# Experiment Π -
# Fun with UV radiation - Blueprint Photography by the Cyanotype Process

Today you will be making a monochrome picture using a blue ‘ink’ called Prussian blue, first made in 1704, accidentally. It seems that a German colormaker mixed cream of tartar, saltpeter ($KNO_3$) and ox blood. After ‘heating, calcination and lixiviation’, green vitrol and alum were added. To the resulting green precipitate was added muriatic acid (HCl) to yield a pretty blue color. This stuff is cool. Prussian blue has the ability to act as a host for large amounts of impurities and has been recently used to lock up radioactivity that was deposited in the uplands of North Wales and Cumbria following the disaster that was Chernobyl.

The cyanotype photographic process was first developed by Sir John Hershel in the 1840’s. Commercial cyanotype paper was available in the late 1870’s and began to be used by architects for copying drawings, known as blueprints. Cyanotype printing became popular among amateur photographers toward the end of the 19$^{th}$ century because of its simplicity and low cost. However, the bright blue color of the prints prevented it adoption by most serious photographers.

The high energy of ultraviolet (UV) radiation catalyzes many chemical reactions. These include undesirable chemical reactions in biological organisms, such as DNA mutations. Actually, UV radiation is composed of three different types: UVA, UVB, and UVC. UVB and UVC are the worst, but they only make up ~2% of the total energy we receive from the sun. High energy UVC photons (less than 290 nm) are almost completely absorbed by ozone and very few reach the earth’s surface. This is fortunate since life as we know it would not exist if there were not the case. The lower the wavelength, the higher the frequency, the higher the energy. The higher the energy of the photon, the higher the likelihood that it will get absorbed by us and molecules in our body will get broken (generally considered a bad thing) It also makes sense that the more of these molecules we get, the worse the reaction is (tanning is bad, right?) What is also important is that the sensitivity of various biological molecules varies with frequency. The long and the short of it is that radiation right around 305 nm (UVB) is seriously bad for you.

We will cover a piece of paper (after coating it is known as cyanotype) with a sensitizer which is a mixture of ferric ammonium citrate and potassium ferricyanide. Exposure of the cyanotype paper you make in lab to UV radiation causes reduction of ferric ($Fe^{+2}$) ions to ferrous ($Fe^{+3}$) ions. A blue image is produced as the ferrous ions react with ferricyanide ions to form insoluble iron(III) hexacyanoferrate(II) or Prussian blue. An image will be produced because you will block some of the UV radiation (take a picture) This image appears as the paper is exposed to the UV light (without any ‘developing’) and this is known as ‘printing-out’. After sufficient exposure, the paper is washed in water to remove the soluble unexposed salts. Upon drying, the final image darkens as a result of either slow oxidation in air or some changes in iron coordination with loss of water. The blue pigment is practically insoluble of water and has been used for printing ink, paint pigment, typewriter ribbon and carbon paper.

What should I be taking a picture of? You can use anything you want, honestly, as long as it is opaque. (What does that mean?) The best things are black and white negatives (big ones) and things printed on transparency sheets. You are given only 1 piece of watercolor paper, so use it wisely. Three dimensions things give cool effects also. Be creative, be original, be you.

**Cyanotype 'picture taking' procedure:**

Note: The sensitizer and paper should be kept away from direct sunlight and fluorescent lights. We will be working under incandescent lights and it will be relatively dark. Be careful.

1. Obtain a piece of watercolor paper, write your name on one side in pencil.
2. As directed by your instructor, carefully apply the sensitizer solution to the naked side of your paper. Apply the solution evenly, with brush strokes in horizontal direction. Then, without applying any more solution, brush in the vertical direction and finally again in the horizontal direction. Do not allow excess solution to remain on the paper.
3. Dry the paper thoroughly using a hair dryer or the oven. Wet sensitizer will stain negatives and other materials. Be careful.
4. Figure out how you are going to set up your picture (when outside) in the room, cover it and get it outside before you uncover it. Acetate sheets should be attached using paperclips or by placing it in a protective sleeve.
5. Take the paper/object combination outside and set it on a table or the ground (level) Remove the protective cover to expose the sensitized paper to direct sunlight. What happens? The length of time needed to see a color change will vary depending on cloud cover, time of day, and other factors.
6. When the exposed paper gets dark, cover it again it with the cloth and take it carefully back into the lab. Remove the cover and run it under cool running water for 10 minutes, to remove all of the chemicals that would later react with light.
7. If you want a darker image, dunk the washed paper in 3% hydrogen peroxide solution for a few seconds and re-rinse the paper.
8. Allow the paper to dry or use the hair dryer/oven to dry the paper.

**Prelab questions** (to be completed on a separate piece of recycled paper)

1. Most photographic work using light sensitive film or paper is done in dark rooms with only dull red light. Why can the paper that you are going to prepare be handled in incandescent light?
2. What is the formula of ferric ammonium citrate?
3. What is the formula of potassium ferricyanide?
4. Calculate the number of UVB photons (305 nm) needed to get 1 kJ of 'bad' energy hitting my skin.