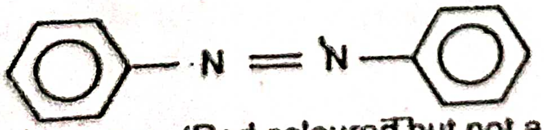
UNIT-1

Introduction

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 brightners. They may also be called as the *white dyes*. They have the special property of absorbing ultraviolet light and re-emiting 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 visible 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 form 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 in 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 auxillary 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.

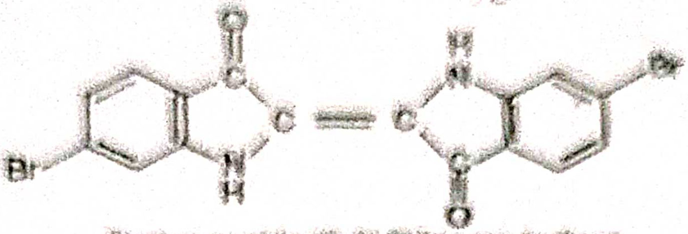
(vii) The shade and fastness of a given dye may vary depending on the substrate due to different interactions of the molecular orbitals of the dye with the substrate, and the ease with which the dye may dissipate its absorbed energy to its environment without itself decomposing.

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 the oldest known dye. It was obtained both from dyer's woad (indigenous in Europe) and from *Indigofera tinctoria* (a native plant of Asia).

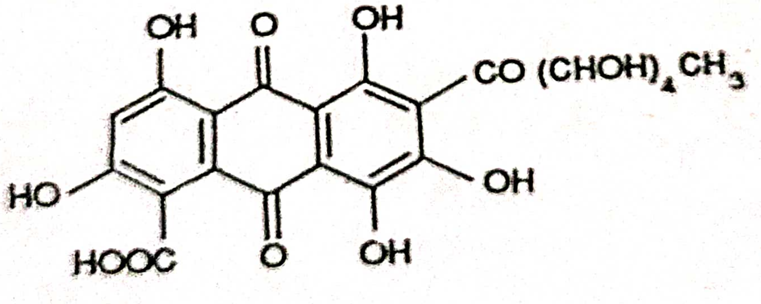
(ii) **Tyrian Purple or Royal Purple.** It was extracted from a gland of the purple snail by a process developed by the Phoenicians. It was very costly. Chemically, it is 6, 6'—*dibromoindigo*.



Tyrian purple (6 6'-Dibromo indigo)

(iii) **Alizarin.** It is the oldest colouring material. It was obtained from the roots of the madder plant which was cultivated extensively in Europe, the near East and India. It is a mordant dye and gives different shades with many matallic salts (mordants), e.g., it gives very fast red colour on an aluminium oxide mordant and a purple to black shade on an iron oxide mordant. Madder, cultivated in Turkey, yielded an exceptionally bright red material which accounts for the name Turkey red.

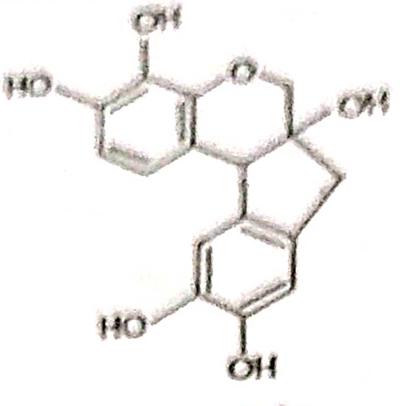
(iv) **Cochineal.** It was obtained from the female insects of the species *Coccus cacti.* It dyed a crimson shade on an aluminium mordant. This dye came to the European dyers from Mexico. Chemically, cochineal is carminic acid.



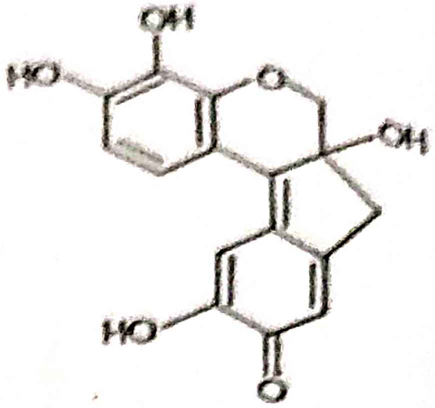
Carminic acid

(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.



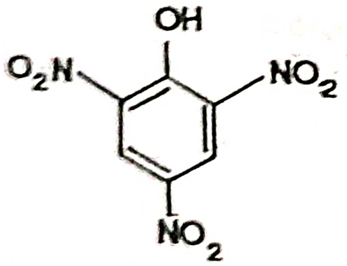
Haematoxylin



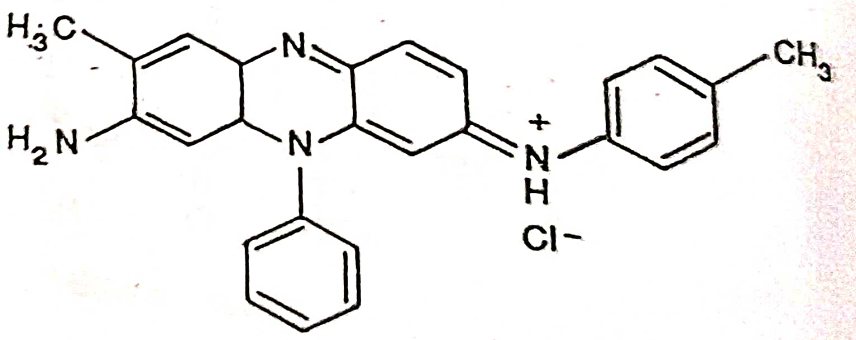
Haematin

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.

Era of synthetic dyes. Picric acid, which was obtained by Woulfe in 1771 by treating indigo with nitric acid, was subsequently occasionally used for dyeing silk but did not attain any significance. For this reason, really incorrectly, William H. Perkin, not Woulfe, was given credit for having produced the first synthetic organic dye. As a young eighteen year old student of Hofmann, William H. Perkin in 1856 decided to make quinine from aniline. Instead of quinine, he obtained a black mass in his reaction. On working up, he found that he had made a purple dye. He started manufacturing the dye himself with great success. He called this dye Mauveine. It is a violet cationic dye.



Picric acid



Mauveine

The brilliant work of Perkin immediately attracted much attention and stimulated other chemists to carry out similar experiments. In this way, in 1859, E. Verguin in Lyon discovered fuchsine. On the other hand, P. Griess discovered diazo compounds which laid the foundation for the development of the azo dyes. The first true azo dye called Bismarck Brown was developed by Martius in 1863.

After the excellent work by Kekule on the quadrivalence of carbon (1858) and on the constitution of benzene (1865), the work was started for the planned preparation of purely synthetic dyes and also for the artificial production of natural dyes. The first success achieved in this direction was the elucidation of the constitution as well as the synthesis of alizarin by Graebe and Liebermann (1868). The elucidation of the constitution and the synthesis of indigo were completed by the research work extending over several decades (Adolf von Baeyer, 1870, K. Heumann, 1890).

In the beginning of 20th century, G. Engi and P. Friendlander developed indigoid dyes. These workers synthesised Ciba Blue 4 B and thioindigo respectively. In 1901, R. Bohn synthesised indanthrone which is the first anthraquinonoid vat dye. In the 20th century, the dyes such as Neolan dyes, (1915) phthalocyanine (1936) and 1,2—metal complex dyes (Irgalan dyes, 1949) were synthesized.

In 1920, R. Clavel and H. Dreyfuss introduced disperse dyes which solved the problem of dyeing hydrophobic fibres. After the Second World War, certain pigments were synthesised which achieved importance for colouring plastics e.g., quinacridone (1948). Later, chromophthalic dyes (1957), reactive dyes for wool (1951/1952, Remalan and Cibalan Brilliant dyes) and especially reactive dyes for cellulose fibres (Procion dyes, 1956) were also synthesised.

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 a 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.

Colour and Chemical Constitution

2.1. 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. 2.1.

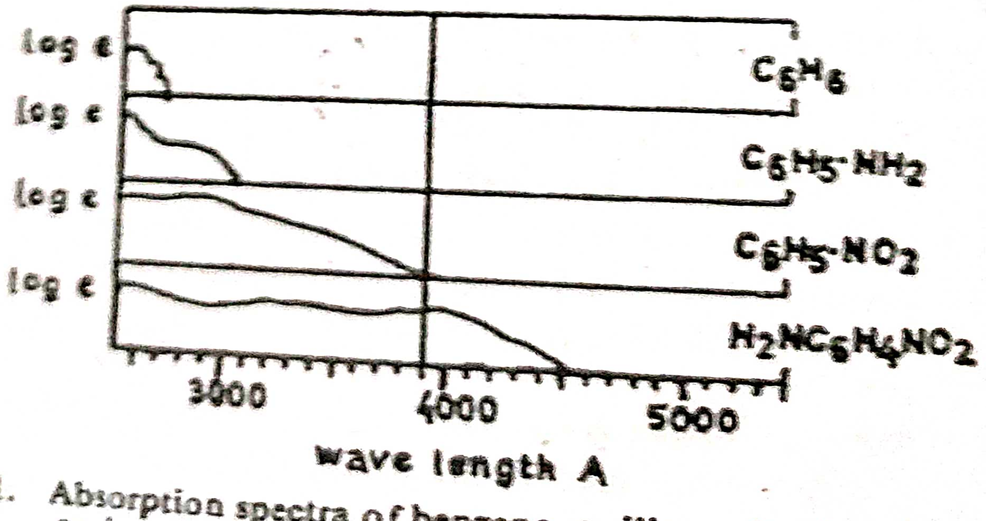


Fig. 2.1. Absorption spectra of benzene, aniline, nitrobenzene, and *p*-nitroaniline.

If a structural change in a dye molecule shifts the absorption from higher to lower wavengths, 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. 2·2) which are obtained by plotting the intensity of absorption against wavelength (λ).

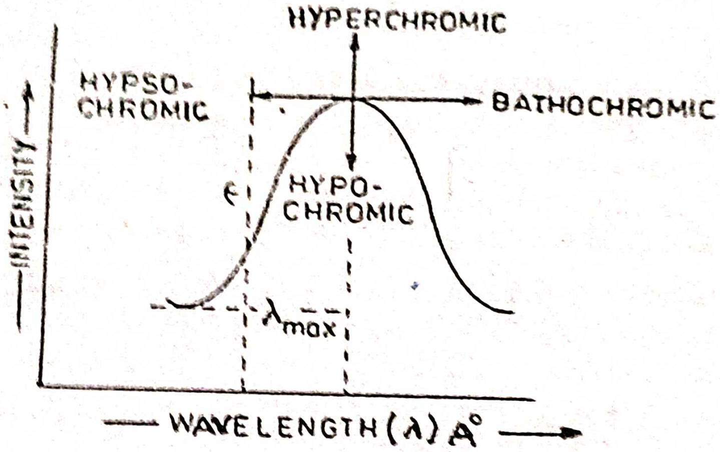
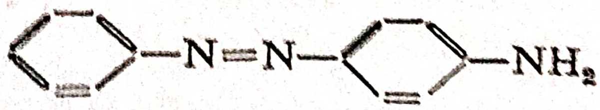


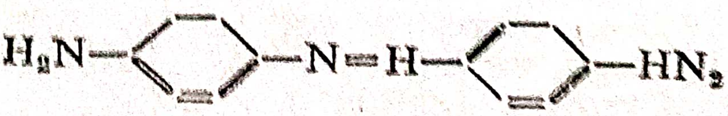
Fig. 2.2. Absorption spectrum of a particular dye.

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

(*i*) The bathochromic 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 bathochromic 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.*

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

2.2. 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 colourled substance.

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 spectral colours) and infrared regions is shown in Fig. 2.3.

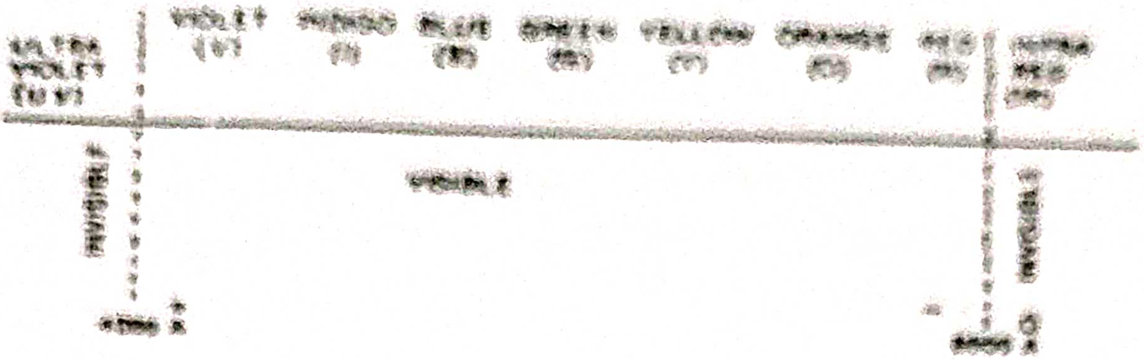


Fig. 2.3. Sequence of U.V., visible with spectral colours and I.R.

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 2.1.

TABLE 2.1

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

2.3. 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)

$$\text{colourled organic compound} \xrightleftharpoons[\text{oxidation}]{\text{reduction}} \text{colourless compound}$$

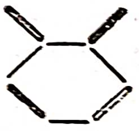
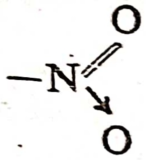
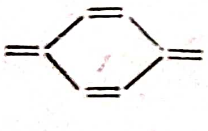
From this example, Graebe and Libermann concluded that unsaturation was responsible for the development of colour.

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 compound 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 methlyhydrazine is produced which is colourless because it does not contain unsaturated group. Some important chromophores are listed in Table 2.2

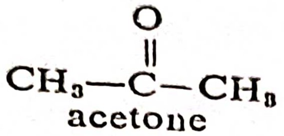
Table 2.2
Some Typical Chromophores

—N=O	nitroso		*o*-quinonoid
$>C=S$	thiocarbonyl	$-\overset{H}{C}=N-$	azomethine
—N=N	azo	 $-N\begin{smallmatrix}\nearrow O \\ \searrow O\end{smallmatrix}$	nitro
—N=N→O	azoxy		
—N=N—NH	azoamino	$>C=O$	carbonyl
	*p*-quinonoid	$>C=C<$	ethylenic

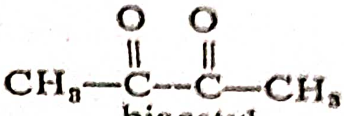
The chromophores listed in the above Table are of two types :

(*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 group, is colourless while biacetyl, containing two 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.


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

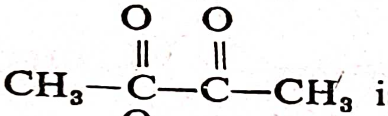
acetone

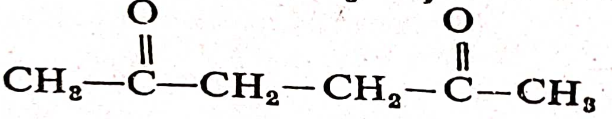

$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$

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 2.3.

Table 2.3

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 associatian 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 R, 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*. When the hydrogen atom in a hydroxyl group $-OH$ or in an amino group, $-NH_2$ by an acetyl group produces hypsochromic effect.

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

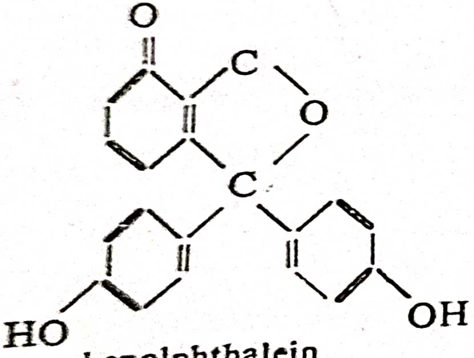
2. Armstrong's theory (Quinonoid theory). According to this theory, all the coloured compounds could be represented by the quinonoid structures (*o*-or *p*-). Thus, if a quinonoid structure could be assigned to a compound, it would be coloured otherwise not. On the basis of this theory, it could be possible to explain the colouring properties of some of the important compounds. For example,

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

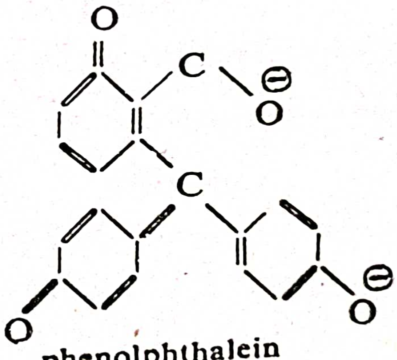
benzene
(colourless)

p-benzoquinone
(yellow)

(*ii*) If phenolphthalein is present in benzoquinone structure, it is coloured. On the other hand, if phenolphthalein is present in benzenoid structure, it is colourless.

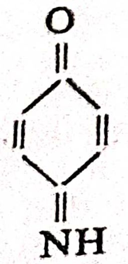


phenolphthalein
(colourless)



phenolphthalein
(red coloured)

Limitations. (*i*) Armstrong's theory could not explain the colouring characteristics of all of the compounds. For example, although iminoquinone and di-iminoquinone have a quinonoid structure, yet they are colourless.



iminoquinone

di-iminoquinone

(ii) A large number of coloured compounds are known which could not be represented by a quinonoid structure. For example, diacetyl, fulvene, and azobenzene are coloured compounds but could not be represented by quinonoid structures.


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

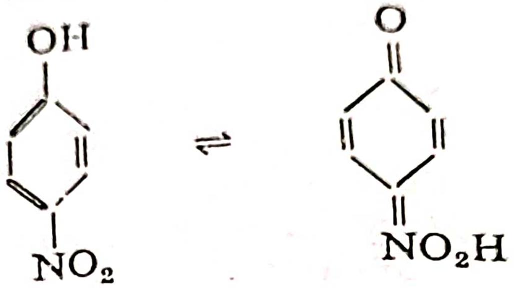
diacetyl


fulvene

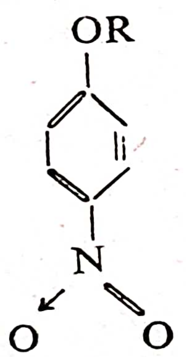
$C_6H_5.N=N.C_6H_5$

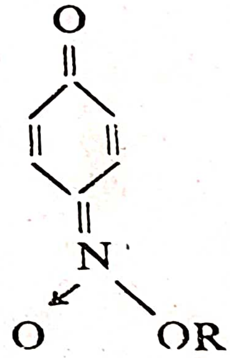
azobenzene

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

~~UNIT : I.~~

UNIT-II

mu· Quinonoid Dyes : Examples and Structures:

⑫ copies

④ copies → spiral

* Anthraquinone and Mordant Dyes :

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).

* The introduction of relatively simple electron donars gives anthraquinone compounds which, according to the strength of the electron donars ($OH < NH_2 < NR_2 < NHAr$), absorb in any desired region of the visible spectrum.

* Dyes based on anthraquinone and related polycyc 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 quinoid group, $>C=O$.

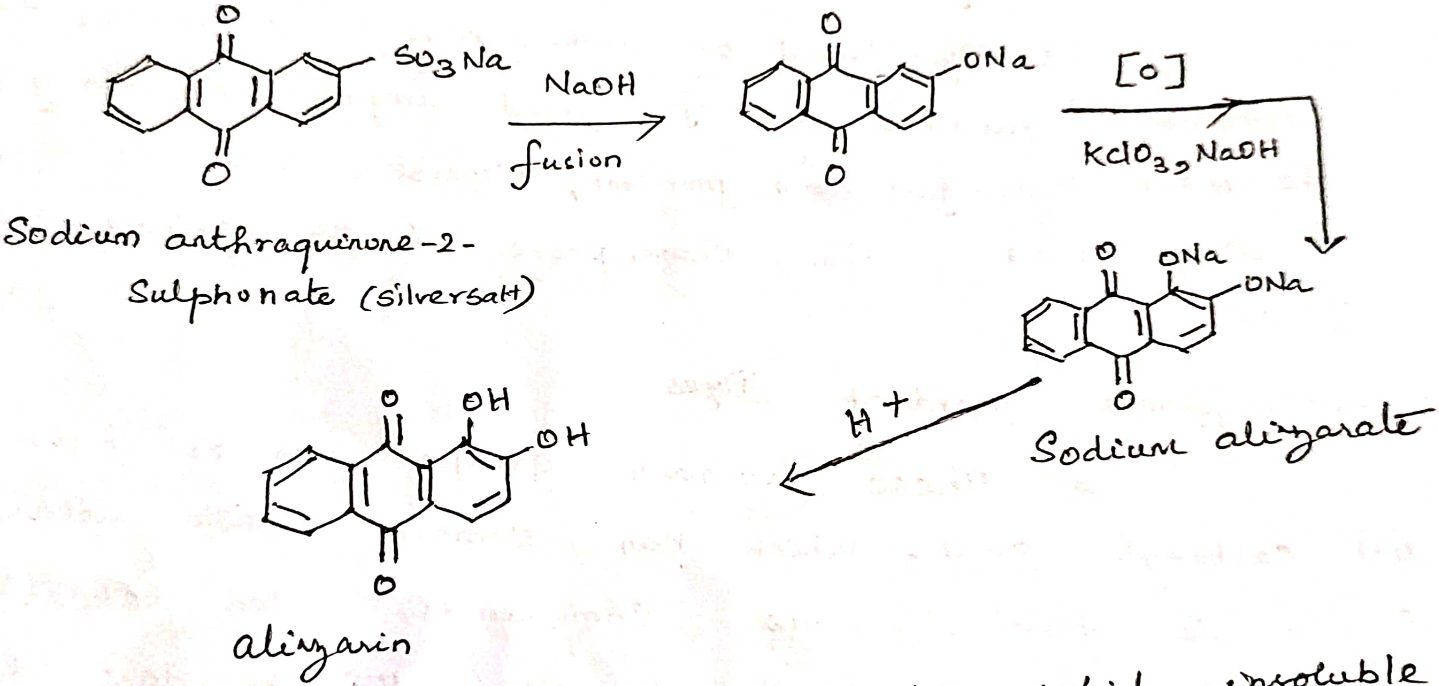
a) Anthraquinone mordant Dyes :

* These contain groups such as hydroxy (or) carboxyl group, which can combine with metal so as to form insoluble compounds called lakes. Th colour of the lake depends upon the mordant i.e., the metal used.

Some of the important anthraquinone morda dyes are as follows :

1) ALIZARIN:

- It is 1,2-dihydroxyanthraquinone.
- It is also known as mordant red 11.
- Previously it was 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 percent paste.



* 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.

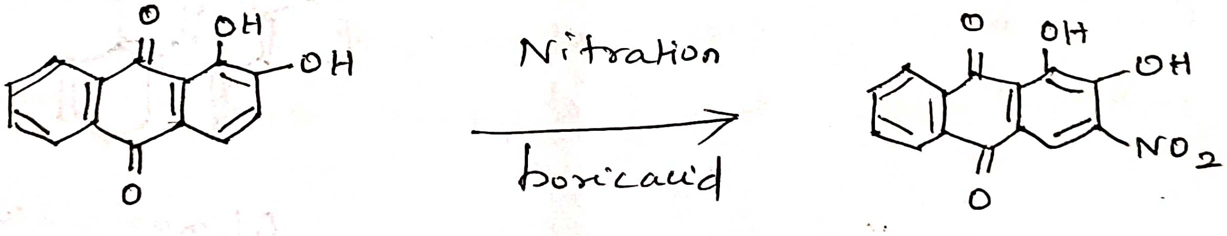
The colours of the lakes along with the respective mordants are given as follows :-

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.

) Alizarin Orange :

It is obtained by nitrating alizarin in the presence of boric acid.

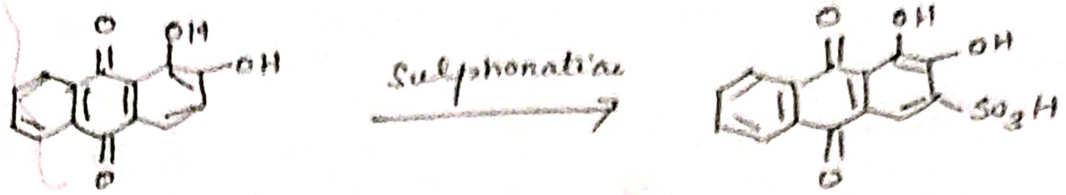


Alizarin

Alizarin Orange.

Alizarin Red S.

It is obtained by the sulphonation of alizarin with fuming sulphuric acid.



alizarin

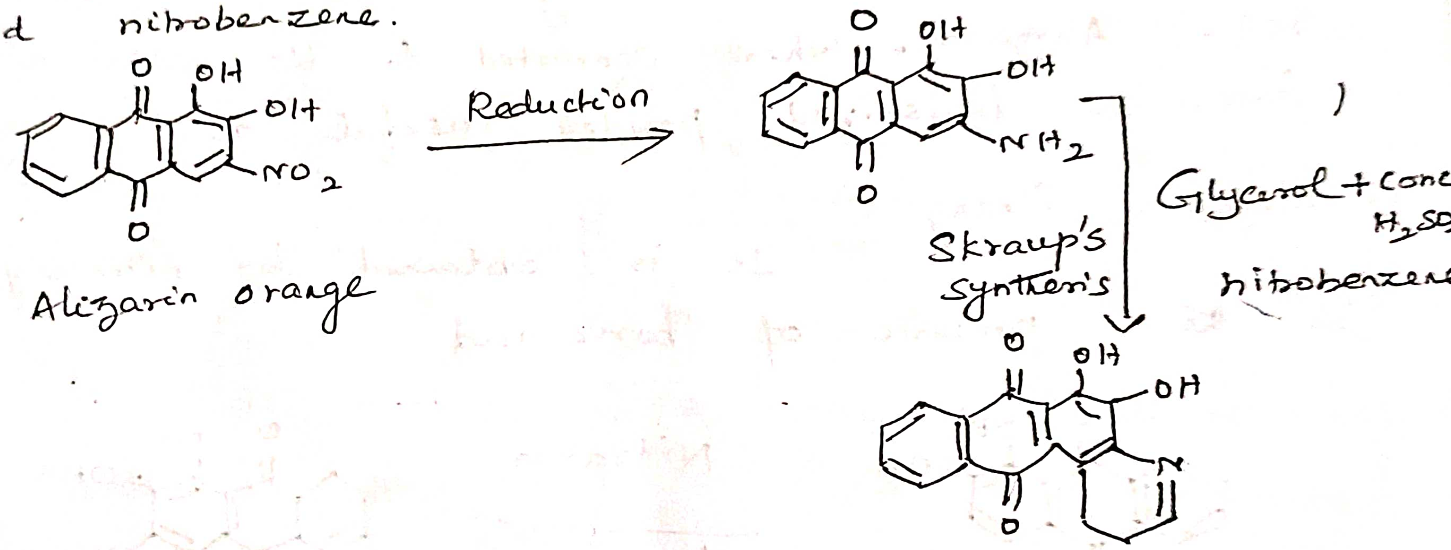
alizarin red S.

Uses:

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 orange

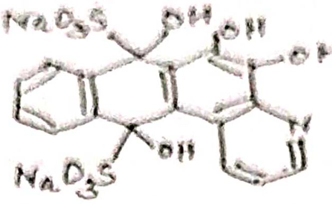
Alizarin blue.

Uses :

Alizarin blue dyes wool a blue colour when mordanted with Chromium.

Alizarin blue S.

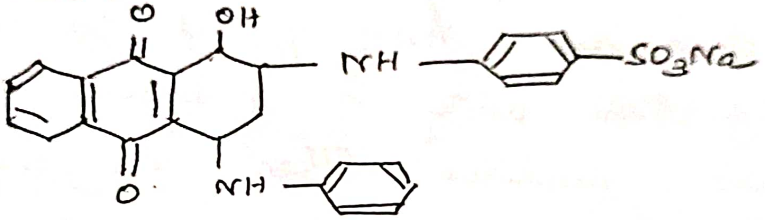
It is the sodium bisulphite salt of alizarin blue. It is soluble in water. It when mordanted with chromium gives a reddish blue lake.



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.

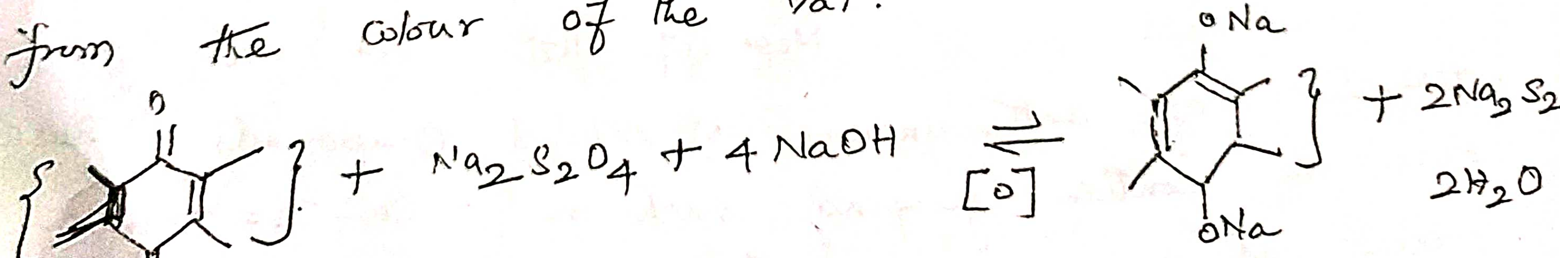
Anthraquinone vat dyes :-

Most of the best vat dyes are derivatives of anthraquinone (or) related compounds. These essentially contain grouping 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 large 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.,

~~Application~~ How to apply vat dyes to cloths.

Inorder 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 cloths 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.



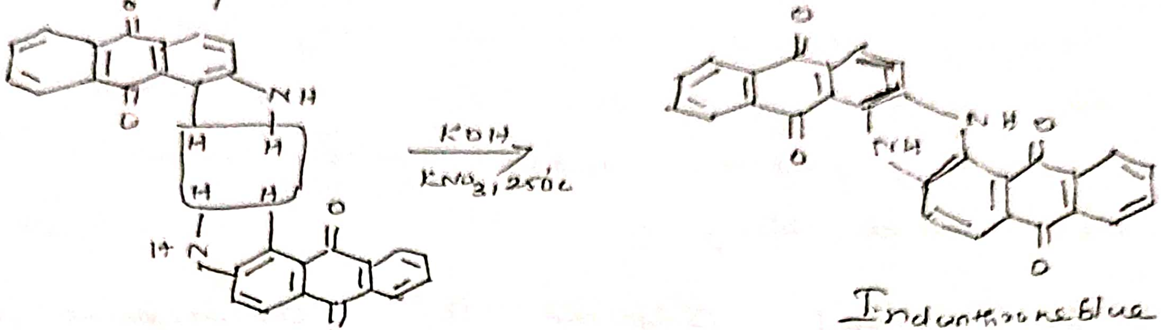
Anthraquinone vat dye (insoluble)

Sodium salt of anthraquinone (soluble)

The important anthraquinone vat dye are :

(i) Indanthrone blue (indanthrone, indanthreane (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 blue4) .

ii) Indanthrone (or) Indanthrene yellow 4GK.

iii) 3- Chloro indanthrone

iv) Indanthrene blue BCS

v) N,N' Dimethyl indanthrone

Phthalocyanines :-

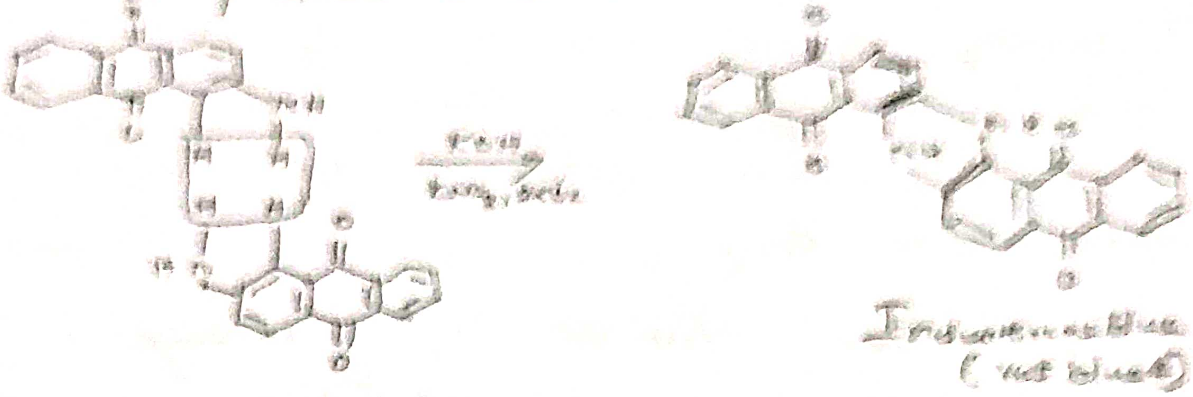
Introduction :

These constitutes 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

The important anthraquinone vat dyes are :

(i) Indanthrene blue / Indanthrone, Indanthrene (or) blue R

It is manufactured by fusing 2-aminoanthraquinone with potassium hydroxide in the presence of potassium chlorate (or) potassium nitrate at [illegible].



Indanthrene blue
([illegible])

(ii) Indanthrone (or) Indanthrene yellow 4GK

(iii) 3- Chloro indanthrone

(iv) Indanthrene blue BCS

(v) N,N'- Dimethyl indanthrone

Phthalocyanines :-

Introduction:
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Unit : II

2.1. Diphenyl methane Dyes - Auramine - Triphenyl methane Dyes - Malachite Green, Crystal violet, Pararosaniline - Preparation and applications

2.2. Indigo dyes - Preparation and applications - Derivativ of Indigo - synthesis and uses of Indigosol and tetrahaloindigo.

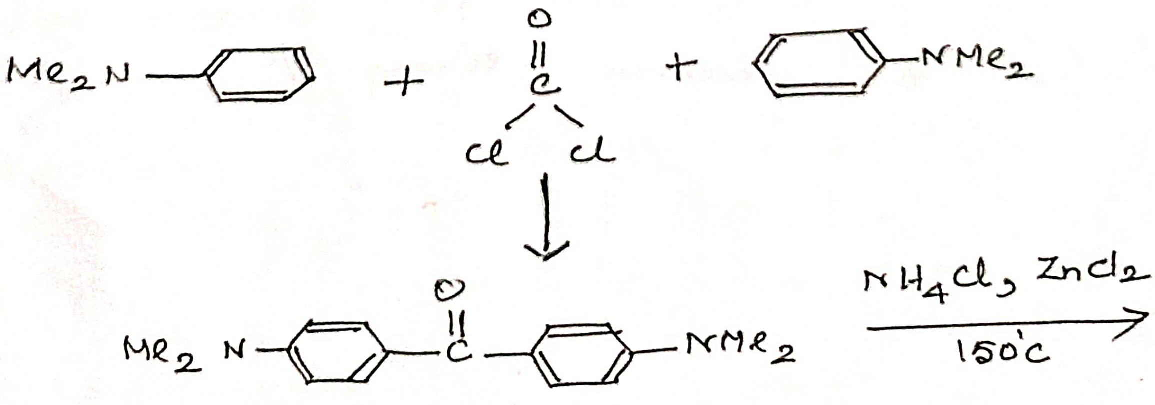
Diphenyl methane Dyes :

* The diphenyl methane dyes are characterised by the presence of a diphenylmethane nucleus. Only few dyes belonging to this class are commercially important.

Examples of Diphenylmethane Dyes :

1. Auramine O.
2. Auramine G.

Preparation : 1. Auramine O : This is prepared by heating michler's ketone with ammonium chloride and zinc chlor at 150 - 160°C. The auramine base so obtained on treatm with HCl is converted into auramine O. The michler's keto required for this synthesis is prepared by condensing N - dimethylaniline with phosgene.



Michler's ketone

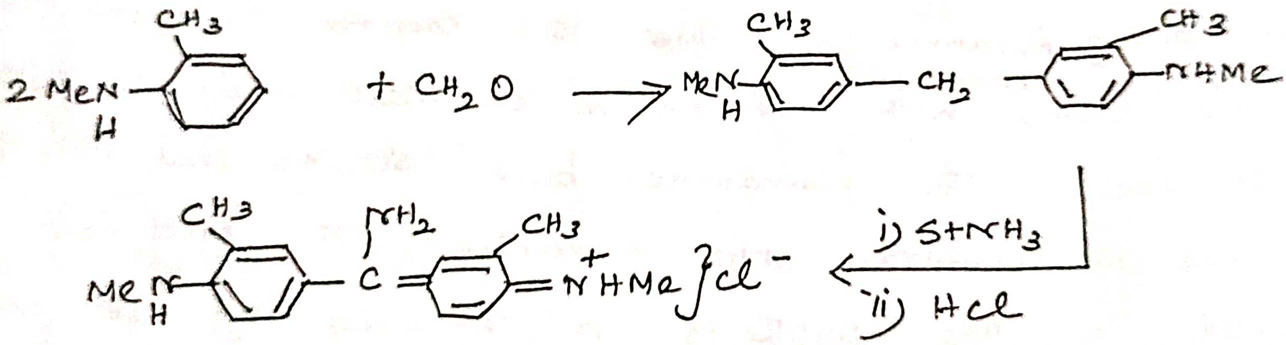
Auramine Base Auramine O

Uses:

- * It is marketed in the form of 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~~

2. Auramine G:

The condensation of N-monomethyl-o-toluidine with formaldehyde yields the product I which on heating with sulphur in a current of ammonia, followed by treatment with hydrochloric acid yields Auramine G.



Auramine G.

* It is greenish yellow dye.

Triphenyl methane Dyes :

* This group of dyes is one of the oldest known synthetic dyestuff groups. They are of brillia colour due to resonance and cover a range of shades from red to blue, including violet and green.

* 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-base.

$$\underset{\text{(Colourless)}}{\text{leuco- base}} \xrightleftharpoons[\text{reduction}]{\text{oxidation}} \underset{\text{Colourless}}{\text{Colour base}} \xrightleftharpoons[\text{alkali}]{\text{acid}} \underset{\text{coloured.}}{\text{dye}}$$

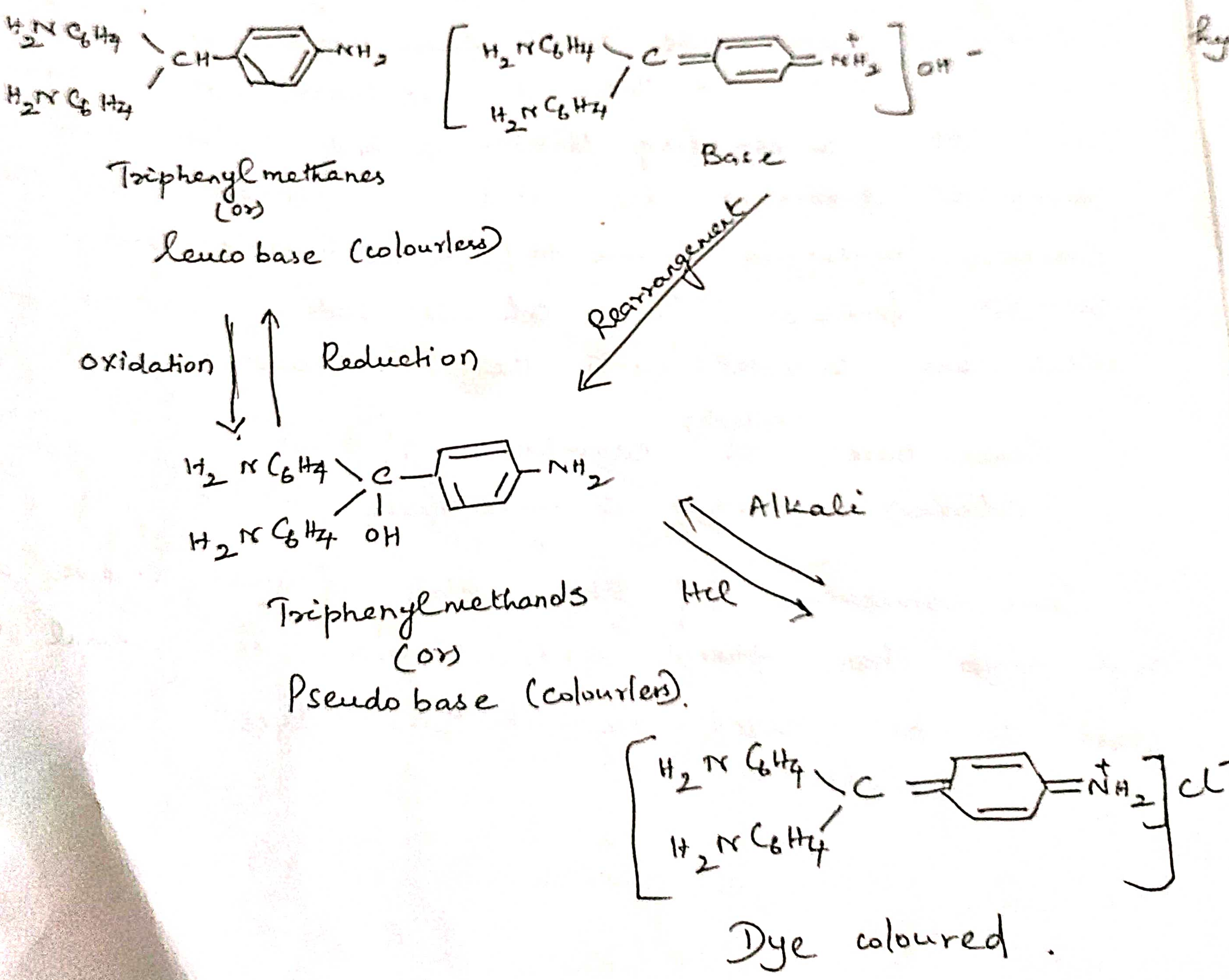
Some structures of this class of dyes involve an aryl group than phenyl and, therefore, in general this class can be called triarylmethane dyes.

The triphenylmethane dyes have been further classified into the following types:

1. Aminotriphenylmethane dyes
2. Hydroxy triphenyl methane dyes

1. Aminotriphenylmethane dyes

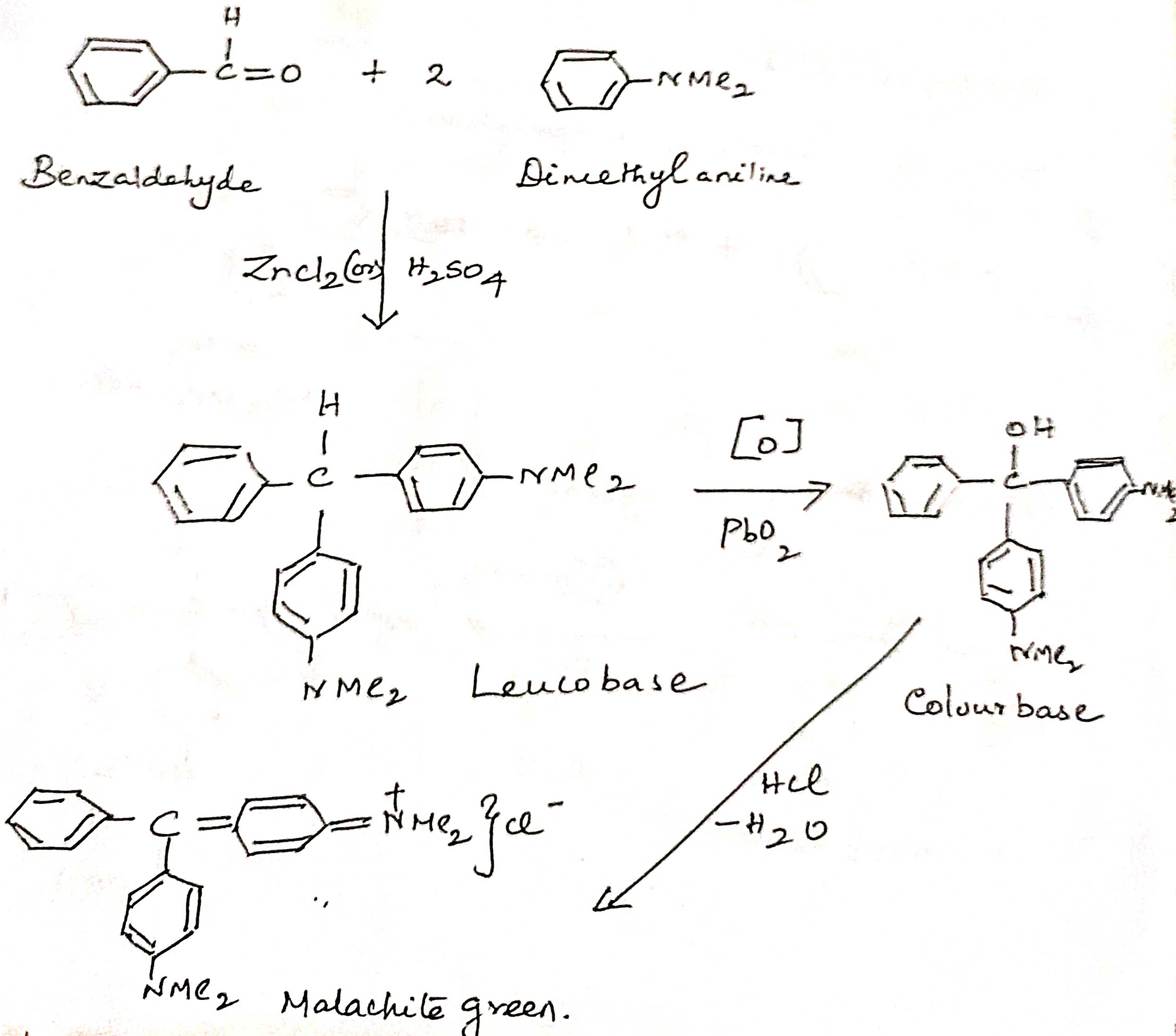
These are the salts which are obtained by the action of mineral acids on certain di- (or) tri-amino substituted triphenylmethanols (colour bases). The colour bases are in turn prepared by the oxidation of the leucobase (triphenyl methanes).



Important triphenyl methane dyes:

Examples: Malachite Green

Preparation: It is prepared by condensation of 2 moles of dimethylaniline with one mole of benzaldehyde at 100°C in the presence of zincchloride (or) conc. sulphuric acid. The leucobase produced is oxidised with lead dioxide in a solution of aceticacid having hydrochloric acid. The resulting base on acidification with excess of hydrochloric acid gives malachite green.



Application ; [illegible] dye

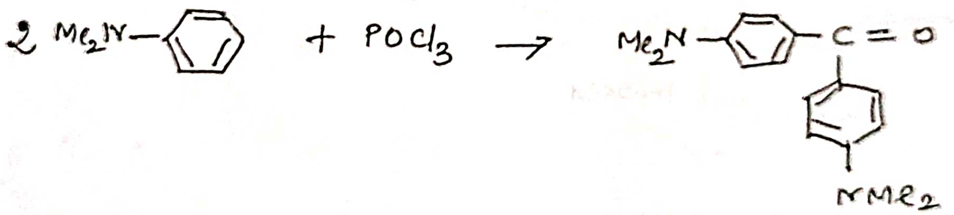
a valuable green dye wool and silk directly, and cotton mordanted with tannin.

2. Crystal violet :

It is hexamethyl pararosaniline or hexamethyl-pararosaniline hydrochloride.

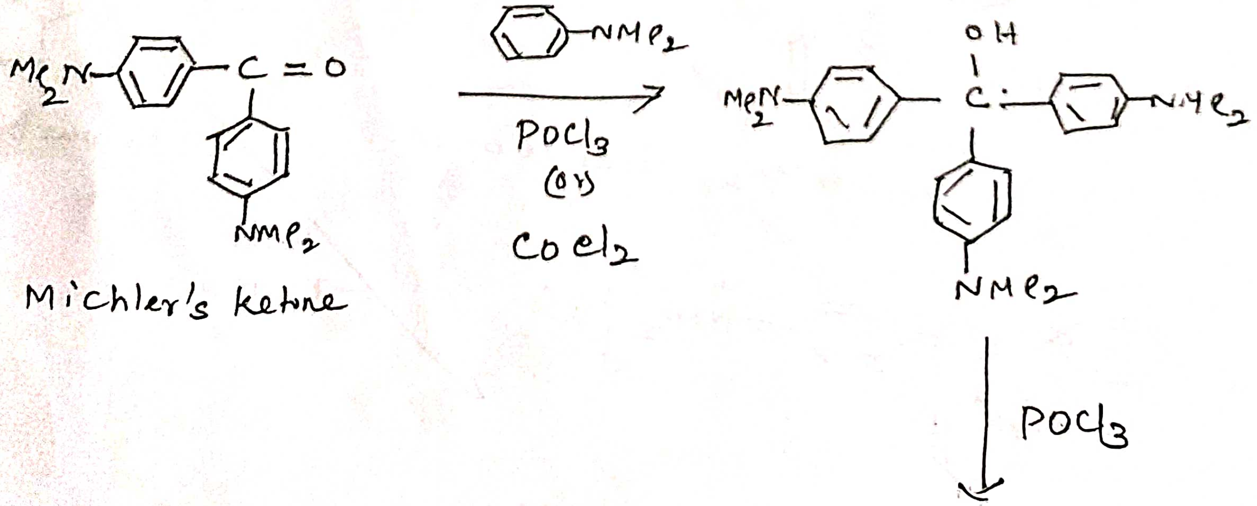
It may be obtained by heating michler's ketone with dimethylaniline in the presence of phosphoryl chloride (or) carbonyl chloride. If the latter compound is used, then crystal violet may be prepared directly by heating carbonyl chloride and dimethylaniline.

Michler's ketone preparation :

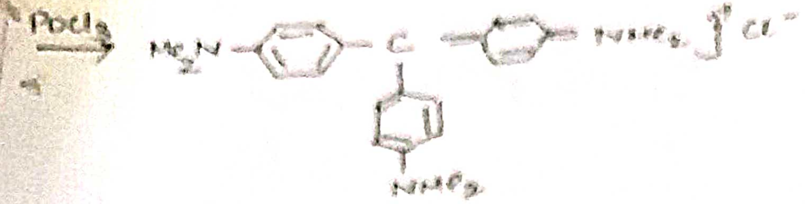


Michler's ketone

Preparation of Crystal violet :



Michler's ketone



Crystal violet

Its weak acid solution is violet, its strongly acid solution is green and its very strongly acid solution is yellow.

Applications :

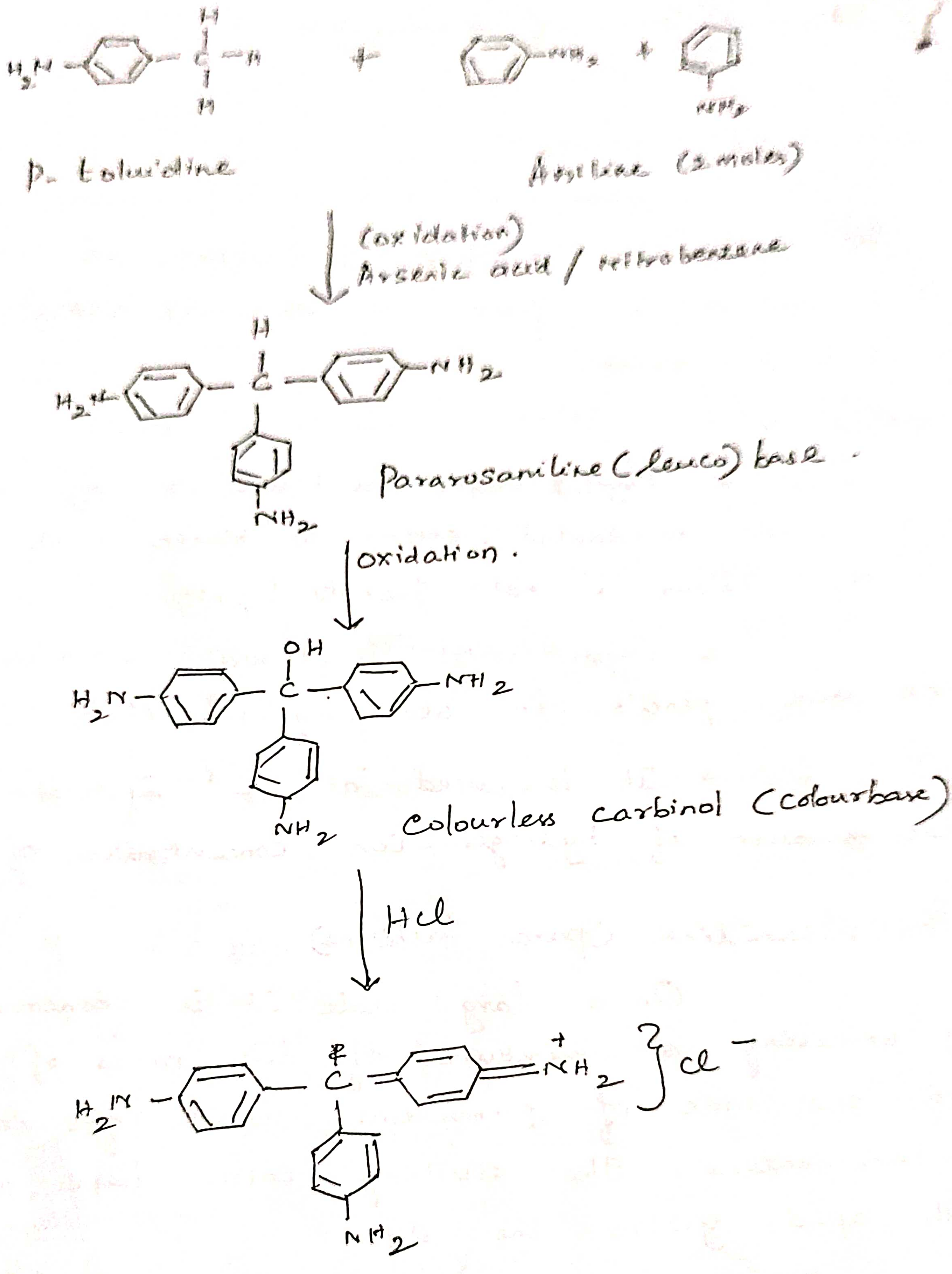
* Crystal violet is used to dye silk, wool and tannin - mordanted cotton to bluish violet colour but the colour is not fast to light.

* 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.

Para rosaniline (para fushsine).

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.



Pararosaniline.

Applications :-

Properties :

* Para 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.

Uses:

It dyes wool and silk directly, producing a violet red colour; cotton must first be mordanted with tannin.

Indigo dyes - Preparation and applications.

Indigoids : These dyes are characterised by the presence of $-\overset{\overset{C=O}{|}}{C} = \; = \; = \overset{\overset{C=O}{|}}{C}-$ group as the Chromophore.

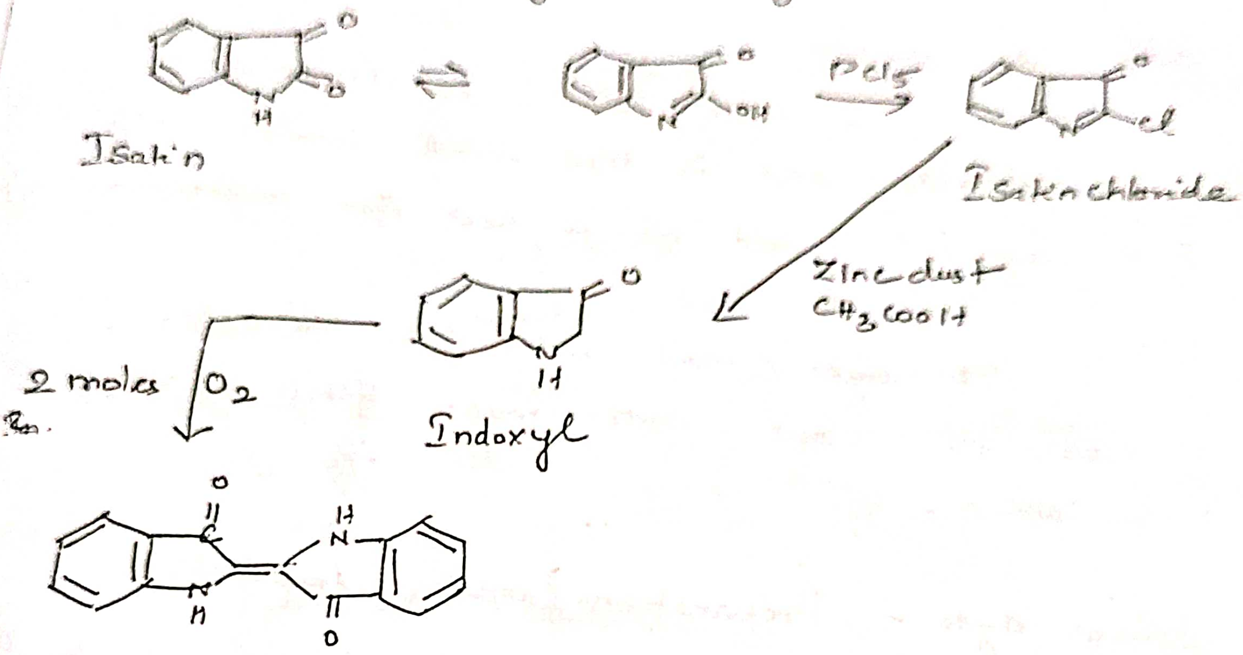
Indigo,

It is the oldest known dye. It occurs n the plants of indigofera group in the form of lucoside - the indican.

Indigo is also known as Indigotin. It is repared by the following methods :

Preparation of Indigo (or) Indigotin:

1) Reduction of isatin chloride (obtained by the action of phosphorus penta chloride on isatin) with zinc dust in glacial acetic acid yields indoxyl which upon oxidation in air gives indigotin.



Indigotin (or) Indigo.

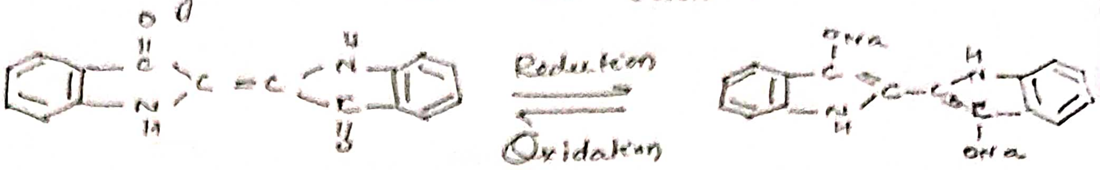
Applications & uses.

Properties: * Indigotion is a dark blue coloured powde

* 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.

Uses * 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

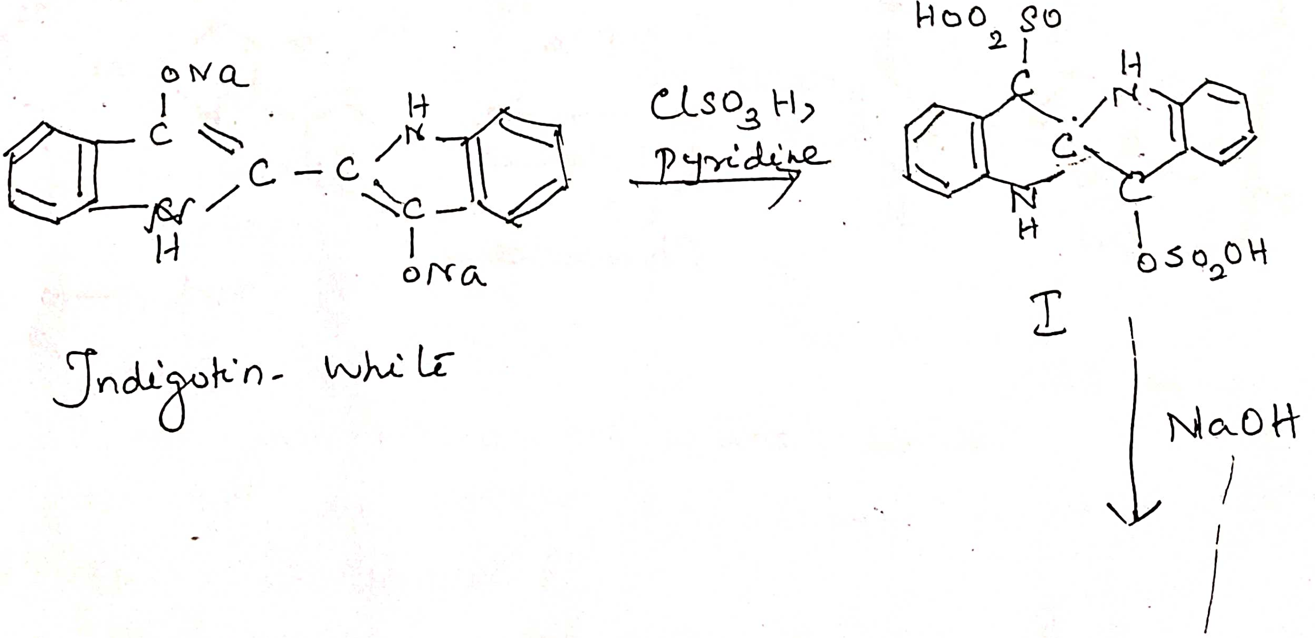
Derivatives of Indigo.

Synthesis & uses of Indigosol and tetrahaloindigo.

Indigosol O :

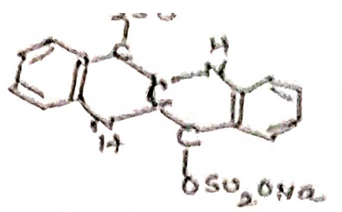
Indigotin- white is not stable. Therefore in ordinary dyeing, indigotin-white is first converted to its disulphonic ester (I) by treatment with chloro. Sulphonic acid in the presence of pyridine. The alkaline solution of ester (I) is called the indigosol O, which is indicated (II),

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.



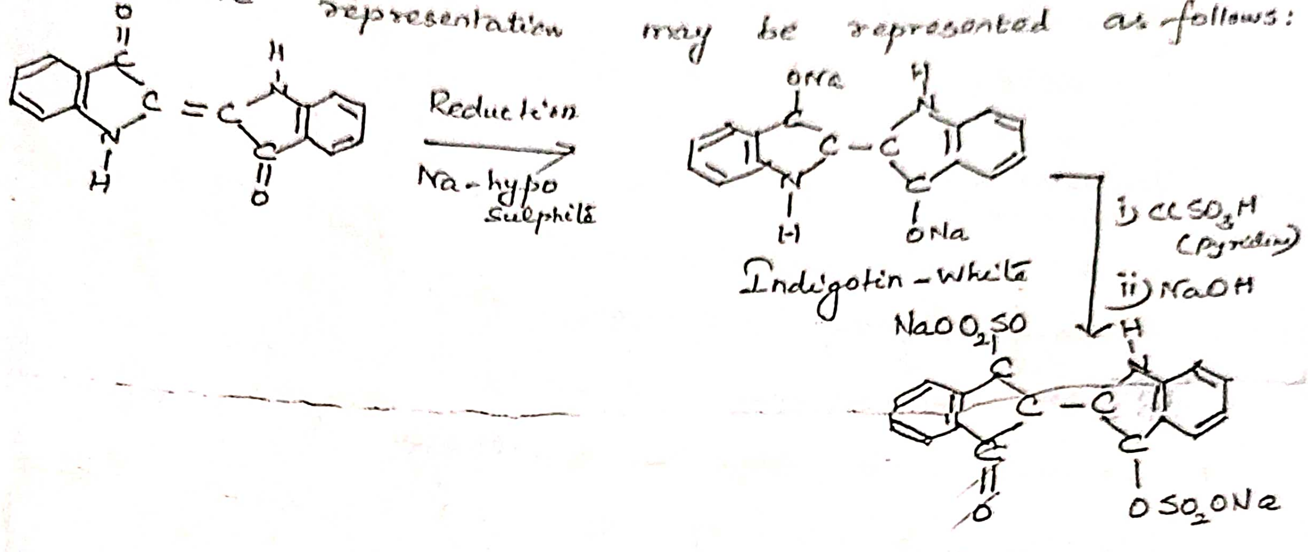
Indigotin- White

I



(II) indigosol O.

The above representation may be represented as follows:

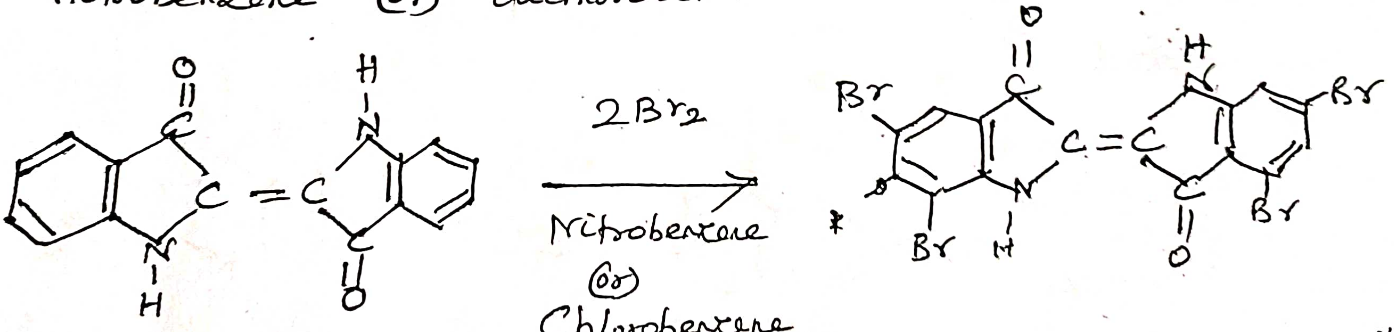


Indigosol-O.

c Tetrahaloindigo

Example :- Tetrabromoindigo ciba blue :-

It is obtained by bromination of indigotin in nitrobenzene (or) dichlorobenzene



Tetrabromoindigo ciba bl

Unit-IV

UNIT : III

3.1. Phthalein Dyes - Phenolphthalein - Preparation and applications.

3.2. Xanthein Dyes - Rhodamine, B, Fluorescein - Eosin - Preparation and applications

Phthalein Dyes :

* These are dihydroxytriphenyl methane derivatives with a carboxyl (or) sulphonic acid group ortho to the centre carbon atom in the third phenyl ring.

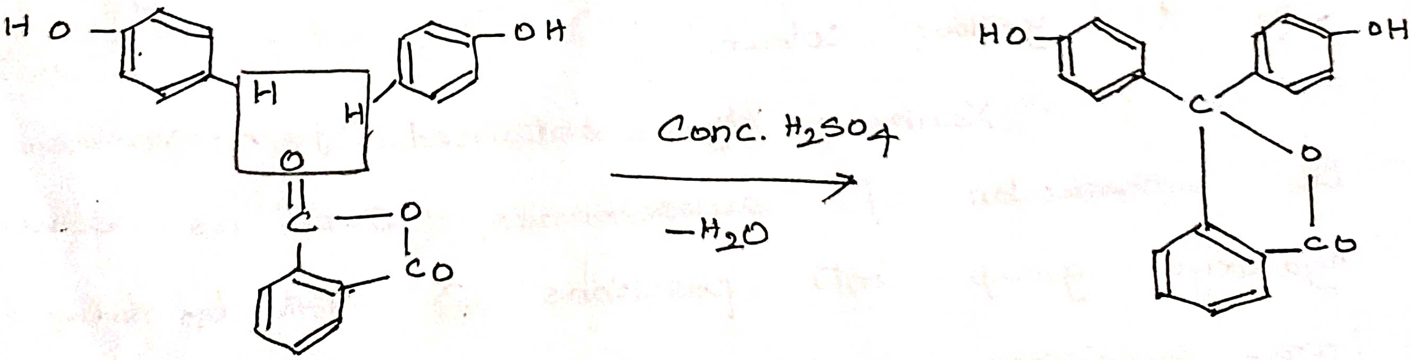
* These are used as indicators because they are sensitive to the action of alkali solutions.

* Phenolphthalein is the most important member of this group.

(a) Phenolphthalein .

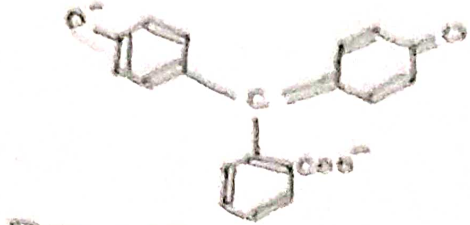
Preparation :

It is prepared by heating phthalic anhydride (1 molecule) with phenol (2 molecules) in the Presence of conc. Sulphuric acid as a condensing agent

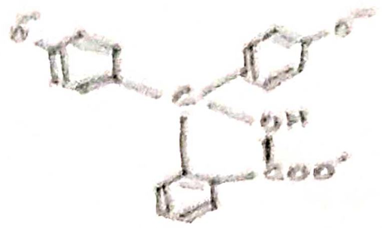


Colourless

* It is a white crystalline Solid.
* Insoluble in water but soluble in alkalis to fo deep pink solution.



Deep pink



Colourless

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.

Applications:

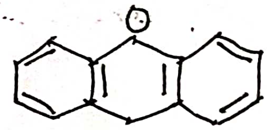
Its 1% solution in alcohol is used as an indicator in acid - alkali titrations. It is also used as a laxative in medicine.

Some other examples of Phthalein are phenol red, bromophenol red. Both these dyes are used in the determination of the hydrogen ion concentrations of solution

3.2 : Xanthein 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- poisitions with respect to the carbon atom linking the two benzene nuclei.



Xanthene (or) Xanthen

Applications :

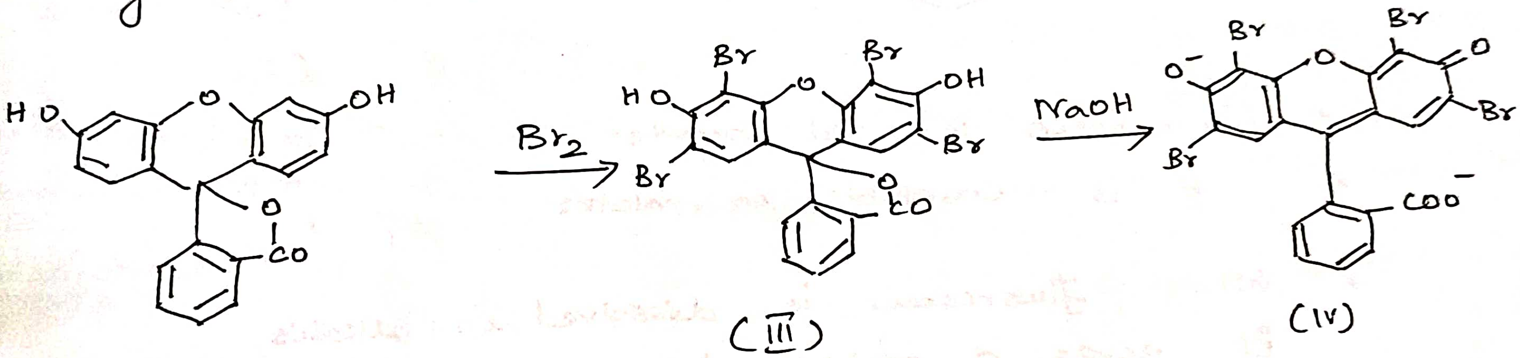
* The sodium salt of fluorescein is known as uranine.

* Uranine is used to dye wool and silk yellow from an acid bath ; the colours are fugitive.

* 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.



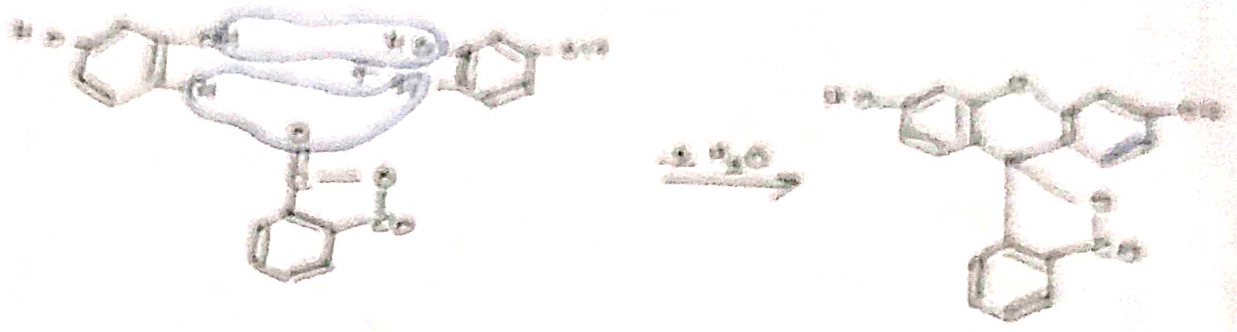
* As eosin is red powder, its structure may not be (III) may be (V) (or) (VI).

* The alkaline solution of eosin shows a yellow green fluorescence which is attributed to the doubly charged structure (IV).

Some important members of this group of dyes are described as follows.

(a) Fluorescein

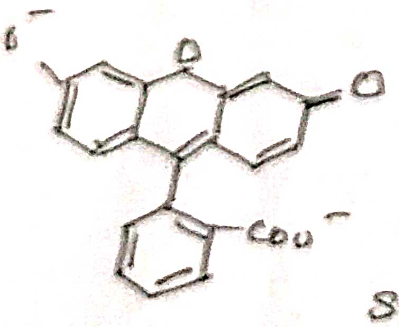
* It is a xanthene derivative obtained by heating phthalic anhydride (1 molecule) with resorcinol (2 molecules) at [illegible] °C with anhydrous zinc chloride.



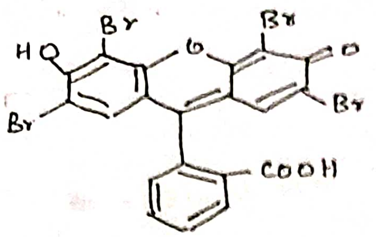
(I)

* Coloured Structure
* Non quinonoid Structure
* Unsatisfactory

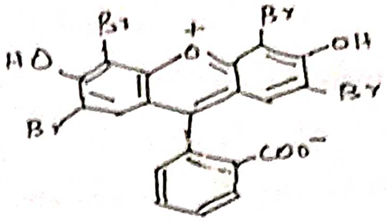
* Fluorescein is red powder.
* It is insoluble in water.
* When fluorescein is dissolved in alkalis, it gives a reddish brown solution which on dilution gives a strong yellowish-green fluorescence.
* The structure of fluorescein anion is (II).



Structure (II).



(V)



(VI).

Applications:

* Eosin is used to dye wool and silk a pure red, with a yellow fluorescence.

* It is also used as the lead Lake Vermilionette for poster printing.

* Most red inks are dilute solutions of eosin.

* Erythrosin is a tetraiodofluorescein and is prepared in a similar manner as eosin.

* It is generally used as a food colouring matter.

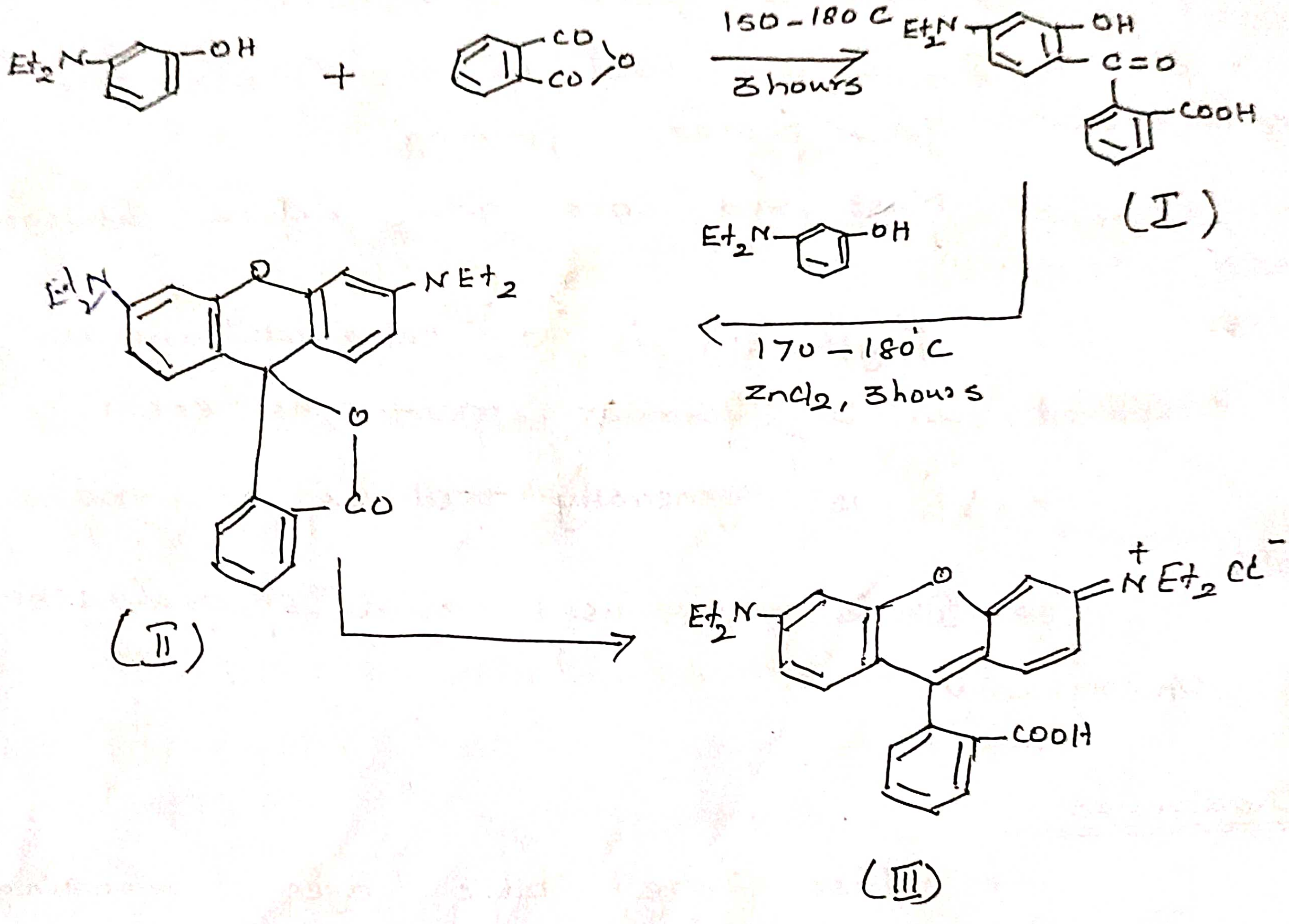
* It is also used as a spectral sensitizer in photography.

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 6G.

Rhodamine B - Preparation:

Rhodamine B is obtained by condensing m-diethylam phenol (1 molecule) with phthalic anhydride (1 molecule) at 150-180°C for 8 hours to yield the reaction product (I), Then the reaction product (I) is condensed with another molecule of m-di-ethylaminophenol 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.



Applications:

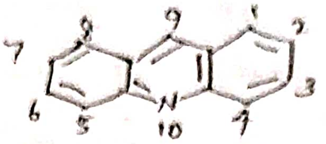
* Rhodamines are generally used to dy Papers.

* They are used for the preparation of red and pink lakes used as pigments.

* They are also used to dye wool, silk and cotton mordanted with tannin where brillant shades of fluorescent effects are required.

Acridine dyes:

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 diphenyl methane and triphenyl methane derivatives. In the later case the third phenyl ring is present in 9 position.

Among the acridine dyes, Acridine orange NO is very important.

a) Acridine Orange NO

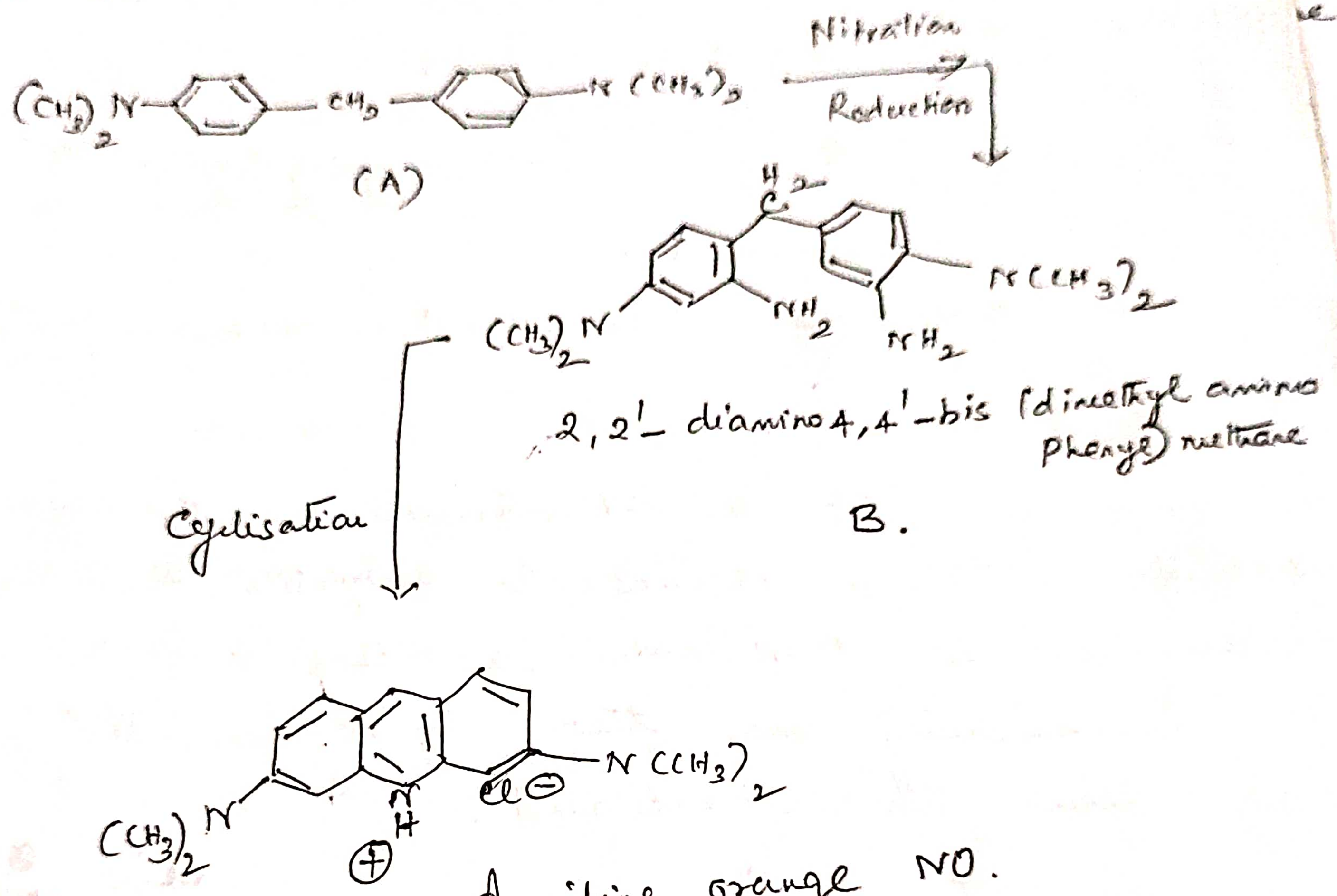
Preparation:

It is prepared from 4,4'-bis (dimet aminophenyl) methane (A) by nitration and subsequent reduction with zinc and hydrochloric acid to yield methane(2,2'-(diamino-4), 4'-bis (dimethyl amino phenyl) which then gets cyclised. The cyclisation of (B) 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 sa

4.2. Cyanamines, Isocyanines and Carbocyanines dyes.- -5-

-2-

Out the dye by the treatment of common salt in the presence of copper sulphate and air at 80°c.



2,2'- diamino 4,4'-bis (dimethyl amino phenyl) methane

B.

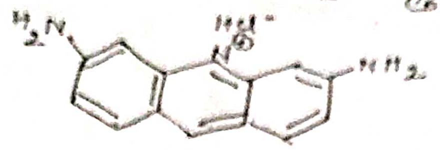
Acridine orange NO.

Acridine Orange NO is used to dye silk orange with a green fluorescent. However at h poor fastness properties. Acridine orange NO is u for leather dyeing and in ink manufacture.

b)

3,6- Diamino acridine

It is obtained by heating a mixture of m-phenylenediamine, glycerol, oxalic acid and zinc chloride and oxidising the leuco compound.

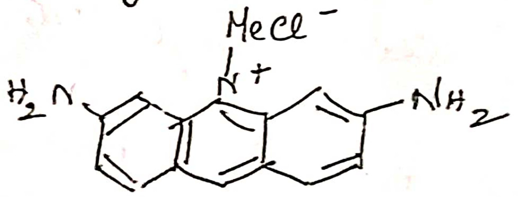


(or)

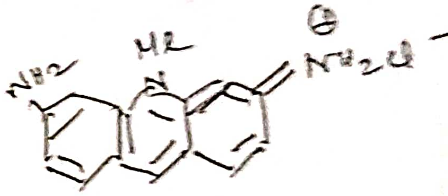
The corresponding sulphate is the antiseptic proflavin.

c) Acriflavin

It is 3,6 - diamino - 10 - methyl - acridinium chloride. It is obtained by acetylating 3,6 - diaminoacr methylating the 10-N atom by means of methyl p - toluenesulphate and then hydrolysing the produ with dilute hydrochloric acid.



(or)



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

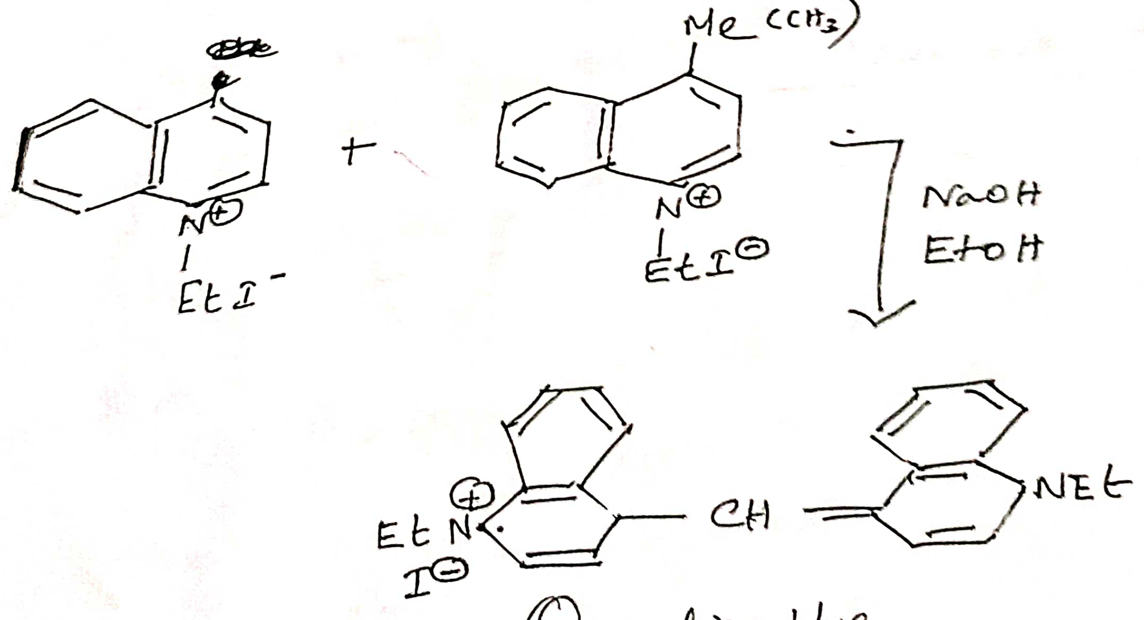
7.2. Cyanines, Isocyanines and Carbocyanines dyes –

Cyanine dyes :– These are the dyes in which the two quinoline nuclei are linked through the 4,4'-position by a =CH- group. The colours of the cyanine dyes are too fugitive. Therefore, these dyes are not used as dyes but used as photographic sensitizers 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.

Quinoline Blue:

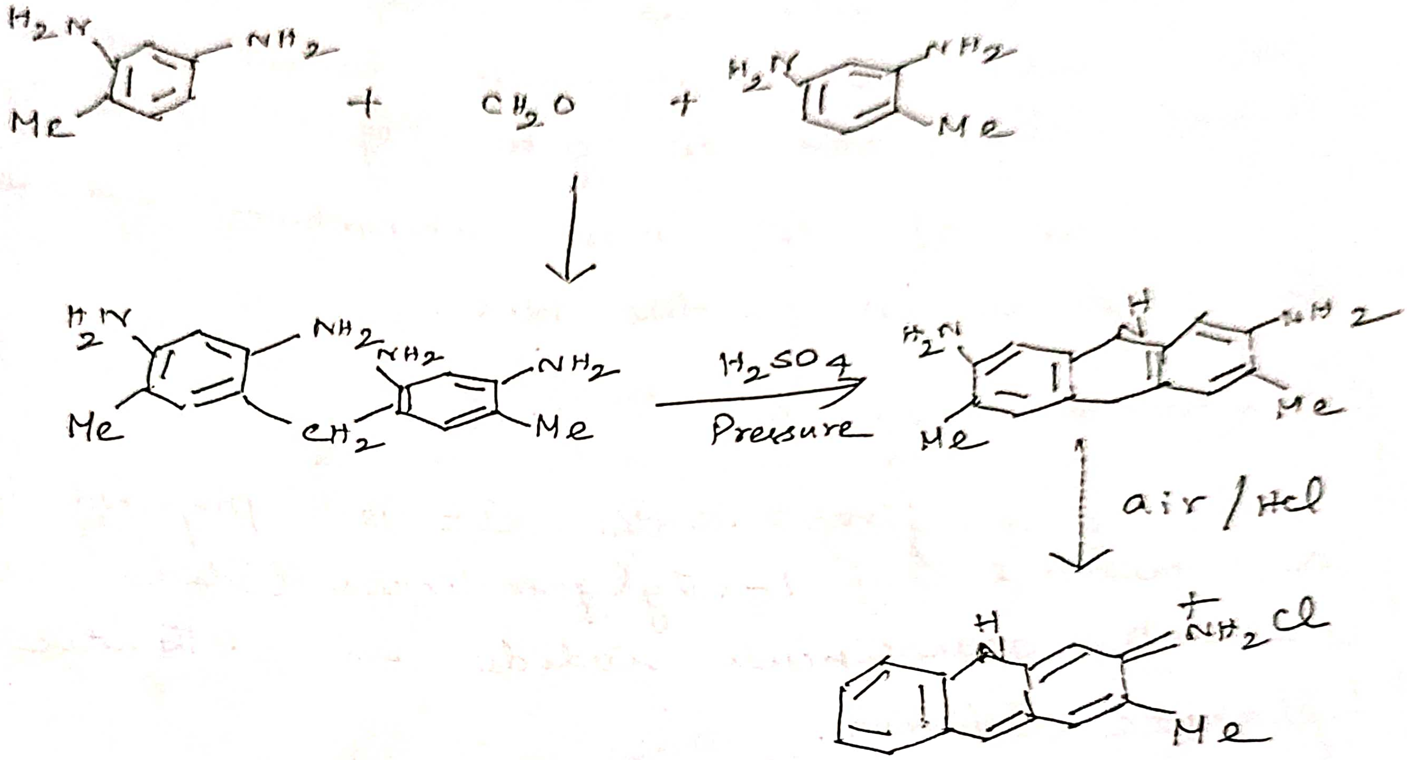
Preparation : It is prepared by heating a mixture of 1-ethylquinolinium iodide and 1-ethyl 4-methyl quinolinium iodide in ethanolic sodium hydroxide solution.



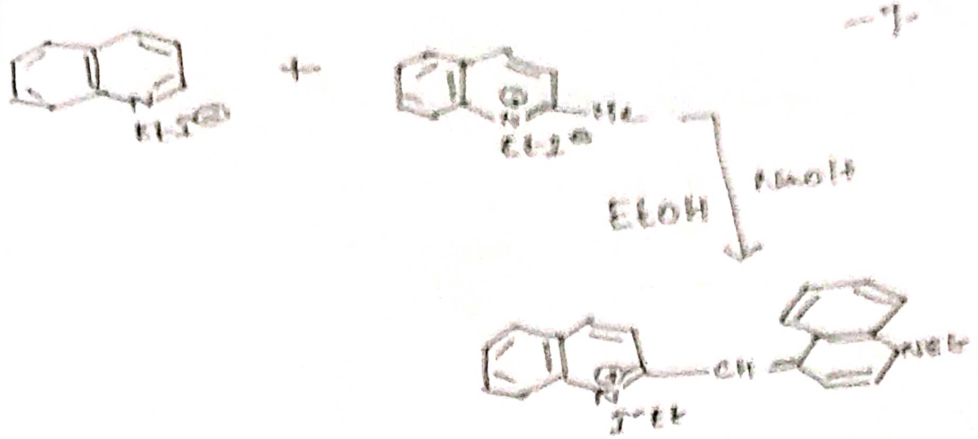
Quinoline blue

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.



Acridine violet



Ethyl Red.

Uses:

It sensitises the photographic plate from Orange to ultraviolet region of the spectrum.

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 carbocyanines is sensitol red (or) pinacyanole.

Sensitor red (or) pinacyanole

Preparation:

Pinacyanole is obtained by heati a mixture of quinaldine ethiodide and ethyl orthoformate in pyridine.

Other examples of cyanine dyes are.

1. Astrazone pink FG
2. Astrazone yellow 3G.
3. Astrazone red 6B.

Applications :

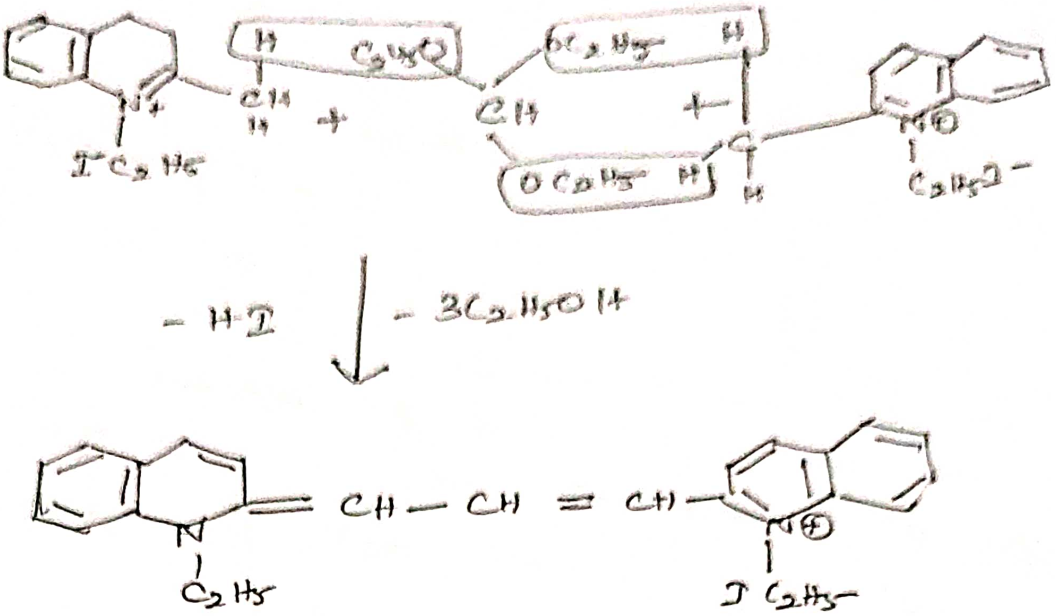
- Quinoline blue are used as photographic Sensitisers.
- Astrazone pink FG used as basic (cationic) dye for polyacrilonitrile fibres (i.e., orlon)

~~* Astrazone yellow 3G~~

Isocyanine dyes:-

In these dyes, the two quinoline nuceli are linked in the 2,4'- positions by a =CH- group. An important example of these dyes ~~are~~ is Ethylred which is prepared by heating a mixture of quinoline and quinald ethiodides in ethanolic Sodium hydroxide Solution.

Preparation :



Sensitol red (or) Pinacyanole.

Uses:

Sensitor red sensitises the photographic plates from red to range of regions of the spectrum.

18

Reactive Dyes

Introduction

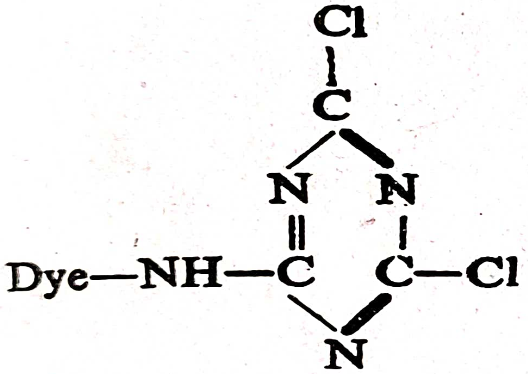
Rys and Zollinger defined a reactive dye as follows :

"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".

This 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.



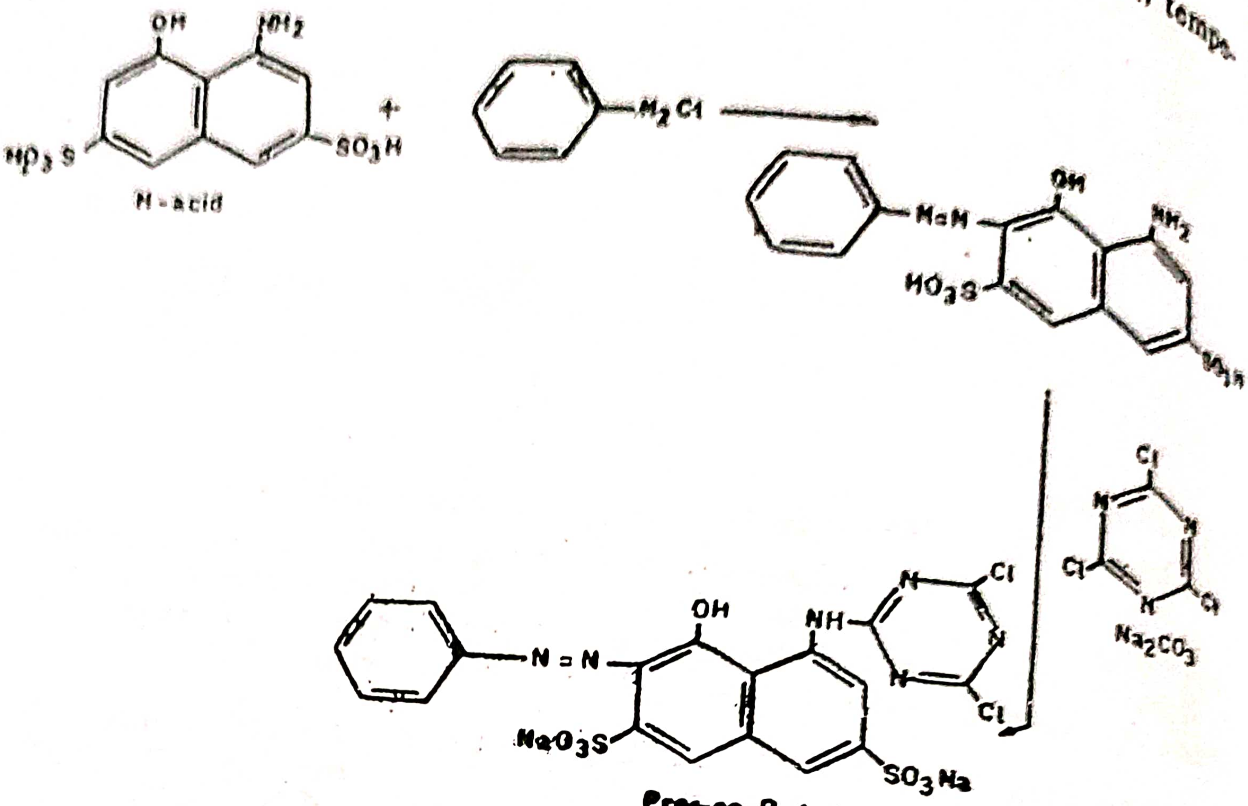
cyanuric chloride is cheap and readily available. The reactivity of the chlorine atom in cyanuric chloride is due to the electron withdrawing properties of the nitrogen atoms.

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 :

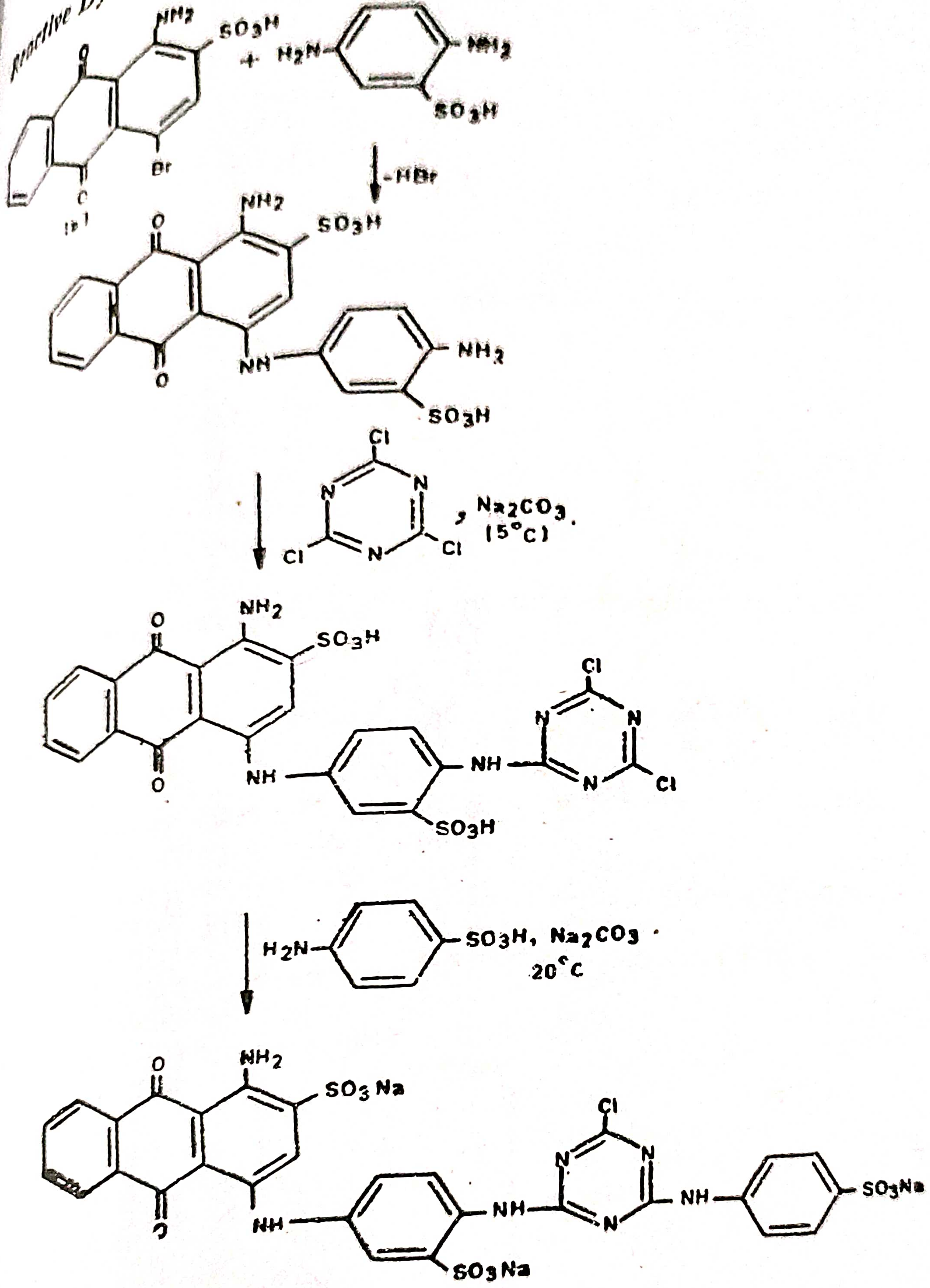
1. **Procion red dye.** It is obtained by coupling diazotised aniline with H acid. The resulting product is then condensed with

cyanuric chloride in the presence of sodium carbonate at low temperature.



Procion Red dye

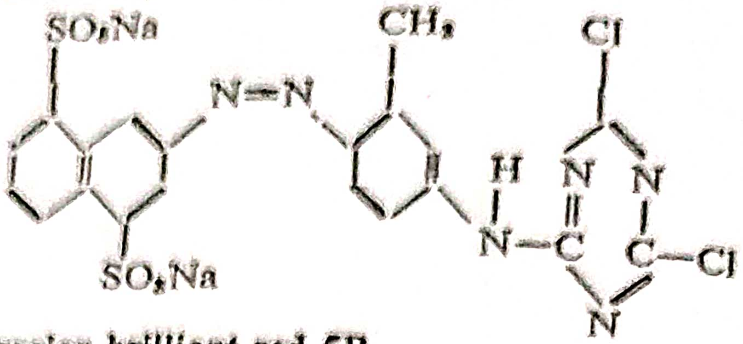
2. Procion blue HB. It is obtained by condensing 1-amino-4-bromo-3-anthraquinone sulphonic acid (*a*) with 2-sulpho-*p*-phenylene diamine (*b*). The resulting product is next condensed with cyanuric chloride in presence of sodium carbonate at low temperature. It is now condensed with sulphanilic acid and ultimately converted into its sodium or potassium salt.



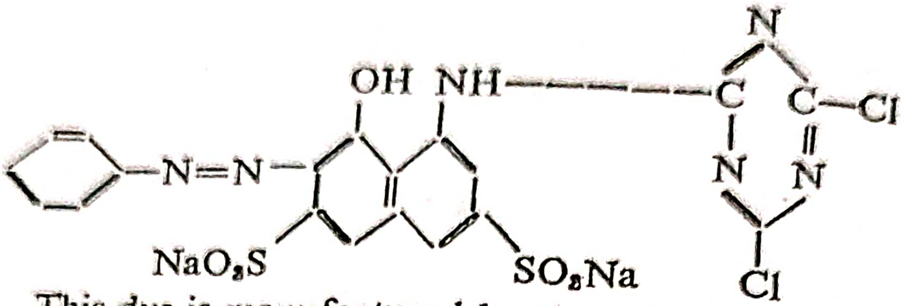
Procion Blue HB

It is used as a reactive dye. It gives a royal-blue shade.

3. Procion yellow R

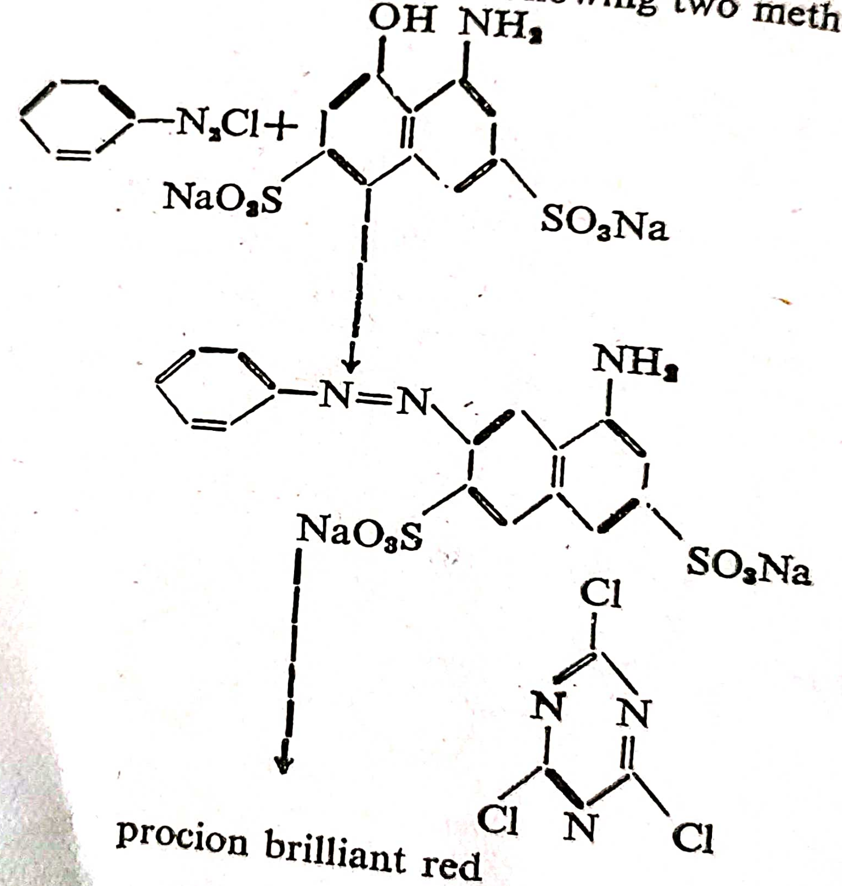


4. Procion brilliant red 5B

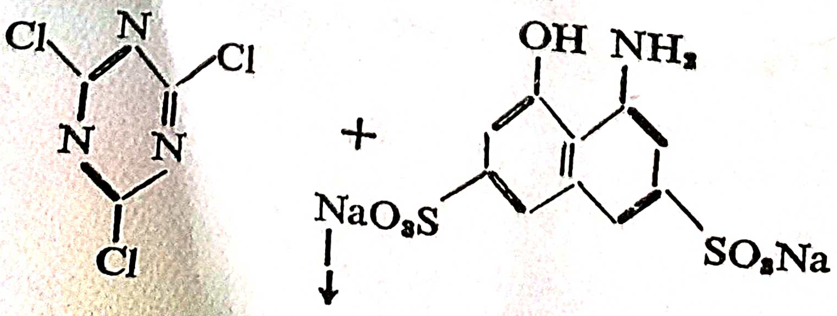


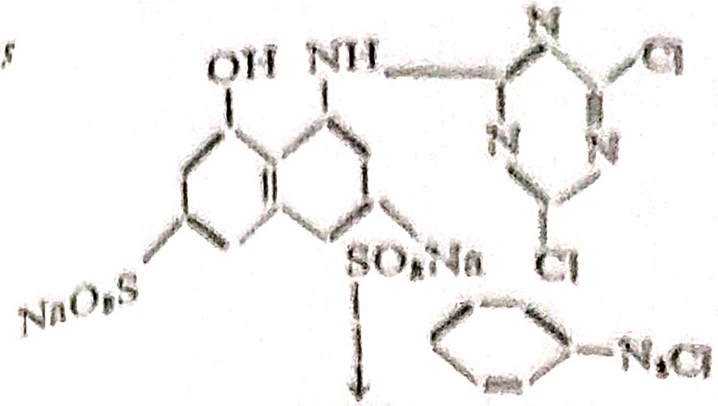
This dye is manufactured by the following two methods :

(i)



(ii)

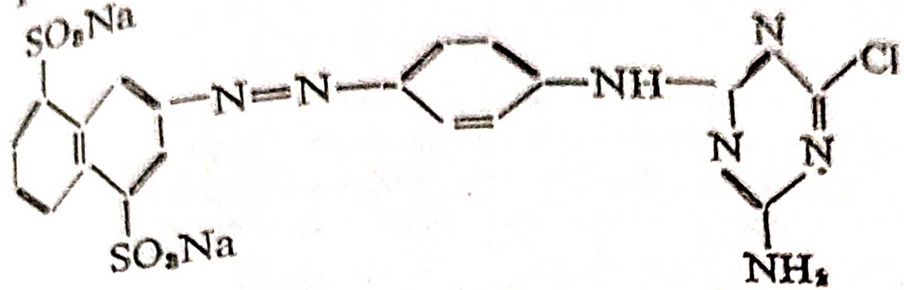




procion brilliant red 5B

In both the above methods (*i*) and (*ii*), the temperature and pH of these reactions have to be controlled in narrow ranges for retaining 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.

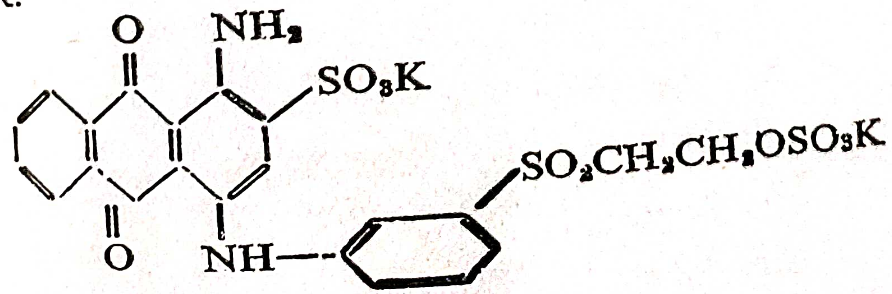
(*ii*) It should not be very costly.

(*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 polyamides. 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 dye is remazol brilliant blue R.



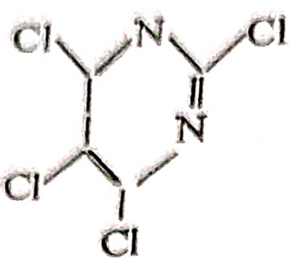
$$\text{Dye}-SO_2CH_2CH_2OSO_3Na + NaOH \longrightarrow \text{Dye}-SO_2CH=CH_2 + Na_2SO_4 + H_2O$$

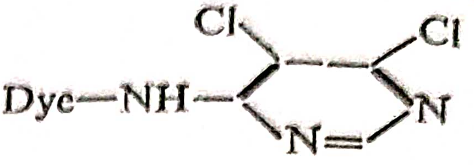
$$\text{Dye}-SO_2-CH=CH_2 + \text{cellulose} \longrightarrow \text{Dye}-SO_2-CH_2.CH_2-O-\text{cellulose}$$

6. Commercial useful reactive dyes

Some commercial useful reactive dyes are as follows :

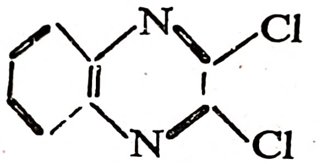
(*a*) *Trichloropyrimidine dyes.* These are derived from tetra-chloropyrimidine. The chlorines present in positions 2, 4 and 6 are reactive whereas chlorine in position 5 is not reactive.



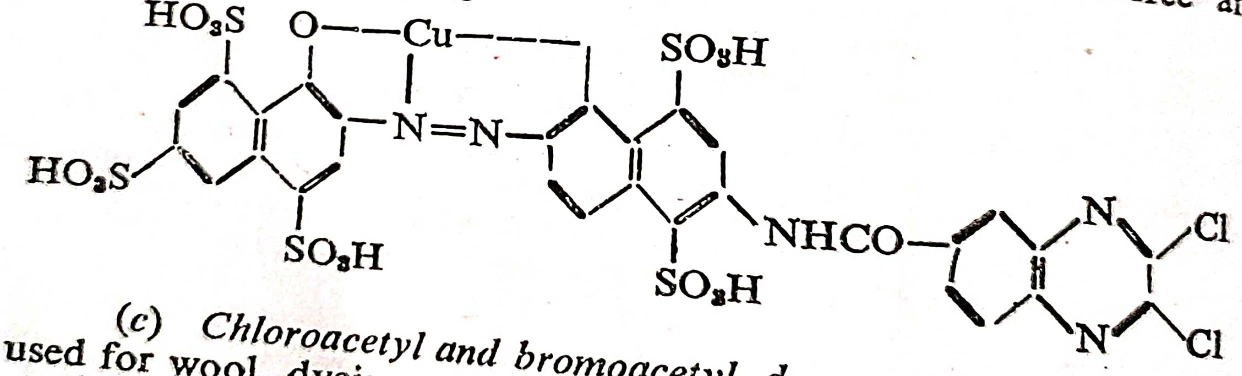


These dyes are marketed as *drimarines* and *reactones.* These are less sensitive to hydrolysis. Dyeing needs high temperature. The reaction with cellulose is similar to chlorotriazinyl system. The 2, 6-Difluoropyrimidine deirvatives are also marketed as reactive dyes, *e.g.*, drimalan, verafix dye, etc.

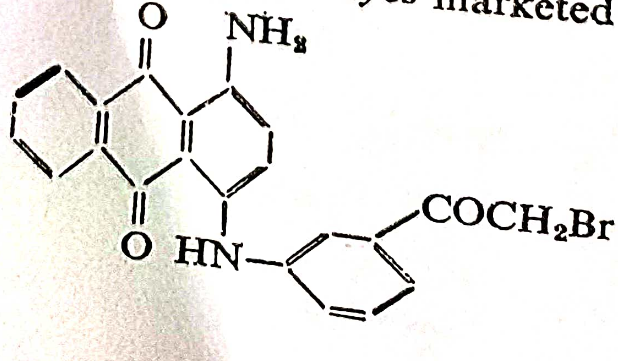
(*b*) *Quinoxaline dyes.* Du Punt and Bayer have marketed these dyes having the following reactive group.



The acid chloride of quinoxaline is condensed with free amino group of an azo dye, *e.g.*



(*c*) *Chloroacetyl and bromoacetyl deys.* These dyes are mainly used for wool dyeing. These dyes are known as *drimalam dyes* marketed by Sandoz and *cibalan dyes* marketed by CIBA.



Introduction :-

The disposal of wastewaters is of widespread national concern industrial activities generate a large number and variety of waste products which are generally discharged into water streams. The nature of industrial wastes depends upon the industrial processes in which they originate. The problem of adequately handling industrial waste waters is more complex and much more difficult than sewage, because industrial waste waters vary in nature from relatively clean rinse waters to waste liquors that are heavily loaded with organic or mineral matters or with corrosive. poisonous, inflammable or explosive substances. organic compounds, however, constitute a large proportion of these wastes which are destroyed only slowly by bacteria and unpleasant odours and tastes are produced. Some industrial, wastes are so objectionable that they should industrial not be added to the public sewage system; other contain so little and such objectionable matter that it is safe to discharge them into a storm drain or directly into a natural body of water such as stream, lake, river, etc., Some industrial wastes adhere to sewers and clog them, acids, H_2S etc. destroy cement, concrete and metals; hot water may cause cracking of tiles and concrete. In addition to immediate danger to human beings, some poisonous chemica may also interfere with biological treatment processes by killing the micr organisms that normally populate in receiving flows. when permitted enter the public sewage system, the industrial wastes becomes a part of sanitary sewage.

Although some of the industrial wastes are known since antiq many of them are quite recent, As the technology develops, newer types of wastes are formed. The great Variety of chemicals wastes produced in the nation's factories forces a Specific treatment in many instances. Some general practices are in use in many fields, and one such Particle is that of storing or layering wastes. This practise serves may purposes, for example, in factories having acid as well as basic waste, it reduces the cost of neutralization. In plants having waste water containing large amounts of organic material, this process decreases the Suspended matter and also results in the reduction of BOD. The use of flocculating agent, such as $FeSO_4$ or alum to remove Suspended solids, and aeration to improve BOD is also common in many industries.

Textile Industry :-

In Textile industry Wastewater is produced. As a result Spinning of weaving cloth. This wastewater contains particulate matter and starch. So ~~Diene~~ Dye ~~Structure~~ Section is part of textile Industry Therefore the wastewater from the dye structure alone, depending upon the dye stuffs used (Vat dye, Sulphur dye and Azo dyes

dyes and dyes stuffs : (characteristic of textile effluent) :

Dye and dyes stuffs used in printing and dyeing of textiles and leather goods are the main reason for causing water pollusion, The term due to condemnation of harmful chemicals.

1) Effect of textile effluent :-

Azo and Benzedine dye which are used in the production f textile will be the main reason for causing water pollusion. he textile effluent which is untreated can be directly ondemnated to water will cause cancer to the human being

(effect). trying these chemicals are consider a criminal affect is most expencially in germany

Pollutents released from textile effluent :-

The Important pollutents released from textile Industry are Zinc , copper Salts are non - Bio - degradable .

(2) Zinc :(effect)

Vomiting , renol damage

copper Salt :-

fever , hip hyper tension , coma ,

Sulphides :-

headache , diarreha , hemolysis .

The drinking water taking from the localities near the textile ~~mill~~ limits may be unfit for drinking purpose. Because of the turbidity , presence of chemicals etc.) due to condemination of textile effluent will ~~cause~~ ~~Simil~~ Severe damage for plant also Because due to the presence of dyes and dyes Compound (Organic Compounds) . These kinds of Organic Compound will enter into water and reduce level of water the plant growth will completely destroyed.

The Animals are effected due to bone diseases and growth retardation .

Waste Water treatment process process :-

1) Airated

Processing techniques used in textile industry :-

It is the ancient Industrial process in india , Totally 700 industry of there in our Country . It is Coimbatore , Erode , Karur

→) Dubai, Mumbai, Ahamadabad).

Textile industry - processing of clothes:-

The processing technique consist of two types of process.

i) Dry process

ii) Wet Process

1) Dry process:-

This process required no water, & therefore no pollution, but this process consist of two operation.

i) Mixing and Blending of cotton

ii) Opening and loosing of fibres

iii) Mechanical ~~area~~ cleaning.

iv) Carding

v) Combing

vi) Spinning.

vii) Splashing and Sizeing

viii) Knitting and waving

(ii) Wet process:

After Weaving the cloth, the cloth appear ash Colour. Therefore we should remove the sizing material which can be processs· got from the Weaving process. Therefore We going the to explain the sizing of Textile cloth.

1) Desizing:-

1) This process Can be done using Enzymes or Dilute ac

2) Kiering process:

1) This process is Used for Removing mass products in Colt

) In this process using soda ash, . sodium silicate, Boric Sa added to the distroy the close are boil.

Bleaching :-

For this process for added hyper chloride, chloride and peroxide added with cloths.

iv) Mersarisation :-

To the processed cloth can be treated with costic soda, glue, Concentration solution so the cloth can be appeared as shiny, stiffness and ready to accept dye

v) Dye :-

For dyeing process various kind of dyes are used, ~~napth~~ naphthol, sulphur, developed dye, vat dye are used in now a days. Also some kind of chemicals and salts are added to this process. Two kind.

b) Printing :-

Two kind of process are used.

1) Manual printing
2) machine printing

So for this process various kinds of pigments metallic compound are can be required.

d) finishing process :-

This is the latest stepping processing.

Effect of Environment By textile industrial wastewater effluent :

i) If it is combine with water and waterbodies like to they causes effect to environment.

i) This heated wastewater, it enter into waterbodie it may increases the heat causes.

ii) [illegible] treatment ?.

It may cause [illegible] nature & water.

iii) So, this heated waste water if enter in to the water Body. It may Increases the heat or thermal solution.

iv) So the oil can be covered the water surface, therefore the exchange of oxygen between air and water will be restricted, therefore the concentration of oxygen will be reduced by water.

v) The Wastewater contain starch, sculphur, hydrosculphide, nitrate will enter into the water and reduces oxygen level.

vi) Due to the condemnation the animals which will be water due to oxygen destriction, so the condemnation sculphur, Chlorine, Aluminium. These damage to leaving water.

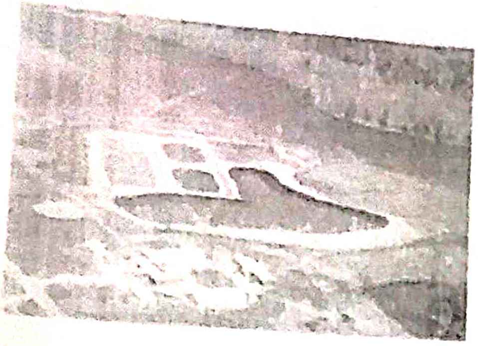
7) If the textile Wastewater enter into Sewages. It will be effect th Sewag due to Sculphur componts and basic. Additionaly Sewa water increases.

8) it will effect the Microorganism growth

9) Due to increases in PH well destroyed affect and indole in water pollution. so these textile effluent also affect in the

10) So, it will affect soil also, it will closest therefore wate adsorption will be restricted increases in basic nature affect in growth of Crobs and plants. Presence of cal and megnisium and reduces growth ~~of~~ and plants

# of Lagoons in Maine



Warren Sanitary District
Warren, Maine

Introduction
This section deals with discussion of data, design considerations and regulatory issues.

General Concepts
This section entails general concepts of biological treatment and nitrification in lagoons and ponds.

Executive Summary
This is the executive summary concluding findings of the Maine Lagoon Task Force

What are lagoon systems?

Lagoons are pond-like bodies of water or basins designed to receive, hold, and treat **wastewater** for a predetermined period of time. If necessary, they are lined with material, such as clay or an artificial liner, to prevent leaks to the groundwater below.

In the lagoon, wastewater is treated through a combination of physical, biological, and chemical processes. Much of the treatment occurs naturally, but some systems use aeration devices to add oxygen to the wastewater. **Aeration** makes treatment more efficient, so that less land area is necessary. Aerators can be used to allow existing systems to treat more wastewater.

Lagoons must be individually designed to fit a specific site and use. Designs are based on such factors as type of soil, amount of land area available, and climate. An important design considerations for lagoons includes the amount and type of wastewater to be treated and the level of treatment required by regulations. Wastewater leaving a lagoon may require additional treatment, or "polishing," to remove disease-causing organisms or nutrients from the wastewater before it can be returned to the environment. If surface applied to crops or grassland in Indiana, a land application permit is needed from the Indiana Department of Environmental Management.

There are several different terms for lagoons. For example, the terms lagoon and pond are often used interchangeably, and names, such as polishing, stabilization, and maturation, can refer to a lagoon's particular role in treatment. This can be very confusing for community leaders and homeowners trying to evaluate lagoon systems.

The following is a brief overview of some of the more common types of lagoons.

Anaerobic Lagoons

The word anaerobic means "without oxygen", which describes the conditions inside this type of lagoon. Anaerobic lagoons are most often used to treat animal wastes from dairies and pig farms, commercial or industrial wastes, or as the first treatment step in systems using two or more lagoons in a series.

Typically, anaerobic lagoons are designed to hold and treat wastewater from 20 to 150 days.* They are relatively deep (usually 8 to 15 feet) and work much like septic tanks.

Inside an anaerobic lagoon, solids in the wastewater separate and settle into layers. The top layer consists of grease, scum, and other floating materials. If not preceded with septic tanks, the layer of sludge that settles at the bottom of an anaerobic lagoon eventually accumulates and must be removed. The wastewater that leaves an anaerobic lagoon will require further treatment.

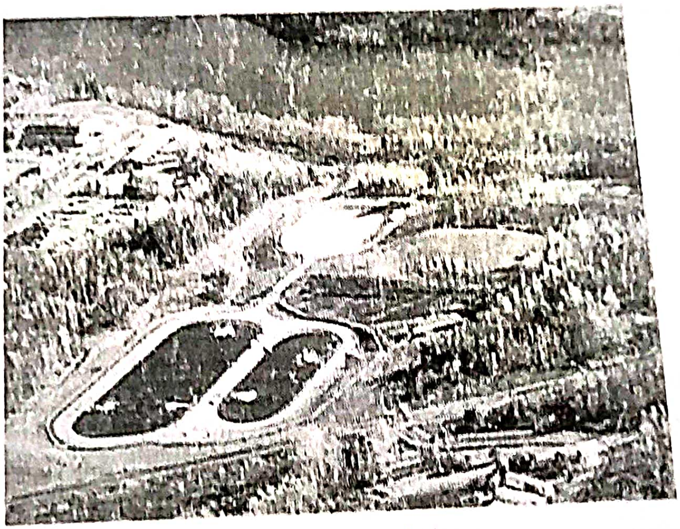
Odor can be a problem with anaerobic lagoons. However, in many cases odor can be managed through a variety of methods, such as adding sodium nitrate, recirculating pond effluent, and through regular maintenance.

Naturally Aerobic Lagoons

Dissolved oxygen is present throughout much of the depth of aerobic lagoons. They tend to be much shallower than other lagoons, so sunlight and oxygen from air and wind can better penetrate the wastewater. In general, they are better suited for warm, sunny climates, where they are less likely to freeze. Wastewater usually must remain in aerobic lagoons from 3 to 50 days to receive adequate treatment.*

Wastewater treatment takes place naturally in many aerobic lagoons with the aid of aerobic bacteria and algae. Because they are so shallow, their bottoms need to be paved or lined with materials that prevent weeds from growing in them.

Sometimes, the wastewater in aerobic lagoons needs to be mixed to allow sunlight to reach all of the algae and to keep it from forming a layer that blocks out the air and sun.



Aerial view of the
Veazie Sanitary District's aerated lagoon system.

Aerated Lagoons

Aerated lagoons are common in small communities. These systems use aerators to mix the contents of the pond and add oxygen to the wastewater. They are sometimes referred to as partial-mix or complete-mix lagoons depending on the extent of aeration. Partial-mix aerated lagoons are often anaerobic lagoons that have been adapted and upgraded to receive more wastewater.

With the exception of wind-driven designs, most aerators require energy to operate. However, energy costs are almost always considerably less than those for other mechanical treatment systems. Aeration makes treatment more efficient, which offsets energy costs in some cases. Aerated lagoons require less land area and shorter detention times.

**Exact detention times for wastewater in lagoons are based on factors such as the particular design, the amount of wastewater to be treated, and the level of treatment desired.*

Discharge Design: A Design Feature That Can Distinguish Lagoons Is How They Discharge Wastewater

- **Continuous Discharge Lagoons.** These lagoons release wastewater continuously to a holding pond, so the rate of output roughly equals the rate of input. The hydraulic flow pattern in the lagoon is designed so the wastewater remains in the lagoon long enough to receive treatment before it reaches the outlet.

- **Controlled Discharge Lagoons.** In these lagoons, wastewater is discharged in controlled amounts, usually once or twice per year. This method is common in cold climates where discharges typically occur after spring thaw and again in fall.

- **Hydrograph Controlled Release Lagoons.** This design can be used for lagoons that discharge directly to surface water. It includes devices that measure the level and quality of the wastewater and receiving water and the velocity of the receiving algae growth is highest.

In Parallel

In parallel means that a system has more than one cell that is receiving wastewater at the same stage of treatment. This system design is particularly useful in cold climates or where lagoons are covered with ice for parts of the year. Because biological processes are involved, wastewater treatment slows down in cold temperatures, making treatment less efficient. Parallel cells are often used during winter months to handle extra loads.

Facultative Lagoons Treat Wastewater Naturally

Like most natural environments, conditions inside facultative lagoons are always changing. Lagoons experience cycles due to variations in the weather, the composition of the wastewater, and other factors. In general, the wastewater in facultative lagoons naturally settles into three fairly distinct layers or zones. Different conditions exist in each zone, and wastewater treatment takes place in all three.

The top layer in a facultative lagoon is called the aerobic zone, because the majority of oxygen is present there. How deep the aerobic zone is depends on loading, climate, amount of sunlight and wind, and how much algae is in the water. The wastewater in this part of the lagoon receives oxygen from air, from algae, and from the agitation of the water surface (from wind and rain, for example). This zone also serves as a barrier for the odors from gases produced by the treatment processes occurring in the lower layers.

The anaerobic zone is the layer at the very bottom of the lagoon where no oxygen is present. This area includes a layer of sludge, which forms from the solids that settle out of the wastewater. Here, wastewater is treated by anaerobic bacteria, microscopic organisms, such as certain protozoa, and sludge worms, all of which thrive in anaerobic conditions.

Names for the middle layer include the facultative, intermediate, or aerobic-anaerobic zone. Both aerobic and anaerobic conditions exist in this layer in varying degrees. Depending on the specific conditions in any given part of this zone, different types of bacteria and other organisms are present that contribute to wastewater treatment.

Throughout facultative lagoons, physical, biological, and chemical processes take place that result in wastewater treatment. Many of these processes are interdependent. For example, on the surface, wind and sunlight play important roles. Surface agitation of any kind adds oxygen to the wastewater. For this reason, facultative lagoons are designed to make the best use of wind in the area.

The amount of wind the lagoon receives is not only important for the oxygen it contributes, but also because it affects the overall hydraulic flow pattern of the wastewater inside the lagoon, which is another physical factor that contributes to treatment.

Time is another important factor in treatment. Facultative lagoons are designed to hold the wastewater long enough for much of the solids in the wastewater to settle and for many disease-causing bacteria, parasites, and viruses to either die off or settle out. Time also allows treatment to reduce the overall organic strength of the wastewater, or its biochemical oxygen demand (BOD). In addition, some of the wastewater eventually evaporates.

Sunlight is also extremely important to facultative lagoons because it contributes to the growth of green algae on the water surface. Because algae are plants, they require sunlight for photosynthesis. Oxygen is a byproduct of photosynthesis, and the presence of green algae contributes significantly to the amount of oxygen in the aerobic zone. The more warmth and light the sun provides, the more green algae and oxygen there is likely to be in the lagoon.

The oxygen in the aerobic zone makes conditions favorable for aerobic bacteria. Both aerobic and anaerobic bacteria are very important to the water to determine when conditions are most favorable for discharge. This method can sometimes eliminate the need for further treatment.

- **Complete Retention Lagoons.** These lagoons are only practical in very dry climates where evaporation rate greatly exceeds rainfall amounts. Wastewater is never released from this type of lagoon. Instead it is allowed to evaporate.

Advantages and Disadvantages of Lagoon Systems

- Lagoon systems can be cost-effective to design and construct in areas where land is inexpensive.
- They use less energy than most wastewater treatment methods.
- They are simple to operate and maintain and generally require only part-time staff.
- They can handle intermittent use and shock loadings better than many systems, making them a good option for campgrounds, resorts, and other seasonal properties.
- They are very effective at removing disease-causing organisms (pathogens) from wastewater.
- The effluent from lagoon systems can be suitable for irrigation (where appropriate), because of its high-nutrient and low pathogen content.
- Lagoon systems require more land than other treatment methods.