

Dyes, Pigments, and Paints

Introduction

In this lab you will synthesize a green pigment, **verdigris**, by a process known since ancient times (Part C) and **Prussian blue**, considered to be the first modern synthetic pigment (Part A). You will reproduce the historically important synthesis of **mauve** dye (Part B). You will prepare **tempera** paint by two methods, including one used the Native Americans of the northwest coast (Part D).

The following introduction to pigments, dyes, and binders is from Joe Lambert, *Traces of the Past: Unraveling the Secrets of Archaeology through Chemistry*.

Coloring materials are usually classified as *dyes* or *pigments*. Dyes are chemically bound to a substrate such as a textile, whereas pigments require another substance, called a *binder*, to help them adhere to the substrate. The human body may have served as the first substrate for dyes, but textiles or fabrics have been the most common over the ages. In addition to textile fibers, dyes have been applied to paper, wood, food, cosmetics, fur, and leather....

Almost all dyes are organic materials - that is, they belong to the large class of chemicals whose structure is based on the element carbon. On the other hand, most early pigments did not contain carbon and hence were inorganic. Water-soluble organic dyes, however, can be converted for use as pigments by embedding them in a solid substrate such as powdered chalk or kaolin clay. The resulting material, called a *lake*, would be powdered and used in the same way as inorganic pigments. Today, however, there are entirely organic as well as inorganic pigments.

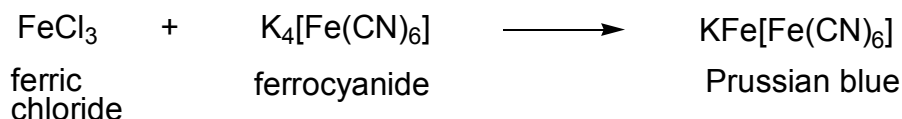
Because pigments do not dissolve in most media, such as water, they require a binder in order to be applied to a substrate. No chemical reaction actually takes place between the pigment and the binder. The binder serves only to incorporate the pigment onto the surface of the substrate, providing another contrast with dyes, which permeate the substrate fully. Normally, binder and pigment are mixed mechanically and then applied together. For underglaze decorations on pottery, however, the pigment is applied first and the transparent glaze, serving as the binder, afterward. In *fresco* painting, the binder is formally applied first in the form of damp plaster prepared from lime (calcium oxide, CaO). The pigments, mixed with lime and water, are then applied to the damp surface. Lime reacts with the atmosphere to form calcium carbonate (CaCO₃, the same material as limestone), so that the pigments are essentially encased in stone.

To serve as a *paint*, pigments are mixed with a carrying agent or solvent as well as a binder. The purpose of the solvent is to keep the mixture fluid until application is complete, after which it evaporates. Chalks and crayons contain pigment and binder but no solvent. The binder in *oil paints* is linseed oil (from flax), tung oil (from the tung tree), or any of a variety of other (usually) plant products; the solvent is an organic material like turpentine. During the drying process the solvent evaporates, and double bonds between carbons (C=C) in the binder combine with other binder molecules, or polymerize, to form larger and larger molecules (polymers). This drying or hardening process is accelerated by light and air. Oils that lack double bonds cannot polymerize and are called semidrying (cottonseed oil, sesame oil) or nondrying (olive oil, coconut oil). They are not suitable as binders. To prevent drying oils from cracking or decaying, the finished product often is covered with a clear film called a *varnish* that provides a seal. Most modern paints use synthetic materials called *acrylics* as binders, but the principle is the same, as the acrylic material (such as vinyl acetate) contains double bonds that polymerize upon application. Synthetic formulations are designed to dry quickly, to use water as the solvent (a *latex paint*), to be flexible, and to have superior hiding power. Their stability over centuries, however, is not known.

Tempera paints use an oil-water *emulsion* as the binder. An emulsion is a stable mixture of two normally immiscible liquids. The process of mixing oil and water requires an emulsifying agent such as gum arabic (from the acacia tree), glue, or egg yolk, or else the two materials will separate. In *watercolor* paint, the pigment is ground very finely and suspended in water with a binder such as gum arabic. *Inks* are liquids used for writing or drawing. The coloring material may be either a pigment or a dye, together with a binder, such as a gum or a glue, and a carrying agent (or *vehicle*), such as water.

Part A. Prussian blue

Ferric ferrocyanide, commonly known as Prussian blue, has a very intense dark blue color and has been used extensively as a pigment in paints and inks, and is responsible for the color of blueprints. The compound contains iron ions in both the Fe^{+2} (ferrous) and Fe^{+3} (ferric) states, with the ferrous ions very tightly associated with CN^- (cyanide) ions. The Prussian blue crystal lattice can accommodate varying amounts of water and metal ions. Therefore the exact molecular formula for Prussian blue can vary from $\text{FeNH}_4[\text{Fe}(\text{CN})_6]$ to $\text{KFe}[\text{Fe}(\text{CN})_6] \cdot 5 \text{H}_2\text{O}$ to $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 15 \text{H}_2\text{O}$. All forms of Prussian blue are insoluble in water although extremely small particles may be easily dispersed to form a blue suspension that looks like a true solution.



Prussian blue was first synthesized unintentionally by a Berlin colormaker named Diesbach. This discovery is described by Philip Ball in *Bright Earth*:

... Diesbach was trying to make one thing and ended up making another, a happy victim of impure reagents. The advance of chemistry has relied heavily on the carelessness of distillers, refiners, and manufacturers, and I mean that with no disrespect.

Diesbach was making cochineal red lake, which required iron sulfate and potash. He secured his potash from an alchemist named Johann Konrad Dippel, in whose laboratory Diesbach was laboring. Presumably in an attempt to economize, Diesbach requested that Dippel give him a batch of potash that had been contaminated with animal oil, which was waiting to be thrown away. Diesbach discovered soon enough that it was a false economy, since his red lake turned out extremely pale. Making the most of a bad job, he attempted to concentrate, it, whereupon it turned purple before becoming deep blue.

Perplexed and lacking much chemical knowledge, Diesbach turned to Dippel for an explanation. The alchemist deduced that the blue color came from a reaction between iron sulfate and the contaminated alkali. More than that he was unable to say, but in retrospect we can see that the alkali had reacted with Dippel's oil, prepared from blood, to make potassium ferrocyanide (a compound still known in German as *Blutlaugensalz*). This then combined with iron sulfate to form the compound that chemists call iron ferrocyanide, known more familiarly (even to them) by its pigment name, Prussian blue.

Procedure

Week 1

1. Using a graduated cylinder, measure out about 5 mL of a 0.5 M solution of FeCl_3 (ferric chloride), to a test tube. Make a note of the color of this solution on your report

sheet.

2. Rinse the graduated cylinder with water and use it to measure about 5 mL of a 0.25 M solution of potassium ferrocyanide, $K_4Fe(CN)_6$, to the test tube. Make a note of the color of the potassium ferrocyanide solution on your report sheet.
3. Stir the mixture in the test tube using a glass stirring rod. Record your observations in your laboratory notebook and on the report sheet. This new substance is Prussian blue.
4. Fold a filter paper circle into a semicircle and then fold in half once again. Open up the filter to form a cone and place it in a funnel. Set the funnel into a test tube in a rack. Pour and scrape the blue precipitate into the funnel and allow the excess liquid to drain into the test tube. The blue material is thick and will take most of the lab period to drain.
5. At the end of the lab period carefully remove the filter paper and wet blue pigment from the funnel, open it up and lay it on a piece of paper towel. Let the pigment dry uncovered on the filter paper in your drawer until the next lab period.

Week 2

6. Carefully weigh an empty vial. Record the mass in your laboratory notebook and on the report sheet. Transfer the dry Prussian blue pigment from the filter paper to the vial. Reweigh the vial and record the mass in your laboratory notebook and on the report sheet.

Part B. Synthesis of Mauve

Over the last 200 years chemists have developed extremely sophisticated methods for the synthesis of large, elaborate organic molecules, including dyes. In Part B of this lab you will reproduce synthesis of mauve dye discovered by William Perkin in 1856.

More about mauve from a discussion between the spirits of earth and water, from "Caveman Chemistry" by Kevin M. Dunn:

Earth spirit: But like I said at the beginning, this chapter is not so much about the gas; it's about the tar. That tar is a complicated mixture of compounds and folks started to wonder what they were and what could be done with them. In 1825 **Michael Faraday** isolated benzene from the destructive distillation of whale oil. Pretty soon everybody and *her* dog were destructively distilling things to see what would come of it. In 1826 Otto **Unverdorben** isolated aniline from indigo and in 1834 **Friedlieb Runge** isolated aniline and phenol from coal tar. So with a second, non-destructive distillation folks started producing chemicals from coal tar, chemicals like benzene, toluene, aniline, phenol, and naphthalene. Folks figured that since these compounds came from the destruction of organic compounds, maybe it would be possible to make good and useful things by putting them back together again.

Water spirit: Gas had become a major industry-

Earth spirit: -but this chapter is more about tar. See, at that time malaria was a problem for the British Empire, on account of its rampant colonialism, and the best treatment for malaria was quinine, extracted from the bark of a south American tree. To promote chemical innovation the British started up the Royal College of Chemistry in 1845, with the great German chemist, **Wilhelm Hofmann**, as director. In 1856 Hofmann's assistant, **William Perkin**, set out to synthesize quinine from coal tar. Perkin reacted aniline with potassium dichromate, a really strong oxidizing agent; the resulting black goo was definitely not quinine, but it made a beautiful purple solution in alcohol. Perkin called it "mauveine" and dropped out of college at the age of 18 to develop his new synthetic dye. British dyers didn't think that mauve would catch on, but the Paris fashion houses liked it so much that Perkin was able to retire at the age of 36. I told you it was a great business.

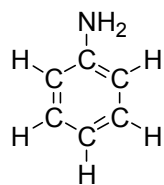
Water spirit: And-

Earth spirit: -once folks knew that it was possible to make artificial dyes from coal tar, new dyes started coming out of the gasworks, so to speak. Variations on the original synthesis produced dozens of dyes from aniline: aniline reds, aniline violets, aniline greens, yellows, browns, and blues. Substituting phenol or naphthalene for aniline produced two more distinct families of artificial colors. There seemed to be few colors which could not be fashioned by art and ingenuity from coal tar.

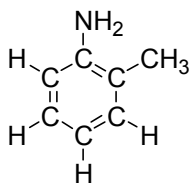
Hofmann's leadership at the Royal College had given the British a head start in synthetic dyes, but when Hofmann returned to Germany in 1865 British dyestuffs dropped the ball. In France, synthetic dye manufacturers charged so much for their products that demand there shifted to natural and imported dyes. But in Germany, the situation was ideal for the development of these new wonder dyes. State-subsidized technical schools fed talented students to the universities; the universities promoted collaborative work, sending students to study in Britain and France; and universities cooperated with industry on joint research projects. Furthermore, with thirty-nine states in the German Confederation, patent enforcement was a problem and the resulting competition produced lean, mean, dye-making machines. German unification in 1871 made patent enforcement easier, but by that time the big players in German dyestuffs were off and running; *Badische Aniline und Soda Fabrik* (BASF) was out of the gate in 1861, followed by *Farbwerke Hoechst* in 1862; *Friedrich Bayer* rounded the bend in 1863, followed by *Kalle & Co* in 1864; and a late starter from 1867 was reorganized in 1873 as *Aktien Gesellschaft für Aniline Fabrikation* (AGFA). Throughout a century of wars, depressions, revolutions, and mergers Bayer, Hoechst, and BASF were the top dogs of the chemical industry.

Water spirit: I guess you could say, "They were buy-y-ing a ta-ar-way to heaven."

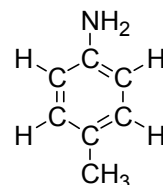
In Part A of the procedure you will reproduce William Perkins' synthesis of mauve. The aniline that he used was not very pure; you will mimic his results by using a mixture of one part aniline, two parts *o*-toluidine, and one part *p*-toluidine. This mixture will be labeled "aniline oil".



aniline



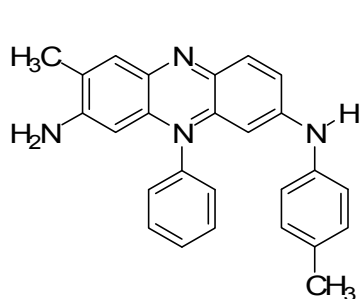
o-toluidine



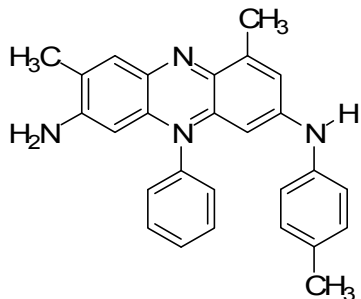
p-toluidine

Rather than dichromate, you will use household bleach as an oxidizing agent. You will use the dye that you produce to dye a swatch of silk fabric.

Because you are starting with a mixture of compounds, the dye that you produce will also be a mixture of compounds. Structures of mauveine A and mauveine B, two of the purple-colored materials produced in this synthesis, are shown below.



Mauveine A



Mauveine B

Procedure

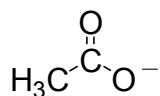
Warning! Mauve will stain some fabrics. Bleach will create white spots on fabric. The starting "aniline oil" in the synthesis of mauve is quite toxic and can be absorbed through your skin.

1. Working with a partner and **wearing gloves**, add one drop of "aniline oil" to 1 mL of white vinegar in a small vial. Aniline oil is a mix of one part aniline, two parts *o*-toluidine, and one part *p*-toluidine.
2. Measure 5 mL ethanol and pour into a small beaker. Add 10 drops of household bleach.
3. Add the ethanol-bleach solution to the aniline oil-vinegar solution and put the cap on the vial. Let this solution stand for one hour. Occasionally check on the solution and record any color changes that you observe.

4. Push two 6x6 in. squares of silk fabric into the vial of dye. Once the silk has taken up the dye, pull it out and spread it out on a few sheets of paper towel to dry. Once dry, wash with soap and water.
5. Attach your dyed silk fabric to your report sheet.

Part C. Preparation of Verdigris

Verdigris is a blue-green pigment made from copper and acetic acid. Neutral copper acetate has the formula $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$. Basic copper acetate contains variable amounts of $\text{Cu}(\text{OH})_2$ and H_2O . Verdigris has been used since ancient times and until the 19th century was the brightest green pigment available.



acetate ion

The following excerpt describing the preparation of verdigris is from *Painters' Colours, Oils, and Varnishes: A Practical Manual* by George H. Hurst, published in 1892.

Common verdigris is prepared in several ways.

1. *French Process.* - The skins and marc of grapes, left after the juice has been pressed out for making wine, are used in France for making verdigris; the material is placed in large tubs, loosely covered over with netting, in which it remains for a few days, when acetic fermentation sets in; when this has commenced sheets of copper (averaging about 8 inches by 4 inches) are thrown in among the fermenting mass - generally old scrap copper is used. They are left in the tub among the grape skins for from 18 to 20 days, the period varying according to the weather; in summer it may be only about 12 to 14 days, but in winter the longer period named is always required. At the end of the time the tubs are emptied and the grape refuse thrown away; the copper sheets are dried, then dipped into water, or, what is better, into bad wine (if that is obtainable), and again dried; by this means a coat of verdigris is formed on the plates, which is scraped off and placed on one side; the plates are redipped and again dried, when another coating of verdigris is formed and scraped off as before; the process is repeated until all the copper has been converted into verdigris. The green is washed with water and then dried, when it is ready for use. At one time almost every vineyard in France and Belgium made verdigris somewhat on the above lines, although there were some variations in the minor details; but, as the consumption of verdigris has decreased considerably, its manufacture has not been so generally followed of late years.

2. *English Process.* - In England verdigris is made by packing plates of copper between clothes soaked in the crude pyroligneous acid obtained in the distillation of wood; this is done in casks; every four or five days the casks are unpacked and the cloths redipped in the acid, and the operation repeated until the sheets of copper begin to have a coat of verdigris; they are then dipped in water and dried; the verdigris on them is then scraped off and the copper is again packed with the cloths; and the process repeated until all the copper has been converted into verdigris. The refuse from the manufacture of cider has been used in making this pigment.

The verdigris is finished for use by washing and drying. The latter has to be done very carefully, as too high a temperature would affect the brilliancy of the tint.

Procedure

You and a partner will prepare verdigris from copper and vinegar. Four different vinegars will be available: red wine vinegar, white wine vinegar, distilled vinegar, and cider vinegar. You will be assigned a vinegar for your verdigris preparation. Part of your assignment is to compare your results with the results of labmates who used different vinegars.

Week 1

1. Working with a partner, clean a small copper strip with copper cleaner. Thoroughly rinse the copper strip with water and place in a 250 mL beaker.
2. Add 20 mL of your assigned vinegar to the beaker, making sure that the copper strip is completely covered. Describe the appearance of the copper strip and vinegar in your laboratory notebook and on the report sheet.
3. Use a piece of tape and a marker to label your beaker with your name(s). Cover the beaker with Parafilm and place it in an oven set at 32°C.

Week 2

4. Describe the appearance of the beaker contents in your laboratory notebook and on the report sheet.
5. Carefully decant the liquid into a clean evaporating dish, leaving any unreacted copper behind.
6. Use a piece of tape and a marker to label your evaporating dish with your name(s) and the type of vinegar used. Place the evaporating dish on the cart provided.

Week 3

7. Examine the residue (verdigris) produced by each team. Record your observations in your laboratory notebook and on the report sheet. Collect your verdigris in one of the vials provided. You will turn your verdigris sample in with your report.
8. Return the evaporating dish to the supply counter.

Part D. Tempera Paint

You will prepare two samples of tempera paint using egg as a binder. For one sample you will use the yolk of a hen's egg. For the other sample you will use salmon eggs to prepare the binder. Salmon eggs were the traditional binder used by the Native American tribes of the coastal northwest. The binder was combined with charred wood or bone for black; iron containing minerals for reds, yellows, and browns; chalky minerals for whites; and ground plants or berries. Other pigments, including Prussian blue and vermilion were obtained through trade. Salmon egg tempera paints were used in the creation of a variety of objects including masks, totem poles, and house front paintings.



Rod Modeste, *The Salmon & Genesis*, silkscreen print, 1982,
from the collection of the Royal British Columbia Museum

Preparation of Binding Media

Each team should prepare one batch of each of the following binders.

Chicken egg tempera binder

1. Obtain one egg. Separate the egg yolk from the white. Discard the egg white. Place the yolk in your palm and pass it from one palm to another until the yolk sac becomes fairly dry. Puncture the yolk and drain it into a small beaker. Dispose of the yolk sac membrane.
2. Estimate the volume of egg yolk and add an equal volume of distilled water. Stir well to form a pale yellow emulsion.
3. Describe the color, texture and viscosity of the binder.

Salmon egg tempera binder

1. Obtain roughly 6-10 salmon eggs. Puncture each egg using a spatula or other sharp object and squeeze the contents into your smallest beaker. Discard the membrane.
2. Use a medicine dropper to add one drop of water for each salmon egg used. Thoroughly mix using a spatula or stirring rod.
3. Describe the color, texture and viscosity of the binder.

Procedure for Preparing Paints

Prepare two samples of paint, one using chicken egg binder and the other using salmon egg binder. You may use any of the pigments provided.

1. Place a small pile (tip end of your spatula only) of dry pigment on a watchglass and add the appropriate binder a few drops at a time. Mix well with a spatula until completely blended. You may need to mix strongly for 25-50 rubs to get thorough blending.

2. Use a paintbrush to apply a sample of your paint to one of the cards provided (Paint a picture!). Label the card with the binder/pigment combination used.

References:

Lambert, Joseph B. *Traces of the Past: Unraveling the Secrets of Archaeology through Chemistry*, Perseus Publishing, Cambridge, MA, 1997

Ball, Philip *Bright Earth: Art and the Invention of Color*, The University of Chicago Press, Chicago, 2001

Hill, Patricia *Laboratory Manual for Chemistry 205*, Millersville University, Millersville, PA, 2008.

Dunn, Kevin M. *Caveman Chemistry*, Universal Publishers, 2003

Hurst, George, H. *Painters' Colours, Oils, and Varnishes: A Practical Manual*, Charles Griffin & Company, London, 1892

Malin, Edward *Northwest Coast Indian Painting; House Fronts and Interior Screens*, Timber Press, Portland, OR, 1999

**Dyes, Pigments, and Paints
Report Sheet**

Name _____
Partner _____
Date _____
TA Name _____

Part A. Prussian blue

1. Observations

Material:	Appearance:
FeCl ₃ solution	
Potassium ferrocyanide solution	
Mixture from step 3	
Prussian blue from step 6	

2. How many moles of FeCl₃ did you start with?

(_____ mL) (1 L / 1000 mL) (0.5 mol/L) = _____ mol

3. How many moles of K₄Fe(CN)₆ did you start with?

(_____ mL) (1 L / 1000 mL) (0.25 mol/L) = _____ mol

4. In this case the limiting reagent is the reactant that you have the fewest moles of. In theory, you can make as many moles of product as you have moles of limiting reagent.

a. What is the theoretical yield of your product in moles? _____

b. Calculate the mass of your theoretical yield, assuming that the formula for your product is KFe[Fe(CN)₆]. Show your calculations.

c. Use the formula shown below to calculate the % of the theoretical that you obtained.

$$(\text{actual yield (g)} / \text{theoretical yield (g)}) \times 100 = \% \text{ of theoretical yield obtained}$$

5. Be sure to turn in your Prussian blue.

**Dyes, Pigments, and Paints
Report Sheet**

Name _____
Partner _____
Date _____
TA Name _____

Part B. Synthesis of mauve

1. Observations

Time:	Appearance of solution:
After _____ minutes	
After _____ minutes	
After _____ minutes	
After _____ minutes	

2. What is the molecular formula for Mauveine A? (In other words, how many C, how many H, and how many N does this molecule contain?)

3. What is the molecular formula for Mauveine B?

4. What is the molar mass for Mauveine B? Show your calculations.

5. Attach your dyed silk fabric to the report sheet.

**Dyes, Pigments, and Paints
Report Sheet**

Name _____
Partner _____
Date _____
TA Name _____

Part C. Preparation of Verdigris

1. Which vinegar did you use? _____

2. Observations

	Observations
Week 1	
Week 2	
Week 3	

3. Compare the appearance of your verdigris to the verdigris obtained by other students in your lab.

Vinegar	Observations
distilled	
red wine	
white wine	
cider	

4. Be sure to turn in your verdigris.

**Dyes, Pigments, and Paints
Report Sheet**

Name _____
Partner _____
Date _____
TA Name _____

Part D. Tempera Paint

Attach your paint tests to the report sheet. Be sure that your tests are labeled with the binder and pigment used.