

Azo colour synthesis for schools

The Azoic Reaction



Colours

Colours can be divided into two groups: Dyes, which are soluble in water and give clear solutions, such as inks, and pigments, which are insoluble in water and give hazy solutions or dispersions, such as paints.

Dyes

Many early dyes were made from plants. Alizarin is an example extracted from the madder root. Alizarin only colours cloth with fastness to water if it has been treated with a metal compound such as aluminium sulphate. The process is called mordanting. The colour obtained depends on the mordant used. An aluminium mordant gives a red colour, tin gives a pink colour and iron gives a brown colour.

The soluble dye reacts with the mordanting metal to produce an insoluble colour by the chelation of the metal ions and within the fibre structure gives a level of water fastness.

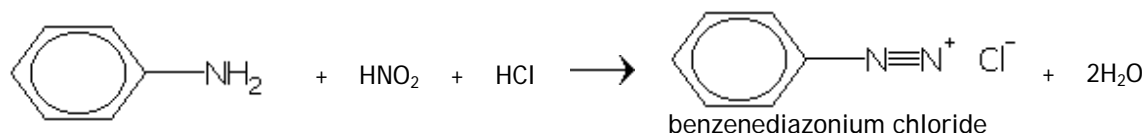
A range of synthetic colours have been developed based on phenylamine (aniline) and other similar chemicals to produce a whole family of azo colours and dyes.

Phenylamine reacts with a solution of sodium nitrite and hydrochloric acid at a temperature below 5°C (remember keeping that test-tube in ice?) to produce benzenediazonium chloride. This type of reaction is known as diazotisation and is used to produce azo linked compounds.

The hydrochloric acid first reacts with sodium nitrite to form unstable nitrous acid.



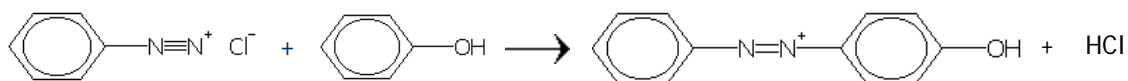
The nitrous acid then reacts with the amine.



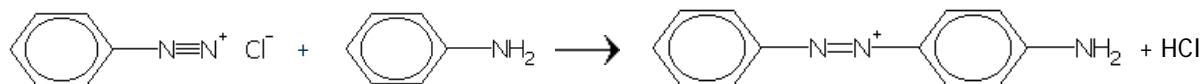
If the temperature is allowed to rise above 5°C, the benzenediazonium chloride decomposes to form phenol and nitrogen gas is given off.

If the benzenediazonium chloride is reacted with another compound containing a benzene ring, called a coupling agent, an azo compound is produced. The diazonium salt acts as an electrophile and is capable of reacting with other compounds containing benzene and similar ring structures. The reaction produces an azo linkage in the new compound. Phenols and amines are used as coupling agents and many are important colours both as soluble dyes and insoluble pigments.

With phenol the following reaction occurs:



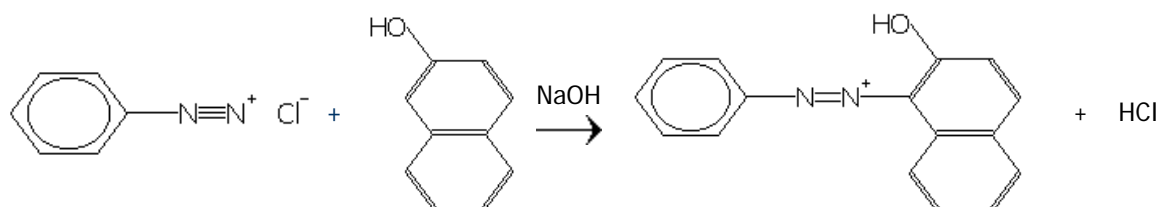
A similar reaction occurs with phenylamine:



The first dye is a yellow-orange shade, the second bright yellow. Many azo dyes are coloured in the range from red through to yellow. Some azo dyes are green, blue or even purple.

Many azo dyes are produced using a derivative of naphthalene, one example of which uses naphthalen-2-ol to produce a red azo dye. Notice how this compound is formed from two benzene rings joined (naphthalene differs since there is no hydroxy group present).

Also note that in this reaction Sodium Hydroxide is needed.

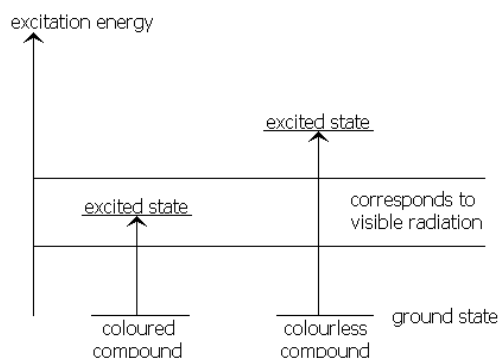


All coupling compounds contain a benzene ring that performs the coupling because it stabilises the delocalised electron structure. Without a coupled benzene ring the compound would remain unstable and break down at over 5°C like benzenediazonium chloride.

The Chemistry of Colour

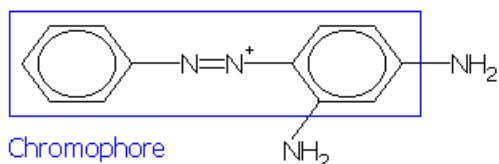
Coloured substances absorb radiation in the visible region of the spectrum. The energy absorbed causes changes in electronic energy. Electrons are promoted from a ground state to an excited state. The electrons excited in this case are the outer bonding electrons or lone pairs.

Not all electronic transitions are brought about by visible light as some require ultra-violet radiation. Those which absorb UV radiation appear colourless (unless they fluoresce). The energy needed to excite an electron in a coloured compound and in a colourless compound is shown below:



Coloured Organic Compounds

A dye molecule is built up from a group of atoms called a chromophore, which is largely responsible for its colour. Chromophores contain unsaturated groups such as C=O and -N=N-, which are often part of an extended delocalised electron system involving arene rings. Chrysoidine is a basic dye shown below:



Attached to the chromophore are two NH_2 groups which interact with the chromophore to produce the orange colour.

Other functional groups may be added which can:

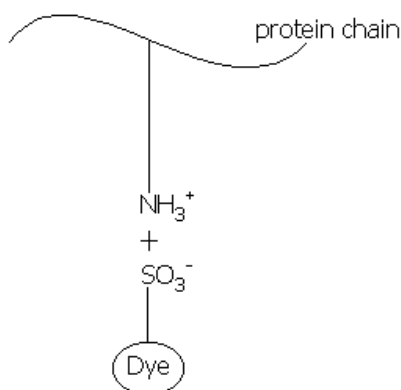
- modify or enhance the colour of the dye
- make the dye more soluble in water
- attach the dye molecule to the fibres of the cloth.

All azo dyes contain the R-N=N-R' arrangement.

How do dyes stick to fibres?

This depends on the dye and the fibre to which the dye is attached.

Protein-based fibres such as wool and silk have free ionisable CO_2H and NH_2 groups on the protein chains which can form an electrostatic attraction to parts of the dye molecule. For example the sulphonate group, SO_3^- , on a dye molecule can interact with a NH_3^+ group on the protein chain.

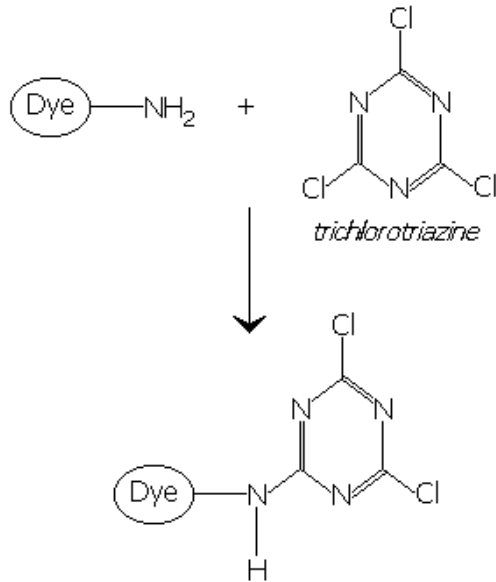


Cotton is a polymer with a string of glucose units joined together. Indigo which is used to dye denim jeans is a vat dye. Indigo is insoluble in water. The reduced form of indigo is soluble. Cotton is soaked in a colourless solution of the reduced form. This is then oxidised to the blue form of Indigo which precipitates in the fibres.

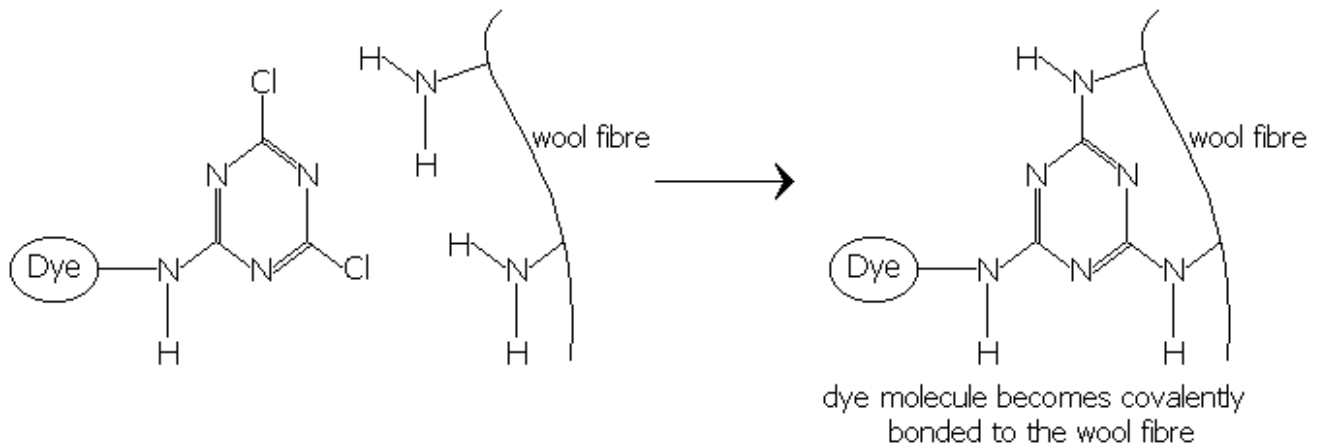
Direct dyes are applied from an aqueous solution and they are absorbed by the cotton cellulose structure. In the presence of sodium chloride salt solutions there is an attraction between the long chain dye

molecules and ionic groups in the cotton, forming an ionic link via hydrogen bonds etc. These dyes have limited water fastness.

Fibre reactive dyes actually form covalent bonds with fibre molecules and are therefore extremely colour fast. A dye molecule is reacted with the molecule trichlorotriazine:



Trichlorotriazine can react with either -OH groups (present in cotton) or -NH groups (present in wool and nylons), thus effectively bonding the dye to the fabric.



Azo Dye Formation in the laboratory

Hazards and safety precautions:



Azo dyes are toxic and may cause genetic mutations.
1-Naphthylamine is absorbed through skin and the respiratory and intestinal tract. It is toxic and carcinogenic.



Sulfanilic acid may act as a skin, eye or respiratory irritant. May act as a sensitizer.
2-Naphthol is harmful if swallowed or inhaled. May be harmful in contact with the skin. Eye, skin and respiratory irritant.



Sodium nitrite is toxic if swallowed. Severe eye irritant. Respiratory and skin irritant.
May act as a carcinogen for chronic exposure.

Safety goggles and protective gloves must be worn. Good ventilation required.

The 1-naphthylamine solution of phenol and the sodium nitrite solution should be made under a fume hood.

Chemicals:

| | |
|---------------------------|--|
| Sulfanilic acid solution: | 1.7 g of sulfanilic acid in 50 ml in of 2 N H ₂ SO ₄ |
| Sodium nitrite solution: | 0.6 g of NaNO ₂ in 10 ml of dist. H ₂ O |
| 1-Naphthylamine solution: | 0.7 g of 1-naphthylamine in 50 ml of 2 N H ₂ SO ₄ |
| 2-Naphthol solution: | 0.7 g of 2-naphthol in 50 ml of 2 N NaOH |

Glass wares:

crystallizing dish 190 × 90
3 beakers 250 ml
beaker 100 ml
3 volumetric pipettes 50 ml
volumetric pipette 10 ml
2 Petri dishes
3 pipette bulbs
3 glass stirring rods

Experimental procedure:

A crystallizing dish is half filled with ice. Four beakers containing the following solutions are placed in a ice bath:

beaker 1: 50 ml of an acidic solution of sulfanilic acid
beaker 2: 10 ml of an aqueous solution of sodium nitrite
beaker 3: 50 ml of an acidic solution of 1-naphthylamine
beaker 4: 50 ml of an alkaline solution of 1-naphthol

The sulfanilic acid solution is mixed with the aqueous solution of sodium nitrite while stirring. Equal volumes of the mixture are poured into the beakers 3 and 4.

Results:

The solutions in the beakers turn red.