

DYES

In the early times the colouring materials were extracted from natural sources like plants and insects. Now a day thousands of such substances are synthesised in factories on a large scale.

Dyes are the organic compounds that are used to impart colour to textiles, foodstuffs, silk, wool and other objects. Dyes are capable of getting fixed to the fabrics/objects permanently and are resistant to the action of water, soap, light, acid, and alkalies.

Every coloured compound cannot be used as a dye. A good dye must have most of the following properties:

- It must have a suitable colour.
- It must be able to fix itself or capable of being fixed to the fabric from the solution.
- When fixed, it must be fast resistant to the action of light, water, soap, detergents, etc. during washing or to the organic solvents during dry cleaning.

Why do dyes or dyed articles appear to have a characteristic colour?

If a molecule absorbs light in the visible region (400 nm to 750 nm) corresponding to green colour, then it will appear violet, which is the complementary colour of green. Similarly, if a dye absorbs blue colour, it will appear yellow which is the complementary colour of blue. Thus, the dyes impart colour to fabric by absorbing the complementary colour.

Unlike most organic compounds, dyes possess colour because they

- 1) absorb light in the visible spectrum (400–700 nm),
- 2) have at least one chromophore (colour-bearing group),
- 3) have a conjugated system, i.e. a structure with alternating double and single bonds, and
- 4) exhibit resonance of electrons, which is a stabilizing force in organic compounds (Abrahart, 1977).

When any one of these features is lacking from the molecular structure the colour is lost. In addition to chromophores, most dyes also contain groups known as *auxochromes* (colour helpers), examples of which are carboxylic acid, sulfonic acid, amino, and hydroxyl groups. While these are not responsible for colour, their presence can shift the colour of a colourant and they are most often used to influence dye solubility. **Table 1** shows the relationships between wavelength of visible and colour absorbed/observed.

Table 1: Wavelength of light absorption versus colour in organic dyes

Wavelength Absorbed (nm)	Colour Absorbed	Colour Observed
400–435	Violet	Yellow-Green
435–480	Blue	Yellow
480–490	Green-Blue	Orange
490–500	Blue-Green	Red
500–560	Green	Purple
560–580	Yellow-Green	Violet
580–595	Yellow	Blue
595–605	Orange	Green-Blue
605–700	Red	Blue-Green

Constitution of Dyes

The colour of a compound is due to the presence of certain groups containing multiple bonds. These groups which impart colour to a compound are called **chromophores** (see figures 1-3). Some examples of chromophores are:

$-\text{NO}_2$ (Nitro), $-\text{N}=\text{O}$ (nitroso), $-\text{N}=\text{N}-$ (azo), quinonoid structures, etc.

At the same time, there are certain groups which they are not chromophores themselves but they deepen the colour when present with coloured compounds. The groups which deepen the colour of a coloured compound are called auxochromes. Some examples of common auxochromes are:

$-\text{OH}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{Cl}$, $-\text{CO}_2\text{H}$, etc.

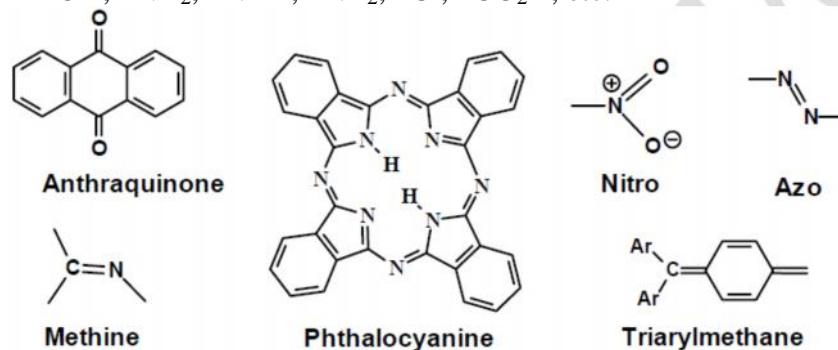


Figure 1: Examples of chromophoric groups present in organic dyes

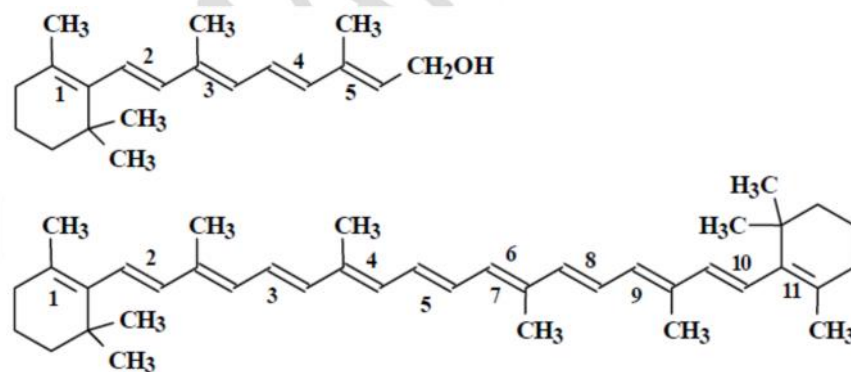


Figure 2: Conjugated systems in Vitamin A (top) and β -carotene (bottom)

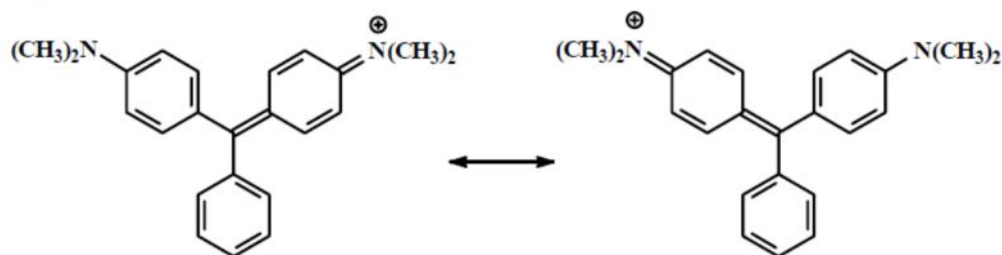


Figure 3: A pair of resonance structures for Malachite Green (C.I. Basic Green 4)

Regarding the requirement of a chromophore generating colour in organic compounds, it is important to note that the chromophore must be part of a conjugated system. This is illustrated through the examples in **Figure 4** where it can be seen that placement of an azo group between methyl groups produces a colourless compound, while a yellow-orange colour is obtained when the azo group is placed between aromatic rings. Similarly, the structures in **Figure 2** demonstrate the importance of having an extended conjugated system. It is evident that doubling the length of the conjugated

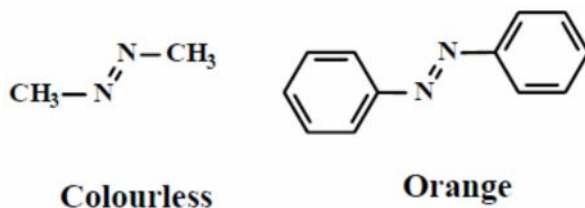


Figure 4: Importance of having a chromophore within a conjugated system

In addition to influencing solubility, auxochromes are essential ring substituents in providing target colours. This is illustrated in **Figure 5**, where the following effects of substituents are shown:

- Adding groups of increasing electron-donating ability to the azobenzene structure has a bathochromic effect (*cf.* OH vs NH₂).
- Electron-donating (NH₂) and electron-accepting (NO₂) groups placed in conjugation provide a bathochromic effect. In this regard, nitro groups are especially beneficial, contributing to their prevalence in disperse dye structures.
- Increasing the number of electron-attracting groups conjugated with the electron-donor has a bathochromic effect.

The electron-donating effects of an amino group are enhanced by adding alkyl groups to the N-atom.

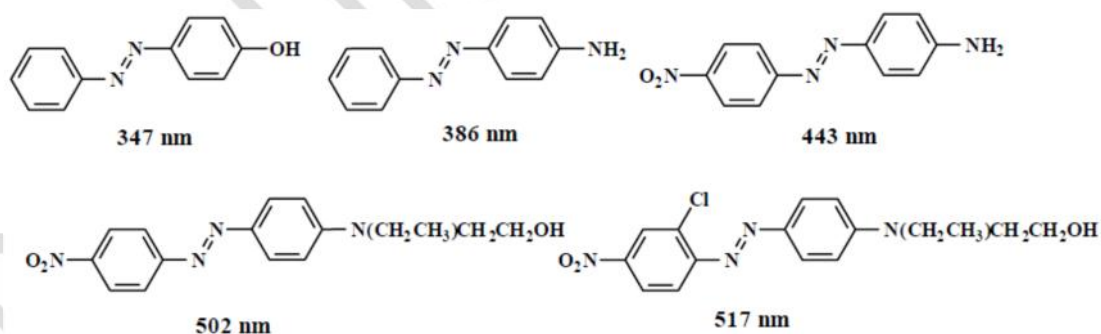


Figure 5: Effects of substituent groups within an azo-dye system

Classification of Dyes

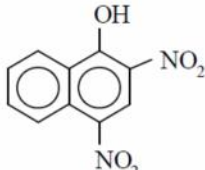
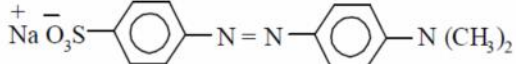
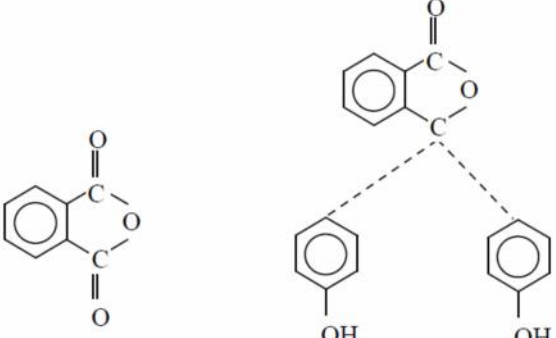
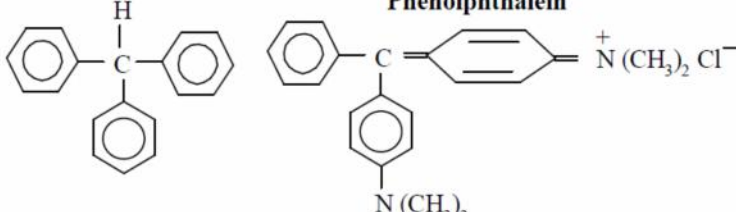

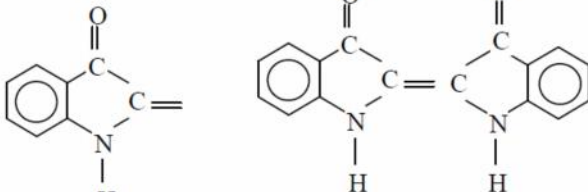
A large number of dyes are used for various purposes. These are classified on the basis of their

- Constitution
- Application

Classification based on constitution:

Depending upon the **characteristic structural units**, the dyes, are classified as given in **Table 2**.

Table 2: Classification of some dyes on the basis of their constitution

Dye type	Characteristic Structural unit	Typical examples
(1) Nitro dyes	-NO ₂	 <p>Martius yellow (2, 4-dinitro-1-naphthol)</p>
(2) Azo dyes	-N=N-	 <p>Methyl orange</p>
(3) Phthalein dyes		 <p>Phenolphthalein</p>
(4) Triphenyl methane		 <p>Malachite green</p>
(5) Anthraquinone		 <p>Alizarin (ruby red)</p>
(6) Indigoid		 <p>Indigo</p>

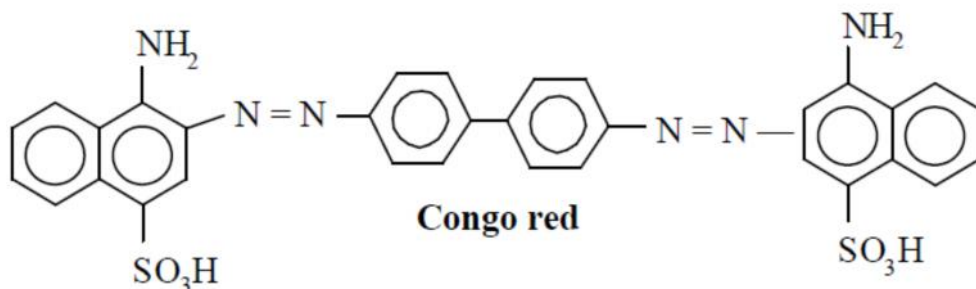
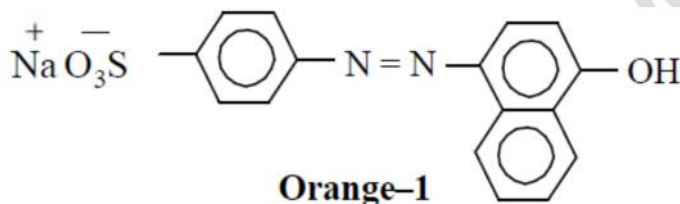
Classification of Dyes on the basis of their applications:

Dyes are classified into the following types on the basis of their applications.

- | | |
|--------------------------|---------------------|
| (i) Acid dyes | (ii) Basic dyes |
| (iii) Direct dyes | (iv) Disperse dyes |
| (v) Fibre reactive dyes | (vi) Vat dyes |
| (vii) Insoluble azo dyes | (viii) Mordant dyes |

(i) Acid Dyes

These are azodyes used in the form of their sodium salt of sulphonic acid ($-\text{SO}_3\text{H}$), carboxylic acid ($-\text{COOH}$) or phenol. The dye can be applied to wool, silk and nylon. These do not have much affinity for cotton and therefore, cannot be used to dye cotton. The common examples of an acid dye are orange – I and congo red.



(ii) Basic Dyes

These dyes contain basic groups like ($-\text{NH}_2$) group or ($-\text{NR}_2$) group therefore these are called basic dyes. These dyes attack the anionic sites present on the fabrics and get attached to them. These are used to dye modified nylons, polyester, wool, cotton, leather, paper, etc. Aniline yellow, malachite green and crystal violet are the basic dyes.

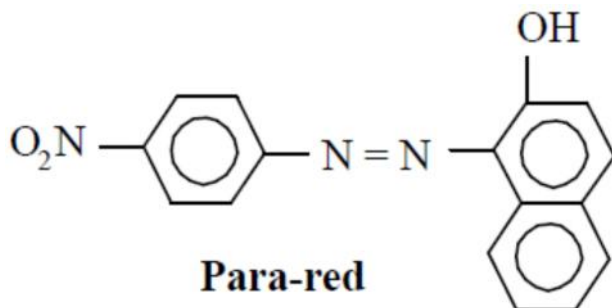
(iii) Direct Dyes

As the name suggest these dyes can be directly applied to the fabrics from their aqueous solution. The direct dyes attach to the fibre by means of hydrogen bonding. These are very effective for dyeing cotton, wool and rayon. Martius yellow (**Table 2**) and congo red are the common examples of direct dyes.

(iv) Ingrain dyes

These dyes are very important because over 60% of the dyes used are **azodyes** or ingrain dyes. The fabric to be dyed is soaked in an alkaline solution of phenol or naphthol and is then treated with a solution of diazotised amine. These are used for cotton, silk, polyester and nylon. The

colour is not very fast because the interaction is only on the surface. For example, para-red is an ingrain dye.



(v) Disperse Dyes

These dyes are usually applied in the form of a dispersion of finely divided dye. The dyes are dispersed in a soap solution in the presence of phenol, cresol or benzoic acid. These are used for nylon, polyester and polyacrylonitrile. Some common examples of disperse dyes are celliton fast pink B and celliton fast blue B.

(vi) Reactive dyes

These dyes attach to the fibre themselves by irreversible chemical reactions. These dyes induce fast colour on the fibres which is retained for a longer time. These dyes are used to dye fibres like cotton, wool or silk. Dyes which are derivatives of 2, 4 dichloro - 1, 3, 5 - triazine are important examples of fibre reactive dyes.

(vii) Vat dyes

Vat dyes are the well-known dyes they are insoluble in water and hence cannot be used directly for dyeing. Therefore, they are reduced to a colourless soluble form (leuco) in large wooden vats with a reducing agent such as an alkaline solution of sodium hydrogensulphite. Under these conditions, the leuco form develops affinity for the cellulose fibre. Then the fabric is exposed to air which oxidises the leuco (colourless) form to coloured form. Therefore, these dyes are mainly used to dye cotton fibres. Indigo is an important example of this type (**Table 2**).

(viii) Mordant Dyes

These dyes require an additional substance (generally a metal ion) for fixing to the fibre. These are used mainly for dyeing wool. The method involves the precipitation of certain mordant material (binding agent) on the fabrics which then combines with the dye to form an insoluble coloured complex called lake. For acid dyes, metal ions are used as mordants but for basic dyes, tannic acid is used as the mordant. For example, alizarin is a mordant dye (**Table 2**). It gives a rose red colour with Al³⁺ and a blue colour with Ba²⁺, a brownish red colour with chromium (Cr³⁺) and a black violet with iron mordant.