

# Dyes

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# Dye

□ A dye is a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and requires a mordant to improve the fastness of the dye on the fiber. Both dyes and pigments appear to be colored because they absorb some wavelengths of light more than others. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments.

# Natural dye

- The majority of natural dyes are from plant sources - roots, berries, bark, leaves, and wood, fungi, and lichens. Textile dyeing dates back to the Neolithic period. Throughout history, people have dyed their textiles using common, locally available materials.
- The discovery of man-made synthetic dyes late in the 19th century ended the large-scale market for natural dyes.

# Synthetic dye

□ The first human-made organic dye, mauveine, was discovered serendipitously by William Henry Perkin in 1856, the result of a failed attempt at the total synthesis of quinine. Many thousands of synthetic dyes have since been prepared. Synthetic dyes quickly replaced the traditional natural dyes. They cost less, they offered a vast range of new colors, and they imparted better properties to the dyed materials.

# Types of synthetic dyes

## □ Acid dyes

Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths.

## □ Basic dye

Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dyebath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.

## □ Direct or substantive dye

Direct or substantive dyeing is normally carried out in a neutral or slightly alkaline dyebath, at or near boiling point, with the addition of either sodium chloride ( $\text{NaCl}$ ) or sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) or sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.

## □ **Mordant dyes**

Mordant dyes require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool.

## □ **Vat dyes**

Vat dyes are essentially insoluble in water and incapable of dyeing fibres directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fibre.

## □ **Reactive dyes**

Reactive dyes utilize a chromophore attached to a substituent that is capable of directly reacting with the fibre substrate.

The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. "Cold" reactive dyes, such as Procion MX, Cibacron F, and Drimarene K, are very easy to use because the dye can be applied at room temperature.

## □ **Disperse dyes**

Disperse dyes were originally developed for the dyeing of cellulose acetate, and are water insoluble. The dyes are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder. Their main use is to dye polyester but they can also be used to dye nylon.

## □ **Azoic dyes**

Azoic dyeing is a technique in which an insoluble azo dye is produced directly onto or within the fibre. This is achieved by treating a fibre with both diazoic and coupling components. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye.

## □ **Sulfur dyes**

Sulfur dyes are two part "developed" dyes used to dye cotton with dark colors. The initial bath imparts a yellow or pale chartreuse color, This is aftertreated with a sulfur compound in place to produce the dark black we are familiar with in socks for instance. Sulfur Black 1 is the largest selling dye by volume.

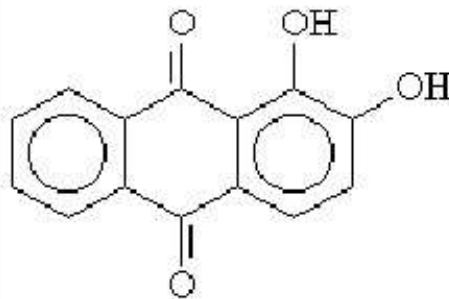
# DYE CLASSIFICATION

## How Do we classify dyes?

There are two practical ways to classify a dye:

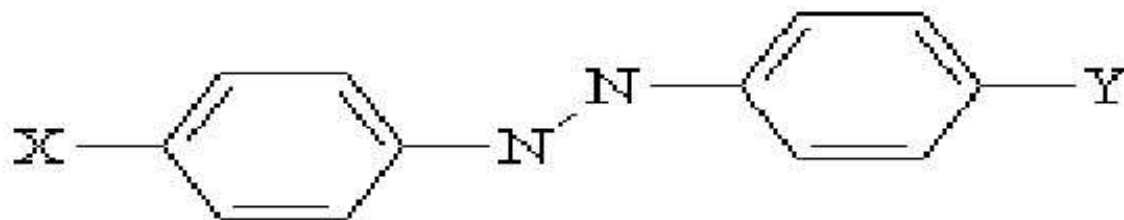
According to its chemical structure.

According to how it is applied to materials.





# On the basis of their structure



Azo dyes are the most important of the dye classes, with the largest range of colours (see Basis of Colour). All azo dyes contain *at least one* -N=N- group. See the Azo Dyes page for more explanation. The next most important dye class contains carbonyl functions (-C=O). This group includes anthraquinones.

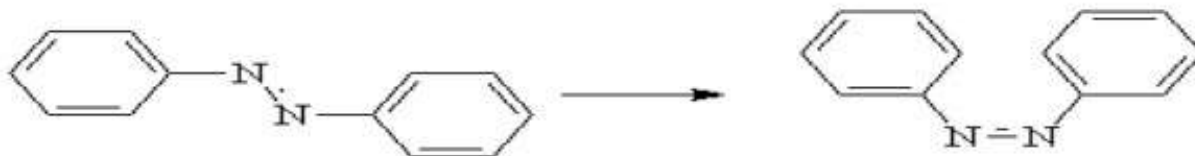
# Azo dyes


The azo compound class accounts for 60-70% of all dyes. As you might expect, they all contain an azo group, -N=N-, which links two  $sp^2$  hybridised carbon atoms. Often, these carbons are part of aromatic systems, but this is not always the case. Most azo dyes contain only one azo group, but some contain two (*disazo*), three (*trisazo*) or more.

## Isomerism in azo dyes

### Geometrical isomerism

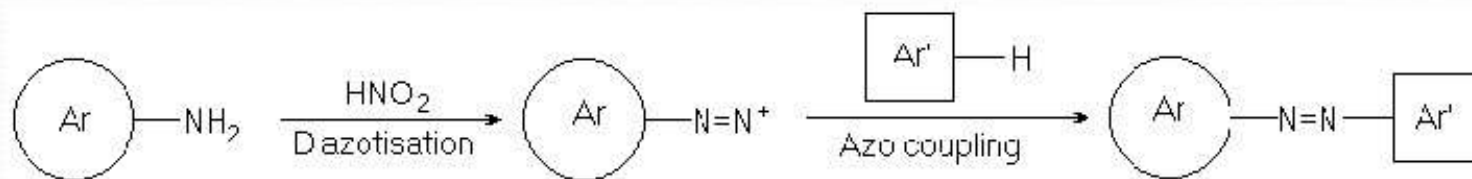
As with any double bond, the planar -N=N- bond shows geometrical isomerism:





This change from trans (preferred) to cis can be effected by exposure to UV radiation. This can lead to photochromism, a light-induced reversible colour change in some dyes, for example C.I. Disperse Red 1. This effect was considered a nuisance and has largely been eliminated by careful development of more stable dyes. But photochromic dyes are beginning to make a comeback in technology like sunglasses and sunroofs in cars.

An overview of azo dye synthesis is shown below:



### Stage 1- Diazotisation

This involves a primary aromatic amine, called the diazo component. It is treated in low temperature, acid conditions with sodium nitrite to form an unstable diazonium salt<sup>2</sup>.

### Stage 2- Azo coupling

The diazonium salt is reacted with a coupling component (for example a phenol or an aromatic amine). This forms the stable azo dye.

# COLOR FASTNESS

## A definition of fastness

"That property of a pigment or dye, or the leather, cloth, paper, ink, etc., containing the coloring matter, to retain its original hue, especially without fading, running, or changing when wetted, washed, cleaned; or stored under normal conditions when exposed to light, heat, or other influences."

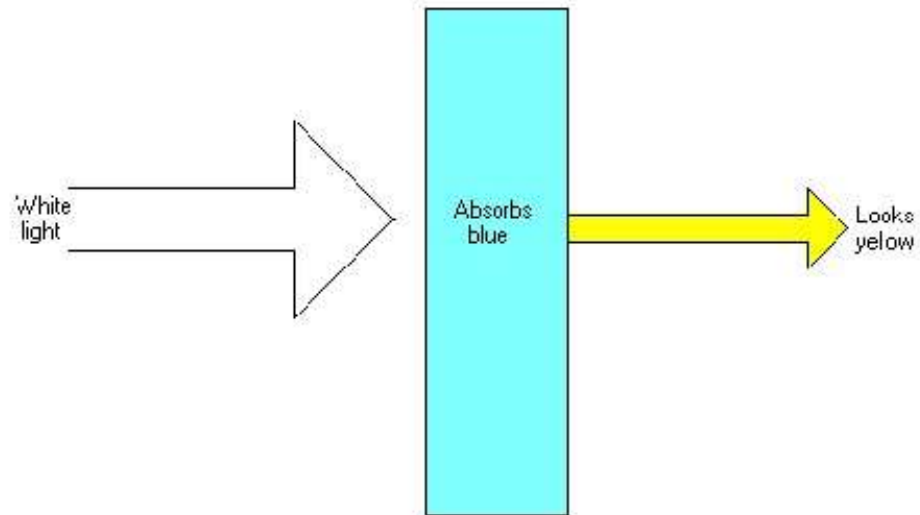
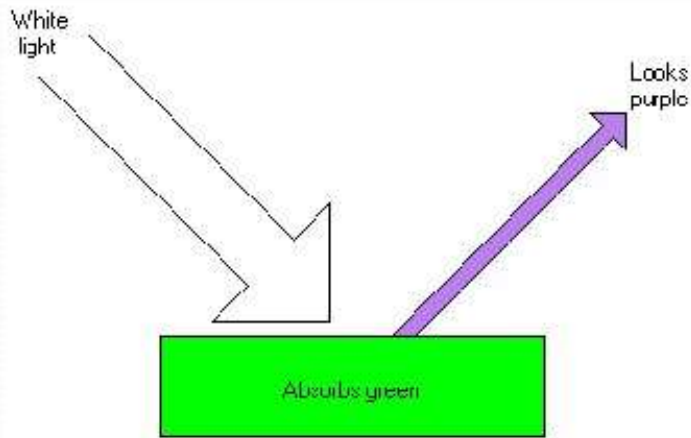
For example, linen is much harder to dye than silk or cotton (although indigo dyes both cotton and linen well- see later). A dye which works well on leather will probably not be suitable for wool.

# BASIS OF COLOUR

## The different colours of white light

Everyone is familiar with rainbows- see the top picture for a well known example! Sunlight is refracted by atmospheric water, producing bands of red, orange, yellow, green, blue, indigo and violet. These combined make up white light. If a light source is deficient in any colour band, the light appears to be coloured in the complementary colour . The table below shows wavelength, the corresponding colour, and its complementary colour

This image shows the effect on white light reflected off a solid object



This image shows the effect on white light transmitted through a solution, or other transparent article

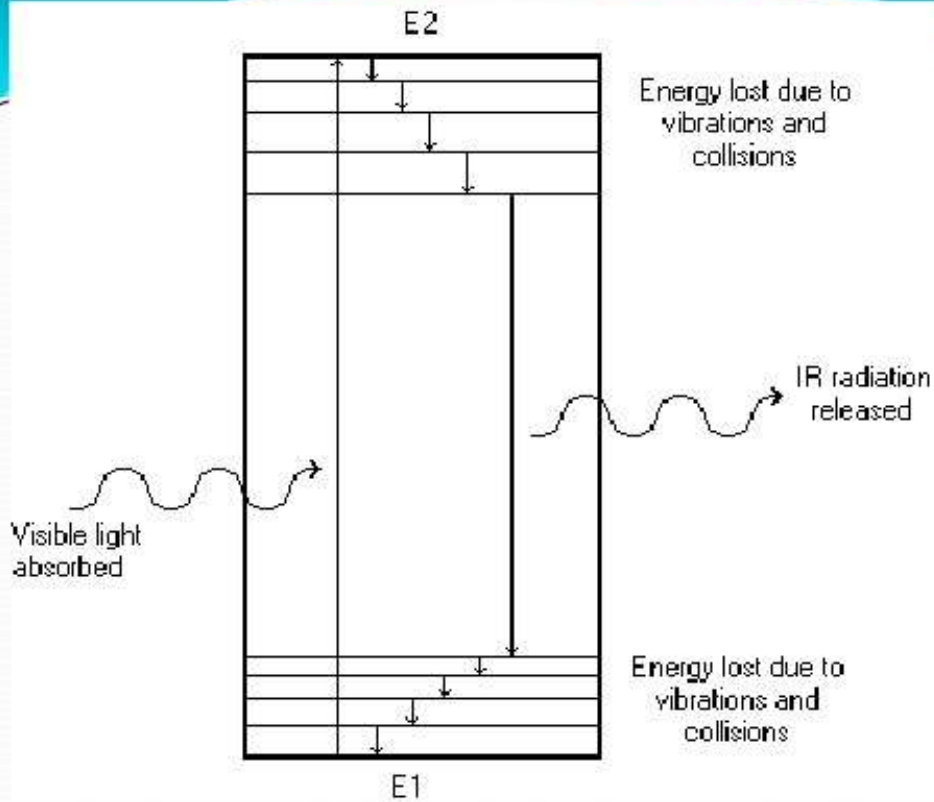
# THE EFFECT OF MOLECULAR ENERGY LEVELS

- Transition metal complexes are coloured due to the distortion of the metal's d-orbitals. Simple molecular excitation, such as in a neon tube, may cause the appearance of colour. This is due to rotation and/or vibration of the molecules-electron shell caused by ligands surrounding the metal ion.
- Electronic motion in conjugated organic systems, and charge transfer.
- Colour in crystalline solids arises from band theory- the blurring of many orbitals through-out the solid. Solids are only coloured if the gap between the Highest Occupied Molecular Orbital (HOMO, the Fermi level) and the Lowest Unoccupied Molecular Orbital (LUMO) is small enough.
- Colour due to refraction, scattering, dispersion and diffraction- these are all due to the geometrical and physical dimensions of a solid or a solution.



The first four mechanisms all rely on some form of energy transfer to move either molecules or electrons from their ground state into some excited state. However, only one of these effectively applies to dye molecules, since dye molecules are almost without exception organic conjugated systems. The overlapping p-orbitals effectively mean that no one electron absorbs more energy than another, since all p-electrons in the conjugated system are smeared above and below the molecule. Conjugated organic molecules absorb specific wavelengths of electromagnetic radiation

If this absorption falls within the visible region, then the light reflected or transmitted is deficient in a particular colour, and the solid (or solution) appears coloured:



The energy of the electronic transition can be calculated from

$$DE = hn$$

where DE is the difference between the two electronic levels, h is Planck's constant and n is the frequency of the absorbed radiation.

## Food dyes

One other class that describes the role of dyes, rather than their mode of use, is the food dye. Because food dyes are classed as food additives, they are manufactured to a higher standard than some industrial dyes. Food dyes can be direct, mordant and vat dyes, and their use is strictly controlled by legislation. Many are azo dyes, although anthraquinone and triphenylmethane compounds are used for colors such as green and blue. Some naturally-occurring dyes are also used.



The End