

MOHAWK

COLLEGE OF APPLIED ARTS AND TECHNOLOGY

**CHEMICAL, ENVIRONMENTAL, AND BIOTECHNOLOGY
DEPARTMENT**

Synthesis and Use of Fabric Dyes

by Professor David Cash

September, 2008

**Mohawk College is the author and owner of these materials
(excluding copyright held by others) and all copyright and
intellectual property rights contained therein.**

**Use of these materials for teaching or other non-commercial
purposes is allowed.**

**Contact information for Mohawk College will be found on
the following page.**

This Experiment is a 3 hour Organic Chemistry laboratory exercise. It is designed for students in the sixth term of a 3-year diploma program in Chemical Engineering Technology.

**For Information or Assistance
Contact:**

**MOHAWK COLLEGE
CHEMICAL, ENVIRONMENTAL, AND
BIOTECHNOLOGY DEPARTMENT**

**Professor Cindy Mehlenbacher
cindy.mehlenbacher@mohawkcollege.ca
905-575-1212 ext. 3122**

**Bill Rolfe (Chief Technologist)
bill.rolfe@mohawkcollege.ca
905-575-2234**

Experiment 5

Synthesis and Use of Fabric Dyes

Brief Description

In this experiment you will synthesize the azo dye **Orange II** and the vat dye **Indigo**. The orange II and the indigo will be used to dye multi-fiber test strips. A soluble food dye or food dye mixture in Kool-Aid or some other drink powder will also be used to dye a multi-fiber test strip.

References

1. **Wade**, 5th Edition, pages 868-874; or 6th Edition, pages 902-908.
2. **Skoog, Holler and Nieman**, Principles of Instrumental Analysis, 5th Edition, pages 330 - 335.
3. **Encyclopedia of Polymer Science and Technology** (library reference section).
4. **Kirk-Othmer Encyclopedia of Chemical Technology** (library reference section).
5. **CHEM CH602 Study Guide: Polymers - Supplementary Notes - Textiles**.

Documentation References (Not available in the Library Resource Centre)

1. **Dianne N. Epp**, Chemistry of Vat Dyes and Chemistry of Food Dyes, Palette of Color Monograph Series, Terrific Science Press, Miami University (Ohio), 1995.
2. **Charles F. Wilcox, Jr.**, Experimental Organic Chemistry, Macmillan, 1984, pages 410 - 412.
3. **J. R. McKee and M. Zanger**, A Microscale Synthesis of Indigo: Vat Dyeing, Journal of Chemical Education, Vol. 68, October 1991, pages A242-A244.

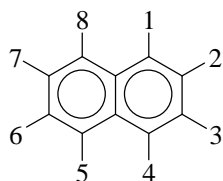
The Preparation Questions are on the Next Page →

Last Revised May 2008 by Professor David Cash

Experiment 5 Preparation Questions

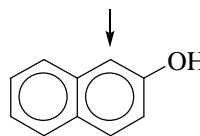
Your Mohawk College ID number is nnnnnnXYZ.

1. You are assigned the substance listed in **Table 1: Some Primary Aromatic Amines** on the next page which has the same number as the **third last digit X** of your Mohawk College ID.
 - a. Draw yourself **by hand or using a draw program** the full structural formula of your compound.
 - b. Draw yourself **by hand or using a draw program** the full structural formula of the **diazonium ion** that would be produced if your assigned compound were reacted with sodium nitrite in hydrochloric acid solution. See **Aromatic Diazonium Ions** on page 5.
2. You are assigned the substance listed in **Table 2: Some Coupling Reagents** on the next page which has the same number as the **second last digit Y** of your Mohawk College ID.
 - a. Draw yourself **by hand or using a draw program** the full structural formula of your coupling reagent. Name the drawing program used. Label the structure with the numbering that matches the name of the compound.
 - b. Draw a second identical structure. **Renumber** the substituents, giving priority in numbering to the acidic functional group instead of to the phenol. Now write the new synonym name of the compound.
3. Draw yourself **by hand or using a draw program** the full structural formula of the **azo compound** that would be produced if your diazonium ion of **Question 1** were reacted with your assigned coupling reagent of **Question 2**. See **Azo Coupling Reactions** on page 5 and **Structure of Orange II** on page 7. Name the drawing program used.



naphthalene - numbering system
for two or more substituents

coupling occurs most rapidly
and almost entirely at position 1
of a 2-naphthol



in substituted
2-naphthols - azo coupling
occurs at position 1

Table 1: Some Primary Aromatic Amines

X	Primary Aromatic Amine	X	Primary Aromatic Amine
0	<i>o</i> -toluidine	5	<i>p</i> -ethylaniline
1	<i>m</i> -toluidine	6	<i>o</i> -isopropylaniline
2	<i>p</i> -toluidine	7	<i>m</i> -isopropylaniline
3	<i>o</i> -ethylaniline	8	<i>p</i> -isopropylaniline
4	<i>m</i> -ethylaniline	9	<i>o</i> -(<i>n</i> -propyl)aniline

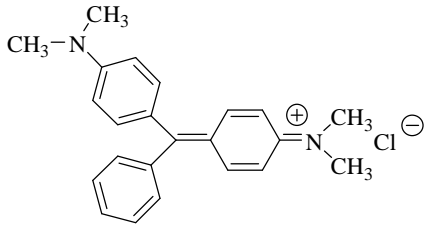
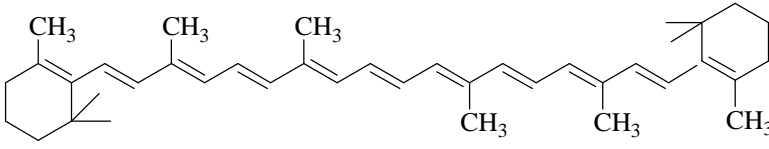
Table 2: Some Coupling Reagents

Y	Coupling Reagent	Y	Coupling Reagent
9	2-hydroxy-3-naphthalenesulfonic acid, sodium salt	4	2-hydroxy-8-naphthalenesulfonic acid, sodium salt
8	2-hydroxy-4-naphthalenesulfonic acid, sodium salt	3	2-hydroxy-3-naphthalenecarboxylic acid, sodium salt
7	2-hydroxy-5-naphthalenesulfonic acid, sodium salt	2	2-hydroxy-4-naphthalenecarboxylic acid, sodium salt
6	2-hydroxy-6-naphthalenesulfonic acid, sodium salt	1	2-hydroxy-5-naphthalenecarboxylic acid, sodium salt
5	2-hydroxy-7-naphthalenesulfonic acid, sodium salt	0	2-hydroxy-6-naphthalenecarboxylic acid, sodium salt

Background and Theory

Chromophores and Auxochromes (see Skoog, Holler and Nieman)

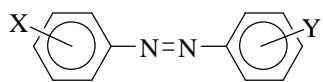
Organic **chromophores** are functional groups, usually conjugated double or triple bond systems, which have low level excited electronic states. These groups absorb energy which may be in or near the visible region of the electromagnetic spectrum. The most common chromophore groups which absorb visible light are long chain conjugated polyalkenes or compounds having multiple aromatic rings connected by sp^2 type carbon or nitrogen bridge atoms.

	
FD&C Green 3 (blue-green colour)	beta-carotene (orange colour)

Auxochromes are functional groups or substituents which alone do not absorb radiation near the visible region, but which as substituents tend to intensify the absorbance of the chromophore, and tend to shift the absorbance of the chromophore to longer wavelengths. Most auxochromes contain unsaturation which conjugates to the chromophore.

Azo Dyes

Azo dyes are the largest and most versatile class of synthetic dyes. They are synthetic organic substances whose molecules contain two aromatic ring systems linked through an azo (dinitrogen) bridge. The first azo dye was synthesized in 1858 by **Griess**, soon after he discovered the diazotisation reaction which is part of the synthesis of an azo dye. The dye **Orange II** or **β -Naphthol Orange** was introduced in 1876.



Azo Compound Structure:
-the aromatic systems may be benzene rings or multi-ring systems
-there may be one or more substituents in each aromatic system

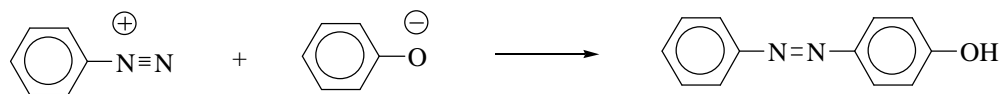
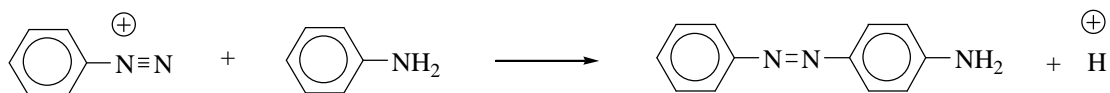
The linking of the aromatic rings through an unsaturated bond like the $N=N$ double bond is called conjugation of the rings. Conjugation of the rings brings the p-electrons of the rings into a combined state that absorbs energy in the visible region of the electromagnetic spectrum. Many useful dyes and chemical indicators are aromatic azo compounds.

Dye substances often have the sulfonic acid functional group as a substituent to one of the aromatic ring systems. This group when neutralized by alkali into the salt form makes the dye more soluble in water and assists in linking the anionic dye molecules to the fibres of cotton, wool or nylon.

Azo Coupling Reactions

Azo compounds are formed by coupling an aromatic diazonium ion with an activated aromatic substrate. Aromatic **diazonium ions** are electrophilic reagents that can attack aromatic rings and replace the hydrogens at activated positions in the ring. The most active positions occur in rings that have either an amine or a hydroxy (phenol) substituent present.

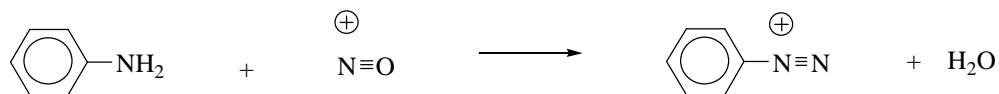
In the case of a phenol-type target molecule, the rate of attack is greatly increased if the phenol is first reacted with strong base to form a phenoxide ion. The reaction is illustrated here with benzenediazonium ion as the electrophile, firstly with aniline as one substrate, and secondly with phenoxide ion (from phenol) as another substrate.



In both aniline (aminobenzene) and phenol or phenoxide ion type substances, **azo coupling** occurs most rapidly at the 4- or *p*- position, opposite the -NH_2 or -OH group, as shown.

Aromatic Diazonium Ions

An aromatic diazonium ion forms when nitrosyl ion reacts with a primary aromatic amine in a reaction called a diazotisation. The positively charged nitrosyl ion is an electrophile, attacking atoms that have unshared electron pairs, such as the nitrogen of an amine group. A new nitrogen - nitrogen bond forms, and after some tautomeric exchanges of hydrogen atoms, a water molecule leaves. The overall reaction is illustrated using aniline as an example.

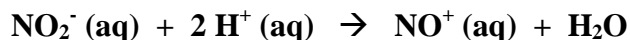


Most aromatic diazonium ions such as the one formed in this experiment must be kept in solution in ice-cold water and must be kept cold. Aromatic diazonium ions form solid salts that are unstable above 5 to 10 °C and are sometimes explosive when dry, but the dissolved salts can remain in an ice-cold solution where they are safe and stable.

The formation of a diazonium ion from an aromatic amine is highly useful in chemical synthesis. Since it is unstable, it can easily be formed and reacted in solution, when the dinitrogen group may be replaced by hydroxy, cyano, fluoro, chloro, bromo, iodo or many other functional groups, including hydrogen. The diazonium ion can also be coupled with aromatic amines and phenols (hydroxy compounds) to form azo compounds, where the dinitrogen group remains in the product molecule.

Nitrosyl Ion

On the addition of strong acid to an ice-cold aqueous solution of sodium nitrite, the nitrite ion reacts with hydrogen ions, producing the nitrosyl ion (NO^+), as shown in the equation below. Nitrosyl ion reacts rapidly with organic amines, both aliphatic and aromatic. The nature of the product(s) depends on whether the amine is primary, secondary or tertiary.

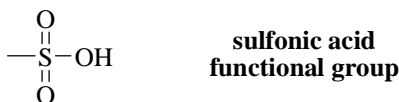


In the case of a primary aromatic amine, the product is an aromatic diazonium ion. Formation of the nitrosyl ion, necessary for the diazotisation reaction, occurs only in strong acid. Addition of hydrochloric acid to a solution of sodium nitrite in water containing some solid ice is the usual method of producing nitrosyl ion.

Sulfonic Acid Functional Group

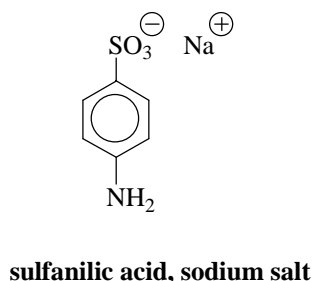
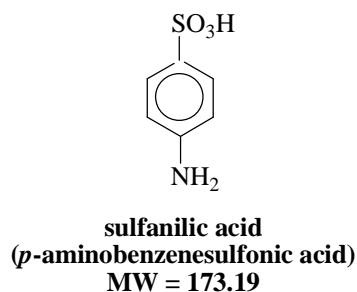
The sulfonic acid functional group consists of a carbon - SO_3H arrangement of atoms. Aromatic sulfonic acids are synthesized by reacting aromatic compounds with concentrated sulfuric acid or other reagents capable of producing the electrophile SO_3 for substitution into the aromatic ring.

Sulfonic acids are strong acids, with a structure similar to that of sulfuric acid. The presence of this group in a molecular structure makes the substance strongly acidic, capable of forming salts by reaction with bases, and potentially soluble in water. Sulfonic acids and their salts are synthesized for numerous purposes, including use as surfactants (synthetic detergents), as water soluble dyes, for ion-exchange use and for use as drugs.



Sulfanilic Acid

Sulfanilic acid (p-aminobenzenesulfonic acid) is related to p-aminobenzenesulfonamide, the parent compound of a range of substances called sulfa drugs. These drugs inhibit the growth of bacteria.



This Section Continues on the Next Page →

Sulfanilic Acid (Cont.)

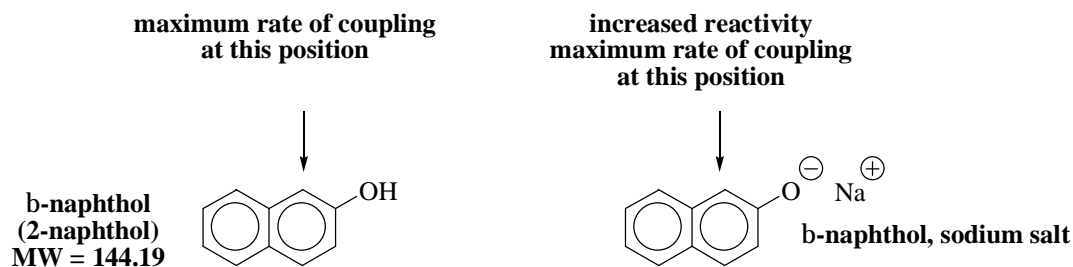
Sulfanilic acid, like all aromatic sulfonic acids, is a strong acid similar in acid strength to sulfuric acid. Solid sulfanilic acid should be considered to be corrosive and hazardous. Sulfanilic acid is not soluble in water or acid, but it is soluble in alkaline solution.

In this experiment, sulfanilic acid will be diazotized and used the resulting diazonium ions will be reacted with β -naphthol to form the azo dye Orange-II. The sulfanilic acid will be made soluble by neutralization with sodium carbonate solution.

β -Naphthol

The naphthalenols (naphthols) and naphthalenediols are intermediates in the synthesis of dyes, agricultural chemicals, drugs, perfumes and surfactants. The chemical and physical properties of all aromatic hydroxy (phenol) type compounds include weak acidity of the hydroxy proton. The solubility of β -naphthol (2-naphthol) in cold water is very small, but on reaction with sodium hydroxide, the phenoxide type salt formed is more water soluble. The reactivity of the phenoxide type ion towards ring substitution is much greater than that of the parent compound.

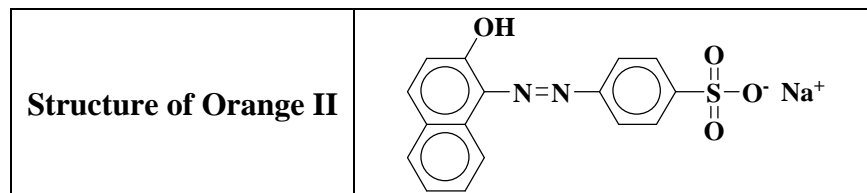
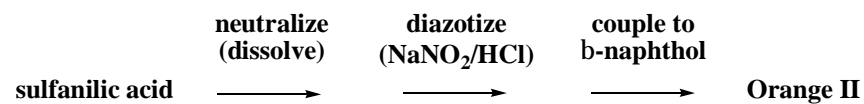
The maximum activation of substitution is at the 1-position (**1 = α = alpha**) in the molecule, next to the hydroxy group in the 2-position (**2 = β = beta**).



Reaction Scheme

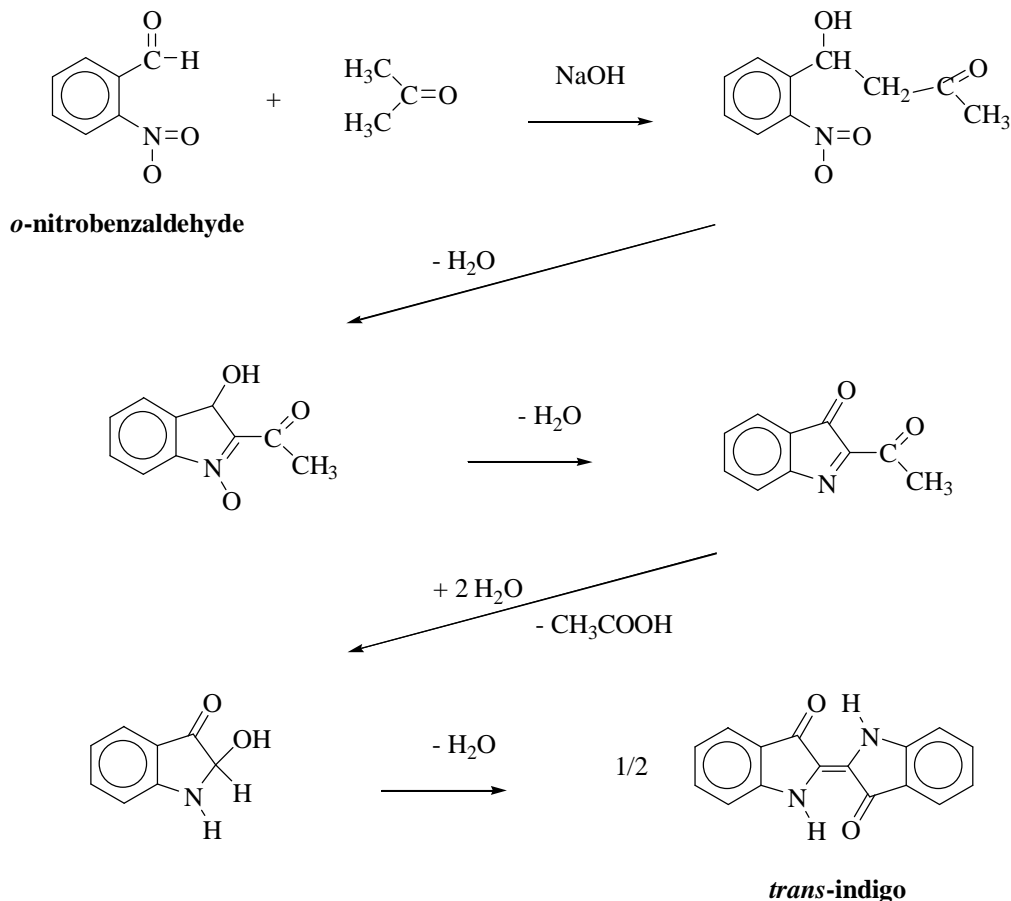
A brief overview of the reaction scheme is:

Synthesis of Orange II (β -Naphthol Orange) - A Fabric Dye



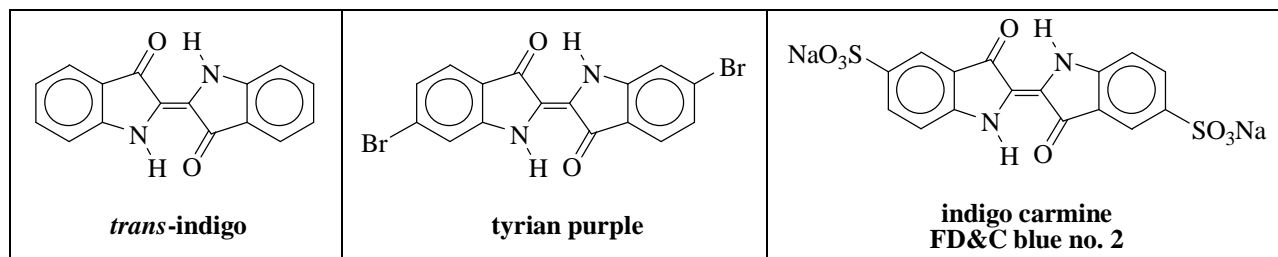
Synthesis of Indigo

There are many synthetic routes to **indigo**. In this experiment, indigo will be produced by a sequence of reactions occurring when ***o*-nitrobenzaldehyde** is reacted with acetone in alkaline solution.



Indigo and Related Dyestuffs

The blue dye of blue denim clothes (**indigo**) is closely related in chemical structure to the purple dye (**tyrian purple**) of the purple trimmed clothes of the Roman emperors Julius and Augustus Caesar and also to the synthetic blue food dye **indigo carmine (FD&C blue no. 2)**.



This Section Continues on the Next Page →

Indigo and Related Dyestuffs (Cont.)

The blue dye of blue denim, called **indigo**, occurs naturally in several plants. Traces of the dye have been found in Egyptian tombs from 3,500 B.C. The Romans imported indigo from India (the origin of the name), where it was extracted from the juices of the plant **Indigoferae sumatrana**. It would be impossible to supply the demand for indigo today from plant sources.

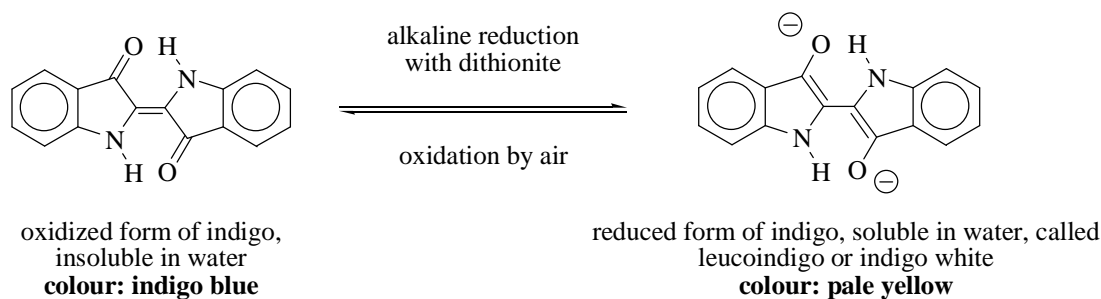
The dye **tyrian or Imperial purple** is obtained from the sea mollusc **Murex**. The production of this natural dyestuff was developed as an industry in the Eastern Mediterranean seacoast region of the city of Tyre. The dyestuff was extremely expensive. In Imperial Rome, the dye was allowed only for the use of the Imperial family.

The synthetic food dye **indigo carmine or FD&C blue no. 2** is one of the dyes recognized as safe for food use in both Canada and the United States.

Vat Dyeing with Indigo

Indigo is insoluble in water and cannot be used as a dye in this form. However, indigo is easily reduced to a soluble ionic form by alkaline reduction with dithionite ion.

Sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) is used as a reducing agent for dyeing and other chemical processes, and as a bleaching agent for paper pulp, straw, china clay, and soap. **Industrial demand for dithionite is about 300,000 tonnes per year.**



The blue colour of the indigo changes to an almost colourless, pale yellow on reduction, and the ionic product is soluble in water. In the soluble form, it is referred to as a **vat dye**.

After the fabric has been soaked in the vat and the dyestuff is attached, the fabric is removed from the vat and washed and dried in air. In air, oxygen slowly oxidizes the **leucoindigo** to its insoluble blue form. The fabric colour changes from yellow to green (yellow + blue) to blue as this process occurs.

Textile Fabrics

Repeated from the CHEM CH602 Study Guide: Polymers - Supplementary Notes

Textile fabrics are made from textile fibres, which in turn are made from **fibre-forming** polymeric materials. Most of these materials are organic polymers. The main classes of natural fibres are the **cellulosic**, such as cotton, linen, hemp, jute, sisal, etc. and the **proteins**, such as wool, hair, silk, etc. The most important classes of synthetic fibre-forming polymers are the polyesters (mainly polyethylene terephthalate), the polyamides (nylons), the polyacrylonitriles (acrylic fibres), and the polyolefins (mainly polypropylene).

Much of the production of fibres goes into fabrics which are then dyed before going on to end uses such as clothing, bedding, towelling, upholstery, rugs, ropes, etc. The amount of such fabrics produced is immense and the amount of dyestuffs required is in the order of several percent of the total mass of fabric. Fibre production, dyestuff production and dyeing are all major economic activities.

Fibre-Forming Polymers

A polymeric substance can form useful fibres if it has the following properties:

- adequately **large** average molecular size;
- highly one-dimensional (**unbranched**) molecular chains;
- **flexible** chains (free rotation of bonds) which can become fairly straight;
- **regularity** of chemical structure and stereochemistry in the chains.

Fabrication of Fibres

The synthesis of a fibre-forming polymer does not in itself produce a fibrous material. The polymeric substance must be physically processed or **fabricated** into a fibre. The polymeric molecules at first are coiled and mixed randomly. To make a fibre the following must occur:

- the molecules must be made to **uncoil**, and **line up** in one direction;
- the **aligned** molecules must **fit together** uniformly;
- regions of crystallinity (called **crystallites**) must form by intermolecular attractions;
- the bulk of the material must be **stretched** out into a fibrous form.

Fabrication is accomplished by **spinning** and **drawing** the polymer mixture.

Spinning consists of melting the polymer and forcing the liquid under pressure through small holes in a die. The passage through the small hole aligns the molecules, which are cooled to form a solid fibre. Alternatively, the polymer may be dissolved in a suitable solvent mixture, forced through a die and then precipitated as a solid by removal of the solvent by evaporation or by mixture with another solvent.

Drawing consists of immediately or later pulling the solid fibre out to several times its original length. This makes the fibre much more crystalline and increases the **tensile strength** greatly.

Dyeing of Fibres and Fabrics

Dyeing of a fibre or fabric consists of attaching an adequate amount of the individual molecules of dyestuff to the polymer chains of the material. The first problem is to diffuse the dyestuff into the fibres. The second problem is to attach the dyestuff permanently. This ability of a dye to remain attached to a fibre is called **fastness**.

- Some fibres are difficult to dye because the individual polymer molecules are packed so closely together, only very small dye molecules can diffuse in to attach to them.
- Some dyes are able to diffuse in, but will not attach strongly, and so are non-fast. For some dyes and fabrics, intermediaries are used to make the attachment. For example, the salts of Al(III), Cr(III) and Mg(II) have been used for thousands of years in the dyeing of wool, where they are called **mordants**. These small, highly charged ions form complex ions with dyestuffs that attach firmly to the wool polymers by further **complexation**.

Multi-Fiber Ribbon Test Fabric

(The U.S. spelling of fibre is used in the name as the material is supplied from the U.S. by a company named Test Fabric Inc.)

Dyeing is a large-scale industrial activity. Dyes are always tested on a small scale before use. A test fabric comprised of multiple fabrics, each made from a different fibre but all in the same swatch or piece is used for the testing of dyestuffs.

The multi-fiber ribbon test fabric used in this experiment consists of 13 different fabrics, each made of a different fibre-forming polymeric material.

Table: Fibres Listed in Order Starting from the Black Marker Stripe

Position	Fibre	Type
1	Acetate	cellulose, monoacetate
2	SEF*	acrylic
3	Arnel - bright	cellulose, triacetate
4	Bleached Cotton	natural cellulose
5	Creslan 61	acrylic
6	Dacron 54	polyester
7	Dacron 64	polyester
8	Nylon 6,6	polyamide
9	Orlon 75	acrylic
10	Spun Silk	natural polyamide
11	Polypropylene	polyolefin
12	Viscose	regenerated cellulose
13	Wool	natural polyamide

* SEF is Self-Extinguishing Fiber, an acrylic copolymer which does not support combustion.

See also:

<http://jkdyes.pbwiki.com/Making%20Sense%20of%20the%20Experiment%3B%20Fabrics%2C%20Dyes%2C%20and%20Intermolecular%20Forces>
(search on: “jkdyes.pbwiki.com” to obtain this URL)

Procedure

This is a long procedure. The partners will have to divide the tasks and work independently to complete the procedure within 2 hours.

Caution. Handle all organic reagents with appropriate care. Phenols, aromatic nitro compounds, and aromatic sulfonic acids are very hazardous.

The product dyes themselves are less hazardous in general than the component reagents. The product dyes will stain hands and clothing.

A. Preparing the Multi-Fiber Ribbon Fabric for Dyeing

The instructor will give you **three (3)** swatches of the multi-fiber ribbon each of **2 cm-width**.

- A-1. Soak all the fabrics pieces which are to be dyed in a small amount of warm water containing a small amount of a surfactant or detergent. For dyeing, it is best to use a **non-ionic** surfactant if possible.
- A-2. Very **gently** squeeze the fabrics several times in the detergent solution to be sure the fabrics are well soaked with the surfactant. **Gently** squeeze the fabrics as dry as possible just before dyeing.

Synthesis of Orange II (Parts B to D)

Record the mass measurements for the synthesis.

Record your observations of colour changes occurring during the procedure.

B. Preliminary Steps

Solution 1

- B-1. Weigh out **0.35 g (± 0.02 g)** of **β -naphthol** (synonyms: 2-naphthol; 2-hydroxynaphthalene).
- B-2. Dissolve or suspend the solid **β -naphthol** in **5 mL** of **1 M sodium hydroxide** in a small erlenmeyer flask.
- B-3. Record the mass data. Stir and cool the mixture in an ice-water bath until its temperature is below **5 °C**. Use a thermocouple and a digital thermometer. This is **Solution 1**. Keep it cold until it is used.

This Section of the Procedure Continues on the Next Page →

B. Preliminary Steps (Cont.)

Solution 2

- B-4. Weigh out **0.43 g (± 0.02 g)** of solid anhydrous sulfanilic acid. **Caution. Corrosive.** Weigh out **0.13 g (± 0.02 g)** of anhydrous sodium carbonate (Na_2CO_3).
- B-5. Add the solids along with **5 mL** of distilled water to a small erlenmeyer flask. Record the mass data.
- B-6. Warm the mixture of sulfanilic acid and sodium carbonate on a steam bath for several minutes. A purple-grey solution will form. Some of the solid may remain undissolved at this point. This does not matter.
- B-7. Cool the flask contents to below **15 °C** using tap water on the outside of the flask, or an ice-water cooling bath. Some solid will be present in the flask.
- B-8. Weigh out **0.19 g (± 0.02 g)** of solid crystals of sodium nitrite (NaNO_2) and place the solid in a small test tube. Record the weighing. Add **1.0 mL** of distilled water to the test tube. Dissolve the solid.
- B-9. Pour the solution of sodium nitrite from the test tube into the erlenmeyer flask containing the neutralized sulfanilic acid prepared in **Step B-7**. Mix well. This is **Solution 2**.

C. Diazotization Reaction

- C-1. Place about **3 g** of crushed ice in a **100 mL** beaker. Add **1.0 mL** of dilute **6 M** reagent **HCl** solution.
- C-2. Add **Solution 2**, the solution of sulfanilic acid and sodium nitrite prepared in **Step B-9** to the ice and **HCl** in the **100 mL** beaker. Stir well, and allow the suspension or slurry to stand for **5 minutes**. Be sure that the solution remains near **0 °C**, using an ice-water bath if needed.

D. Orange II Azo Dye Formation

- D-1. After the mixture of **Step C-2** has had **5 minutes** to react, pour **Solution 1**, the cold solution of **β -naphthol** in sodium hydroxide prepared in **Step B-3**, into the suspension (slurry) of diazotized **sulfanilic acid** of **Step C-2**.
- D-2. Stir well and heat the entire mixture in the **100 mL** beaker on a steam bath for **5 minutes**. Most but not all of the solid will dissolve. A **dark red colour** of the dissolved product dye should be apparent. This beaker will be the dye vat.

E. Dying with Orange II

- E-1. Dilute the solution in the 100 mL beaker from **Part D** to **50 mL** by adding distilled water. See **Part A** for the fabric preparation instructions. Add one prepared multi-fiber ribbon test strip to the dye vat.
- E-2. Heat the mixture in the 100 mL beaker on a steam bath and stir **very gently** occasionally with a stirring rod for **10 minutes** or as long as possible.
- E-3. Observe and record any colour changes seen as the dyeing progresses.
- E-4. Remove the dyed fabric with tongs. Rinse the fabric gently in a small beaker with warm running tap water or with several portions of hot tap water until the water runs clear. Observe whether the dye is **fast** (remains on the fibre), or washes out of the fibre. Hang the fabric to dry.
- E-5. Rinse the fabric again after drying, and dry again. This latter step may be done at home. Note if any dye runs out during the second washing.
- E-6. Note the **colour** and **depth of colour** of each individual fabric in the multi-fiber ribbon strip on a scale of 0 to 10.

F. Synthesis of Indigo

Check that the bench ventilation and fume hood ventilation fans are switched on.

- F-1. **Caution. Very Hazardous.** Weigh out **0.50 g** of *o*-nitrobenzaldehyde into a **100 mL** beaker. **Move into a fume hood.**
- F-2. Add **5.0 mL** of **acetone** and stir or swirl until dissolved.
- F-3. Add **5.0 mL** of distilled water and stir well.
- F-4. Add **2.5 mL** of **1 M NaOH** and stir. The blue colour of the indigo will appear.

The reaction is strongly exothermic, and the solution may boil. Allow the mixture to stand for **5 minutes**. Remove from the fume hood.
- F-5. Recover the product solid by a vacuum filtration. Wash the solid product first with **10 mL** of water, then with **10 mL** of ethyl alcohol. Place the washings into the organic discard.
- F-6. Allow the solid on the filter paper to dry in air until it is needed for dyeing.

G. Vat Dyeing with Indigo

- G-1. Transfer as much of the dried product **indigo** as possible into a **250 mL** beaker. Add **60 mL** of a solution of **1 M NaOH**.

The indigo is insoluble and will not dissolve.

- G-2. Heat the mixture as hot as possible on the steam bath and then add about **1 g** of dry **sodium dithionite**.

The indigo will react to form the soluble leucoindigo and will dissolve as a clear, yellowish solution. Some of the unreacted insoluble blue indigo solid will remain on the surface of the solution.

- G-3. Add about **50 mL** of distilled water to the solution. Keep the solution on the steam bath throughout the dyeing process.

- G-4. See **Part A** for fabric preparation instructions.
Add one prepared multi-fiber ribbon test strip to the dye vat.

- G-5. Soak the multi-fiber test strip in the beaker for **10 minutes** or as long as possible. Stir the fibre **very gently** occasionally with a stirring rod.

- G-6. Note and record the colour of the fibres at all stages of the process.

This is vat dyeing. Lighter or darker colours may be obtained by altering the dyeing time.

- G-7. Remove the dyed fabric with tongs into a clean beaker. Note the colour on the fabric immediately, and watch as it changes over several minutes in air.

- G-8. Rinse the fabric gently in a small beaker with warm running tap water or with several portions of hot tap water until the water runs clear. Observe whether the dye is **fast** (remains on the fibre), or washes out of the fibre. Hang the fabric to dry.

- G-9. Rinse the fabric again after drying, and dry again. This latter step may be done at home. Note if any dye runs out during the second washing.

- G-10. Note the **colour** and **depth of colour** of each individual fabric in the multi-fiber ribbon strip on a scale of 0 to 10.

H. Dyeing with a Powdered Drink Mixture Containing Soluble Food Dyes

- H-1. Add the contents of a powdered drink package (**Kool-Aid**[®] or similar) to about **50 mL** of distilled water in a **250 mL** beaker. Heat the mixture on a steam bath until it is hot.

The drink mixture is acidic.

- H-2. See **Part A** for fabric preparation instructions.
Add one prepared multi-fiber ribbon test strip to the dye vat.
- H-3. Keep the solution on the steam bath throughout the dyeing process.
Soak the multi-fiber test strip in the beaker for **10 minutes** or as long as possible.
Stir the fibre **very gently** occasionally with a stirring rod.
- H-4. Note and record the colour of the fibres at all stages of the process.
- H-5. Remove the dyed fabric with tongs. Rinse the fabric gently in a small beaker with warm running tap water or with several portions of hot tap water until the water runs clear.
Observe whether the dye is **fast** (remains on the fibre), or washes out of the fibre.
Hang the fabric to dry.
- H-6. Rinse the fabric again after drying, and dry again. This latter step may be done at home.
Note if any dye runs out during the second washing.
- H-7. Note the **colour** and **depth of colour** of each individual fabric in the multi-fiber ribbon strip on a scale of 0 to 10.

Report Instructions

Synthesis of Orange II

- R-1. Report all of the mass measurements and the observations of colours seen in every part of the procedure.
- R-2. Draw yourself **by hand or using a chemical drawing software application** the full structural formula of the diazonium ion prepared from sulfanilic acid.
Name the drawing program used. **Name the ion.**

Dyeing with Orange II

- R-3. Report all of the observations made during the dyeing with **Orange II**.
- R-4. **Attach the dyed multi-fiber ribbon to the report as part of a labeled display.**

Synthesis of Indigo

- R-5. Report all of the observations made during the preparation of **Indigo**.

Vat Dyeing with Indigo

- R-6. Report all of the observations made during the vat dyeing with **indigo**.
- R-7. **Attach the dyed multi-fiber ribbon to the report as part of a labeled display.**

Dyeing with a Powdered Drink Mixture Containing Soluble Food Dyes

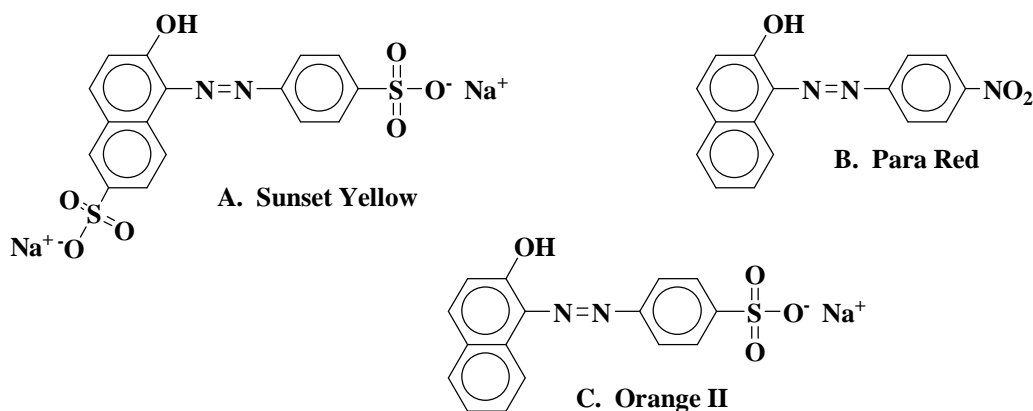
- R-8. Report the Brand and flavour of drink powder used. Report all of the observations made during the vat dyeing with the **soluble food dye mixture**.
- R-9. **Attach the dyed multi-fiber ribbon to the report as part of a labeled display.**

Results of Dyeing

- R-10. Tabulate descriptions of the colour and depth of colour observed **on each individual fibre** (on a scale of 0 to 10) for the each of the three dyeing experiments of the multi-fiber ribbon.

See the **Table** on page 12 for the names and order of the 13 fibres on the ribbon.

Post-Laboratory Questions

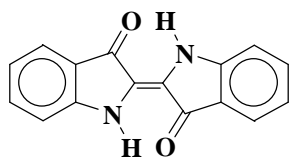


1. Substance **A** above is **Sunset Yellow**, a yellow-orange **very water soluble** food colour. Substance **B** is **Para Red**, a red fabric dye that is **very insoluble** in water. Substance **C** is **Orange II**, an orange fabric dye that is **moderately soluble** in water.
 - a. Draw the three structures by hand or using chemical drawing software. Name the drawing program used.
 - b. What is common to the chemical structures of the three dyestuffs? Show the common region on the structures. This is the **chromophore** of the three molecules.
 - c. Which parts of the molecules promote solubility in water? **Show** these parts on the structures. **Explain** in each case why water solubility is enhanced. This is the basis of the differing water solubility of the three molecules.
2. One of the many synonyms of **Sunset Yellow** (Structure **A** above) is **6-hydroxy-5-(4-sulfophenylazo)-2-naphthalenesulfonic acid, disodium salt**.
 - a. Draw the structure of Sunset Yellow by hand or using chemical drawing software. Name the drawing program used. Show on the structure the numbering system used in the name. **Explain** in words each part of the name.
 - b. Draw the structure of the azo substance of one of the partners of **Experiment 5 Preparation Question 3** by hand or using chemical drawing software. Name the drawing program used.
 - c. Name the azo compound you have drawn using the same system as in **Part 2a** above. **Show** on the structure the numbering system used in the name. **Explain** in words each part of the name.

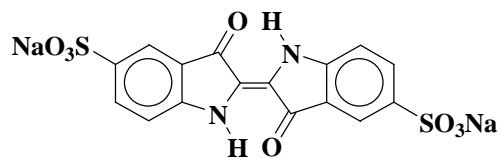
Bonus Questions - Answer No More Than Two Questions

1. Identify each of the 13 fibres in the multi-fiber ribbon according to its chemical type (cellulosic; modified cellulosic; polyamide; polyester; polyacrylic; polyolefin). For each fibre type, state the name or chemical type of the monomer or monomers in the chain, and the modifying groups if present. Use a table format for your answers. Give your reference(s).

2.



trans-Indigo



Indigo Carmine (FD&C Blue No. 2)

Indigo Carmine is a blue, very water-soluble food colour dye. This substance might be synthesized by the method used in this experiment to synthesize Indigo, if the properly substituted sulfonate derivative of *o*-nitrobenzaldehyde were available.

- Draw the structure of the required sulfonate derivative of *o*-nitrobenzaldehyde by hand or using chemical drawing software. Name the drawing program used.
 - Devise a synthesis of the required substance starting from benzene. Pay attention to the sequence of the synthesis, and the activating / deactivating and orienting nature of the substituents to the benzene ring.
3. As demonstrated in this experiment, water soluble anionic dyestuff molecules are able to adhere well to **wool**, **silk**, and **nylon** fibres. They do not adhere well to **polyesters**, **polyacrylics** or **polypropylene**.

Research this topic. What kinds of dyestuffs are used to dye the other fibre types? Give your reference(s).