

Natubhai V. Patel College of Pure & Applied Sciences
B.Sc. Semester VI
Industrial chemistry/Industrial chemistry (Vocational)
US06ICH01/US06CICV01: Dyes and intermediates
UNIT – 1

SYLLABUS

Introduction, Classification of Dyes on the basis of mode of applications to the fibres and chemical constitution of the Dyes. Applications of Dyes to fibres, colour shades and fastness properties

1.0 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.

1.1 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.

1.2 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

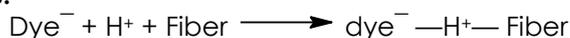
1.2.1 Classification of dyes according to application

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 give 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 dye **require a pretreatment** of **fiber** with a mordant which bind the dye. The **mordant** gets attached to the fiber and then combines with the dye to form an **insoluble complex** called a '**Lake**'. **Mordents** 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.

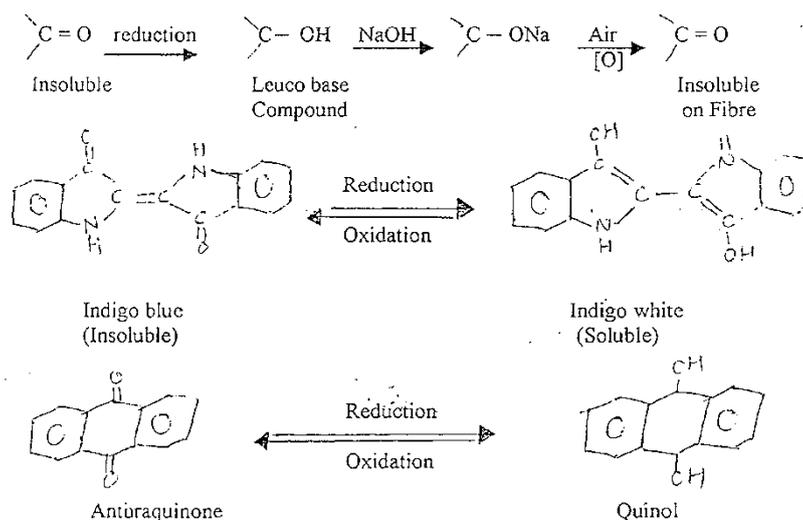
7. Ingrain Dyes

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. Sulfur Dyes

These dyes are **insoluble dyes** and when **reduced** with sodium sulfide they become **soluble**. These dyes are adsorbed on the fiber and on exposure to air they are **deoxidized 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.

Sulfur dye **contain sulfur 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 -NH₂ 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.

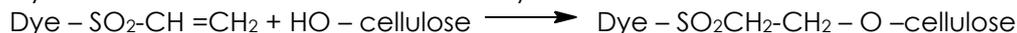
E.g. Cellitone scarlet B and cellitone fast violet 6B

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

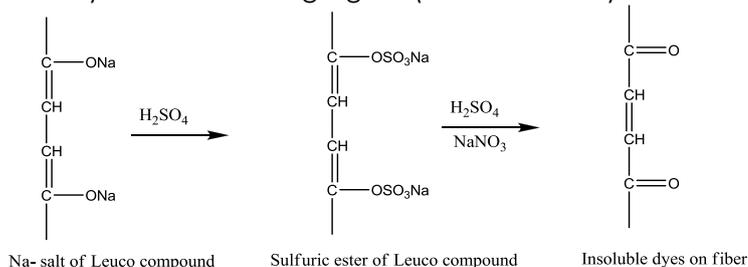
used in manufacture of stains, varnishes, inks, lacquors, typewriter ribbons, candles, shoe polishes, soap and cosmetics etc.

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.

1.2.2 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	—	Safranine 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

1.3 COLOUR AND CHEMICAL CONSTITUTION

1.3.1 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.

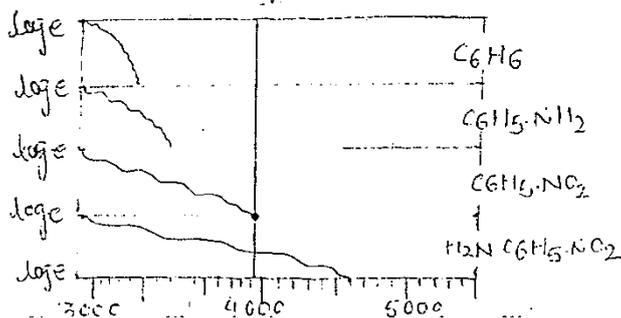


Figure: Absorption spectra of benzene, aniline nitrobenzene and p-nitroaniline

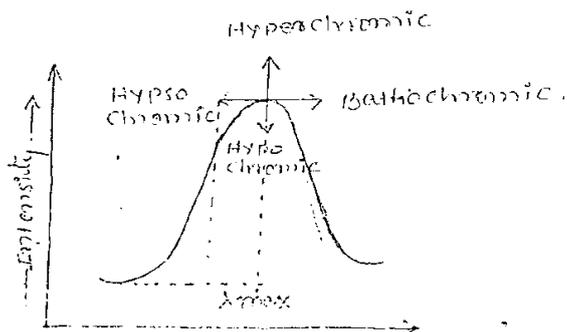
If a **structural change** in a dye molecule **shifts** the **absorption** from higher to **lower wavelengths**, it will lighten the colour of the dye in accordance to the following sequence

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**

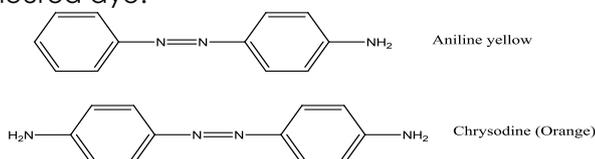
Changes in the structure of a dye due to which the **intensity of absorption increases** are said to be **hyperchromic** on the other hand, structural changes which **decrease the intensity of absorption** are termed as **hypochromic**.

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 -NH₂ groups in a dye molecule. For example, when an additional -NH₂ 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 pararosaniline (red dye) nucleus to give crystal violet(violet colour)
 - NH₂ → —NH(CH₃)₂ Bathochromic effect
 - OH → —OCH₃ or —OCOCH₃ Hypsochromic effect
- 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.
 - NH₂ → —NH₃⁺C1⁻ and —OH → O⁻Na⁺ Bathochromic effect

1.3.2 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°A**. 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°A						8000°A	

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

1.3.3 Relation between colour and chemical constitution

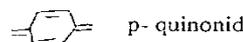
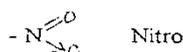
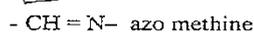
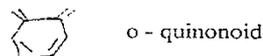
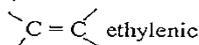
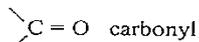
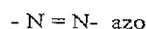
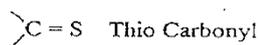
The colour of compound is related to its chemical constitution. **Graebe and Libermann** have stated that **reduction** of coloured organic compound results in the **loss of colour** and **oxidation** of the reduced compound **regenerates** the **original colour**. Hence they concluded that unsaturation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

1.4 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**.

1.4.1 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



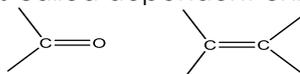
There are **two types of chromophores**

1.4.1.1 Independent chromophores

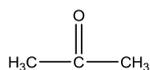
When a **single chromophores** is sufficient to impart colour to the compound, then it is called independent chromophores e.g. -N=O, NO₂, -N=N, -N=NO, -N=N-NH, p-quinonoid etc.

1.4.1.2 Dependent chromophores

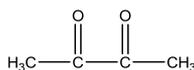
When **more than one chromophores** are required to impart colour to a compound, then it is called dependent chromophores



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



Acetone (Colourless)



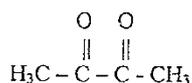
Biacetyl (Yellow)

Similarly Diphenylpolyenes having formula

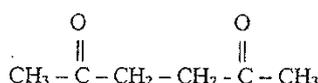
Ph-(CH = CH)_n-Ph here if,

- 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**.

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

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

1.4.2.1 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.

1.4.2.2 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.

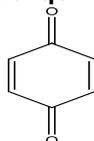
1.5 ARMSTRONG'S THEORY

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

- **Benzene is colourless whereas benzo-quinones are coloured**

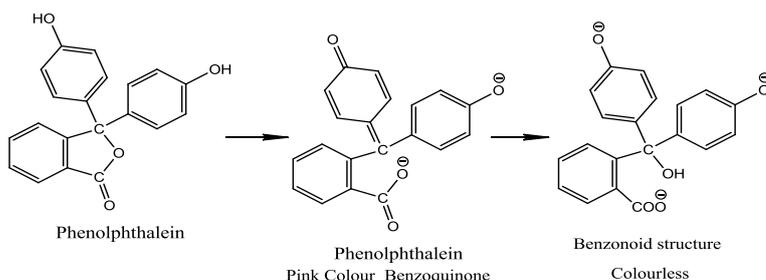


Benzene (colourless)



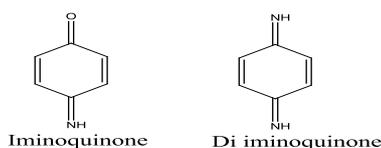
p-benzoquinone (yellow)

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

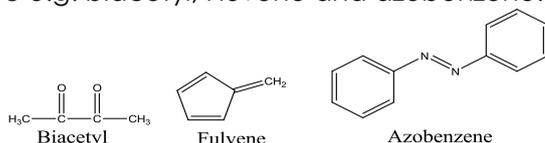


1.5.1 Limitations

- 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**.

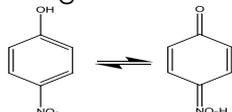


There are other **compounds**, which are **coloured, but do not have quinonoid structure** e.g. biacetyl, Fulvene and azobenzene.

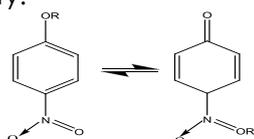


Armstrong attempted to explain the colour of **p-nitrophenol**, on the basis of **quinonoid structure**, but there was **no evidence** for their **existence of a structure**.

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.

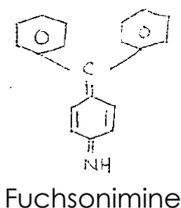


For example the groups $-\text{NO}_2$ and $-\text{ONa}$, both are present then impart colour, but if present alone do not do so. This means that the two groups must be interchange to yield a new structure for the molecule. This phenomenon is known as chromo-isomerism.

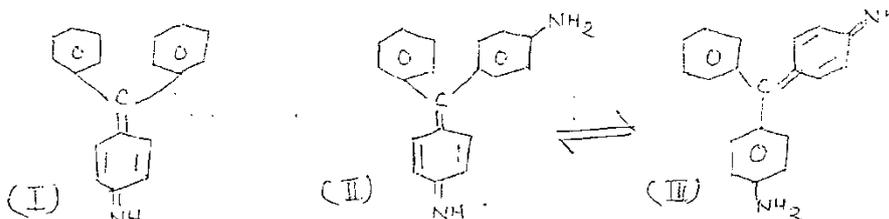
1.6 BAEYER'S THEORY

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.



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



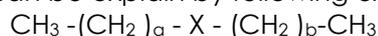
Fuchsonimine (Colourless)

Doebner's Violet (Coloured)

1.7 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.

1.8 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.

1.9 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,

ΔE = Quantum energy

h = Plank's constant

E_1 = Energy of excited state

λ = Wavelength of the absorbed radiation

E_0 = Energy at ground state

c = Velocity of light

v = Frequency of light

The **amount of energy absorbed** i.e. ΔE **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 ΔE lie between 71.0 and 35.5 kcal/mole as we go from 4000 to 8000 \AA .

As the electrons occupy definite orbital, it means that ΔE 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 consist of a 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 bands because of the value of E which is 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 the molecule absorbs light very slowly, and vice versa. Thus if the group which is introduced in a molecule, decreases the symmetry and increases the transition dipole of the molecule, the intensity of the absorbed light will increase.

1.10 VALENCE BOND THEORY OR RESONANCE THEORY

1.10.1 Postulates of theory

The π -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 π -electron of the **aromatic ring**. This increase in resonance **increases** the **intensity of absorption of light** and shifts the absorption band 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.
 $N=O > C=S > N=N > C=O > C=N > C=C$ (light)
 ← Dark

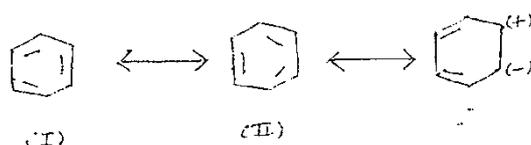
The colour deepens in the opposite direction.

- 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.

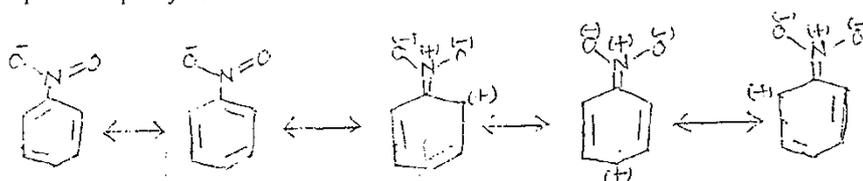
1.10.2 Consider the following examples.

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

In benzene, **two Kekulé 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**.

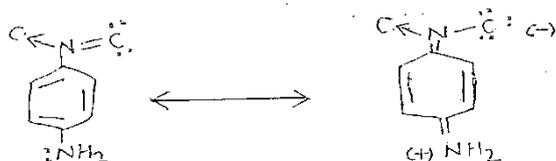


In **nitro benzene** charged structures contribute much more to its **resonance hybrid**. And due to **loss of symmetry** of the molecule, the absorption is shifted to longer wavelength, thereby producing **pale yellow**.



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**.

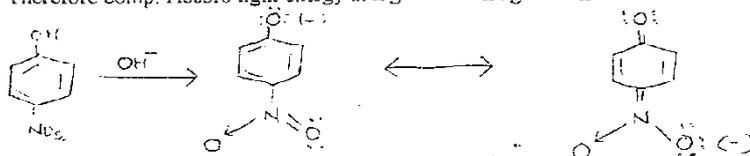


The **comparison** of the **dipole moment** for nitrobenzene (0.21D) aniline (1.48D) and p-nitroaniline (6.1D) also gives an idea that there is relatively high contribution of the charged structure to resonances, hybrid of p-nitro aniline.

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

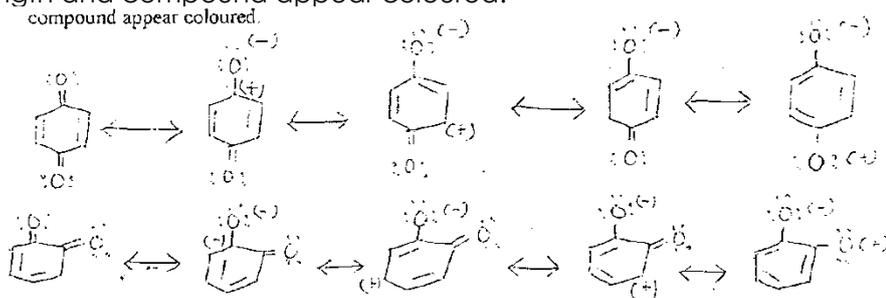
b) Pure p-nitrophenol is colourless but yellowish in alkaline solution.

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.

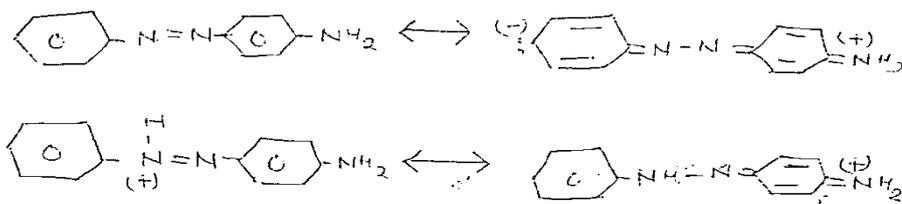


c) p- or o-quinones has yellow colour which can be explained by resonance theory

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.

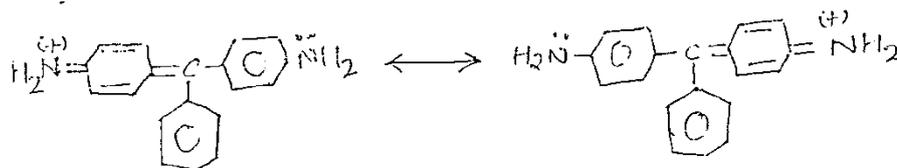


d) Explain p- aminoazobenzene is yellow but in acidic solution it becomes violet.



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.

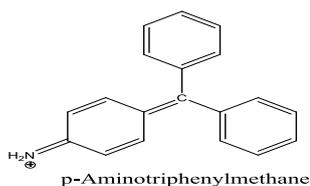
e) All the triphenylmethane dyes has much deeper colour this can be explain by resonance theory.



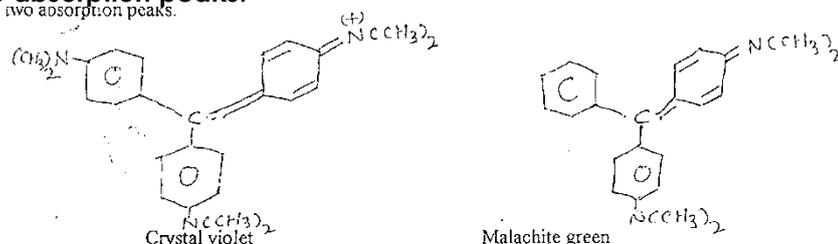
Doebner's violet

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 (λ_{max} 5900 \AA) while malachite green has two absorption peaks.



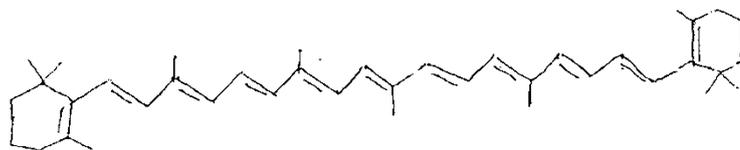
Malachite green, the molecule is **unsymmetrical** and as **two axes of polarisability** differing in degree lying at right angle, also here the possibility of the **oscillation for +ve charge is restricted to two benzene ring**, hence it shows **two peaks** at 4230 - 6250 \AA .

Crystal violet has **center 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

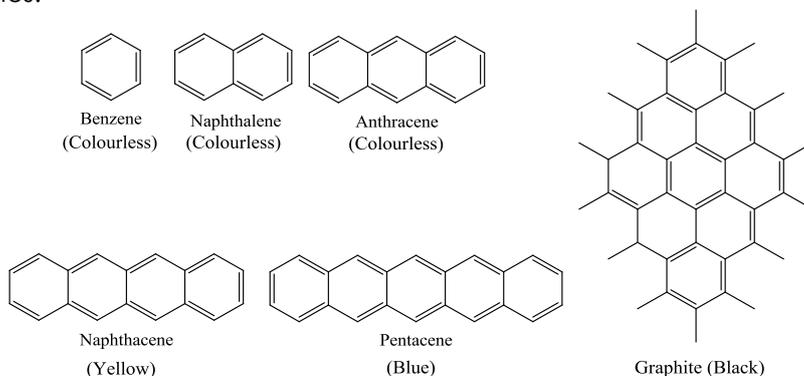
The **longer** the **conjugation** in a molecule, the **deeper** will be the **colour** because the conjugation system of the **double bonds** provides a **long path** of resonance. This **shifts** the **absorption to longer wavelength**. E.g. diphenylpolyenes. The colour change as 'n' increases which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



β - 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.

1.11 MOLECULAR ORBITAL THEORY

According to this theory, the excitation of a molecule means the transference of one e-from an orbital of lower energy to higher energy. This electrons may be σ , π or n.

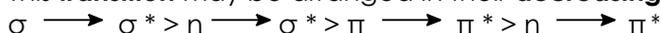
The higher energy states are commonly known as "Anti bonding" orbital. It's association with σ and π bonds are called σ^* and π^* but there are no antibonding orbitals associated with 'n' electrons because they do not form bonds.

σ^* Anti bonding
π^* Anti bonding
n Loan pair, non-bonding
π Bonding
σ 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) $\sigma \rightarrow \sigma^*$ (2) $n \rightarrow \sigma^*$ (3) $n \rightarrow \pi^*$ and (4) $\pi \rightarrow \pi^*$

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



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

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

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

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

Considered the data of following table

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

From above absorption it is concluded that as conjugate of double bond increases, energy required for $\pi \rightarrow \pi^*$ 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 NO₂ 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.

1.12 DYEING

The **process** which is used to **transfer the color to the substrate using dyes** is generally known as **dyeing**. A colored substance is useful as a dye only if it can be attached to a fiber. The **method of applying a dye depends** upon the following **three** important factors.

- Type of the dye
- Nature of the dye
- Type of the fiber

Wool and silk may be regarded as **amphoteric proteins** and they have a **natural affinity** for substances containing **acidic or basic groups** with which they react as a result of salt formation. In other words, dyeing properties of wool and silk are similar and both of them can be **dyed directly** by introducing into a solution of either an acidic or a basic dye.

Cotton, linen and rayon's, on the other hands are composed of natural cellulose molecules. They **do not show** any **affinity** for many dyes direct to wool and silk. They may however, **react with substances** known as **substantive dyes**. Cellulose fibers, such as cotton, linen etc. can also be dyed by making use of processes of vatting, mordanting and formation of dye on the fiber.

1.13 TYPES OF FORCES INVOLVES DURING DYING OF FIBER

The dyeing of fiber involves one or more of the following types of forces

1.13.1 Ionic interactions

These interactions are **due to ionic sites of opposite charge** in the fiber and the dye molecules, **E.g.** Dyeing of wool with acid dyes having fairly simple structures involves the formation of salt type chemical links between dye anions and cationic groups in the fiber. The resulting dyeing; however, had poor fastness to wet treatment, because the salt type chemical links formed between dye anion and cationic fibers can be broken easily. **Basic dyes** are **attached to** silk, wood, or acrylic fibers containing anionic sites through the salt type linkages. **Fastness to washing** on wool as well as silk is rather **poor in majority of cases**, but **good** in cases of **poly acrylonitrile fibers**. This probably due to partly in differences in the strength of salt bonds and partly to the hydrophobic nature.

1.13.2 Hydrogen bonds

The hydrogen bonds are involved in dyeing of wool, silk and manmade fibers. **Several hydrogen bonds formed** between the dye molecule and the structure of fiber at a time are responsible for strong holding of the dye molecule to the fiber structure. The dyeing of cellulose cannot be explained on the basis of hydrogen bonding, because water has more affinity for cellulose than dye molecule.

1.13.3 Vander Waal's Interaction

In dyeing, Vander Waal's interactions take place **because of interactions** between **π orbital's** of the **dye** and the **fabric molecules** in linear fashion. These interactions become stronger between similar groups, **e.g.**, alkyl, aryl in polyester dyes. The dye will attach to the fiber only when the total effect of Vander Waal's interaction becomes greater than a critical requirement. Moreover, Vander Waal's forces are **effective only** when the dye and fiber are brought in contact by salt type link or by some other means.

1.13.4 Covalent bonds

Such **bonds are formed** between **dye** and **fiber molecules** because of the reactions between a reactive dye and a group such as -OH. These dyes are fast to washing. For example, when a reactive dye having dichloroazine reactive system is brought in contact with a cellulose structure, possessing alcoholic hydroxyl groups, one of the chlorine atoms undergoes reaction with the -OH groups of the fiber and dye is attached to the fiber through covalent bonding.

If **dyeing** is done is **aqueous medium**, one Cl atom is replaced by the oxygen atom of -OH groups present originally in the cellulose, while other Cl atom is replaced by -OH groups by reaction with water.

On the **basis of various types of interactions** taking place between fiber and dye, it may be **concluded that**

- **Cotton** may be dyed by direct dyes, vat dyes, sulfur dyes, ingrain dyes, reactive dyes, solubilized vat dyes and pigment emulsions.
- **Silk** may be dyed with direct dyes, mordant dyes, acid dyes, and basic dyes.
- **Wool** may be dyed with acid dyes basic dyes, reactive dyes and acid mordant dyes.
- **Polyae fibers**-such as nylons may be dyed with acid dyes, disperse dyes and disperse reactive dyes.
- **Polyester fibers** may be dyes only with disperse dyes.
- Modified polypropylene fibers are dyed with only specially-selected dispersed dyes.
- **Polyacrylonitrile** fibers may be dyed by cationic dyes or disperse dyes with some limitations.

1.14 CROSS DYEING

The **versatility** of the **new fibers** has now been **increased by incorporating dye sites** of varying nature in order to achieve dyability with a predetermined class of dyes. Polyesters, acrylics, polyamide fibers etc. have now been manufacturing in such a manner that they can be dyes with basic, cationic, acid, anionic or disperse dye. Textile fabrics and carpets etc are now fabricated in such patterns that they can be dyed with **three different colours** from **one dye bath** having **three different types of dyes**. The process is **known as cross-dyeing** and has become popular as a low cost or cheap method or coloration.

1.15 BASIC OPERATIONS IN DYEING

The basic operation of the dyeing process involves the following important steps:

1.15.1 Preparation of the fiber

The **raw fibers** are generally **associated** with **foreign materials** such as oils, waxes, lubricants etc used during spinning. The fibers are also associated with **sizing materials** and **dirt possessing**. The fibers are **thus scoured with soap** and **detergents** before they are subjected to dyeing. This step **helps** the dye liquor **to penetrate** through the fibrous material and hence gives **uniform** and **level dyeing**. There are various important factors such as nature of fibers, depth of the shade and the processing material to which the dyed material is subjected to, on which this treatment depends.

1.15.2 Preparation of the dye bath

The dye bath can be **prepared by** adding **requisite amount of chemicals** and other necessary **ingredients** to the solution of **water soluble** acidic, basic, and direct dyes. The **insoluble vat dyes** in the dyeing bath are necessary to be reduced with alkaline hyposulfite in order to convert them into soluble leuco compounds. The fibers are air oxidized after dyeing as a result of which original colour is developed on the fibers.

In addition to dye, some **other ingredients** such as wetting agents, carriers, salts, etc have also been added to the dye bath to improve certain properties. **E.g.** Carriers improve the rate of dyeing of hydrophobic fibers like polyester fibers, because they act as swelling agents. The colourless retarders slow down the dyeing process to the desired level by competing with dye for the reactive sites on the fiber. When wool is dyed with acid dyes, acetic acid is used as a retarded.

1.15.3 Application of the dye

The **fiber** is dyed by **immersing** in the **dye bath** for a **special period** and at **optimum temperature**. In case of level dyeing, **stirring** is also necessary because **level dyeing** shows uniformity of the dye on the fiber and generally **depends upon three** following factors.

- Nature of dye.
- Absorptive power of fiber.
- Condition of the dyeing.

Dyeing can be carried out either by **hand operation** or on a **machine**. In **hand operation**, the fibrous material is moved in an open vat containing the dye colour. The **process on a machine** is continuous and **two types** of dyeing **machine** are generally used. In **one type** of continuous dyeing process, the dyeing bath is maintained stationary and the

fabric is moved in it. This agitates the liquor placed, in the dyeing bath. The excess dye is squeezed out by passing the yarn or fabric through a pair of rollers. In **second type** of continuous dyeing process, the fabric is properly supported and dye liquor is allowed to pass through it under pressure in one direction. The direction of flow of dye liquor is reversed at regular intervals. As the dyeing continues, there is a gradual decrease in the concentration of dye but there is a gradual increase in concentration of dye on the fiber. A stage is reached when dyeing bath contains almost no dye and then it is said to be exhausted.

1.15.4 Finishing

Dyed fibers are finally finished by making use of a **number of finishing process**. These processes are **used to produce** luster, resistance to shrinkage, crease, and other desirable qualities of feel and appearance.

It should be noted that **dyeing processed** are generally performed **using water** as the medium, hence **water should** be very pure as well as soft. The sequence of operations may also be different for different fibers. **E.g.** in the dyeing of wool, finishing treatment is carried out first and then dyeing operations are performed. In dyeing of cotton, dyeing process is performed between two preparatory treatments.

1.16 GENERAL METHODS OF APPLICATION OF DYES ON FIBRE

A **coloured substance** may be **used as a dye only** if it can be **attached to a fiber**. The method of applying a dye depends upon:

- Nature and type of dye
- Type of fiber.

For wool and silk are amphoteric proteins and have affinity for substance containing acidic or basic groups with which they combine by salt formation. Wool and silk have similar dyeing properties and can therefore, be dyed directly by introduction into a solution of an acidic or a basic dye. Example of direct dyes for wool and silk are Meldolas Blue, methylene blue, Martius yellow, Alizarin etc.

Cotton, nylon and rayon are composed of natural cellulose molecules and show no affinity for many dyes direct to wool and silk. **Cellulosic fabrics** can be dyed by vatting, mordanting and formation of dye on the fiber itself. They are also expected to combine with substantive dyes by adsorption or hydrogen bonding.

The **vat process** and one process for **indirect application of azo dyes** are conducted in **alkaline solution** and cannot be used for dyeing **wool** and **silk** because these are very sensitive to alkali.

Cellulose acetate and **nylon** are almost neutral solution and differ from cellulose because they have no hydroxyl groups available for hydrogen bonding. Hence cellulose acetate and nylon are hydrophobic fiber which are resistant to the usual cotton dyes.

Cellulose acetate and nylon are best dyes from an aqueous dispersion of a water insoluble azo or anthraquinone dye in presence of soap acting as dispersing agent. The dye enters the fiber in the form of a solid solution. Dyes containing free amino and hydroxyl groups have affinity for hydrophobic fibers under these conditions.

1.17 METHODS OF DYEING

1.17.1 Direct dyeing

Direct dyeing mainly **depends upon** the following important factors.

- Absorptive power of the fiber
- **Nature** of the fiber
- **Dyeing condition**

Moreover, the **dye** applied should be **fast to** light, washing, bleaching and other treatments. We have seen that wool and silk can be dyed directly either by acidic **or** basic dyes. In order to get faster and brighter shades, mordant dyeing is usually preferred. The dye **bath** can be **prepared by dissolving** the **dye** in **cold water** and then **adding** small amounts of

Na_2CO_3 and H_2SO_4 or CH_3COOH . The fabric to be dyed is then introduced into the dyeing bath and temperature of the bath is gradually increased to 60°C . Now some exhausting agents such as NaCl or Glauber's salt is added and temperature is further raised to boiling. After the dyeing is complete, the fabric is rinsed cold and dried. The **washing fastness is improved by after treatments** of the dyed fiber in a separate bath. These **treatments include**

- Development with diazonium salts.
- Diazotization and development.
- Treatment with HCHO .
- Treatment with copper salts.
- Treatment with chromic fluoride or sulphate etc.

There are **various fibers** such as cotton, linen and rayon which **do not show** much **affinity** for many dyes which are used for dyeing **wool** and silk. **These fibers** can however be **dyed** with **substantive dyes** by direct dyeing process. The dye is first dissolved in hot water, 5-20% Na_2SO_4 and 0.5-2% Na_2CO_3 are added to the dye bath. Fibers are now introduced in the dyeing bath and temperature of the bath is raised first to 60°C and then to $80-85^\circ\text{C}$. Complete dyeing takes place in about an hour.

Synthetic fibers, being hydrophobic are resistant to cotton dyes. These synthetic fibers can however be dyed efficiently from an aqueous dispersion of water insoluble anthraquinone or azo dye in presence of soap or a dispersing agents. As a result the dye enters the fibers in the form of a solid solution.

1.17.2 Vat dyeing

Vat dyeing is one of the good methods of **dyeing cotton** with **very insoluble natural dye** indigo. The process depends upon the fact that indigo is **reduced to a** colorless di-hydro or **leuco derivative**, which is soluble in alkali. When fabric is immersed in the alkaline solution of a reduced dye (vat), the leuco compound is adsorbed and on withdrawal and exposure to the air is **oxidized to** the dye. The latter gets fixed to the cotton-fiber or cloth. Satisfactory results are obtained when leuco compounds or anion had affinity for the fiber through hydrogen bonding. The reducing agent used for reduction of dye is $\text{Na}_2\text{S}_2\text{O}_4$ (sodium hydrosulphite).

For vat dyeing, the **dye bath** is generally **prepared by adding** the **paste of dye** in **water** and a **dispersing agent** to **water** which **contains** caustic soda and hydrosulphite. Such dyes are called vat dyes. There are at present several hundred such dyes other than indigo. Vat dyes are quinonoid substances that can easily reduce to hydro-quinoid compounds re-oxidisable by air. **Vat dyeing** is now carried out by **a continuous process**. The cotton cloth from a roll is conveyed over a system of rollers into a solution of reduced dye, where the cloth is impregnated with vat liquor. It is then led into a chamber where a leuco compound is properly fixed to impregnated fabric by steaming and acetic acid or per-borate. The fabric is finally passed into soaping, rinsing and drying baths.

Thus vat dyeing is carried out **partly by a continuous process** in which cotton cloth is impregnated with vat liquor. It is then steamed for proper fixation of leuco compound to the fabric and then passed through a bath containing oxidizing agents such as chromate, and acetic acid or per-chlorate. As a result, colour is generated; finally it is soaped, rinsed and dried.

1.17.3 Mordant dyeing

In this method cotton is dyed in such a manner that acidic or basic groups capable of combining with a basic or an acidic dye are fixed on it. The **processing agent between cloth and dye** is called **mordant** and hence the **process** is called **mordant dyeing**.

Alizarin is a principal coloring material of this class. For **production of colour** known as **Turkey red, cotton was impregnated first** with rancid oil, olive oil containing lime and **then with** a solution of aluminum sulphate and **finally steamed**. The **mordanted cloth** was then treated with aqueous suspension of the dye. The colloidal metal hydroxide adheres to the fiber and dye molecule reacts with metallic mordant to form **a complex salt or lake**. This **process** is however very much **time consuming** and takes about **4 months** for completion.

In **modern methods, sulfonated castor oil** is used **instead of olive oil**. The colour can be varied by using other metals. For example chromium mordant gives brownish red colour and iron mordants give violet colour.

Wool and **silk** can also be dyed by the same method. Dyes of a number of chemical types can be applied to cloth mordanted with metal oxides which provide basic groups to the fiber. Acidic groups suitable for binding basic dyes can be affixed to cotton by impregnating cotton cloth with tannic acid which is fixed on the fiber with potassium antimonyl tartrate, tannic acid contains a number of acidic groups some of these are bound as antimonyl groups in fixation, while other are free to bind basic dyes (tri-phenyl methane).

1.17.4 Substantive dyeing

Congo red is a substantive dye capable of dyeing cotton directly. It is fugitive and so sensitive to acid.

1.17.5 Disperse dyeing

Disperse dyeing which was **originally developed** for **cellulose acetate** and **polyacrylate fibers**, has **now** been **used** for **polyester fibers**. In this type of dyeing the **dye is pasted into the fiber** with **water** at about **35-40°C** and then **suitable dispersing agent** and **carrier** such as biphenyl, o-phenyl phenol or trichlorobenzene are added to the dye bath and temperature of the dyeing bath is raised to **80°C**.

Disperse dyes have also been applied by a dry heat or thermosol process to the polyester fiber.

1.17.6 Formation of dye on the fiber

Azoic dyes are produced **inside textile fiber** by **azo coupling**. The process consists in impregnating the fiber with an alkaline solution of the coupling agent and then treating the coupling component simultaneously from aqueous dispersion. Finally the product is treated with nitrous acid to develop with colour.

1.17.7 Dyeing with reactive dye

Impregnation by padding and **dyeing in dye bath** are the two important methods which are used for **dyeing fiber with reactive dye**.

In **impregnation method**, the dye is dissolved in one vessel and wetting agent, Na_2SO_4 and sodium bicarbonate are dissolved in another vessel. Before dyeing bath solutions are mixed and cotton fabric is padded through the mixed solution and then dyed above 100°C the NaHCO_3 liberated the alkali which is capable of fixing the reactive dye on the cotton fabric. Na_2SO_4 prevents the movement of dye during drying.

Dyeing in dye bath with certain reactive dyes can be performed in cold, using 2-3% of the dye in presence of relatively high concentration of NaCl .

1.17.8 Formation of dye on the fiber

Azo dyes can be applied to **cotton fibers** by **soaking cotton** in an **alkaline solution** of phenol and then in an **ice cold solution** of a **diazonium salt**. The **azo dye** is developed **directly** on the **fiber** and azo dyes **applied in this manner** are **called ice colours**.

In **ingrain dyeing**, the cotton impregnated with an amine is diazotized and then developed by immersion in a solution of phenol. The **first ingrain dye** was **Primulin Red**.

Dyes on fiber are also **produced** by **oxidation of aromatic amines**. E.g. aniline black is made by impregnating cotton with aniline hydrochloride solution, an oxidizing agent, an oxygen carrier and hygroscopic salt. The cloth is dried at 35°C . The dark bottle green coloured fabric is then immersed in a bath containing aniline, dichromate, diluted H_2SO_4 and finally dried at about 80°C . Jet black coloured aniline black dye is produced on the fiber.

1.17.9 Dyeing of wool with acid dye

Dyeing of wool with acid dyes can be carried out by preparing dyeing bath in which dye is dissolved in cold water and small quantities of Na_2SO_4 and H_2SO_4 or CH_3COOH are added. The fiber is now introduced in to the bath and temperature of the bath is gradually raised. The complete dyeing takes place in about 90 minutes at the boiling temperature. The dyed fiber is rinsed and finally dried.

1.18 FASTNESS PROPERTIES

The **ability** of the **dye** in **association with** a given substrate **to withstand** various **agencies** (like sunlight, washing, dry cleaning, water, perspiration etc.) **in processing or in use** is called **Fastness Properties**.

The various kinds of fastness have been given **quantitative expression** by carefully standardized comparative tests.

In **1934** the **Fastness test committee** of the **society of dyes & colourists published methods** for the **determination** of light, perspiration and washing fastness.

Methods were described for preparing the standards, **carrying out the tests** and **assigning numbers** to indicate the **degree of fastness**. **Fastness to light** is graded from **1 to 8** and **all other fastness** properties from **1 to 4 or 5**, the **fastness increasing** with **increasing numbers**.

The alteration in depth and tone of a dyeing are only examined visually, an absolute assignment of grades is not possible and it is necessary to make a comparison with a set of standard dyeing on which the same tests are simultaneously carried out.

1.18.1 Colour fastness

These measure the resistance of the textiles when they are exposed to various agencies. The usually practice is to apply the dye on the fabric in specified strength and subjected to the various agencies. For this, a **scale** of **1 to 5** is employed. In this scale, **1** means **Poor** and **5** means **Excellent**.

1.18.2 Sublimation fastness

A dyed fabric is kept in contact with undyed piece and subjected to heat. Alternation in colour and degree are noted. This fastness is **graded** from **1 to 5** where 1 denotes lowest rate in sublimation while 5 denotes highest rate in sublimation.

1.18.3 Burnt gas fumes fastness

A dyed piece is exposed to oxides of nitrogen. Alternation in colour is assessed. This test is largely used for synthetic fibers.

1.18.4 Rubbing (dry and wet) fastness

Transfer of color from **textile material** is **undesirable** and causes much trouble to both textiles finishing and processing as well as during wear of garments. This test is applicable to textiles made up of all fibers in the form of yarn and fabrics. The specimens are fastened. Crock meter, which causes a **piece of standard white cloths** (starch free 96x100 cotton fabric long type) **to rub against** the **colour specimen** under **controlled conditions** of pressure and speed. The rubbing fingers are covered with white cloths both for dry and wet test and slide back and forth for twenty rubbing stocks. The colour transfer to white cloth is compared with grey scale. The grey scale for alteration in colour consists of **grades** as **1 to 5**.

Observation	Grade	Qualitative assessment
No dye stain on un-dyed fabric	5	Excellent
Slight dye stain on un-dyed fabric	4	Very good
Moderate stain on un-dyed fabric	3	Good
Distinct stain on un-dyed fabric	2	Fair
Very much dyed stain on un-dyed fabric	1	Poor

1.18.5 Fastness to perspiration

This test is applicable to all fibers. Since **human perspiration** can be **acidic** or **alkaline**, so both acid and alkaline solutions have to be used for the test. Each solution contains 10gm of NaCl and 1gm di-sodium hydrogen phosphate per liter, the acid solution contains in addition 1gm lactic acid and the alkaline solution 4gm ammonium carbonate. The tests are carried out in glass tubes which are placed in a drying oven. The test specimen is made up by taking a piece of the dyed or printed fabric its length and width similar to test piece. The 4 tests corresponds to **grades 1 to 4** differ only in the **time of treatments** 40 min, 2, 6, & 18 hours.

Test specimen and test cloths are thoroughly wetted with the acid solution so that the weight of the two is about trebled. The two pieces are then rolled together and place in oven or desiccators. A similar test is performed with alkaline solution. On removal, the specimens are dried without rinsing, and the fastness graded according to the maximum numbers of the test in which the staining of the multi-fiber test cloth is no greater than Munsell Neutral Value Scale No-8 and there is no appreciable migration and change in colour.

1.18.6 Light fastness

The dyed textiles are often exposed to light and hence it is essential that the **color** should **not fade** on **exposure** to **light** so the study of light fastness of dye becomes essential. The dyed patterns are exposed to light along with standard dyed patterns of specific rating,

such standard samples are blue wool standard developed produced in Europe and are identified by numerical designations **1 to 8**. Higher the rating betters the lighting fastness.

Rating	Qualitative assessment	Rating	Qualitative assessment
8	Outstanding	4	Fairly good
7	Excellent	3	Fair
6	Very good	2	Poor
5	Good	1	Very poor

1.18.7 Wash fastness

The wash fastness of dyed pattern is another important property desired of a dye. The dye textile materials are often washed with soap detergents thus it becomes very necessary that the colour should not fade on washing. For wash fastness study **five test methods** are developed by **Indian Standard 58%**. The dyed pattern tested with another piece made of the fiber indicated in the following table.

Test pieces	Second pieces
Cotton	Viscous
Viscous	Cotton
Acetate	Viscous
Polyamide	Viscous or Cotton
Polyester	Viscous or Cotton
Linen	Viscous
Acrylic	Viscous or Cotton

The **study carried out** by **IS test method** in the **following manner**

The test piece was placed in container with 12 S.S. balls. To it 50 ml soap soda solution (5gm soap and 2gm anhydrous sodium carbonate in 1000 ml distilled water) at 50 °C was added. The test pattern was treated for 30 minutes then the pattern was removed from the container, rinsed twice with cold water for 10 minutes and squeezed. The stitches were removed and test specimen was opened out and dried in air. The change in color was evaluated on grey scale. Scales for alteration of color consisting of 1 to 5 grades are as follows.

Observation	Grade	Qualitative assessment
Shade unaltered	5	Excellent
Very slight loss in depth	4	Very good
Appreciable loss or alteration	3	Good
Distinct loss or alteration	2	Poor
Great loss or much alter	1	Fair