restored and white effect is produced. Thus the colour compensation is done by addition process. The intensity of reflected light is increased and the fabric appears brilliant white.

The mechanism of fluorescent brightening agent can be represented by the following diagrams.







The optical brighteners should have the following desirable properties.

(*i*) They should not affect or be affected by detergent action.

(*ii*) They should be soluble in water and should be absorbed by fabric (substantive).

(*iii*) They should have fastness to light.

(*iv*) They should not contain chromophoric groups so that they themselves are not coloured.

(*v*) The molecules should have linear and planar structure so that they are easily attached to the fibre.

The optical brighteners are mainly applied to cellulosic fibres. They can be directly mixed with the detergents. They can also be added to molten polymer during the manufacture of synthetic fibres.

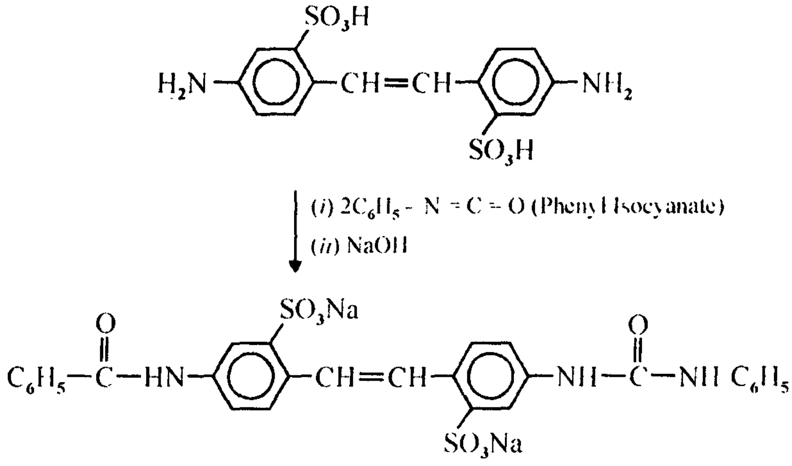
Types of Optical Brightners

The optical brightners can be classified into following types depending on chemical structure.

1. Stilbene Derivatives

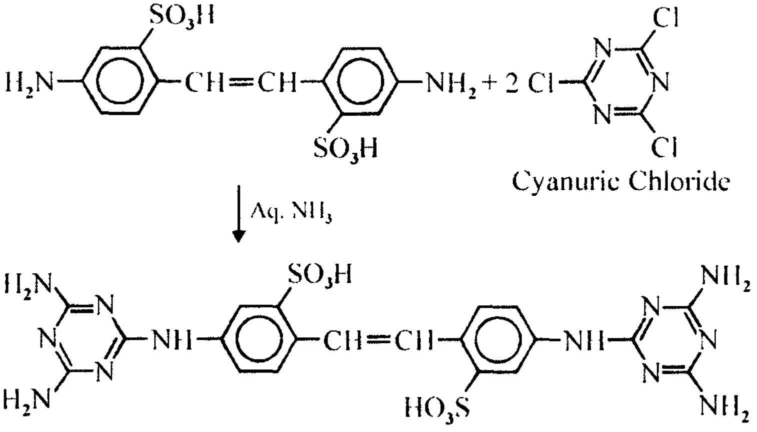
Majority of optical brightners are derivatives of stilbene (diphenylethene) containing naphtho, benzothiazole, or triazinyl rings. The basic compound is 4, 4'-diamino stibene-2, 2'-disulphonic acid.

Example (i)



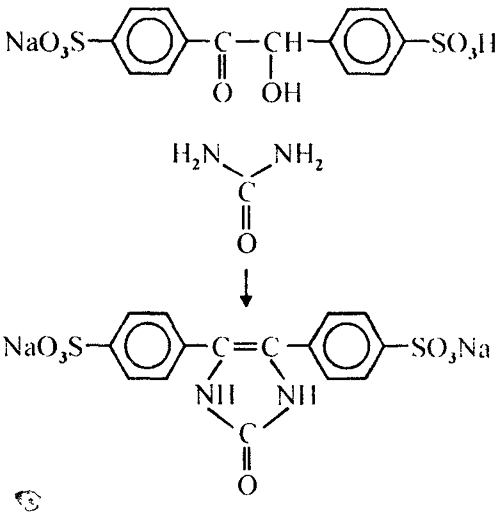
Blankophor R

Example (ii)



Tinopal BV

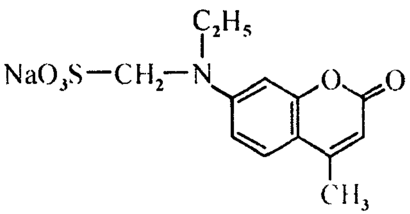
Example (iii) : The urea derivative of stilbenes which is sulphonated, is used as brightner for wool.



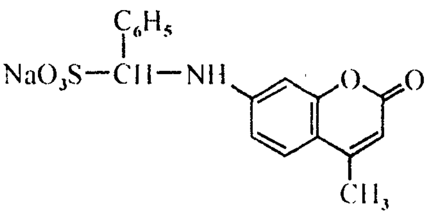
Blankophor WT

2. Coumarin Derivatives

The derivatives of 7-amino coumarin are used as optical brightners. The formaldehyde bisulphite derivative, benzaldehyde bisulphite derivative, or acid salt of 7-amino coumarin are used.



7-Ethyl amino-4-methyl coumarin formaldehyde bisulphite derivative



7-amino-4-methyl coumarin benzaldehyde bisulphite.

The triazinyl derivative of 7-amino-3-phenyl coumarin are supplied to natural fibres like cellulose and wool. They can also be added to molten polymers like polyamides, polyesters, polyurethanes, etc. They have good fastness to light.

Q.25. Discuss the pollution of dyeing in industry.

Ans. One of the main threatening problems in the industrial world facing today and applicable to dyestuff is the pollution problem. The dyestuff industrial wastes in the form of atmospheric gases and waste waters have been found to be polluting the neighbouring area.

The handing and production of carcinogenic intermediates regularly involved in the production such as benzidine and its derivatives α-, and β-naphthylamines, diphenylamine. *etc.*, has created setback in the production of dyes. Further benzidine and its derivatives are being banned all over the world and being replaced by the new comparatively much safer diamines because of their carcinogenic nature. For example, the β-naphthylamine is no more in practice for making its derivatives but is replaced by a much safer sulphonic acid, Tobias acid (β-naphthyl-amine-α-sulphonic acid).

In dye industry, the processes where lead salts, mercury salts, etc.; were essential are abandoned or replaced by new safer methods.

The above developments are notable from ecology point of view. It is hoped that the future development of intermediates and dyes to be exploited commercially will be thoroughly investigated first from the point of view of ecology and safety of human beings and animal as well as plant kingdom.

For the pollution control, newer techniques have been introduced and are further being developed by absorbing the industrial gases and giving appropriate treatments to waste waters to minimise pollution. An expensive study had been made on careful handing of solvents, cyanides, etc. The developments are notable from ecology point of view.