Dyes and Dyeing

Polar versus Nonpolar Compounds

Introduction

The art of dyeing dates back thousands of years to the use of natural dyes extracted from plants and animals. Some dyes, such as Tyrian purple obtained from shellfish, were so rare that only emperors and kings could afford to wear purple—hence the term "royal purple." The modern dye industry started 150 years ago with the discovery of "mauve," the first synthetic dye. Since then, thousands of dyes have been developed to work with all types of fabrics.

Concepts

- Chemical bonding
- Polar vs. nonpolar bonds
- Ionic bonds
- Hydrogen bonding

Background

Dyes are organic compounds that can be used to impart bright, permanent colors to fabrics. The affinity of a dye for a fabric depends on the chemical structure of the dye and fabric molecules and on the interactions between them. Chemical bonding thus plays an important role in how and why dyes work.

The chemical structures of six common fabrics—wool, acrylic, polyester, nylon, cotton, and acetate—are shown in Figure 1 on page 2. Cotton and wool are natural fibers obtained from plants and animals, while acrylic, polyester, and nylon are synthetic fibers made from petrochemicals. Acetate, also called cellulose acetate, is prepared by chemical modification of natural cellulose. All fabrics, both natural and synthetic, are polymers. Polymers are high molecular weight, long chain molecules made up of multiple repeating units of small molecules. The structures of the repeating units are enclosed in brackets in Figure 1. The number of repeating units (n) varies depending on the fiber and how it is prepared.

Wool is a protein—a naturally occurring polymer made up of amino acid repeating units. Many of the amino acid units have acidic or basic side chains that are ionized (charged). The presence of many charged groups in the structure of wool provides excellent binding sites for dye molecules, most of which are also charged. Cotton is a polysaccharide composed of glucose units attached to one other in a very rigid structure. The presence of three polar hydroxyl (–OH) groups per glucose repeating unit provides multiple sites for hydrogen bonding to ionic and polar groups in dye molecules. Acetate is cellulose in which some of the –OH groups have been replaced by acetate groups ($–OCOCH_3$). The presence of acetate side chains makes acetate softer and easier to work with than cotton but also provides fewer binding sites for dye molecules.

Nylon was the first completely synthetic fiber. It is a polyamide, made up of hydrocarbon repeating units joined together by highly polar amide (–CONH–) functional groups. The amide groups provide sites for hydrogen bonding to dye molecules. The repeating units in polyester are joined together by ester (–COO–) functional groups. Finally, acrylic fiber is poly(acrylonitrile). Each repeating unit contains one nitrile ($–C{\equiv}N$) functional group.

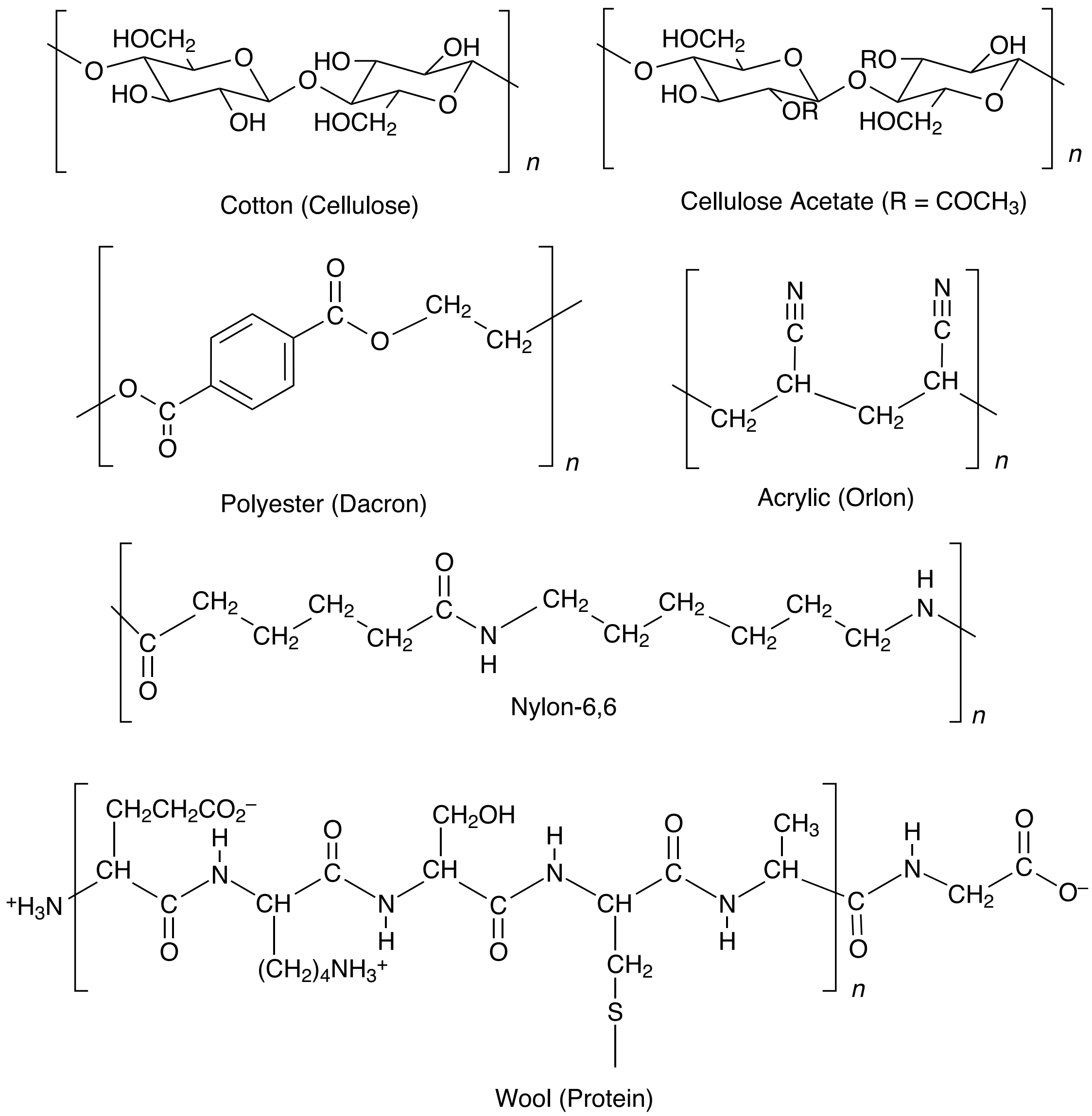


Figure 1. Chemical Structures of Fabric Molecules.

Dyes are classified based on both the structure of the dye and the way in which the dye is applied to the fabric.

- Direct dyes are charged, water-soluble organic compounds that bind to ionic and polar sites on fabric molecules. Direct dye molecules contain both positively and negatively charged groups and are easily adsorbed by fabrics in aqueous solution. Simple salts such as sodium chloride and sodium sulfate may be added to the solution to increase the concentration of dye molecules on the fiber.
- Substantive dyes interact with fabrics primarily via hydrogen bonding between electron donating nitrogen atoms (–N:) in the dye and polar –OH or –CONH– groups in the fabric.
- The ability of a dye to bond to a fabric may be improved by using an additive called a mordant. Mordant dyes are used in combination with salts of metal ions, typically aluminum, chromium, iron, and tin. The metal ions adhere to the fabric and serve as points of attachment for the dye molecules.

Experiment Overview

The purpose of this activity is to investigate the interaction of dyes with different fabrics. The dyes are methyl orange, malachite green, and crystal violet (direct dyes); congo red (a substantive dye); and alizarin (a mordant dye). See Figure 2 for the structures of the dye molecules. The dyes will be tested on a multifiber test fabric that contains strips of six different fibers—wool, acrylic, polyester, nylon, cotton, and acetate (Figure 3).

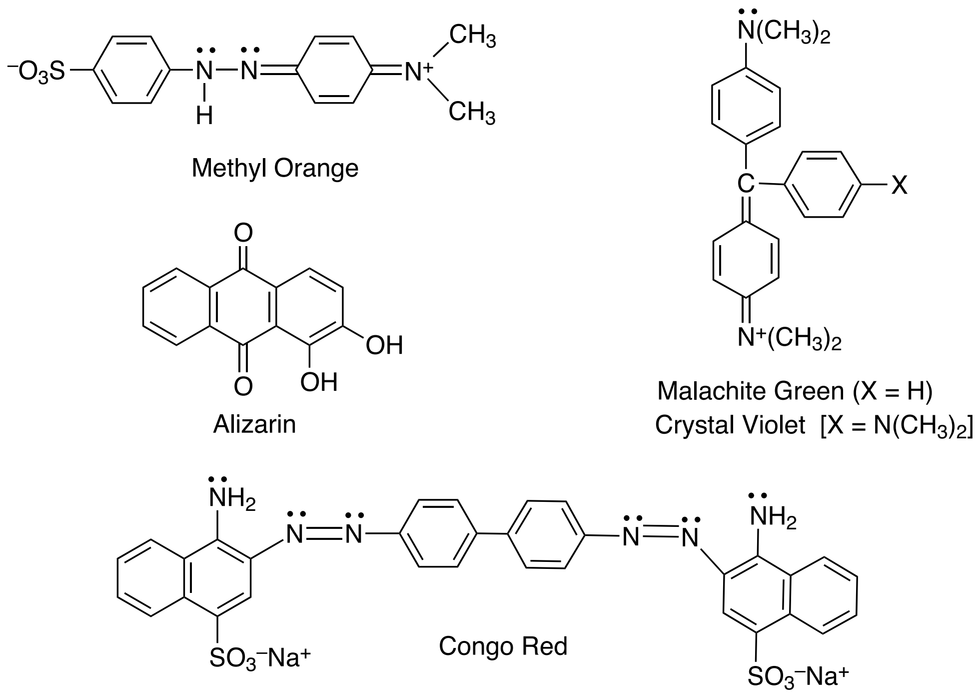


Figure 2. Chemical Structures of Dye Molecules.

Safety Precautions

All of the dyes are strong stains and will stain skin and clothing. Methyl orange, crystal violet, and malachite green are toxic by ingestion and irritating to body tissue. Sulfuric acid is corrosive and toxic by ingestion. Alizarin red is a body tissue irritant. The dye baths are very hot, near boiling. Exercise care to avoid scalding and skin burns. Avoid contact of all chemicals with eyes and skin. Wear chemical splash goggles and chemical-resistant gloves and apron. Please consult current Material Safety Data Sheets for additional safety, handling, and disposal information. Remind students to wash their hands thoroughly with soap and water before leaving the lab.

Preparation

Preparation Materials

Alizarin red, 1% solution, 60 mL
Aluminum potassium sulfate (alum), $AlK(SO_4)_2 \cdot 12H_2O$, 2 g
Calcium oxide, CaO, 1 g
Congo red, 0.1% solution, 150 mL
Crystal violet, 1% solution, 25 mL
Malachite green, 1% solution, 25 mL
Methyl orange, 2 g
Sodium carbonate, Na_2CO_3, 4 g
Sodium sulfate decahydrate, $Na_2SO_4 \cdot 10H_2O$, 10 g
Sulfuric acid solution, H_2SO_4, 1 M, 25 mL
Water, distilled
Aluminum foil, 25-foot roll
Beakers, 400-mL, 12†
Boiling stones, 10 g
Forceps or tongs, 30
Hot plates, 6†
Multifiber test fabric, 4 ft*
Paper towels
Pencils, 10
Permanent markers, 10
Scissors, 10
Stirring rods, 10
Wash bottles, 30

*Cut the multifiber test fabric into 12-cm strips and distribute.

†To ease congestion and improve safety, set up several dyeing stations around the lab. We recommend using 200 mL of dye solution in 400-mL beakers for each dye bath. To achieve even dyeing of fabrics, do not immerse more than three pieces of fabric in any one dye bath at the same time. Large (7″ × 7″) hot plates will accommodate two 400-mL dye baths.

Preparation of Dye and Mordant Solutions

Directions are given for preparing 200 mL of each solution. *Prepare two baths for each dye.* Dye baths may be used continuously during the day by different class sections.

Alizarin Red: Dilute 25 mL of 1% alizarin red solution with 175 mL of distilled or deionized water in a 400-mL beaker. Place a boiling stone in the dye solution and heat to near boiling on a hot plate.

Aluminum Potassium Sulfate (Alum): Dissolve 0.7 g of alum $[AlK(SO_4)_2 \cdot 12H_2O]$ in 200 mL of distilled or deionized water in a 400-mL beaker. Add 0.4 g of calcium oxide and stir to dissolve. Place a boiling stone in the solution and heat to near boiling on a hot plate.

Congo Red: Dilute 70 mL of 0.1% congo red solution with 130 mL of distilled or deionized water in a 400-mL beaker. Add 2-g of sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$) and 1.5 g of anhydrous sodium carbonate (Na_2CO_3) and stir to dissolve. Place a boiling stone in the dye solution and heat to near boiling on a hot plate.

Crystal Violet: Dilute 10 mL of 1% crystal violet solution with 190 mL of distilled or deionized water in a 400-mL beaker. Place a boiling stone in the dye solution and heat to near boiling on a hot plate.

Malachite Green: Dilute 10 mL of 1% malachite green solution with 190 mL of distilled or deionized water. Place a boiling stone in the dye solution and heat to near boiling on a hot plate.

Methyl Orange: Dissolve 0.7 g of methyl orange in 200 mL of distilled or deionized water. Add 2.5 g of sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$) and 5 mL of 1 M sulfuric acid and stir to dissolve. Place a boiling stone in the dye solution heat to near boiling on a hot plate.

Materials

Aluminum foil, 12-in square
Distilled water and wash bottle
Forceps or tongs
Multifiber test fabric, 12 cm
Pencil
Permanent marker
Scissors
Stirring rods
Paper towels

Dye baths *(prepared by teacher)*
Alizarin red
Congo red
Crystal violet
Malachite green
Methyl orange

Mordant bath *(prepared by teacher)*
Aluminum potassium sulfate (alum), $AlK(SO_4)_2$

Procedure

1. Cut the multifiber test fabric crosswise to obtain six 2-cm multifiber strips. Each test strip should contain all six fabric samples. Notice that the wool fabric is cream-colored, not white. Use a pencil to mark the wool ends with a "W." Label the strips with your initials.
2. Obtain a 12-inch square piece of aluminum foil. Using a permanent marker, write the names of the dyes to be tested (see the "Dye baths" in the *Materials* section) in separate locations on the aluminum foil. Label a sixth section "Alizarin + Alum."
3. All of the dyes are strong stains. Avoid getting any dye solution on your skin, clothes or books. To avoid contamination, rinse tongs or forceps with water before inserting them into a new dye bath.

Part A. Direct Dyes

4. Fold a multifiber test strip in half. Using forceps or tongs, immerse the test strip into the crystal violet dye bath. *Caution:* The dye baths are very hot. Exercise care to avoid scalding or skin burns.
5. After 5–10 minutes, remove the dyed test strip from the bath using forceps. Hold the fabric above the dye bath for a few minutes to allow excess dye solution to drain back into the dye bath.
6. Pat the test strip with paper towels and rinse the dyed test strip under running water from the faucet or a wash bottle. Continue rinsing the test strip until all of the excess dye has been removed and the rinse water is colorless.
7. Place the rinsed test strip in the appropriately labeled section on the aluminum foil and allow it to air dry.
8. When the fabric is dry, record the dye color produced by each direct dye on each type of fiber. See the Data Table.
9. Repeat steps 4–8 with new test strips in the malachite green and methyl orange dye baths.

Part B. Substantive Dye

10. Repeat steps 4–8 with a new multifiber test strip in the congo red dye bath.

Part C. Mordant Dye

12. Use a pencil to write "Alum" on the side of a multifiber test strip.
13. Using forceps or tongs, immerse the "alum"-labeled test strip into the boiling mordant bath (aluminum potassium sulfate solution).
14. After 15–20 minutes, remove the test strip from the mordant bath. Allow the fabric to cool slightly and then wring it out over the bath to remove excess liquid.
15. Immerse both the mordanted test strip and an untreated multifiber test strip in the alizarin dye bath.
16. After 5–10 minutes, remove the test strips from the dye bath. Rinse and dry the test strips as described in Part A, steps 5–7.
17. In the Data Table, record the colors produced by alizarin on the mordanted and untreated test strips.

The Color of Chemistry

Data Table

	Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Methyl Orange						
Malachite Green						
Crystal Violet						
Congo Red						
Alizarin						
Alizarin + Alum						
	Wool	Acrylic	Polyester	Nylon	Cotton	Acetate

Post-Lab Questions *(Use a separate sheet of paper to answer the following questions.)*

1. Describe the colors produced by methyl orange on the different fabrics in the multifiber test fabric. Compare the results with the relative color intensities predicted in the *Pre-Lab Questions*. Explain any differences between the predicted and actual results.
2. Compare the general ease of dyeing the six different fabrics in the multifiber test fabric. Which fabric(s) consistently developed the most intense colors, regardless of the type of dye used? Which fabric was the most difficult to dye?
3. Consult Figure 1: What feature stands out as unique in the structure of the fabric that was the easiest to dye? What feature stands out as unique in the structure of the fabric that was hardest to dye?
4. Consult Figure 2: Which two dyes have very similar structures? Compare the relative color intensities produced by these dyes on the different fabrics in the multifiber test fabric. Are the color patterns (from lightest to darkest) similar for these two dyes? Explain.
5. Compare the color patterns produced on the different types of fabrics by methyl orange (a direct dye) and congo red (a substantive dye). Suggest a possible reason for any differences based on the chemical bonding interactions of direct versus substantive dyes (see the *Background* section).
6. Show by means of a diagram one hydrogen bond that might form between a glucose unit in cotton and congo red. *Hint:* Hydrogen bonds have the general form X–H --- :Y, where X and Y are highly electronegative atoms such as N, O, F, and Y has an unshared pair of electrons.
7. Compare the colors produced by alizarin on the untreated and mordanted test strips. What is the principal advantage of

using a mordant? What fabric was almost impossible to dye except with a mordant?

Teacher's Notes

The Color of Chemistry

Disposal

Consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste. The dye solutions may be washed down the drain with plenty of excess water according to Flinn Suggested Disposal Method #26b.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
Systems, order, and organization
Constancy, change, and measurement
Content Standards: Grades 9–12
Content Standard B: Physical Science, structure and properties of matter, chemical reactions.

Lab Hints

- If three students are working together, each student may be responsible for testing two dyes. For best results, allow the fabrics to dry overnight before recording the final results. Students may test the colorfastness of the dyed fabrics at home, if desired. Make sure excess dye has been completely rinsed out of the fabric strips before allowing students to take the samples home.
- Place lots of paper towels, absorbent lab mats or newspaper all around the dye baths. This will help keep the room clean. Instruct students to store books, bags, and other personal items away from the lab area to avoid staining them.
- Students may bring fabrics from home to dye. Suitable fabrics include cotton T-shirts, acrylic socks or yarn, polyester sheets, etc. Scavenge fabric stores for inexpensive bolts of white cloth (read the labels!). Pure (100%) white cotton, polyester, acetate, and nylon are easy to find and relatively inexpensive. Wash fabrics before dyeing to remove sizing and other fabric finishes.
- Other multifiber test fabrics containing 8 or 13 different fabrics are available from Testfabrics, Inc. See their Web site at www.testfabrics.com.
- Congo red is an acid–base indicator. The red color of fabrics dyed with congo red will turn blue when placed in a mild acid solution, such as 0.1 *M* HCl. The blue color disappears and the red color returns when the congo red–dyed fabric is placed in a washing soda (sodium carbonate) bath.
- Malachite green and crystal violet are often paired with tannic acid as a mordant for difficult-to-dye fabrics. The toxic heavy metal salt antimony potassium tartrate is required as an adjunct to "fix" the tannic acid to the fabric. Since using antimony in the lab would necessitate dedicated heavy metal waste disposal, the use of tannic acid as a mordant was omitted from this experiment. Fabrics mordanted with tannic acid must be thoroughly dried before dyeing.
- Students may experiment with other metal salts as mordants for alizarin—some interesting color changes result. Using iron(II) sulfate as the mordant imparts a rich brown color to the dyed fabric.

Teaching Tips

- The "Mystery Nylon Factory" demonstration kit available from Flinn Scientific (Catalog No. AP2088) provides a good lead-in to this activity. Use the nylon rope trick demonstration to introduce polymers and their unique charac teristics. One point worth mentioning is that individual polymer molecules do not all have the same molecular weight.

Polymers are polydisperse—the molecular weight is an average based on the number of molecules having different molecular weights in a sample (the so-called number-average molecular weight).

- One of the most famous dyes is indigo, which is used to dye blue jeans. Indigo is a so-called vat dye—the dye is first reduced to a colorless, water-soluble form, which is then applied to a fabric. The ingrained dye is re-oxidized back to its colored form when the fabric is exposed to air. The history and chemistry of dyeing with indigo are investigated in "Dyeing with Indigo," a student laboratory kit available from Flinn Scientific (Catalog No. AP6166).

Sample Data *(Student data will vary.)*

Data Table

	Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
Methyl Orange	Red-orange	White	Pale yellow	Orange	Light yellow	Yellow
Malachite Green	Dark green	Blue-green	Pale green	Light green	Blue-green	Turquoise
Crystal Violet	Dark purple	Lavender	Light blue	Dark blue	Royal blue	Dark blue
Congo Red	Red	Pink	Light pink	Bright pink	Dark red	Red
Alizarin	Violet	Pale pink	Pink	Lavender	Mauve	Cream
Alizarin + Alum	Dark purple	Purple	Purple	Purple	Purple	Purple
	Wool	Acrylic	Polyester	Nylon	Cotton	Acetate

(Optional) Use the space below to write down any observations concerning the colorfastness of the dyes.

All of the dyes were colorfast. There were a few exceptions:

- *The color of malachite green on cotton faded after washing.*
- *The color of crystal violet on both cotton and polyester also faded after washing.*

Answers to Post-Lab Questions *(Student answers will vary.)*

1. Describe the colors produced by methyl orange on the different fabrics in the multifiber test fabric. Compare the results with the relative color intensities predicted in the *Pre-Lab Questions*. Explain any differences between the predicted and actual results.

   Observed color intensity:

   Wool > nylon > acetate > cotton > polyester > acrylic

   The color of methyl orange ranged from dark red-orange on wool and bright orange on nylon to essentially colorless (white) on acrylic.

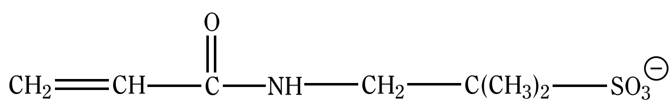
Acetate was dyed lemon yellow, while cotton and polyester were light yellow and pale yellow, respectively. ***Note to teachers:*** *Student predictions in the Pre-Lab Questions will vary. Most should predict that wool will show the greatest affinity for the dye, and thus the most intense color with methyl orange. The results for nylon may be a surprise, since there are no charged groups shown in the structure of nylon. Students may notice, however, that both nylon and wool contain amide-linking groups in their repeating units—maybe the polar amide groups interact very strongly with the dye via hydrogen bonding.*

2. Compare the general ease of dyeing the six different fabrics in the multifiber test fabric. Which fabric(s) consistently developed the most intense colors, regardless of the type of dye used? Which fabric was the most difficult to dye?

Wool consistently developed the most intense colors with all of the dyes except congo red. Even with congo red, however, wool was only a shade paler than cotton, which gave the most intense color. Nylon, cotton, and acetate were also relatively easy to dye. They gave fairly intense colors with at least four out of the six dyes tested. Polyester was the most difficult fabric to dye.

3. Consult Figure 1: What feature stands out as unique in the structure of the fabric that was the easiest to dye? What feature stands out as unique in the structure of the fabric that was hardest to dye?

Wool contains many charged groups in its structure. None of the other fabrics show any charged groups in their normal repeating units. Polyester is unique in that it appears to be the least polar of all the fabrics. Polyester has no –X–H (where X = O or N) groups capable of forming hydrogen bonds with electron donor sites in dye molecules. ***Note to teachers:*** *Students may notice that acrylic fiber is similar to polyester in that is lacks polar groups capable of hydrogen bonding to electron donor sites in dye molecules. The dyeability of acrylic is improved commercially by incorporating small amounts of charged monomers such as AMPS (see below) into the growing polymer.*



Structure of AMPS

4. Consult Figure 2: Which two dyes have very similar structures? Compare the relative color intensities produced by these dyes on the different fabrics in the multifiber test fabric. Are the color patterns (from lightest to darkest) similar for these two dyes? Explain.

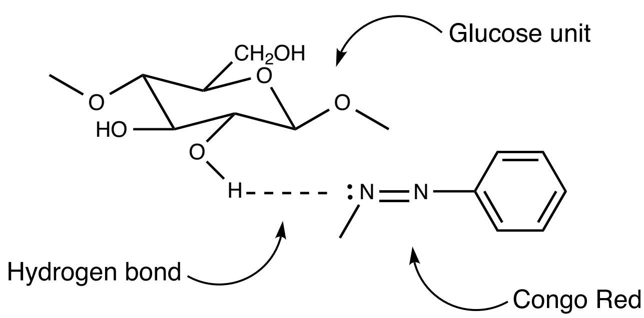
Crystal violet and malachite green have similar structures and produced similar color patterns with the six fabrics in the multifiber test fabric. The observed color intensity produced by crystal violet and malachite green was:

Wool > cotton, acrylic, and acetate > nylon >> polyester.

5. Compare the color patterns produced on the different types of fabrics by methyl orange (a direct dye) and congo red (a substantive dye). Suggest a possible reason for any differences based on the chemical bonding interactions of direct versus substantive dyes (see the *Background* section).

Congo red dyed every fabric! It gave nice bright reds of almost equal color intensity with four of the fabrics (wool, nylon, cotton, and acetate) and light pink colors with acrylic and polyester. Methyl orange showed a much greater variability in the colors that it produced on different fabrics (see Question #1). Binding of methyl orange may depend on its ability to form ionic bonds with fabric molecules. Congo red binds to fabrics via hydrogen bonding. More fabrics are capable of hydrogen bonding than ionic bonding.

6. Show by means of a diagram one hydrogen bond that might form between a glucose unit in cotton and congo red. *Hint:* Hydrogen bonds have the general form X–H --- :Y, where X and Y are highly electronegative atoms such as N, O, F, and Y has an unshared pair of electrons.



7. Compare the colors produced by alizarin on the untreated and mordanted test strips. What is the principal advantage of using a mordant? What fabric was almost impossible to dye except with a mordant?

The effect of the mordant was unique—it produced almost equal color intensity (shades of purple) on every fabric in the multifiber test fabric. The untreated test strip showed large variations in the color shade produced with alizarin. The mordanted test strip was simply purple almost all the way across. The only exception was wool, which was darker than the rest of the fabrics on the mordanted test strip. The effect of the mordant was most significant on polyester, which was almost impossible to dye using any other dyes.

Reference

This activity was adapted from *Flinn ChemTopic™ Labs*, Volume 5, Chemical Bonding; Cesa, I., Editor; Flinn Scientific: Batavia IL, 2004.

Flinn Scientific—Teaching Chemistry™ eLearning Video Series

A video of the *Dyes and Dyeing* activity, presented by John Little, is available in *Polar versus Nonpolar Compounds*, part of the Flinn Scientific—Teaching Chemistry eLearning Video Series.

Materials for *Dyes and Dyeing* are available from Flinn Scientific, Inc.

Materials required to perform this activity are available in the *The Color of Chemistry—Student Laboratory Kit* available from Flinn Scientific. Materials may also be purchased separately.

Catalog No.	Description
AP6632	The Color of Chemistry—Student Laboratory Kit
A0265	Aluminum Potassium Sulfate, 100 g
A0260	Alizarin Red, 1% Solution, 100 mL
C0263	Calcium Oxide, 100 g
C0127	Congo Red Indicator Solution, 0.1%, 100 mL
C0132	Crystal Violet Solution, 1%, 100 mL
M0148	Malachite Green Solution, 1%, 20 mL
M0076	Methyl Orange, 25 g
S0052	Sodium Crabonate, 500 g
S0225	Sodium Sulfate, 100 g
AP6135	Multi-Fiber Test Fabric

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.