

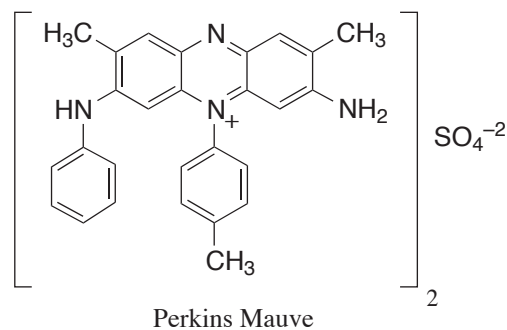
## Supplement to Experiment 9

### Essay: Dyes and Dyeing

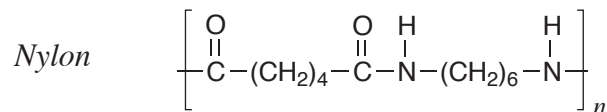
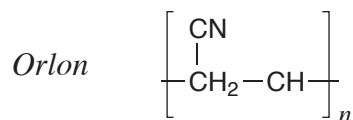
The dyeing of cloth is an ancient art. Prior to 1856, all dyes came from plant or animal sources. In that year, William Henry Perkin accidentally discovered the first synthetic dye while trying to synthesize quinine from allyltoluidine. Instead of quinine he produced a purple solution which proved to be a good dye for fabrics. The purple dye came to be known as Perkins Mauve, and Perkin went on to found the British coal tar dye industry. (He retired from the business world at age 36 to devote full time to chemical research.)

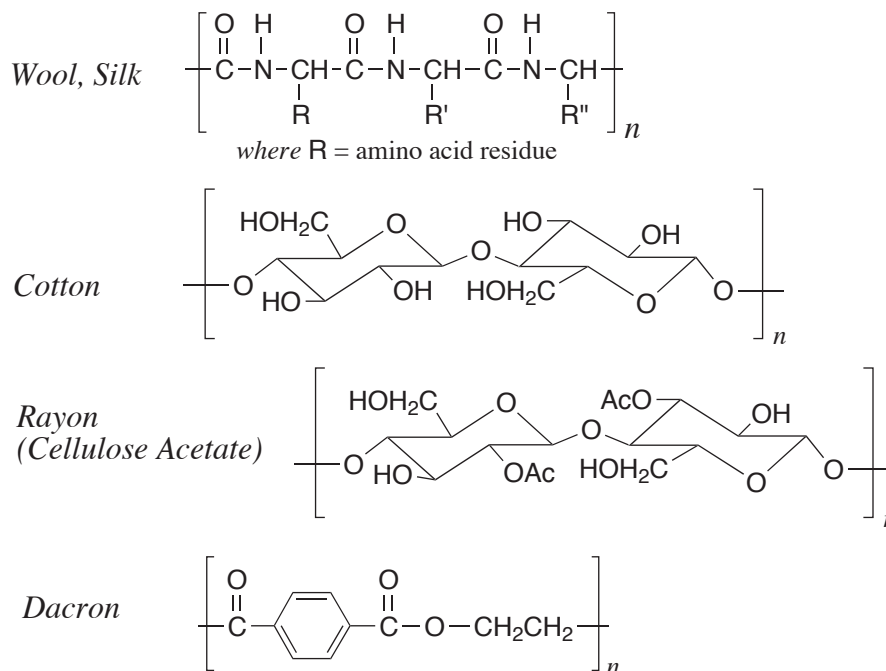
The founding of the first dye company is considered the birth of the organic chemical industry.

Although numerous colored compounds and, thus, potential dyes have been produced since the 1850s, the successful dyeing of a cloth sample depends both on the structure of the fibers in the cloth and the structure of the dye.



The structures of some common fibers are given below. Wool, silk, and cotton are natural fibers. Wool and silk are polypeptides, or polymers made of amino acid units. The acidic and basic amino acids present in these polymers provide many polar groups to which a dye can bind. Cotton, which is pure cellulose, has many hydroxyl groups ( $-OH$ ) which can form hydrogen bonds to dyes. Rayon (or acetate) is cellulose in which some of the hydroxyl groups have been acetylated. Thus, rayon has fewer hydrogen bonding sites and is more difficult to dye than cotton. The synthetic fibers (nylon, dacron, and orlon) have fewer polar sites than the natural fibers. Nylon, a polyamide, is made by polymerizing a dicarboxylic acid and a diamine. It can be synthesized so that either  $-NH_3^+$  or  $-COO^-$  groups predominate at the ends of the chains. Dacron is a polyester made by polymerizing ethylene glycol and terephthalic acid. Orlon is a polymer of acrylonitrile.

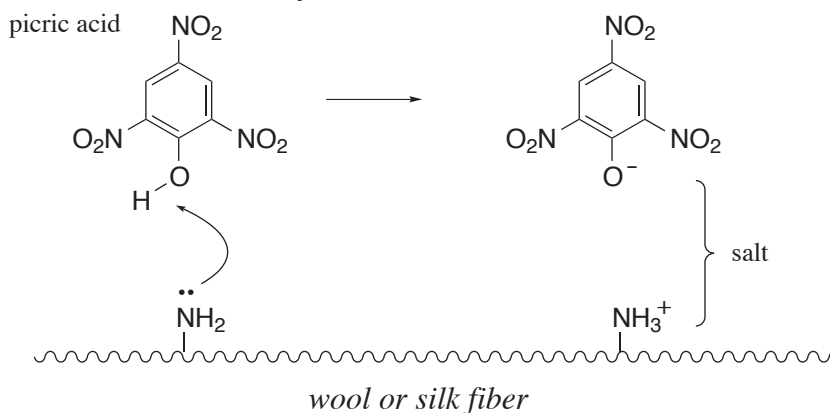




In order to dye the various types of fibers, numerous methods have been developed. Dyes have come to be classified according to the dyeing method most commonly employed in their use. These classifications are: direct dyes, disazo dyes, ingrain or developed dyes, mordant dyes, vat dyes, fiber reactive, disperse dyes, and optical brighteners. Some dyes fall into more than one of the above classifications; dyes are sometimes also classified according to their structural class, e.g., azo, triphenylmethane, anthraquinone, etc.

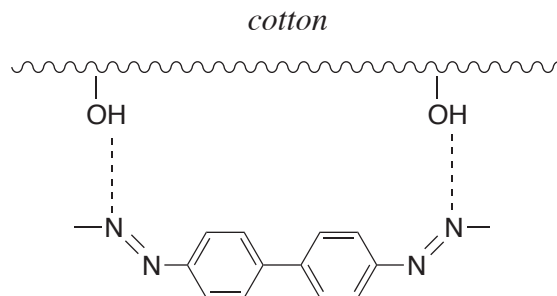
## Direct Dyes

A direct dye forms a strong ionic bond with the fabric. The dye either contains or is capable of forming a positive or negative charge which is electrostatically attracted to a negative or positive charge on the fiber. For example, the direct dye picric acid is a strong acid and interacts with the basic side chains in wool to form a salt linkage between itself and the fiber. On the other hand, malachite green bonds to the acidic side chains in the wool fibers. Malachite green is a member of the important triphenylmethane structural class of dyes.



## Disazo Dyes

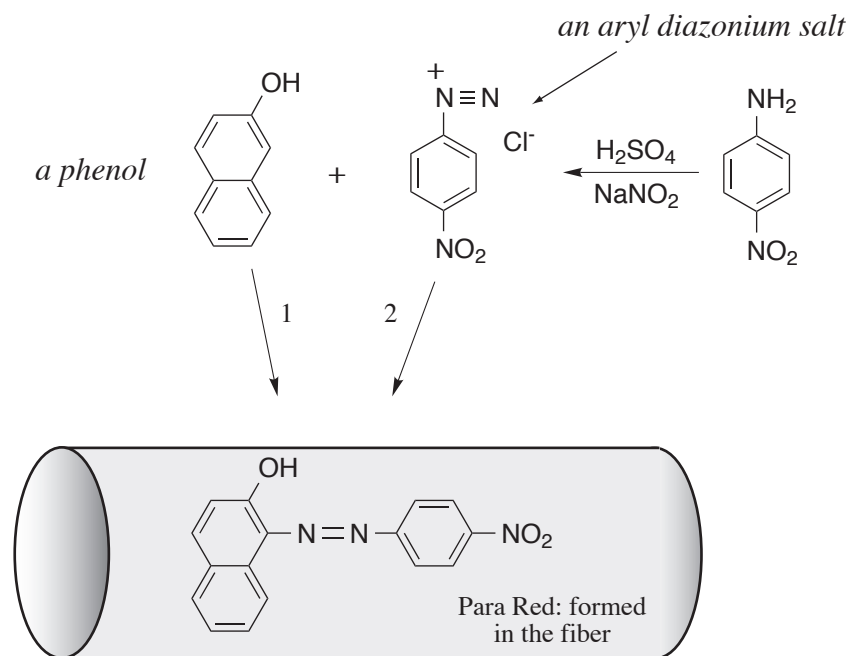
Also called substantive dyes, this type of dye contains two azo linkages. Disazo dyes link via hydrogen bonding to the hydroxyl (–OH) groups in a fabric. Cotton and sometimes rayon (depending on the amount of acetylation of the hydroxyl groups) can be dyed directly with disazo dyes. Congo red (a benzidine dye) is a disazo dye.



## Ingrain Dyes

Also called developed dyes, these dyes are actually made inside the fibers of the fabric. The fabric is treated with the two components used to synthesize the dye. These precursor molecules are small enough to diffuse into the pores and spaces between the fibers in the fabric. They then react to form the dye, which is trapped inside or “in the grain” of the fibers because of the large size of the dye molecule.

An example of an ingrain dye is para red (“American flag red”), an ingrain dye for cotton. The fabric is soaked first in a solution of the coupling component  $\beta$ -naphthol and then in a solution of diazotized *p*-nitroaniline.

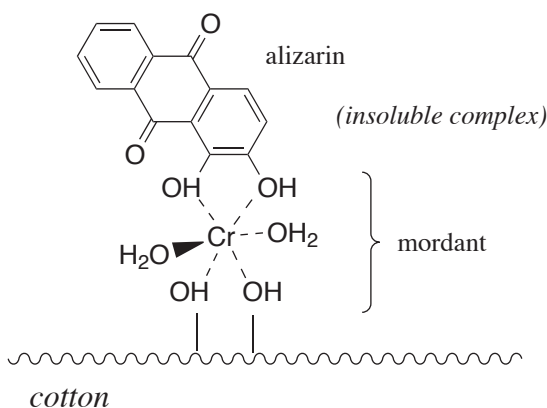


Para red is one member of a large structural group of synthetic dyes called “azo dyes”. Synthesized by the coupling of aryl diazonium salts with various aromatic amines and phenols, azo dyes encompass a broad range of colors, including yellows,

oranges, reds, browns, and blues. It is the structure of each particular dye that determines the color that will be exhibited. In general, the more the conjugated  $\pi$  system of a molecule, the longer the wavelength of visible light it will absorb, and the observed color will change accordingly. (White  $\rightarrow$  yellow  $\rightarrow$  orange  $\rightarrow$  red  $\rightarrow$  green  $\rightarrow$  blue.) Azo dyes are discussed in Loudon (5<sup>th</sup> ed. section 23.10, pp. 1139-1144).

## Mordant Dyes

Certain dyes form chelated complexes with heavy metals such as copper, chromium, tin, iron, and aluminum. Cotton, wool, and silk can also coordinate with these metals. To dye a fabric with a mordant dye, the fabric is first treated with a mordant, or the salt of a heavy metal. The fabric is then treated with the dye, the dye complexes with the mordant, and is thus linked to the fabric. Different metals (mordants) can lead to different colors with the same dye. Alizarin (an anthraquinone dye) is a typical mordant dye, shown in a chelated complex with cotton using chromium as the mordant.

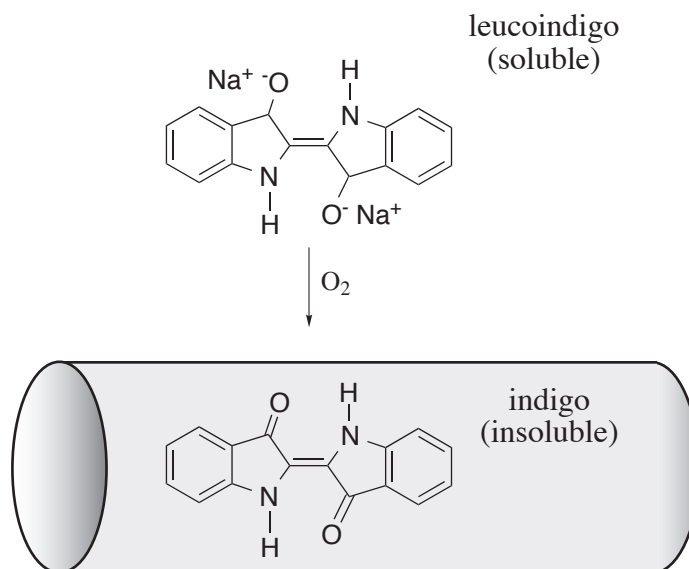


With some mordant dyes, especially the triphenylmethane dyes (e.g., malachite green and crystal violet, cationic dyes) tannic acid is used as the mordant. Tannic acid is actually a mixture of tannin structures and is isolated from the bark of different plants.

## Vat Dyes

Vat dyes can be used for all fibers, both natural and synthetic. Most vat dyes are soluble (and colorless) in water in their reduced form, but become insoluble and colored when oxidized. They are introduced to the fabric in their soluble form and then oxidized or “developed” to precipitate them both on the inside and outside of the fabric fibers. The vat dye indigo (a quinonoid dye) is used to dye blue jeans. It is very insoluble in all solvents, and thus is fast. However, since it is not covalently bound to the fabric, and only adheres to the surface of the fiber, it is subject to removal by abrasion. This explains why the knees and other parts of blue jeans sub-

ject to wear will gradually turn white. It also accounts for the appearance of the currently popular “stone-washed” jeans.



Indigo has an interesting history. In ancient times, indigo was isolated from plant sources, such as *Indigofera*. In India, it was used to dye cloth and in Egypt, mummies were sometimes wrapped with indigo-dyed ribbons. It became known in Europe after the discovery of the sea route to India. It was used for dyeing wool by the Gauls, and “their wives and daughters painted their bodies with it, when they appeared naked at the sacred festivals. Caesar relates the same of the Britons, who however did it in order to appear more terrible in battle”.<sup>\*</sup> In the sixth century in France and in Germany, indigo was isolated from a plant known as “woad”. The first chemical synthesis of indigo was reported by Adolf von Baeyer in 1880. This introduction of synthetic indigo met with violent opposition from growers of woad, and the use of synthetic indigo was prohibited in England, Germany, and France. The French king, Henry IV, “even went so far as to issue an edict, condemning to death any one who used that pernicious drug called ‘devils food’.”<sup>†</sup>

## Disperse Dyes

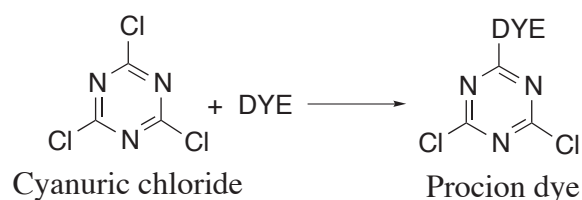
Disperse dyes are similar to vat dyes in that they are applied to the fabric in soluble form and remain on the fabric as a water-insoluble precipitate. These dyes are soluble in an organic solvent and insoluble in water. They may be used to dye the fabrics like dacron and rayon that have few groups present to allow any direct dye-fiber interactions. Many of the dyes used above can be used as a disperse dye: para red is a common disperse dye.

<sup>\*</sup> from *The Rise and Development of Organic Chemistry*, Carl Schorlemmer, p. 253, 1894.

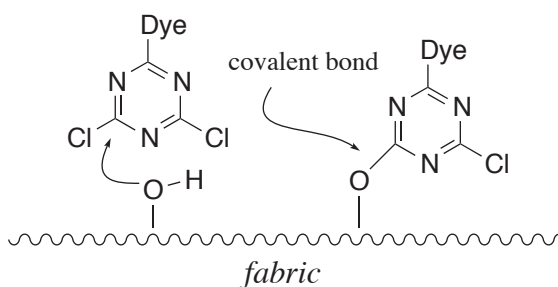
<sup>†</sup> *ibid.*

## Fiber-Reactive Dyes

This is the newest type of dye. These dyes attach to the fiber by reacting with either an amino or a hydroxyl group in the fiber to form a covalent bond. The main class of these dyes are the procion dyes, based on cyanuric chloride. The dye



molecule and the fiber molecule must each contain either an  $\text{-OH}$  or an  $\text{-NH}_2$  group, each of which replaces one of the chlorines in cyanuric chloride. The result is that the dye is covalently attached to the fiber through cyanuric chloride.

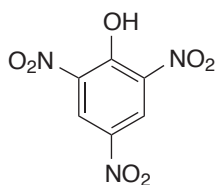


## Optical Brighteners

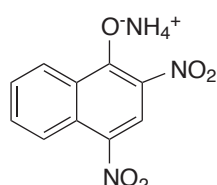
Many detergents contain a blue-white fluorescent dye that is adsorbed on the cloth during the washing process. These dyes fluoresce, that is, absorb UV light and reemit light in the visible blue region of the spectrum. This blue color counteracts the pale yellow color of white goods, which develops because of a buildup of soil embedded in lipid.

## Representative Dyes

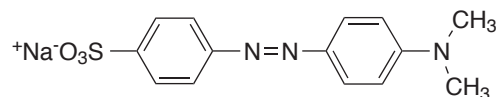
The following compounds are dyes which represent the types discussed above.



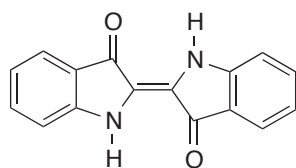
Picric Acid  
(direct)



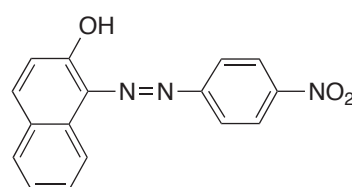
Martius Yellow  
(direct)



Methyl Orange  
(direct)



Indigo  
(vat)



Para Red  
(ingrain, disperse)

