

**Natubhai V. Patel College of Pure & Applied Sciences****T. Y. B.Sc. (Industrial chemistry)****IC – 302: Unit Process, Synthetic dyes and Pharmaceuticals****UNIT – 3****Syllabus**

Dye introduction, classification of dyes on the basis of structure and methods of application (two examples in each class). Chemistry of Azo, Anthraquinone, reactive and disperse dyes. Synthesis of Direct Black EW, Eriochrome black T, Tartrazine, Congo Red, Naphthol Blue Black-6B, Metanil Yellow, Indanthrene Yellow-4GK, Procion Brilliant Red, Reactive Yellow 3, Methyl Orange, Eriochrome Red-B dyes.

**3.0 INTRODUCTION**

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**.

All the dyes may not necessarily be coloured substances. Previously dyes were obtained from animal and vegetable sources. Today most of the available dyes are synthetic dyes prepared from aromatic compounds, which are obtained from coal tar or petroleum.

**3.1 REQUISITES OF A TRUE DYE**

All colored substances are not dyes. However, requisites of true dye are as follows:

- It must have a **suitable colour**.
- It must have an **attractive colour**.
- It must be **able to attach** itself to **material** from solution or to be capable of fixed on it. e.g. azobenzene is coloured but cannot fix itself to a fabric. Therefore, azobenzene is not a dye.
- 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**.
- 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 under suitable conditions of concentration, temperature and pH.
- When a **dye** is fixed to a substrate it must be **fast to** washing, dry cleaning, perspiration, light, heat and other agencies.
- The **shade** and **fastness** of a given dye may **vary depending** on the **substrate** due to **different interactions** of the molecular orbital's of the dye with the substrate.

**3.2 CLASSIFICATION OF DYES**

Dyes are **classified in various ways** according to

- The methods of application to the fiber
- Their chemical constitution
- The types of materials to be dyed
- The intermediates from which they are prepared

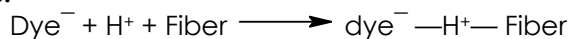
**3.2.1 Classification of dyes according to application**

Dyes are classified according to application method, for convenience of the dyer.

**1. Acid Dyes**

These dyes are usually the **sodium salts** of the **colour acids** which may **contain sulphonic acid or phenolic group**. These dyes give very bright colour and have a **wide range** of **fastness properties**.

Acid dyes are **used to dye** fibers having **basic groups**, such as wool, silk and polyamides and are applied under acidic condition that causes **protonation of the basic groups**.



Generally the acid dyes can be **removed by washing**. The **rate of removal** depends on the rate at which the dye can diffuse through the fiber under condition of washing and the **rate of diffusion** depends on temperature, size & shape of dye molecule and number & kind of linkage formed on fibers.

**E.g.** Picric acid, metanil yellow, naphthol yellow, orange II etc

## 2. Basic or Cationic dyes

They have a **basic amino group** which is protonated **under acidic condition** of fibers. This gives intense and brilliant shades but has poor light fastness.

These are **used for dyeing** silk and wool directly but for dyeing cotton the basic dye needs mordant like tannic acid or some synthetic organic substance.

**E.g.** Methyl violet, methylene blue, crystal violet, rhodamine etc

## 3. Direct Dyes

They usually **bear sulphonic acid groups** and become strongly adsorbed on cellulose. However it is **not acid dyes** because **sulphonic acid groups** are **not used** as a means of **attachment to the fiber**. The **dyeing process** with this type of dye is **reversible** because they are held in cellulosic fiber by **adsorption**. They have **poor fastness** to washing but may be improved by treating with resins and dye fixing agents. **E.g.** Congo red

**Special types** of direct dye having amino groups which is first diazotized and then coupled on the fiber to improve washing fastness. **E.g.** Direct Black K 17

## 4. Mordant or Adjective Dyes

These dyes have **poor affinity** for fiber, these dyes **require a pretreatment** of fiber with a mordant which binds the dye. The **mordant** gets attached to the fiber and then combines with the dye to form an **insoluble complex** called a '**Lake**'. **Mordants** such as aluminum, chromium and iron salt are used depending upon the fiber and the class of dyes.

- **Chromium salts** for dyeing wool and for printing cotton with mordant azo dyes
- **Aluminum salts** for dyeing and printing cotton with alizarin
- **Iron salts** for printing of cotton with o-nitrosophenol.

## 5. Azoic Dyes

These dyes are **produced inside textile fiber** by **azo coupling**. The dye is fast to washing. A **variety of colours** can be developed by **proper choice of diazo and coupling components**. In usual procedure, the fiber is first impregnated with an alkali solution of the coupling component. This is then treated with a solution of the diazonium compound. Finally the dyed goods are soaped and rinsed.

The major application of azoic dyes is dyeing and printing of cellulosic fiber especially cotton giving shades of high standard light fastness.

## 6. Oxidation Dyes

These dyes are **produced by oxidation of colourless compound**. **E.g.** aniline is oxidized in cotton with sodium dichromate in the presence of a metal catalyst to produce an aniline black. This process of dyeing is an **economical way** to produce **full black shades**. The appearance and fastness of the dyeing may be varied over wide range by choice of oxidant condition and catalyst.

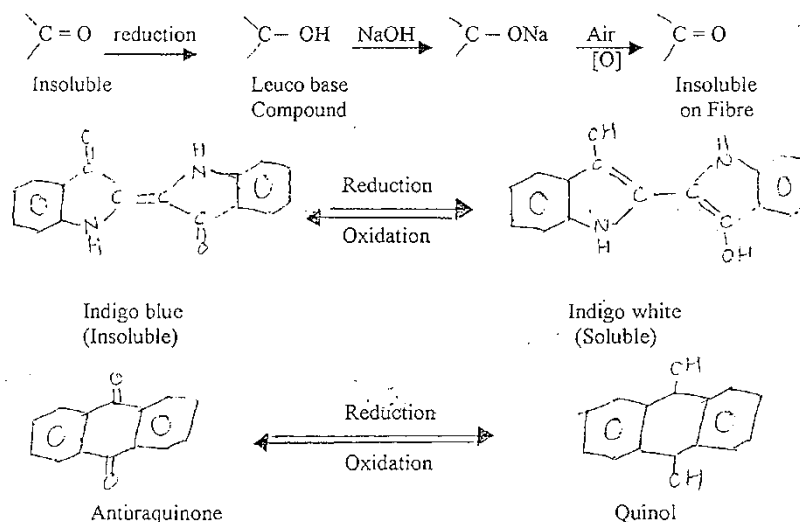
## 7. Ingrain Dyes

The term **ingrain applicable** to all types of **dye formed on the substrate** by the development or coupling of **intermediate compounds** which **are not themselves true finished dyes**. These groups thus included azoic and oxidation dyes e.g. the very bright blue copper phthalocyanine is produced inside cotton fiber. These types of dyeing are extremely fast to that light and washing.

## 8. Vat Dyes

These are **insoluble**, but their **reduced forms** which are **soluble**. These dyes are applied in their reduced forms which are obtained by treating it with reducing agent such as alkaline sodium hyposulphite in large wooden vats from which the name Vat dyes has come.

The cloth is immersed in the vat, having a reduced vat dye for sufficient time, then it dried in air, **due to oxidation** of dye on fiber the original **insoluble coloured dye** is obtained which is very fast to washing, light and bleaching as well e.g.



These dyes offer excellent fastness; these dyes are most often used on cotton fabrics which are subjected to the severe conditions of washing and bleaching. It can also be used for dyeing wool silk and cellulose acetate.

### 9. Sulphur Dyes

These dyes are **insoluble dyes** and when **reduced** with sodium sulphide they become **soluble**. These dyes are adsorbed on the fiber and on exposure to air they are **reoxidised to original insoluble dye** inside the fiber and they become very resistant to removal by washing but their brightness and fastness to bleaching are often inferior.

Sulphur dye **contain sulphur both** as an integral part of chromophore and in attached polysulfide chain

**E.g.** Heating m-dinitrophenol with sodium polysulfide gives m-toluenediamine which is fused with sulfur gives brown sulfur dye.



### 10. Disperse Dyes

These dyes are **water insoluble** dyes originally introduced for dyeing cellulose acetate and are usually applied from fine **aqueous dispersion**.

The molecules are generally small and some -OH or -NH<sub>2</sub> groups to give finite water solubility at dyeing-temperature.

Dispersed dye may be applied by a dry heat process to polyester fibers. Here the dye achieves molecular form by sublimation from the solid dye to the fiber process. **Extremely small sizes of particles** are important to the fiber process. It gives excellent washing fastness. This dye is also used to dye cellulose acetate, nylon polyester and polyacrylonitrile fibers.

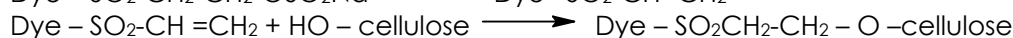
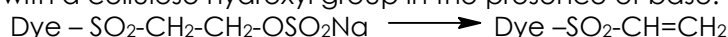
**E.g.** Cellitone scarlet B and cellitone fast violet 6B

### 11. Reactive Dyes

They are relatively new class of the dye, which **forms covalent bond** with fibers possessing hydroxyl and amino groups.

An important type of reactive dye has chlorine atoms which react with hydroxyl groups in cellulose when applied in presence of alkali. It is evident that there is an ether linkage between the dye and fiber is established.

Another important type of this dye involves an activated vinyl group, which can reacts with a cellulose hydroxyl group in the presence of base.



These dyes offer excellent fastness to washing, as they become the part of fiber. The other property depends on the structure of colored part of molecule and by what means it gets attached to the reactive part. **E.g.** Procion red dye and Procion brilliant red

## 12. Solvent Dyes

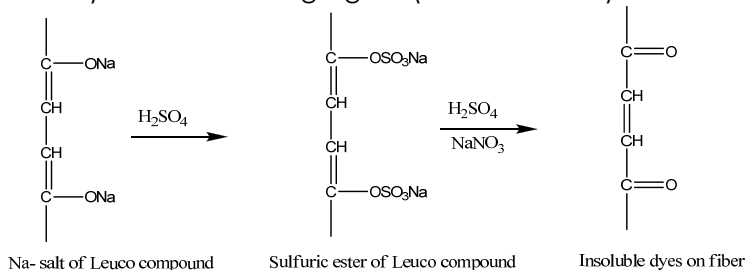
These dyes do not contain sulphonic acid or other water soluble groups and are **soluble in organic solvent**. The nature of which varies according to application. They are used in manufacture of stains, varnishes, inks, lacquors, typewriter ribbons, candles, shoe polishes, soap and cosmetics etc.

Instead of water, **tetrachloro ethylene** as used in suitable dyeing processes especially for the dyeing of the polyester fibers.

### 13. Solubilised Vat Dyes

It is difficult to store the sodium salts of leuco compounds of vat dyes because they are prone to air oxidation.

However, the solubilised vat dyes, the sulphuric esters of leuco compound are fairly stable and could be stored without oxidation. They are vat dyes derivatives from with the parent vat dye could be produced on the fiber by the oxidation with an acid (dilute sulphuric acid) and on oxidizing agent (sodium nitrate).



## 14. Sulphurised vat dyes

The method of application is **similar to those vat dyes** because they have either a quinonoid structure or other structure basically similar to that of quinonoid. They are prepared by thionation of certain anthraquinone and indophenol derivatives.

## 15. Disperse Reactive Dyes

These dyes have **dual characteristic** properties. They are obtained as microfine aqueous paste and have reactive grouping. These are **applied on polyamide** fiber from **aqueous dispersion** as a dispersive dye and subsequently **dyed as a reactive** dye under alkaline conditions to facilitate the reaction of the dye with the fiber.

## 16. Synthetic fiber Dyes

**Nylon:** As it is basic, it may be **dyed with acid** as well as with **disperse dyes**. Although acid dyes have good wet as well as light fastness, they cause the variation in the nylon fiber and hence not much used, similarly for acid mordent dyes.

When the disperse dyes are used to dye nylon, they give wet fastness but do not build heavy shades with good wet fastness.

**Terylene (polyester, Dacron):** It is **dyed by the disperse dyes**, which slowly penetrate but their wet fastness is good sometime diphenyl or orthophenyl phenol is used with dispersed dye in dyeing of terylene because they acts carriers for accelerating the penetration in the fabric.

**Orlon (polyacrylonitrile):** It is acidic, it may be **dyed with basic dyes** and also with **disperse dyes** or certain **vat dyes**, the drawback of disperse dye is that they do not have good penetration in to fabric, which can be increase by dyeing at 120°C under pressure.

### 3.2.2 Classification of dyes according to its chemical constitution

The most appropriate system for the classification of dyes is by chemical structure. This has many advantages as

- It readily identifies dyes as belonging to a group which has characteristic properties. For example azo dyes (strong and cost effective) and anthraquinone dyes (weak and expensive)
- It produces a manageable no. of groups (about a dozen )
- Most importantly, it is the classification used most widely by both the synthetic dye chemist and the dye technologist.

The dyes are classified according to its chemical constitution as follows:

Class	Subclass	Examples
Nitro	—	Naphthol yellow S

Class	Subclass	Examples
Nitroso	—	Fast Green O
Azo	Monoazo	Acid Orange II
	Bisazo	Congo Red
	Trisazo	Direct Black EW
	Polyazo	—
	Mordant azo	Eriochrome Black T
	Stilbene azo	Chrysophenine G
	Pyrazalone azo	Tartrazine
Diphenyl methane	—	Auramine O
Triphenylmethane	—	Malachite Green
Xanthene	—	Fluorescein
Acridine	—	Acridine orange NO
Thiazole	—	Basic Yellow T
Indamine indophenol	—	Toluylene Blue
Azine	—	Safranin T
Oxazine	—	Capri Blue GN
Thiazine	—	Methylene Blue
Cyanine	Methine	Astrafloxine FF
	Quinoline	Kryptocyanine
Sulphur	—	Sulphur Black T
Lactone	—	Resoflavine W
Aminoketone	—	Helindon Brown CR
Hydroxy Ketone	—	Alizarin Dark Green W
Anthraquinonoid	—	Perlon Fast Green 3B
Indigoid	—	Indigo
Sulphurized Vat dyes	—	Hydron Blue R
Phthalocynine	—	Monastral Fast Blue BS

### 3.3 COLOUR AND CHEMICAL CONSTITUTION

#### 3.3.1 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 **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** e.g.

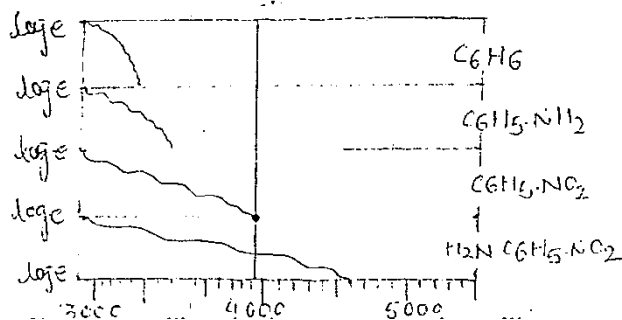


Figure: Absorption spectra of benzene, aniline nitrobenzene and p-nitroaniline

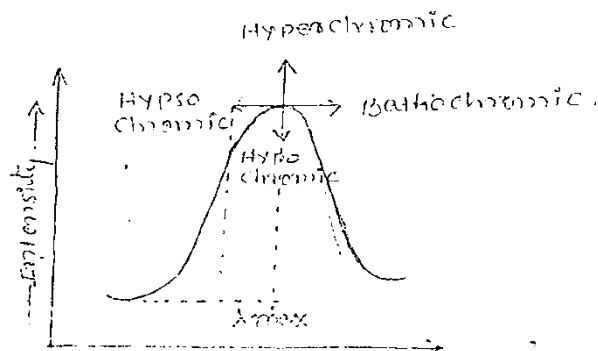
If a **structural change** in a dye molecule **shifts** the **absorption** from higher to **lower wavelengths**, it will lighten the colour of the dye in accordance to the following sequence

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**

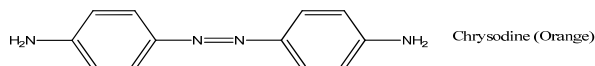
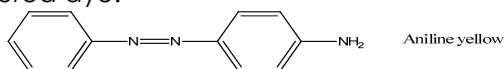
Changes in the structure of a dye due to which the **intensity of absorption increases** are said to be **hyperchromic** on the other hand, structural changes which **decrease the intensity of absorption** are termed as **hypochromic**.

Bathochromic, hypsochromic, hypochromic and hyperchromic effects are represented by the absorption spectra as show in the figure

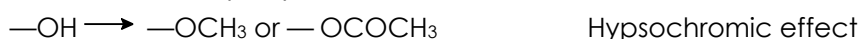


The introductions of certain group in a dye molecules cause the Bathochromic and Hypsochromic effects. This is summarized in the following facts:

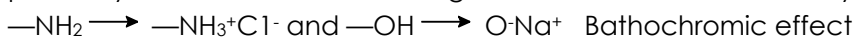
- The **bathochromic effect** is produced by the **introduction of** additional **auxochromes** such as -OH and -NH<sub>2</sub> groups in a dye molecule. For example, when an additional -NH<sub>2</sub> group comes in the aniline yellow, chrysodine is produced which is in orange coloured dye.



- In addition to the auxochromes, the **o-and p- directing groups** when presence on the aromatic ring also **deepens** the colour. For example alkyl, aryl and halogens deepen the colour and are **therefore known as Bathochrome**.
- When the **alkylation of amino group** is done, it **produces** the **bathochromic effects** 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 pararosiline ( red dye) nucleus to give crystal violet( violet colour)



- 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.



### 3.3.2 Colour

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

The ordinary light can be categorized in following three groups or types

Part of Light	Range of Wavelength of light
Ultraviolet light	1000 - 4000° A
Visible part (White light)	4000-7500°A
Infrared	7500-1,00,000° A

The **range of wavelength visible to human eyes** is consisting of electromagnetic radiation's covering rays of wavelength in the **region 4000 to 8000 $\text{\AA}$** . In this region (visible region) **seven different colours** namely violet, indigo, blue, green, yellow, orange and red are present (**VIBGYOR**). The sequence of UV, visible and IR is shown below.

Ultraviolet (UV)	Violet (V)	Indigo (I)	Blue (B)	Green (G)	Yellow (Y)	Orange (O)	Red (R)	Infra Red (IR)
Invisible	visible						Invisible	
	4000 $\text{\AA}$						8000 $\text{\AA}$	

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

- If the white light **reflected completely**, the substance will appear **white**
- If the white light is **absorbed completely**, the substance will appear **black**.
- If **all the wavelengths** of white light are **absorbed except a single narrow band**, which is **reflected**, the **colour of the substance** will be colour of the reflected band.
- If only a single band of white light is absorbed, the substance will have the complementary colour of the absorbed band, which is shown below.

Wavelength	Colour absorbed	Colour visualized
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

### 3.3.3 Relation between colour and chemical constitution

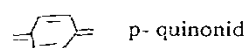
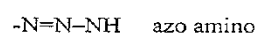
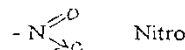
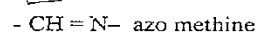
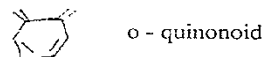
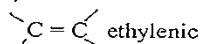
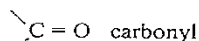
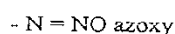
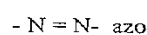
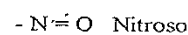
The colour of compound is related to its chemical constitution. **Graebe and Libermann** have stated that **reduction** of coloured organic compound results in the **loss of colour** and **oxidation** of the reduced compound **regenerates** the **original colour**. Hence they concluded that unsaturation was responsible for development of colour.

### 3.4 WITT'S THEORY

According to this theory, there existed a relationship between colour and chemical constitution, a dye is made up of two parts, **chromophores and auxochromes**.

#### 3.4.1 Chromophores

The colour usually appears in an organic compound if it contains certain **unsaturated group called Chromophores**. (Chromo-colour and phores -bearing) Typical chromophores are shown below



There are **two types of chromophores**

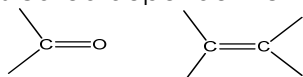
#### 3.4.1.1 Independent chromophores

When a **single chromophores** is sufficient to impart colour to the compound, then it is called independent chromophores e.g. -N=O,  $\text{N}_2$ , -N=N, -N=NO, -N=N-NH, p-quinonoid etc.

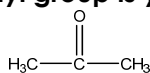


### 3.4.1.2 Dependent chromophores

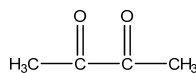
When **more than one chromophores** are required to impart colour to a compound, then it is called dependent chromophores



**Acetone containing one carbonyl group is colourless while biacetyl containing two carbonyl group is yellow**



Acetone (Colourless)



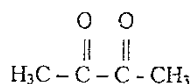
Biacetyl (Yellow)

### Similarly Diphenylpolyenes having formula

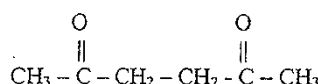
$\text{Ph}-(\text{CH}=\text{CH})_n-\text{Ph}$  here if,

- $n = 1$  or  $2$  the compound is colourless
- $n = 3$  the compound is yellow
- $n = 5$  the compound is orange
- $n = 7$  the compound is copper - Bronze.
- $n = 11$  the compound is violet - black

Shade of the colour is also influenced by the **proximity of chromophores**, If these are **separated by other groups**, the compounds become **colourless**.



Biacetyl (yellow coloured)



Diketo hexane (colourless)

Compound **containing Chromophores** then it is called as **Chromogen**.

### 3.4.2 Auxochromes

The presence of **certain groups** in a **chromogen** leads a **deepening** of the **colour**, even though they are **not chromophores** and **do not impart colour** to the compound when present **without chromophores**, Witt's called these groups as **auxochromes**. (Auxein means to increase and chroma means colour) Some typical auxochromes are as shown below.

Amino	-NH <sub>2</sub>	Chloro	-Cl
Methyl amino	-NHCH <sub>3</sub>	Methyl	-CH <sub>3</sub>
Dimethyl amino	-N(CH <sub>3</sub> ) <sub>2</sub>	Methoxy	-OCH <sub>3</sub>
Sulphonic acid	-SO <sub>3</sub> H	Cyano	-CN
Hydroxy	-OH	Acetyl	-COCH <sub>3</sub>
Carboxylic acid	-COOH	Acetamide	-CONH <sub>2</sub>

These **auxochromes serve two functions**

- They **increase** the **intensity** of the colour.
- They **make the chromogens a dye** by fixing it the fabric or the material to dyes either by association or by salt formation.

### Auxochromes are of two types

#### 3.4.2.1 Bathochromic Auxochromes

These are the groups which increases the depth of the colour. These shift the absorption maximum from the violet towards the red and bring deepening of colour. It is called "Red Shift" e.g. H-atoms are replaced by 'R' in amino group.

#### 3.4.2.2 Hypsochromic Auxochromes

These are the groups which decreases the depth of colour. These shift the absorption maxima from red toward violet and result in the fading of colour. It is called "Blue shift" e.g. H-atom is replaced by acetyl group in hydroxyl or amino group.

### 3.5 ARMSTRONG'S THEORY

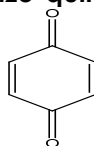
According to theory, all the **coloured compounds** could be represented by **quinonoid structures**



- **Benzene is colourless where as benzo-quinones are coloured**

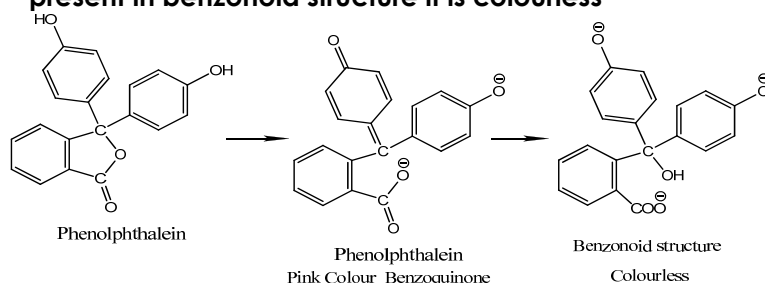


Benzene (colourless)



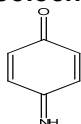
p-benzoquinone (yellow)

- **If phenolphthalein is present in benzoquinone structure it is coloured, and if it is present in benzenoid structure it is colourless**

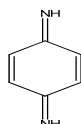


### 3.5.1 Limitations

- This theory could not explain colouring characteristics of the entire compound, e.g. even though **iminoquinone** and **di-iminoquinone** have **quinonoid structure**, yet they are **colourless**.

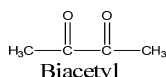


Iminoquinone

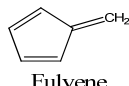


Di iminoquinone

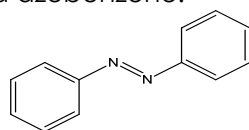
There are other **compounds**, which are **coloured**, **but do not have quinonoid structure** e.g. biacetyl, Fulvene and azobenzene.



Biacetyl



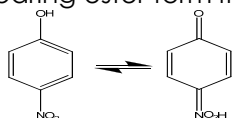
Fulvene



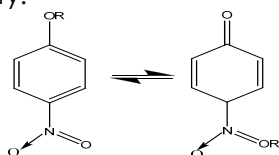
Azobenzene

Armstrong attempted to explain the colour of **p-nitrophenol**, on the basis of **quinonoid structure**, **but** there was **no evidence** for their **existence of a structure**.

Then Hantzsch proved that there exists the phenomenon tautomerism in nitrophenol is by preparing ester form it.



According to Hantzsch the change in colour of compound could be attributed to a change in structure from benzenoid to quinonoid or vice versa i.e. colour is an additive property.

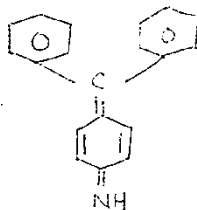


For example the groups  $-\text{NO}_2$  and  $-\text{ONa}$ , both are present then impart colour, but if present alone do not do so. This means that the two groups must be interchange to yield a new structure for the molecule. This phenomenon is known as chromo-isomerism.

### 3.6 BAEYER'S THEORY

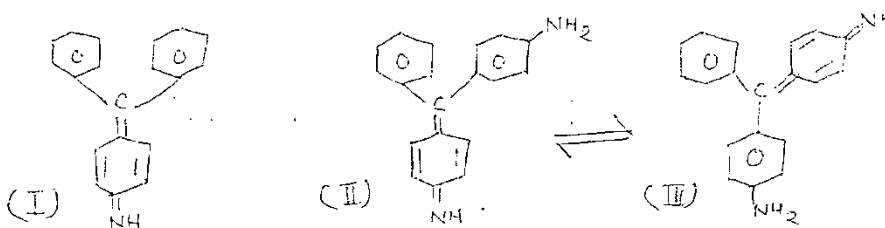
According to this theory, the **colour**, is might be **due to** the **structural oscillation** of the **quinonoid** condition between the **two benzene rings**.

- **Fuchsonimine, (I) is colourless, but if amino groups is introduced in one of the benzene rings, it introduces deeply coloured Doebner's violet.**



Fuchsonimine

This is because of structural oscillation of the quinonoid condition between two benzene rings as shown in figure (II) & (III).



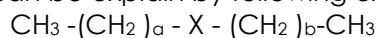
Fuchsonimine (Colourless)

Doebner's Violet (Coloured)

### 3.7 NIETZKI'S THEORY

According to this theory, the **colour** of dye is **deepen** by the **addition of substituent** and due to **increase in molecular weight**.

But for the **deepening** of colour, **nature of the group** added is important and not its weight this can be explain by following example



Here X is chromophores, if X remain same and a & b are having different values, the depth of colour is not affected or no deepening of colour occurs.

### 3.8 WATSON'S THEORY

**Besides the length of conjugated chain**, other factor are also has effect on colour change of compound. If **weight of dye is increased without changing the length of conjugated chain**, the **shade** becomes **deeper**, because vibration becomes slower due to increase in molecular weight, e.g. Fluorescein on bromination gives eosin (tetra bromo-fluorescein) which has much deeper colour then Fluorescein due to the molecular weight.

### 3.9 MODERN THEORIES OF COLOUR AND CONSTITUENTS

There are two most important theories called valence bond and molecular orbital theory. These theories are based upon following concepts.

#### 1. Quantization of light energy

Light is quantized in the units of energy called quanta or photons.

#### 2. Absorption of Radiation by molecules

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 absorbed energy is to raise the energy of the molecule from ground state to excited state.

$$\Delta E = E_1 - E_0 = hc/\lambda, = hv$$

Where,

$\Delta E$  = Quantum energy

$E_1$  = Energy of excited state

$E_0$  = Energy at ground state

$v$  = Frequency of light

$h$  = Plank's constant

$\lambda$  = Wavelength of the absorbed radiation

$c$  = Velocity of light

The **amount of energy absorbed** i.e.  $\Delta E$  **depends** upon the **structural configuration of dye**. For instance

- If the **electrons** are **tightly bound**, as in **saturated compound**, no light of visible region will be absorbed and hence the **compound** will appear **colourless**.
- If the **electrons** of a molecule are **loosely bound** as in **unsaturated compounds**, the **absorption** may occur in the **visible region** and the **substance** will then appear **coloured**.

For a coloured substance the values of  $\Delta E$  lie between 71.0 and 35.5 kcal/mole as we go from 4000 to 8000° A.

As the electrons occupy definite orbital, it means that  $\Delta E$  and hence frequency of light absorbed must have definite values. As each values of a frequency is associated with a particular line of spectrum. Thus the spectrum of the compound will consists of large number of lines corresponding to a large number of excited states of the large number of molecules constituting the compound. These lines then appear as band because of value of E which very close to each other. The existence of the bands in definite parts of the spectrum which produces the color.

### 3. Dipole moment

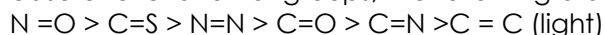
The **molecule** can **absorb light** only if its **dipole moment changes**. The more the molecule is symmetrical, the smaller the transition dipole and molecule absorbs light very slowly, and vice versa. Thus if the group which is introduce in a molecule, decreases the symmetry and increases transition dipole of molecule, the intensity of the absorbed light will increased.

## 3.10 VALENCE BOND THEORY OR RESONANCE THEORY

### 3.10.1 Postulates of theory

The  **$\pi$ -electrons of groups of atom** (i.e. chromophores) which may get transferred from **ground state** to **excited state** by the **absorption of radiation**, thus **producing** the **colour**.

- **Auxochromes** are groups, which tend to **increase resonance** by **interacting** the **unshared pair** of the **electrons** on nitrogen or oxygen atoms of the auxochromes with  **$\pi$  -electron** of the **aromatic ring**. This increase in resonance **increases** the **intensity of absorption of light** and shift the absorption bend to longer wavelength deepening the colour.
- The **dipole moment changes** as a result of the **oscillation of electron pairs**. For the ease of excitation of groups, the following order has been observed.



← Dark

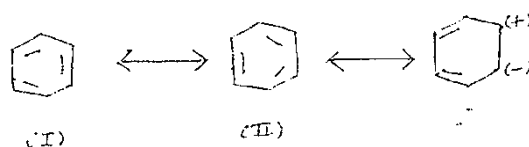
The colour deepens in the opposite direction.

- The more the possibility and **longer the path** for a **charge to oscillate** in a compound, the more long wavelength of light will be absorbed. And therefore **more deeper** would be the color of the compound.

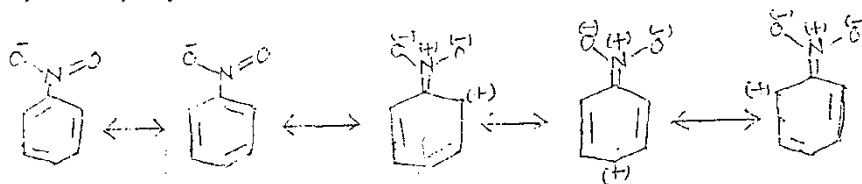
### 3.10.2 Consider the following examples.

**a) Explain Benzene is colourless, nitrobenzene is pale yellow and p-nitro aniline is dark yellow**

In benzene, **two kekule structures** (I & II) are major structures **contributing** to its **resonance hybrid**. Also a number of **charged canonical structures** are possible (as shown in figure III). But they contribute relatively little to either ground or excited state and thus benzene **absorbs** in the **U.V. region** also benzene is **symmetrical**. Therefore, it is colourless. Also it has **no chromophoric group**.

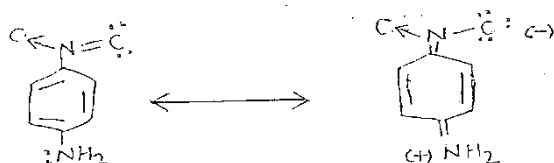


In **nitro benzene charged structures contribute** much more to its **resonance hybrid**. And due to **loss of symmetry** of the molecule, the absorption is shifted to longer wavelength, thereby produces **pale yellow**.



Due to chromophore also colour deepens.

Similarly in **p-nitroaniline** the **contribution** of the **charged structure** is **still large** and hence the light of longer wavelength is absorbed. Thus deepening colour occurs to **dark yellow**.

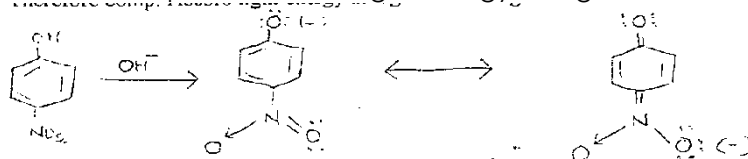


The **comparison** of the **dipole moment** for nitrobenzene (0.21D) aniline (1.48D) and p-nitroaniline (6.1D) also gives an idea that there is relatively high contribution of the charged structure to resonances, hybrid of p-nitro aniline.

Here in p-nitroaniline each of amino and nitro groups cooperatively helps the other in shifting the actual state of the molecule in the direction of charged structures.

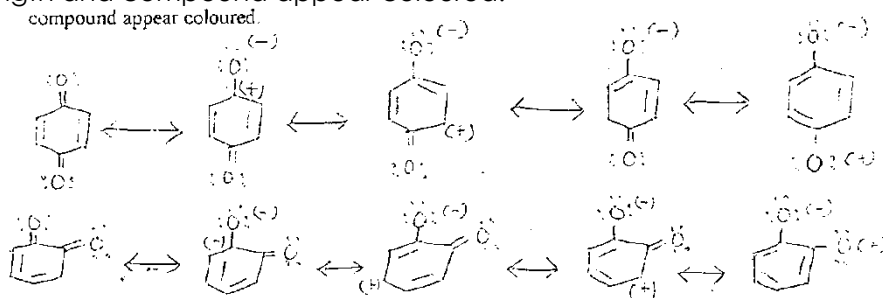
**b) Pure p-nitrophenol is colourless but yellowish in alkaline solution.**

It is evident from the fact, that in **alkaline solution** the **nitrophenol** exists as **nitrophenoxide ion** in which only the charged structures are contributing to its resonance hybrid. Therefore compound absorb light energy at higher wavelength.

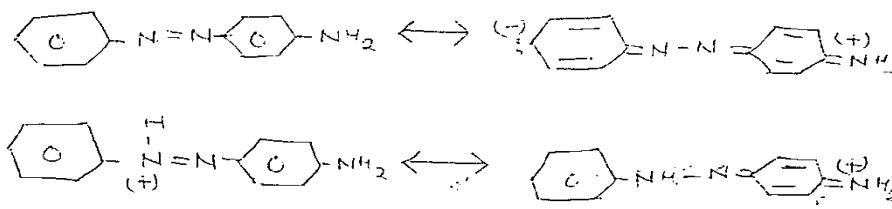


**c) p- or o-quinones has yellow colour which can be explained by resonance theory**

Here due to **two oxygen atoms**, there occurs **greater contribution** of the charged structure to the **resonance hybrid**. Thus these compound absorbed light of the higher wavelength and compound appear coloured.

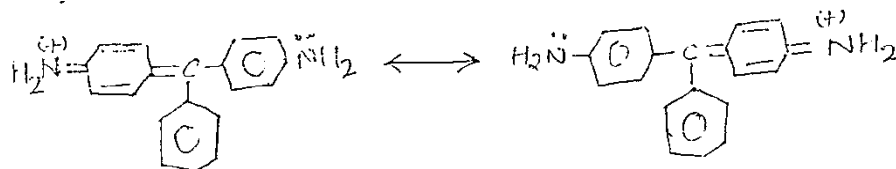


**d) Explain p- aminoazobenzene is yellow but in acidic solution it becomes violet.**



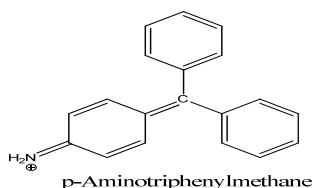
The **deepening** of colour is due to **contribution** of **both charges structures** in resonance hybrid, while in case of **p-aminoazobenzene** only **one charged structure** **contribute** to the resonance hybrid.

**e) All the triphenylmethane dyes has much deeper colour this can be explain by resonance theory.**

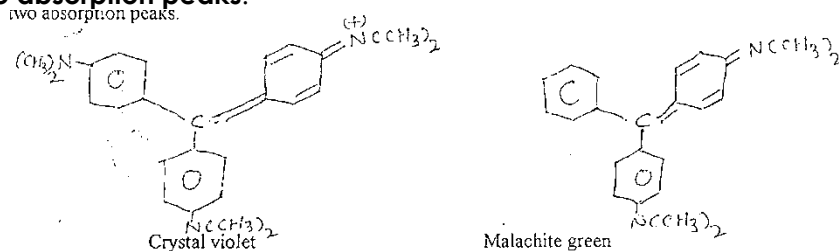


Doebner's violet

This is due to the **delocalisation of unit electrical charge** over a long path. If **one** of the **amino group** of Doebner's violet is **replaced by H-atom** then the molecule formed i.e. **p-amino triphenylmethane** is **colourless** because here **no oscillation of +ve charge** takes place.



**f) Crystal violet has one principle absorption peak ( $\lambda_{max}$  5900Å) while malachite green has two absorption peaks.**



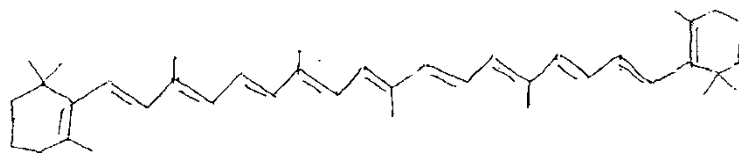
**Malachite green**, the molecule is **unsymmetrical** and as **two axes of polarisability** differing in degree lying at right angle, also here the possibility of the **oscillation for +ve charge** is **restricted to two benzene ring**, hence it shows **two peaks** at 4230 - 6250Å.

**Crystal violet** has **centre of symmetry** in which **all three benzene rings** participate in resonance as shown in above structures. **Polarisability** becomes **equal in all directions** in the **plane of the molecule** and hence there is only **one absorption peak**. Also the **oscillation for +ve charge** is **not restricted**, but oscillates in all benzene rings.

**g) Effect of conjugation on resonance**

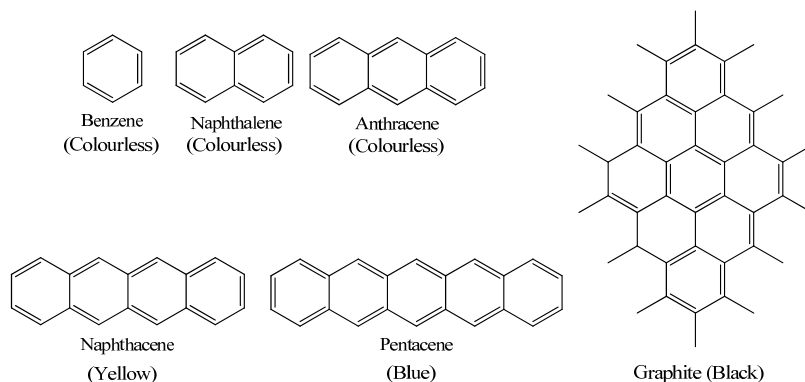
The **longer** the **conjugation** in a molecule, the **deeper** will be the **colour** because the conjugation system of the **double bonds** provides a **long path** of resonance. This **shifts** the **absorption to longer wavelength**. E.g. diphenylpolyenes. The colour change as 'n' increases which shift the change absorption to higher wavelength side and colour becomes deeper.

According to **Lewis and Calvin** the **deepening** of colour with **increase** in **length of conjugation** which has been attributed to increase in number of electrons which are participating in conjugation. In some compound increasing in conjugated system is also able to increase the deep colour, which do not have aromatic nucleus.



$\beta$  - carotene ( orange red)

As the **number of fused rings increases**, the **colour deeper** more and more for examples.



If the **conjugated system** also has **atoms** as **N, O, S**, etc, it **absorbs** light of **longer wavelength** than the corresponding compounds which consists of conjugated system of only the carbon atoms.

### 3.11 MOLECULAR ORBITAL THEORY

According to this theory, the excitation of a molecule means the transference of one e<sup>-</sup> from an orbital of lower energy to higher energy. This electrons may be  $\sigma$ ,  $\pi$  or n.

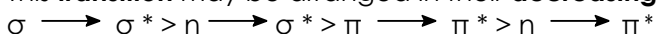
The higher energy states are commonly known as "Anti bonding" orbital. It's association with  $\sigma$  and  $\pi$  bonds are called  $\sigma^*$  and  $\pi^*$  but there are no antibonding orbitals associated with 'n' electrons because they do not form bonds.

$\sigma^*$	Anti bonding
$\pi^*$	Anti bonding
n	Loan pair, non-bonding
$\pi$	Bonding
$\sigma$	Bonding

Figure: schemes showing molecular orbitals

The **electronic transition** can occur by the **absorption of ultra-violet** and **visible radiation**. Although **several transitions** are possible only the **following types are allowed**.  
 (1)  $\sigma \longrightarrow \sigma^*$  (2)  $n \longrightarrow \sigma^*$  (3)  $n \longrightarrow \pi^*$  and (4)  $\pi \longrightarrow \pi^*$

This **transition** may be arranged in their **decreasing order of energy**.



$\sigma \longrightarrow \sigma^*$  type of **transition** requires a **very large amount of energy** as  $\sigma$  - electrons are very tightly bonded. The saturated hydrocarbons which do not have any  $\pi$  or n electrons may undergo only  $\pi \longrightarrow \pi^*$  transition and are **not absorbed** in the ordinary **ultraviolet region** e.g. ethane absorb at 1350°A.

If a compound has non-bonding e<sup>-</sup> pair then  $n \longrightarrow \sigma^*$  transition take place also in addition to the  $\sigma \longrightarrow \sigma^*$  transition. Compounds having **non-bonding electrons** on **hetero atom** like O,N,S etc. can undergo  $n \longrightarrow \sigma^*$  transitions also in addition to the  $\sigma \longrightarrow \sigma^*$  transition. But non-bonding electrons are much more loosely held then the  $\sigma$  electrons. Therefore the energy required for  $n \longrightarrow \sigma^*$  will be much lower than that for  $\sigma \longrightarrow \sigma^*$  transitions and hence they are usually absorbed in **ordinary U.V. region** e.g methyl iodide shows  $\lambda$  max. at 2580°A. while trimethylamine at 2270°A.

$n \longrightarrow \pi^*$  and  $\pi \longrightarrow \pi^*$  are of lower energy than both the  $\sigma \longrightarrow \sigma^*$  and  $n \longrightarrow \sigma^*$  transition and therefore, take place at longer wavelengths.. Furthermore,  $\pi \longrightarrow \pi^*$  transitions are of lower energy than the  $n \longrightarrow \pi^*$  but require more energy than the  $n \longrightarrow \sigma^*$ .

E.g. Acetaldehyde shows two absorptions, one at 1800°A. Corresponding to  $\pi \longrightarrow \pi^*$ , while the other at 2900°A, corresponding to  $n \longrightarrow \pi^*$  transition.

Considered the data of following table

Compound	Transition	Absorption band (max)
H <sub>2</sub> C = CH <sub>2</sub>	$\sigma \longrightarrow \sigma^*$ , $\pi \longrightarrow \pi^*$	1750°A
H <sub>2</sub> C = CH-CH - CH <sub>2</sub>	$\pi \longrightarrow \pi^*$	2170°A
B-Carotene	$\pi \longrightarrow \pi^*$	4510°A

From above absorption it is concluded that as conjugate of double bond increases, energy required for  $\pi \longrightarrow \pi^*$  transition decrease and absorption shift to longer wavelength.

- Explain **Benzene** which is **symmetrical**, possesses **no transition dipole**, **does not absorb visible light** and is colourless. While **nitro-benzene** is **not symmetrical** and thus its C-atoms are unequally charged. The introduction of  $\text{NO}_2$  group in the benzene molecule extends its conjugation, the decreases the energy difference between the highest level of the ground state and the lowest level of the excited state and hence absorption are expected at longer wavelength then the benzene and thus nitrobenzene appears **yellow**.
- Consider **aniline** molecule, in which the **lone pair of electrons** present on nitrogen atom is in conjugation with the benzene ring and therefore it **possesses dipole transition** due to this aniline absorbs light of longer wavelength than that of benzene. In acid solution the lone pair of electron of nitrogen atom is coordinated with proton. This destroy conjugation and transition dipole due to this the absorption maxima of anillinium ion is almost the same as that of benzene.

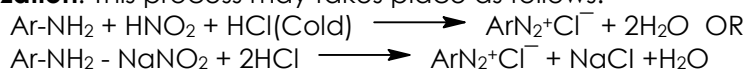
### 3.12 AZO DYES

#### 3.12.1 Introduction

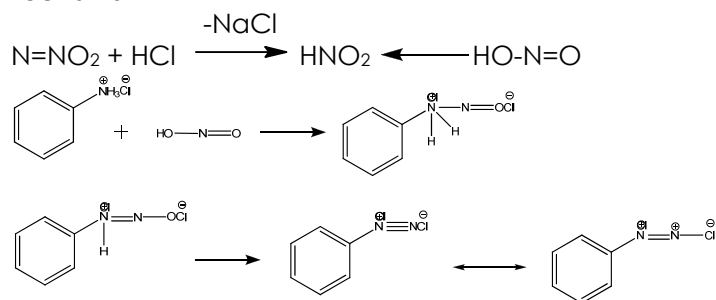
The **chromophoric system** of this class is the **azo groups -N=N-**, in **association with one or more aromatic systems**. There may be **more than one azo group** present in the dye molecule and thus one speaks of **monoazo, bisazo, trisazo, tetra-azo** and **polyazo dyes** according to whether there are one, two, three, four or more azo groups present in the dye molecule.

#### 3.12.2 Diazotization

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 **Ar-N=N<sup>+</sup>Cl<sup>-</sup>**. This new compound **Ar-N=N<sup>+</sup>Cl<sup>-</sup>** is **called diazo** compound and the **formation** of this compound is called **diazotization**. This process may takes place as follows.



#### 3.12.3 Mechanism



#### 3.12.4 Effects of substituent's on diazotization

**Diazotization** of aromatic amine found to **depend upon** the **nature** and **position** of **substituent's** 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  $-\text{NO}_2$  groups and therefore require special methods for their diazotization.

Diazotization may also give rise to **difficulties** through **low solubility** in **aqueous acid** the presence of **easily replaceable groups** such as  $-\text{SO}_3\text{H}$ ,  $-\text{NO}_2$  or the presence of **easily oxidizable groups** such as  $-\text{OH}$ ,  $-\text{CHO}$ . Accordingly a number of methods have been developed to overcome these difficulties.

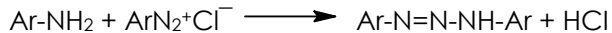
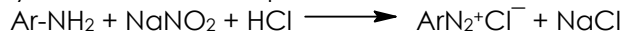
#### 3.12.5 Methods of diazotization

Diazotization can be carried out by different methods which are as follows.

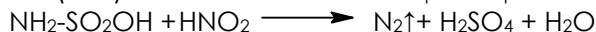
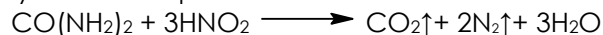


### 1. Direct Methods

Direct diazotization 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 diazotized with only one mole of acid present, then a diazo-amino compound formed.



**Completion of diazotization** 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 diazotization process may be destroyed either by urea or sulphamic acid because nitrous acid reacts with the second component.



As the **diazonium ion decomposes** in the **presence of metals**, the **diazotization** is **carried out** in wooden vats or rubber-lined steel vessels or glass-lined steel vessels.

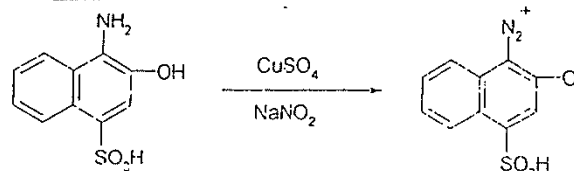
The direct diazotization may also be carried out in acetic acid with amyl or ethyl nitrite.

### 2. Reverse methods

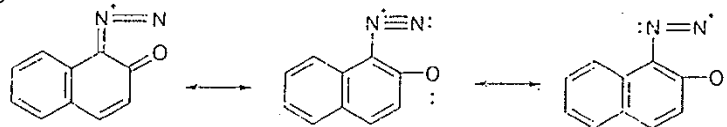
In the reverse method, a solution of **amine** and solution of **sodium nitrite** are **run into** the solution of the **acid**. This method is used for Naphthylaminesulphonic acids which give insoluble diazo salts due to the formation of Zwitter ion. The diazonium salts are explosive and care must be exercised in handling them.

### 3. Special Method

**Aminophenol** are readily **oxidized** by **nitrous acid** to the **quinones** and therefore, special methods are developed for diazotization. The diazotization 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 25% solution, cool to 20°C. To the solution is added copper sulphate followed by sodium nitrite.



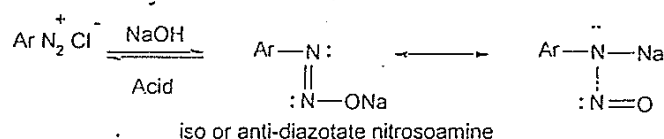
The diazo-oxide obtained is more stable than other diazo ions and may be subjected to even further reactions such as nitration, halogenation etc. The diazo-oxides undergo coupling reaction. Their resonance structures are



#### 3.12.6 Stabilization of azo compounds

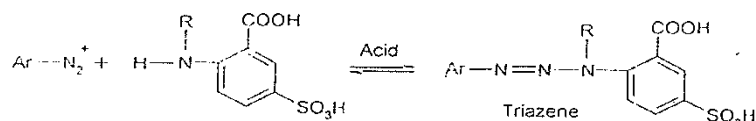
Most of the **diazonium salts** are **not very stable** except the nitro substituted benzene diazonium salts, diazo oxides and zwitter ions. Almost all the dry diazonim salts are **explosive**. However, there is a great need for the dyer and printer for the diazonium salts to produce different shades on the fiber 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.



- Diazoamino compounds** are produced by reacting 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  $\text{CH}_2\text{NHCH}_2\text{COOH}$  and other amino acids. The aromatic amines used are Sulphoanthranilic acid or 2-alkylamino-5-sulphobenzoic acids.



- Diazosulphonates** are obtained when diazonium solution is treated with naphthalene-1, 5-disulphonic acid, e.g.  

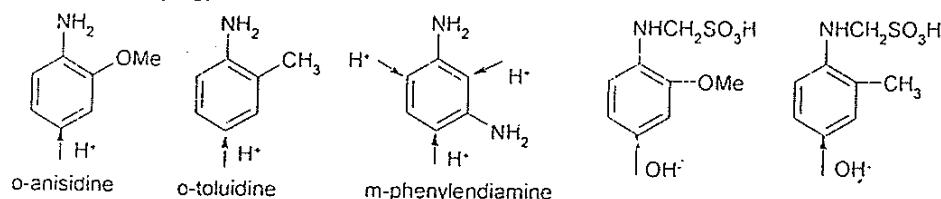
$$\text{ArN}_2^+\text{Cl}^- + \text{HO}_3\text{S-Ar}' \longrightarrow \text{Ar-N=N-O-O}_2\text{S-Ar}' + \text{HCl}$$
- The diazoarylsulphonate on redissolving in water** is in equilibrium with the diazo salt on coupling the diazoaryl sulphonate further breaks up. Diazoaryl sulphonate are prepared from diazoamino compounds, e.g. p-amino diphenylamine diazonium salt, variamine blue B and blue BB.
- Doublesalts** are obtained by treatment of diazonium solution with zinc chloride solution when the double salt  $(\text{ArN}_2^+\text{Cl}^-)_2\text{ZnCl}_2$  is formed and crystallized out, e.g. benzidine, aminoazo, benzene etc.
- Stabilised fluoborates** are also obtained by treatment of diazonium solution with fluoboric acid.

### 3.12.7 Coupling components

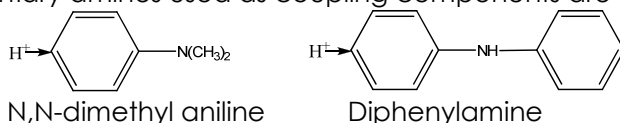
#### (A) Benzene derivatives

##### 1. Amines

**Primary aromatic amines** are useful as coupling components. Some important examples are as follows:

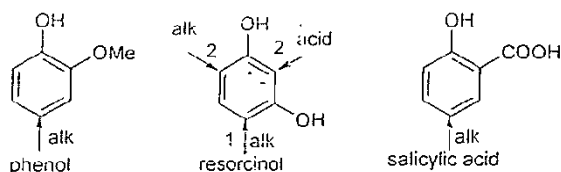


The **arrows indicate the usual coupling position**. Coupling is generally **carried out under acid conditions** with an **energetic diazo component**, if **less energetic diazo components** are to be coupled with the amine, the amino groups has to be protected by first forming the methansulphonic acid by reacting the amine with formaldehyde and bisulphite. The resulting compounds may be coupled under alkaline conditions. However, the methansulphonic acid group is subsequently removed by hydrolysis. Examples of secondary and tertiary amines used as coupling components are as follows:



##### 2. Hydroxyl derivatives

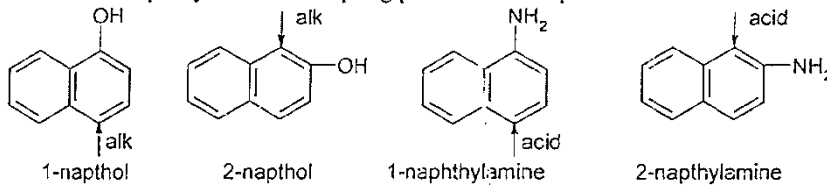
Phenol couples under alkaline conditions principally in the 4 -position. In resorcinol coupling takes place in the 4 - position and then according to the pH at which the coupling is done. **E.g.** pH = 5 - 8, position 2; pH > 8, position 6. Recorcinol couples principally in the 4 - position.



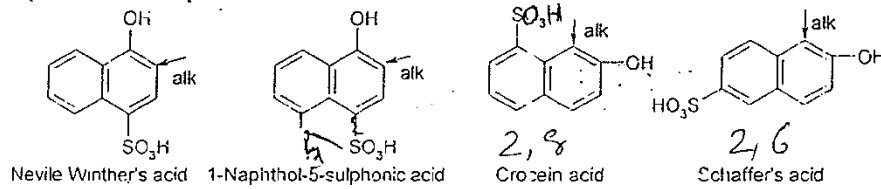
#### (B) Naphthalene derivatives

##### 1. Naphthols and Naphthylamine

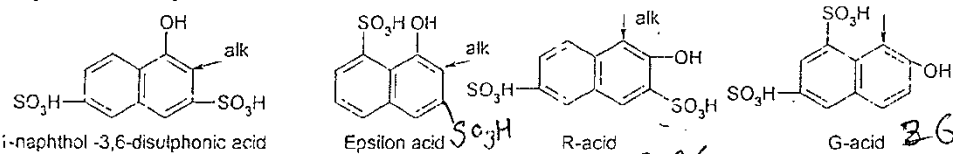
Coupling positions of naphthols are shown as



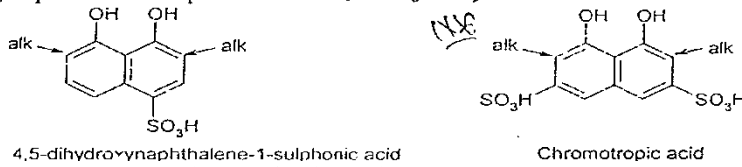
**2. Naphtholmonosulphonic acids**



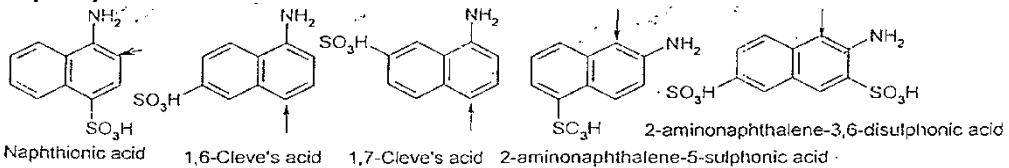
**3. Naphtholdisulphonic acids**



**4. Dihydroxynaphthalene sulphonic acids**

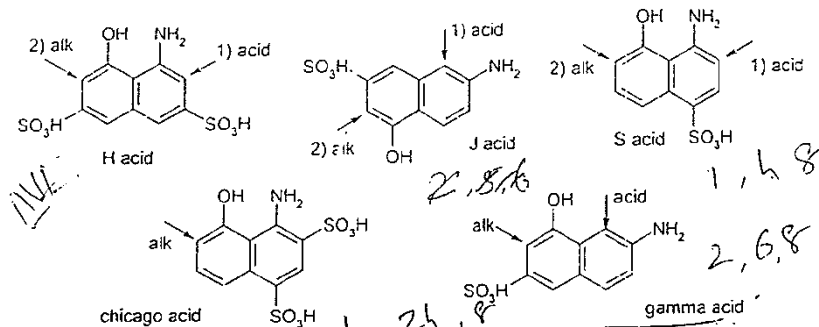


**5. Naphthylamine sulfonic acid**



**6. Amino naphthol 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, leather dyes.

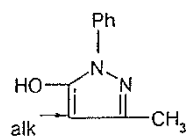


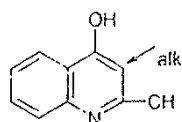
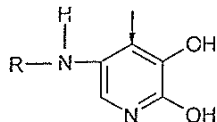
**7. Methylphenyl pyrazole**

It couples at position 4. It is used in the manufacture of direct and acid dyes and especially in mordant dyes.

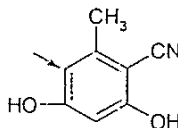
**8. Acetoacetanilide**

It is used for making a number of direct and acid dyes.



**9. Quinoline – 2,4 – diol****10. Dihydroxypyridines**

where R = alkyl

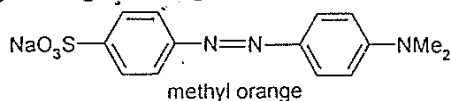
**3.12.8 Types of azo dyes**

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 fibers** as follows.

1. Acid azo dyes
2. Basic azo dyes
3. Direct or substantive azo dyes
4. Ingrain azo dyes
5. Mordant azo dyes
6. Synthetic fiber dyes
7. Stilbene – azo dyes

**1. Acidic azo dyes**

These dyes have been characterized by the **presence** of an **acidic group** such as  $-SO_3H$ ,  $-COOH$  or phenolic  $-OH$  group. The **acidic group** makes the dye **more soluble** and **act** as **auxochromes**. **E.g.** Methyl orange / Orange III ( Sulfanilic acid to N,N-dimethyl aniline.)

**2. Basic azo dyes**

These have  $-NH_2$  or  $-NH-R$  groups are the **auxochrome**. The chromophoric system is

present as cations. **E.g.** Aniline Yellow (Aniline to Aniline)

**3. Direct or substantive azo dyes**

The azo dyes described earlier are used to dye the proteinous fibers (e.g. Wool, Silk and leather) directly but they need mordant for dyeing cellulosic fibers (e.g. Cotton, linen, paper etc). However, certain azo dyes are known which could dye directly the cellulosic fibers without a mordant such azo dyes are called direct or substantive azo dyes. **E.g.** Congo-Red (Benzidine to 2-Naphthionic acid).

**4. Ingrain azo dyes**

These are **water insoluble azo dyes** which are formed on the fiber. 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 diazotized amine. The most important example of this group is Para red (p-NA to  $\beta$ -naphthol).

**5. Mordant azo dyes**

These are the azo dyes, which when **fixed** on the **fiber**, are capable of forming **complex metallic compounds** when **treated** with **metallic salts** such as sodium dichromate, sodium chromate or chromium fluoride. Chromium is the most widely used metal in mordant azo dyes. Most of the dyes belonging to this group are monoazo dyes but they include a few diazo dyes. Their great importance is due to 'their high fastness' to light and washing. **E.g.** Diamond black-F (5-amino salicylic acid  $\rightarrow$  1-naphthylamine  $\rightarrow$  1-naphtho-4-sulfonic acid).

**6. Synthetic fiber dyes**

Several dyes are known which are used to dye synthetic fibers such as Rayon, Terylene, Nylon, Polyacrylonitrile etc. These may be acidic, basic or, disperse dyes **E.g.** Cellitone scarlet-B. (p-NA N-ethyl-N( $\beta$ -hydroxy ethyl)-aniline.

**7. Stilbene azo dyes**

These are **yellow and orange direct azo dyes** used for Cellulosic fibers. Although these dyes have azo groups, they are not prepared by process diazotization and coupling.

**3.12.9 Subclasses of Azo dyes**

Azo dyes can also put into various subclasses such as monoazo, bisazo, trisazo, mordant azo, stilbene azo, polyazo and pyrazolone.

**3.12.10 Nomenclature used in the subclasses of azo dyes (LAPWORTH'S NOTATION)**

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.

**A:** It represents an Arylamine used as diazonium components, further such components used are denoted by A1, A2 etc. Examples of A are aniline, O-toluidine etc.

**D:** It is an Aryldiamine like benzidine having two diazotizable groups. Examples of "D" are benzidine, 4,4'-diaminostilbene-2,2'-disulphonic acid etc.

**E:** It is the second component or coupling component. Example of "E" are phenol,  $\beta$ -Naphthol, dimethylaniline etc.

**Z:** It is a coupling component having dual coupling positions. Examples of Z are H-acid, gamma acid, J acid etc.

**T:** It is a coupling component having three coupling position. Examples of "T" are Resorcinol, m-phenylene diamine.

**M:** It is the middle component having one coupling position and one diazotizable amine which can further couple with a coupling, component. Examples of "M" are 1-naphthylamine, J-acid etc.

**3.12.11 Different types of azo dyes**

**A  $\rightarrow$  E**

E.g. Orangc-II (Sulfanilic acid  $\rightarrow$   $\beta$ -naphthol)

**A  $\rightarrow$  Z  $\leftarrow$  A1**

E.g. Naphtho Blue Black-6B (Aniline  $\rightarrow$  H-acid  $\leftarrow$  p-NA)

**E1  $\rightarrow$  D  $\leftarrow$  E**

E.g. Congo Red (Naphthionic acid  $\leftarrow$  Benzidine  $\rightarrow$  Naphthaionic acid)

**A  $\rightarrow$  M  $\rightarrow$  E**

E.g. Cloth Red-B (ortho toluidine  $\rightarrow$  ortho toluidine  $\rightarrow$  1-Naphthol-4-sulfonic acid means NW-acid).

**A  $\rightarrow$  Z-L-Z  $\leftarrow$  A1**

E.g. Chlorazol Scarlet 4-BS (Aniline  $\rightarrow$  J-acid Urea  $\leftarrow$  p-amino acetanilide)

**3.13 ANTHRAQUINONE DYES****3.13.1 Introduction**

**Anthraquinone**, the **basic system** of these dyes, has a **faintly yellow colour**, 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 ( $\text{OH} < \text{NH}_2 < \text{NR}_2 < \text{NHAr}$ ) absorb in any desired region of the visible spectrum. Dyes based on anthraquinone and related polycyclic aromatic quinones are of great importance. In Anthraquinone dyes Quinonoid group and C=O are chromophore.

**3.13.2 Classification**

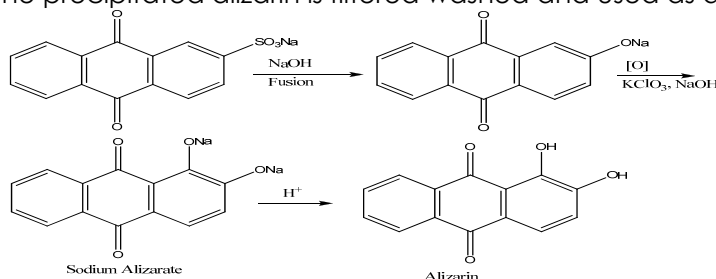
1. Anthraquinone Mordant dyes.
2. Anthraquinone Vat dyes.
3. Anthraquinone Acid dyes.
4. Anthraquinone Disperse dyes

### 3.13.2.1 Anthraquinone mordant dyes

These **contain** groups such as **hydroxyl or carboxyl group** which can combine with metal ions so as to form insoluble compounds called lakes. The colour of the lake depends upon the mordent i.e. the metal used. Some of the important anthraquinone mordant dyes are as follows.

#### 1. Alizarin

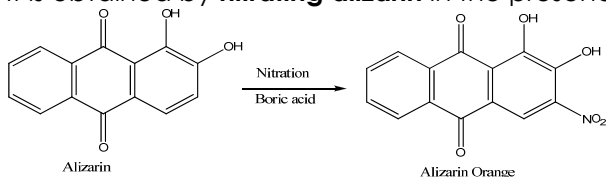
It is **1, 2-dihydroxyanthraquinone**. It is also known as **Mordant R-11**. It is obtained by heating under pressure, silver salt (sodium anthraquinone-2-sulphonate, so called because of its silvery crystals), caustic soda, potassium chlorate and water in a steel autoclave at about 180°C. The resulting melt is blown into water and acidified to decompose the sodium alizarate, the precipitated alizarin is filtered washed and used as a paste (2.0%).



Alizarin is a **red crystalline solid** insoluble in water but soluble in alcohol and alkali. It is a mordant dye and colour is mainly depends on the type of mordant.

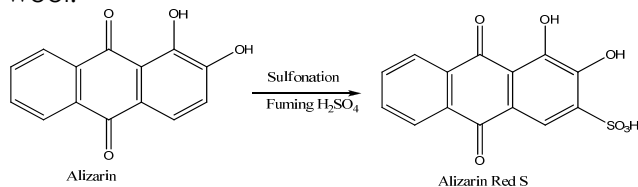
#### 2. Alizarin Orange

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



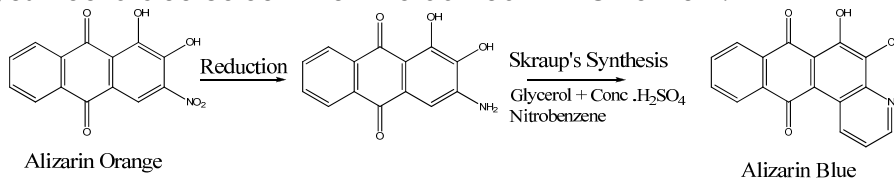
#### 3. Alizarin Red-S

It is obtained by the **Sulfonation of alizarin** with fuming sulfuric acid. It is used for dyeing wool.



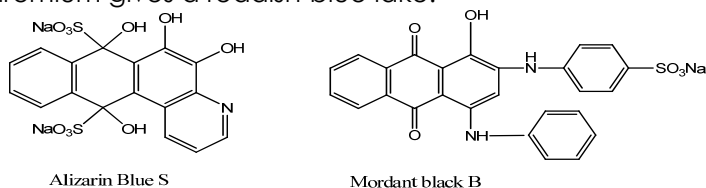
#### 4. Alizarin Blue

It is obtained by **reducing alizarin orange** to 3-aminoalizarin followed by **Skrup's synthesis** of quinoline, i.e. by heating with glycerol, conc. H<sub>2</sub>SO<sub>4</sub> and nitrobenzene. Alizarin blue dyes wool a blue colour when mordanted with Chromium.



#### 5. 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.



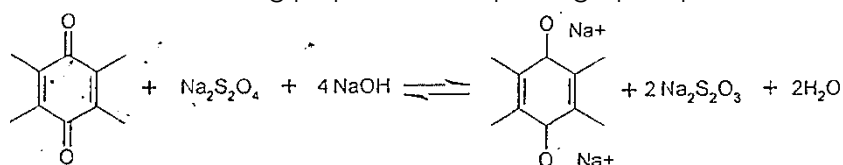
### 6. Mordant Black-B

It is made by **condensing aniline** with **1,2,4-trihydroxyanthraquinone** and **sulphonating** the **resulting base**. It is applied to wool with a chromium mordant and is quite fast to light and washing.

#### 3.14.2.2 Anthraquinone vat dyes

Most of the **vat dyes** are **derivatives** of **Anthraquinone** or **related compounds**. These essentially contain grouping such as  $-\text{CO}-\text{CH}=\text{CH}-\text{CO}-$  present as a quinonoid ring system or  $-\text{CO}-(\text{CH}=\text{CH})_n-\text{CO}-$  where "n" is a suitable integral and  $-(\text{CH}=\text{CH})_n$  part is involve either through the fused heterocyclic or through the, polycyclic system These have a high molecular weight and are insoluble in water. 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 some time and **finally exposed to air**.

These dyes are mainly used for dyeing cotton, wool, nylon, silk, calico-printing etc. These are also used for colouring pulp, cements, photographic prints etc.



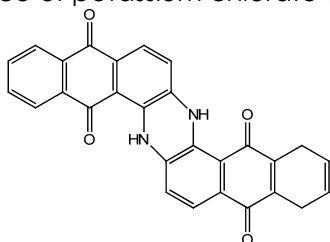
Anthraquinone vat dye (insoluble)

Sodium salt of an Anthraquinol (soluble)

The important anthraquinone vat dyes are:

#### 1. Indenthron blue / Indanthrone / Indanthrene / Vat Blue-4

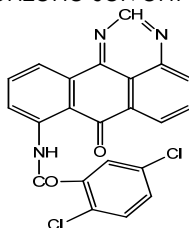
It is manufactured **by fusing 2-amino anthraquinone** with **potassium hydroxide** in the presence of potassium chlorate or potassium nitrate at 250°C.



Indanthrone blue

#### 2. Indanthrone / Indenthrene Yellow-4GK

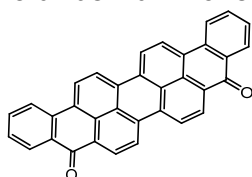
It is prepared by condensing **2,5-dichlorobenzoyl chloride** with **1,9-anthra pyrimidine**. The latter compound is obtained by condensing 1,5-diaminoanthraquinone with formamide in nitrobenzene solvent in the presence of copper compound.



Indenthrene Yellow 4GK

#### 3. Manufactured from benzanthrone

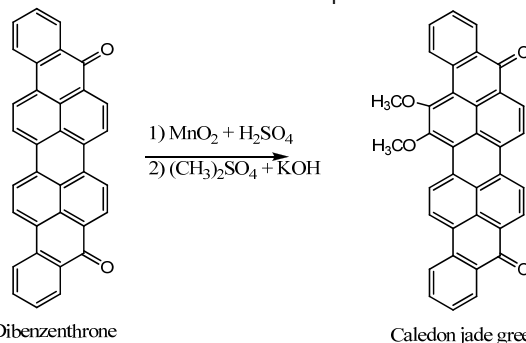
Several important vat dyes have been manufactured from benzanthrone. Among these are **di-benzanthrone** (Vat Blue-20) and **Caledon Jade Green**.



Dibenzanthrone



**Di-benzanthrone** when **oxidized with manganese** by methylation with dimethyl sulfate in nitrobenzene and in the presence of alkali yields **Caledon Jade Green**.

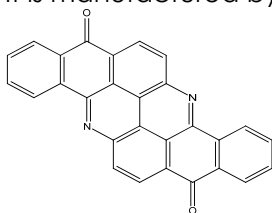


Dibenzenanthrone

Caledon jade green

#### 4. Flavanthrone / Flavanthrene / Indenthrene Yellow

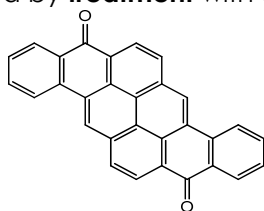
It is manufactured by **fusing 2-amino anthraquinone** with **caustic potash** at 350°C.



Flavanthrone

#### 5. Pyranthrene / Pyranthrene / Indanthrene Golden Orange-G

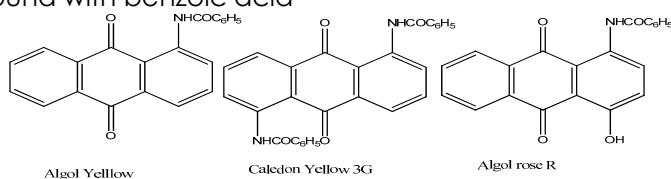
It is manufactured by **heating 1-chloro-2-methyl anthraquinone** with **copper powder** followed by **treatment with alcoholic KOH**. It is yellow dye and is very fast.



Pyranthrene

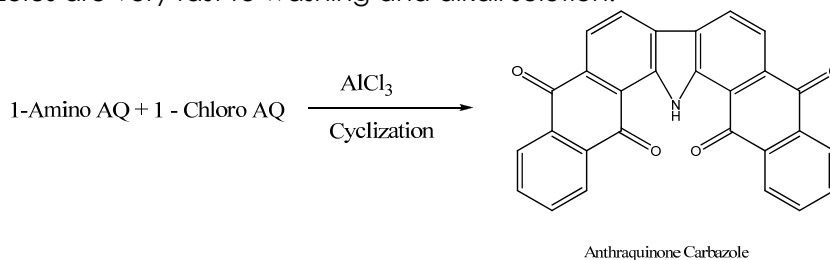
#### 6. Algol dyes

There are many dyes belonging to this class but **Algol Yellow is important**. Chemically it is 1-benzoylamino anthraquinone which is prepared by heating the corresponding amino compound with benzoic acid



#### 7. Anthraquinone Carbazoles

These are prepared by the **cyclization** of a **suitable dianthraquinoyl amine**. For example, a yellow coloured dye is obtained by condensation of (1-aminoanthraquinone followed by cyclization with anhydrous  $\text{AlCl}_3$ . Anthraquinone Carbazoles are very fast to washing and alkali solution.

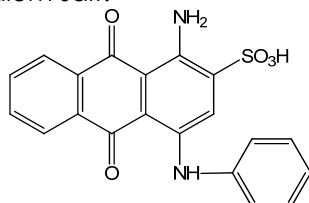


Anthraquinone Carbazole

### 3.13.2.3 Anthraquinone acid dyes

These dyes are **water soluble anthraquinone derivatives** which are used for dyeing wool, silk, nylon, leather and paper. These have **soluble sodium sulfate groups**. These are among the fastest of those dyes which are applied to wool from a sulfuric 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 sulfonated and brominated to give Bromamine acid. Condensation with aniline yields Solway Ultrablue-B which is isolated as the sodium salt.

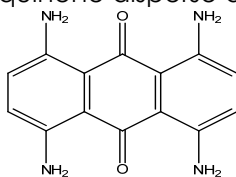


Solway ultrablue B

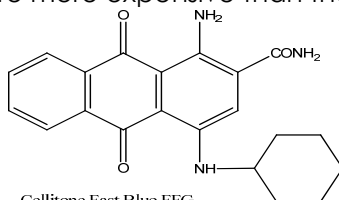
### 3.13.2.4 Anthraquinone disperse dyes

These are simple **insoluble derivatives of Anthraquinone**. These dyes are mainly used for dyeing of Acetate Polyester, Polyamide and synthetic fibers. 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**. Anthraquinone disperse dyes are more expensive than the insoluble azo dyes.



Durarol Brilliant Blue CB



Cellitone Fast Blue FFG

## 3.14 REACTIVE DYES

### 3.14.1 Introduction

It is a coloured organic compound which has a **suitable reactive group**, capable of forming **covalent bond** between **carbon of the dye molecule** and **N, O, SH or OH** group of **substrate**. Reactive dyes offer excellent fastness to washing since the dye becomes a part of the fiber by forming a covalent bond. In 1956 first reactive dye was introduced by ICI for the dyeing and printing of cellulose fibers. These reactive dyes were containing cyanuric chloride (2, 4, 6-trichlorotriazine) as a reactive system.

### 3.14.2 Application

They are applied to cellulosic fabric by a variety of dyeing process.

#### a) Batch dyeing process

In this process the **fibers** are **dyed** in a **batch containing salt**, a temperature is usually according to the reactivity of the dye concerned. Thus **Procion-M dyes** are applied from cold bath at 50-60°C and **Remazol dyes** at moderate temperature. Dyeing is completed within **half an hour** and at this stage **Na<sub>2</sub>CO<sub>3</sub>** is **added** to bring about fixation. This requires half to one hour in all case. Hydrolyzed dye is removed in final treatment with soap or detergent.

#### b) Semi continuous Process

This process is known as **hot bath processes**. The **fiber** to be dyed is **padded** with a **solution** of the **dye, alkali** and **wetting agent** at **20-30°C** and then allowed to stand until fixation is completed. The alkali used may be NaOH, Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub> for fixation. Finally remove unfixed dye by washing.

#### c) Continuous Process

It is carried out by **padding cloth** with a **neutral solution** of reactive dye, drying then passing it successively through a bath of caustic soda solution, a streamer, soap bath and

dryer. In the case of dye of fairly low reactivity, the alkali may be applied with the dye. For light shade decomposition can be minimized by using  $\text{NaHCO}_3$  in place of  $\text{NaOH}$  and the reaction time is reduced to a few minutes by the use of higher temperature.

### 3.14.3 Limitation of Reactive dyes

- Poor sublimation fastness.
- Lesser number of shades.
- Require more and skilled labors.
- More cost and technical knowledge is required.

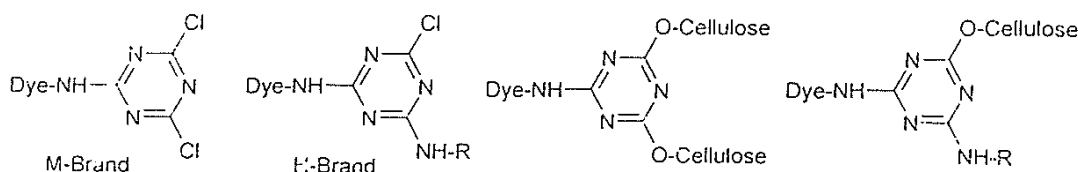
### 3.14.4 Classification of Reactive dyes

Reactive dyes are classified on the basis of types of reactive system present in to the dyes. **Reactive systems are mainly two types**

1. Nucleophilic substitution system (Mono and dichloro triazine, tri chloro pyrimidine etc.)
2. Nucleophilic addition system (vinyl Sulfone, acrylamide etc.)

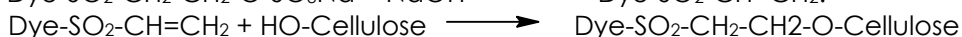
#### 1. Procion dyes

This **class of dye** contains **Cyanuric-chloride** as a reactive system. In alkaline condition it is applied and become part of substrate. They are mainly **two types M-brand** (Cold Brand) and **H-brand** (Hot Brand), e.g. Procion Brilliant Red-M5B (Aniline  $\rightarrow$  Cyanurated H-acid in alk.)



#### 2. Remazole dyes

The **basic structure** of dye is  $\text{Dye-SO}_2\text{-CH}_2\text{-CH}_2\text{-O-SO}_3\text{Na}$  (Sodium sulfato of ethyl Sulfone). It is first marketed by F-Hoechst in 1953 for Wool and Nylon. The sodium sulfato of ethyl Sulfone group is hydrolyzed by alkali and give vinyl Sulfone group which formed covalent bond with substrate.



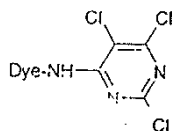
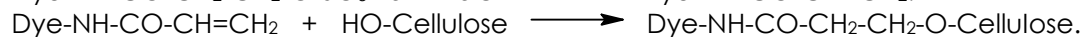
**E.g.** Remazole Brilliant Blue-R (Bromamine acid + m-amino phenyl sodium sulfato of ethyl Sulfone).

#### 3. Trichloro pyrimidine dyes

These dyes are derived from **trichloro pyrimidine**. The chlorine group at 2, 5 and 6 are reactive site through it can form a bond with substrate. General formula of dye is

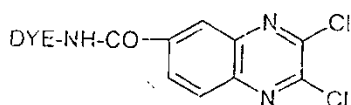
#### 4. Acrylamide dyes

Structure which yield **acrylamide-group** on **treatment** with **alkali**. These dyes are Nucleophilic addition reactive system type dyes and principally used for wool and cellulose dyeing.



#### 5. Quinoxaline derivative

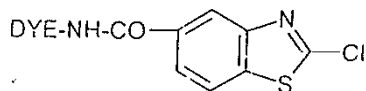
The general structure of this class is as under.



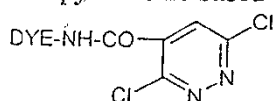
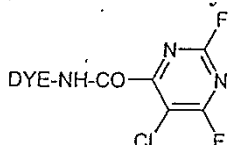
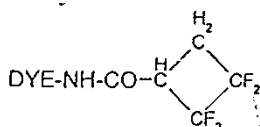
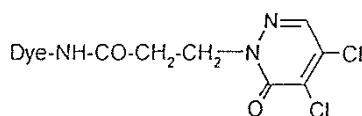
The reactive system is di-chloro quinoxaline. They are marketed as Leuafix by BAYER and Du-Pont.

**6. 2-Chloro Benzthiazole based reactive dyes**

The reactive system of this class is **2-chloro benzthiazole**. The general formula is as under

**7. Chloropyridazine based reactive dyes**

The general structure of dyes is as under and this class of dyes is marketed as Solidazole by BAYER and REATEX by Franc-Color.

**8. 2,6-difluoro-5-Chloro Pyrimidine based reactive dyes****9. Tetra fluoro butane based reactive dyes****10. 4, 5 dichloro-6-pyridazole based reactive dyes****11. Chloro acetyl or Bromo acetyl based reactive dyes**

These classes of dyes are mainly **used** for the **Wool dyeing**. On which halogen acetyl group is reactive system and marketed by CIBA and SANDOZ.

Dye-CO-CH<sub>2</sub>-X, Where X =-Cl OR-Br.

**3.15 DISPERSE DYES****3.15.1 Introduction**

Disperse dyes are **colored organic compounds**, which are only **very slightly soluble** in **water** and therefore, **dyeing** is carried out with **aqueous dispersion**. The disperse dyes have proved to be the **most successful type** of dye for the coloration of **cellulose acetate fibers** and are widely manufacturing in the form of powder or paste containing the requisite quantities of dispersing agent. It is **also used** on polyamide, poly-acrylonitriles, polyesters and cellulose triacetate.

Disperse dyes are essentially **low molecular weight derivatives** of azo, anthraquinone and other compounds. They **melt** at **above 150°C** and are **crystalline materials** which are ground with **dispersing agents** to produce **particles** of **0.5-4 μm** in **size** and which produce a stable dispersion in the dye bath. They are essentially **non-ionic** in **nature** and **contain** aromatic or aliphatic amino, mono and di-substituted amino and hydroxyl groups in their molecular structure. They have relatively low solubility in water under the dyeing conditions but it is at least 0.1 mg/liters.

**3.15.2 Dispersion**

Dispersion of disperse dyes can be achieved follows

- By using powerful dispersing agent.
- By attaching alkanol, carboxyl amide and other groups to the dye molecule,

- By using powerful dispersing agent. During the manufacturing, commercial disperse dyes are milled with a dispersing agent e.g. the sodium salt of a cresolnaphthalene sulphonic acid formaldehyde condensate plus a little sodium alkylnaphthalene sulphonate, thus enabling the particle size to be reduced to 2-4  $\mu$ , which is the maximum size for satisfactory dispersion.

### 3.15.3 Effect of Dispersing Agents

Certain dispersing agent are capable of **penetrating** cellulose acetate, but in view of the very small amounts involved it seems unlikely that the presence of dispersing agent within the fiber will have any appreciable effect on the rate of diffusion of the dye, although this would presumably not be the case if the effect of affinity or diffusion rate was appreciable.

Dispersing agents **increase** the **solubility** of the dye in the aq. phase, with **increasing temperature**, the **normal solubility** of the dye will **increase**, so that the effect of the dispersing agent in increasing the dyeing rate will be less marked. The dispersing agent also maintains a much more satisfactory dispersion thus penetrating the absorption of large particles of dye on to the surface of the fiber as well as assisting leveling by increasing solubility.

### 3.15.4 Leveling Agent

Selected **non-ionic surface active agents** can also be used to increase the solubility of disperse dyes in water. The results in the **following benefits**, particularly when dyeing is carried out at temperature below the normal boiling point:

- Increased **rate of migration**, leveling and fiber penetration.
- Increased **rate of dyeing** of the relatively insoluble, more complex dyes. This is of advantage when disperse dyes of better than average wet fastness are applied to acetate and nylon.
- Less **tendency for** listing and ending in jig dyeing.

### 3.15.5 Classification

Disperse dyes can be classified according to their application on different fibers such as polyester, polyamide, polyacrylonitrile etc.

**But chemically it can be classified into three well defined groups**

- The **azo group** containing mostly monoazo derivatives.
- The **nitrodiphenylamine derivatives**.
- The **anthraquinone derivatives**.

Beside the simple anthraquinone, many derivatives having attached carboxylic or heterocyclic rings such as benzantraquinones, benzantrones, anthrapyridones, anthrapyrimidines, anthrapyrimidones are reported to be disperse dyes.

Almost all the classes contain amino or substituted amino groups, but no solubilising sulphonic acid groups.

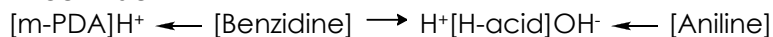
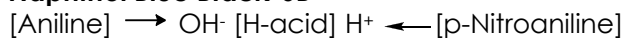
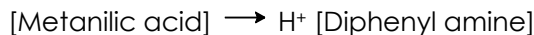
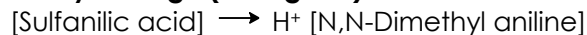
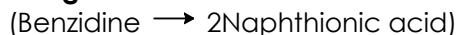
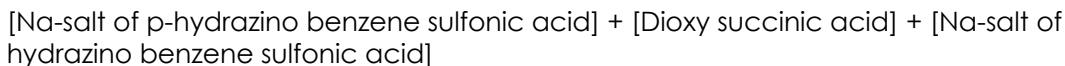
Generally the anthraquinone derivatives are used for deeper shades like red, violet and blue. The less deep shades are obtainable from the azo series. However Duranol Brilliant yellow G3, ICI (3-methoxy benzantrone) has been found to give yellow shade on cellulose acetate.

The shade of anthraquinone dyes for acetate depend upon the kind of auxochromes, their number and orientation, Auxochromes in the alpha position are more effective in shade changes, than those in the beta position. In general the effect of the auxochromes is additive. Introduction of substituent's such as halogen, hydroxyl, alkoxy, nitro, cyano, and other groups is reported to improve the fastness properties.

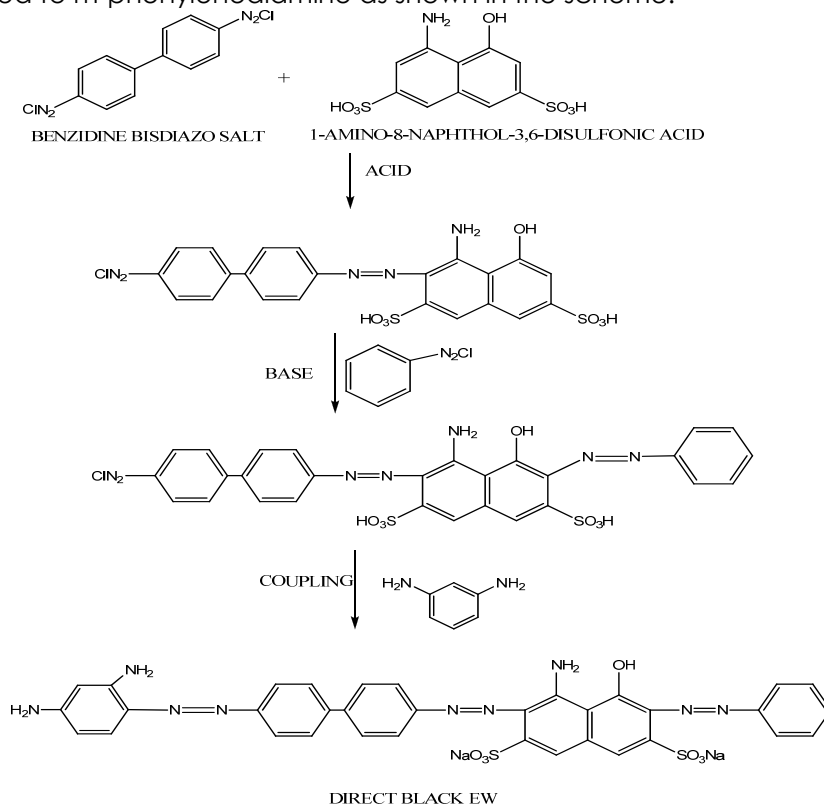
Strong salt forming groups and groups promoting water solubility generally decrease the affinity of dye.

#### Examples of Disperse dyes

- Disperse Yellow-3 (p-aminoacetanilide  $\rightarrow$  p-Cresol).
- Disperse Black-1 (p-NA  $\rightarrow$   $\alpha$ -naphthylamine).
- Disperse Yellow-9 (p-PDA + 1-chloro 2,4-dinitrobenzene).
- Disperse Yellow-11 (1, 4-diamino-2-methoxy AQ).
- Disperse Blue-1 (1, 4, 5, 8-Tetra AQ).

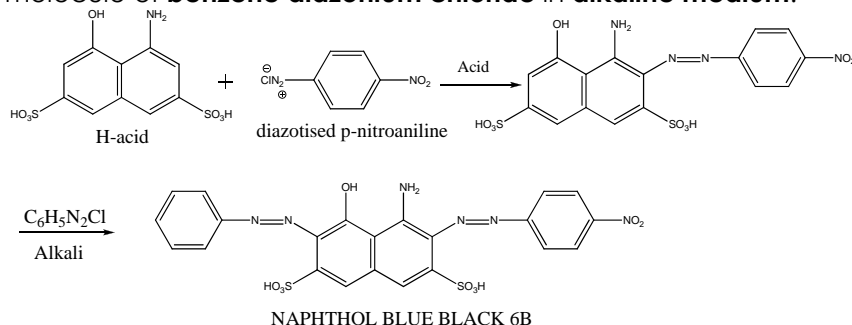
3.16 **IMPORTANT SYNTHESIS OF DYES**1. **Direct Black-EW**2. **Naphthol Blue Black-6B**3. **Metanil Yellow**4. **Methyl Orange (Orange-III)**5. **Congo Red**6. **Indanthrene Yellow-4GK (Indanthrone )**7. **Eriochrome Black-T**8. **Eriochrome Red-B**9. **Procion Brilliant Red**10. **Tartrazine**11. **Reactive yellow-3**1. **Direct Black EW**

It is **trisazo** type dye. Prepared by **first acidic coupling** of H-acid with benzidine tetraazo, **second alkaline coupling** of the monoazo dye on H-acid part with phenyl diazonium salt and lastly the **third acidic coupling** of the bisazo diazonium compound thus obtained to m-phenylenediamine as shown in the scheme.



## 2. Naphthol blue black 6B/ Amino black 1 OB)

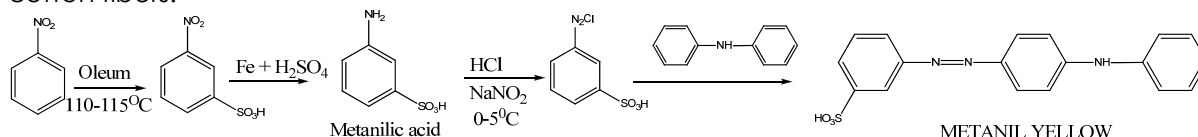
It is prepared by **coupling H-acid** ( 1-amino-8-naphthol-3,6-disulfonic acid) with one molecule of **diazotized p-nitroaniline** in an **acid medium** followed by **coupling** of the product with one molecule of **benzene diazonium chloride** in **alkaline medium**.



It is important acid dye used for dyeing wool for black shades of moderate fastness.

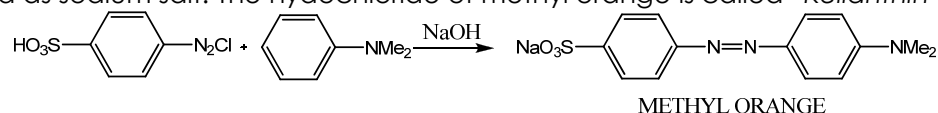
## 3. Metanil Yellow

It is **acidic azo dye**. The starting compound is **nitrobenzene**. It is **sulfonated** using oleum (fuming sulfuric acid) followed by **reduction** with iron and sulfuric acid gives metanilic acid. Metanilic acid is **diazotized** and **coupled** with diphenylamine gives metanil yellow. Since Diphenyl amine is insoluble in water, coupling reaction has to be carried out by emulsifying diphenylamine in water before coupling. Metanil Yellow is used for dyeing silk and cotton fibers.

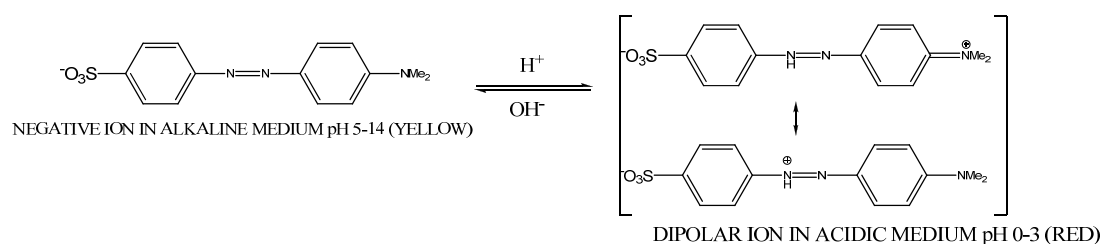


## 4. Methyl orange /orange III

Chemically it is sodium **p-dimethylaminoazobenzene - p' - sulfonate**. It is acidic azo dyestuff is obtained by coupling diazotized sulfanilic acid with dimethyl aniline. Dye generally isolated as sodium salt. The hydrochloride of methyl orange is called "Kelianthin"



Methyl orange is not generally used as dye because it is sufficiently fast to light and soap. However, Its sodium salt is used as indicator in acidimetry and alkalimetry because its sharp colour change over small pH range. It gives yellow colour in alkaline solution (above pH 4.4) and red in acidic solution (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.

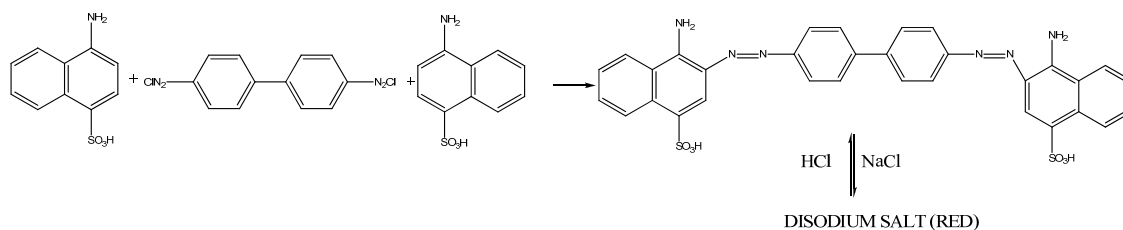


## 5. Congo red

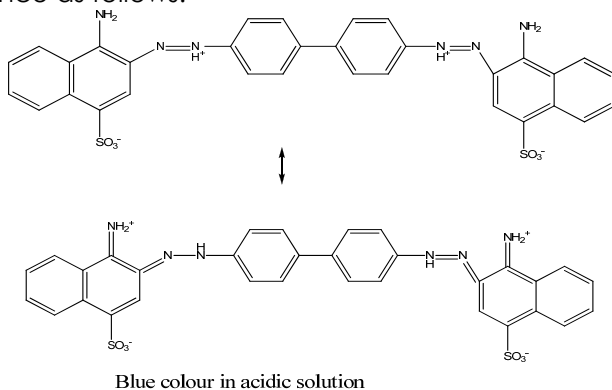
It is **Basic azo dye**. It is simple benzidine bisazo dyestuff. Prepared by **coupling** tetraazotised (bis diazotised) benzidine with two molecules of naphthionic acid. Blue dye so obtained is converted into its disodium salt having red colour using NaCl.

The **red salt** is capable of dyeing cotton only.





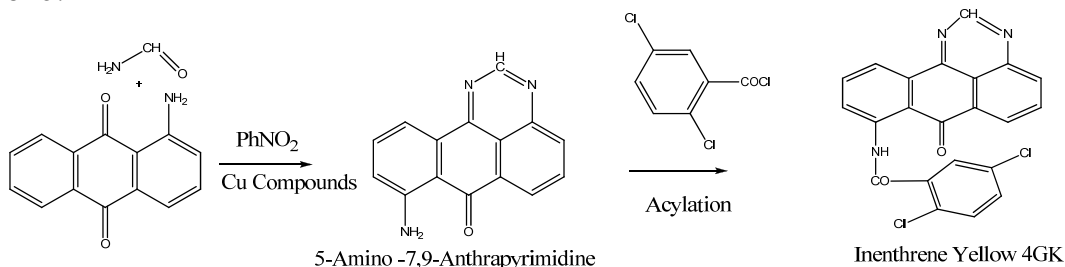
**Red salt** is very sensitive to acids, the colour turns from red to deep blue in the presence of strong mineral acid and dull purple in by organic acid. The change in colour from red to blue in the presence of inorganic acids may be explained due to occurrence of resonance as follows.



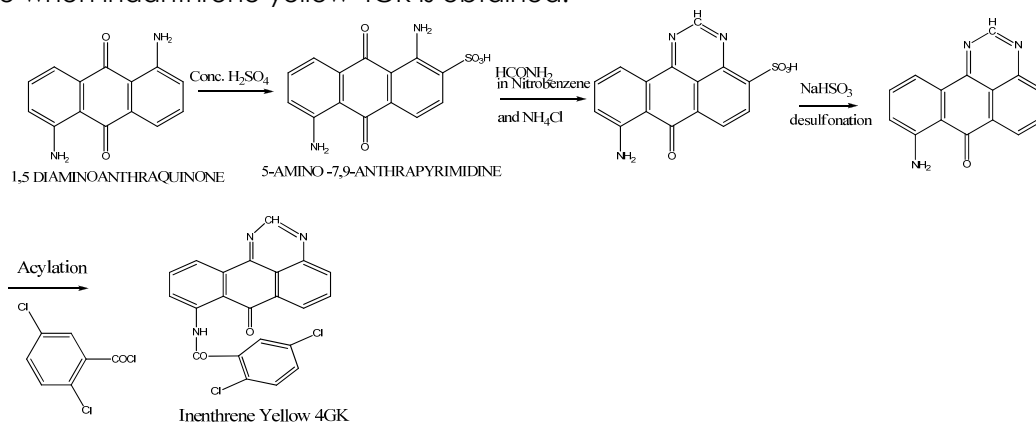
Congo red is used as an indicator in acid-base titration. Congo red paper is used for testing acidity of the solution.

#### 6. Indenthrene or Indenthrene Yellow 4GK

It is **anthraquinone vat dye**. Prepared by **condensing** 2,5-dichlorobenzoyl chloride with 1,9-anthra pyrimidine. The latter compound is obtained by condensing 1,5-diaminoanthraquinone with formamide in nitrobenzene solvent in the presence of copper compound.



It is also prepared from 1, 5 – diaminoanthraquinone which is sulfonated with conc.  $\text{H}_2\text{SO}_4$  to give 1, 5 – diaminoanthraquinone-2-sulfonic acid. The later compound on heating with formamide in nitrobenzene in the presence of  $\text{NH}_4\text{Cl}$  followed by desulfonation with  $\text{NaHSO}_3$  yields 5-amino-1, 9-anthrapyrimidine. This is acetylated with 2, 5-dichlorobenzoyl chloride when indanthrene yellow 4GK is obtained.

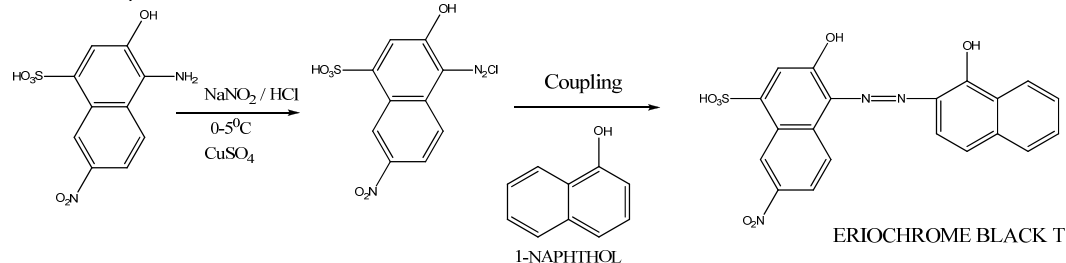


It is used as a vat dye. However it is no longer prepared.

### 7. Eriochrome Black T

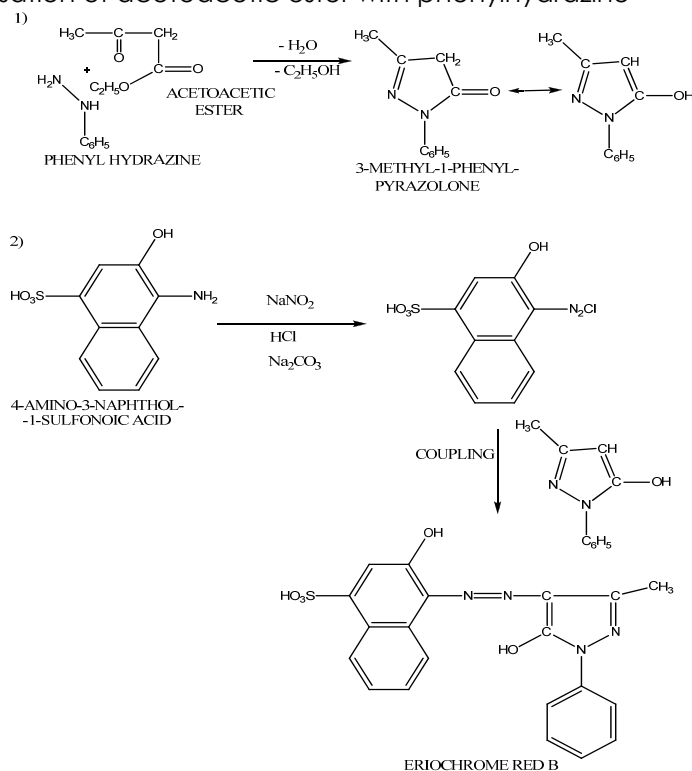
It is **mordant azo dye**. It is used in large quantities due to high light and wet fastness. Prepared by diazotizing 4-amino-7-nitro-3-naphthol-1-sulfonic acid in presence of a small quantities of  $\text{CuSO}_4$  followed by coupling the product with 1-naphthol.

It is mainly used as an indicator in EDTA titrations.



### 8. Eriochrome Red B

It is **mordant azo dye**. Prepared by **coupling** 3-methyl-1-phenyl pyrazolone with diazotised 4-amino-3-naphthol-1-sulfonic acid. 3-methyl-1-phenyl pyrazolone obtained by condensation of acetoacetic ester with phenylhydrazine



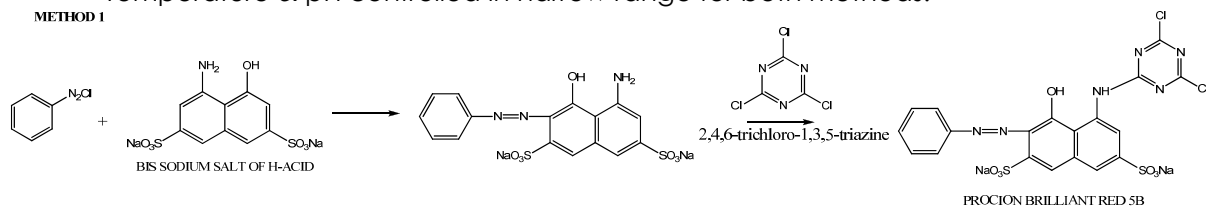
It is fast to light and washing.

### 9. Procion Brilliant Red 5B

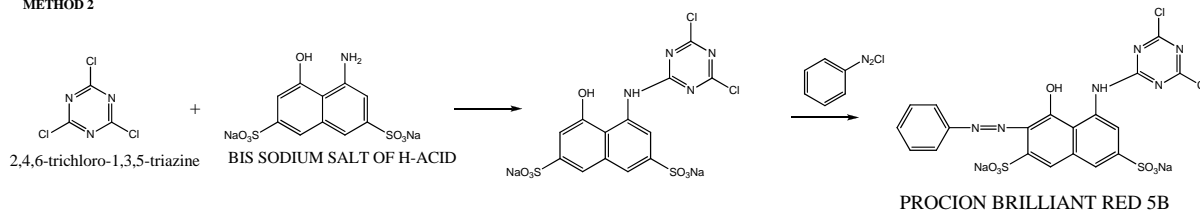
It is **reactive dye**. Prepared by **coupling** between phenyl diazonium chloride with bisodium salt of H acid. Resulting product then reacted with 2,4,6-trichloro-1,3,5-triazine gives Procion brilliant red 5B.

It is also prepared by reaction between 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride) and Na- salt of H-acid then coupling with phenyl diazonium chloride  
Temperature & pH controlled in narrow range for both methods.

METHOD 1



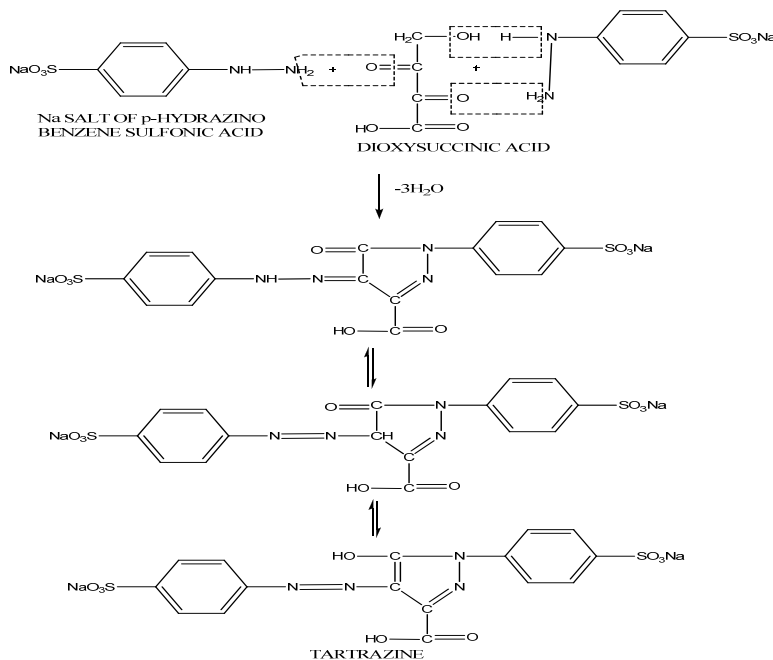
METHOD 2



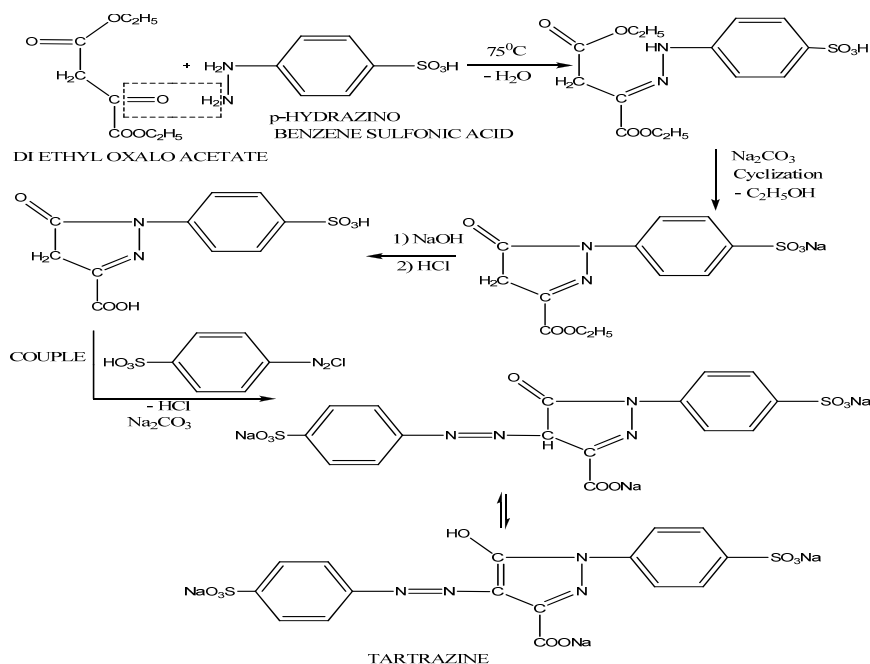
10. Tartrazine

It is an **acid azo dye**. Which may be prepared by the following **two methods**.

1. It may be **prepared by** condensing two molecules of p-hydrazino benzene sulfonic acid with one molecule of dioxysuccinic acid



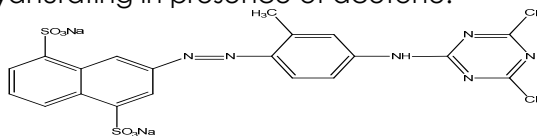
2. It may also, **prepared by** condensing one molecule of p-hydrazinobenzene sulfonic acid with one molecule of diethyl oxaloacetate . The product then coupled with diazotised sulfonic acid to yield tartrazine.



It is mainly used for dyeing wool fabric yellow with moderate fastness and silk with poor fastness.

### 11. Reactive Yellow 3

It is obtained by first preparing azo dye from diazotized C –acid and m-toluidine and then cyanurating in presence of acetone.



The diazotization of C –acid (1mole) is carried out by convectional method and the coupling with m- toluidine (0.99mole) is carried out in acidic medium. The pH of reaction mixture during coupling is found to have an appreciable effect on the colour and yield of the product. Since the diazonium salt of C – acid has a very low solubility in highly acidic conditions, so either increases the volume for smooth and complete coupling or raise the pH to above 5.4 to 6.0. Raising the pH increase the solubility of the diazonium salt coupling is more smooth and yield of final dye is also increased.

The cyanuration of the dye is carried out by preparing slurry of cyanuric chloride by dissolving it in acetone to made 20% solution and the solution then added to ice water mixture. The prepared solution used for cyanuration. The use of acetone reduces the time of cyanuration.

### 3.17 EXERCISE

1. Give an account of each of the following group of dyes with respect to mode of their application
 

	Each carry
1. Acid dye	2 or 3
2. Base dye	marks
3. Direct dye	
4. Mordant dye	
5. Vat dye	
6. Solubilised vat dye	
7. Sulfurized vat dye	
8. Solvent dye	
9. Disperse dye	
10. Sulfur dye	
  
2. Write the synthesis of each of following
 

	Each carry
1. Direct black EW	2
2. Eriochrome black T	marks
3. Tartrazine	
4. Congo red	
5. Naphthol blue black 6B	
6. Metanil yellow	
7. Indanthrene yellow 4GK	
8. Procion brilliant 4A	
9. Reactive yellow 3	
10. Methyl orange	
11. Eriochrome red B	
  
3. Define dye. Explain requisites of a true dye 05
4. Write a notes on
 

	Each carry
1. Bathochromic auxochromes	2 or 3
2. Hypsochromic auxochromes	marks
3. Dependent and independent chromophores	
4. Postulate of valance bond theory	
5. Armstrong's theory	
6. Witt's theory	
7. Baeyer's theory	

8. Anthraquinone dye
9. Reactive dye
10. Azo dye
11. Classification of azo dyes
12. Methods of diazotization
13. Solubilised vat dye
14. Stabilized azo compounds
15. Mordant dyes
5. Discuss the role played by change in dipole moment in explaining the colour of substance 03
6. Give a brief account of different theories that explained the relation between colour and chemical constitution 07
7. Give reasons Each
  1. Benzene is colourless, nitrobenzene is pale yellow whereas p-nitro aniline is orange carry
  2. Ethylene is colourless whereas  $\beta$ -carotene is orange red 3
  3. Acetone is colourless, diacetyl is yellow and triketopentane is orange marks
  4. p-amino azobenzene is yellow but in acidic solution it becomes violet
  5. p-amino triphenylmethane is colourless whereas Doebner's violet is deeply coloured
  6. p- nitroaniline is colourless but yellow in alkaline solution
8. Give classification of dyes on the basis of their mode of application 05
9. What mean by reactive dyes? Give its detail classification 04

### **3.18. FURTHER READING**

1. Synthetic dyes by Gurdeep R. Chatwal