

Exploring Photographic Chemistry

Introduction

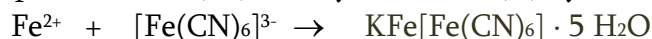
Photography is the process of making pictures by means of the action of light. The idea of a camera has been around since 350 BC when Aristotle used lenses to focus images onto walls. Leonardo da Vinci described a camera obscura before 1519. This device was a box with a lens in one end and a ground glass plate where the image was focused. However, it was not until 1835 that the first successful photographic process was invented by L.J.M.Daguerre. Daguerre actually made his first photograph using a “camera obscura”. Today, photography is widely used by all of us, although most people have no real understanding of the chemistry behind the process.

Photography is based upon the fact that light energy causes certain chemicals to react (photochemistry), forming a latent image on film or paper. Black and white film consists of light sensitive silver compounds mixed in a gelatinous base. This gelatin material is applied to either the surface of a plastic polymer (film) or to the surface of paper (prints). When a picture is taken or a print is made, these chemicals are briefly exposed to light energy. After exposure, the film or print must be developed. Processing, which always takes place in the dark to prevent further photochemical reaction, involves the following four steps. First, the film or print is treated with a chemical solution called a developer, which makes the recorded image visible. Second, the film or print is washed in a stop bath to stop the chemical reaction and remove any excess developer. Third, the film or paper is placed in a fixer, which removes any of the unreacted, light sensitive material. And finally, the film or paper is washed extensively to remove the fixer solution.

PART 1: Cyanotypes

Blueprint paper, used for architectural drawings, is another photosensitive substance. The use of blueprints or cyanotypes dates back to the 1840's when Sir John Herschel discovered the light sensitivity of certain iron salts. While the basic principles of exposure and development are similar, the photochemicals are different. In this case the picture can be developed using water.

To make a blueprint, paper is treated with a solution of potassium ferricyanide ($K_3Fe(CN)_6$) and ferric ammonium citrate ($Fe(NH_4)$) to produce the photosensitive compound, iron (III) hexacyanoferrate (III), $Fe[Fe(CN)_6]$. When paper or cloth coated with this chemical is exposed to light, the light reduces the ferric ion (+3) to ferrous ion (+2). The ferrous ions then react with potassium ferricyanide to produce iron (III) hexacyanoferrate (II) by the following reaction:



Iron (III) hexacyanoferrate (II), an insoluble, deep-blue colored compound called Prussian blue, forms the blue part of the final blueprint. Prussian blue can exist with different amounts of cations and water in the crystal lattice, so the exact molecular formula can vary depending upon conditions. To fix the image, the paper is washed with water to remove the unreacted water-soluble salts, leaving the areas not exposed to light as white areas on the blueprint.

In this part of today's experiment you will produce cyanotypes using watercolor paper and a white cloth square.

Directions

1. Each student should obtain a piece of watercolor paper and cloth square.
2. Each group should prepare the following solution to be used by all group members.
 - 1.2g ferric ammonium citrate
 - 0.6g potassium ferricyanide
 - 20 mL of water
3. Stir until dissolved and describe the color of the mixed solution.
4. Place the paper in one of the plastic trays under the hood. Using a flat foam brush, coat one side completely wiping coating first in one direction and then in the other.
5. Dry the paper using a hairdryer.
6. When dry, print the dry paper by using a large negative image on top of the paper and exposing it to sunlight or a UV light source.
7. When the exposed regions of the paper are changed in color to a deep blue-green, unclip the frame and remove the objects or negative.
8. Wash the paper with a gentle stream of tap water to remove the soluble unreacted light sensitive chemicals.
9. Dry the blueprints with a hairdryer.
10. Repeat the process for the cloth square.

Discussion Questions

What develops the image? What works as the fixer for the image? Compare your paper and cloth cyanotypes... how are they similar and how are they different? Write balanced chemical equations for the reactions observed.

When turning in your abstract for this experiment, include your cyanotypes and salted-paper prints labeled with the type of binder used.

PART 2: Salted Paper Prints

One of the first methods tried for making photographs involved first treating paper with a salting solution containing a weak binding agent and a chloride salt. When the treated paper is dry then it is coated again with a solution of silver nitrate. This treatment deposits light-sensitive silver chloride right in the fiber of the paper. The paper can then be exposed in a camera obscura, pinhole camera, or printed out under a negative to produce an image. Sometimes this method was referred to as photogenic drawing. Today you will prepare these salted paper prints.

Two different salting solutions and the silver nitrate sensitizing solutions have been prepared for you. The composition of these solutions is given at the end of the experiment for your own future reference. Each student will try two different salting formulas, (1) gelatin-based and (2) starch-based, and compare the results of the two.

Directions

1. Obtain 2 pieces of 4 x 5 watercolor paper. Mark one side which will remain untreated with the type of salting solution used on each.
2. Apply the salting solution (either gelatin or starch) to one side of a piece of heavy watercolor paper with a sponge brush. It is important to get an even coating so spread the solution first in one direction, then spread again at a right angle to the first direction, then spread a final time in the first direction. This may be carried out under normal lighting. You can allow the paper to dry naturally or using heat. Once dry, the treated paper will keep indefinitely. Be sure it is completely dry before proceeding to step 2.
3. In subdued light, brush sensitizing silver nitrate solution onto the dry salted paper using the same technique as previously to ensure even coating.
4. Heat dry the paper or let it dry in the dark. The paper will keep about a week if dry and in the dark.
5. Print the dry paper by placing negative image on top of the paper and exposing it to sunlight or a UV light source. The image should be allowed to change to a rather deep or dark tone with shadows having a bronze or metallic sheen.
6. Wash the print in several changes of tap water until all cloudiness in the water has been removed. The print tone will lighten and become reddish.
7. Fix the image by soaking for 10 minutes in a solution of fixer (also called hypo, a solution of sodium thiosulfate) with frequent agitation.
8. Wash fixed prints for about 10-15 minutes in a running water bath.

Gelatin Salting Formula		Starch Salting Formula	
Water	280 mL	Water	280 mL
Gelatin	2 g	Corn starch	5 g
Sodium citrate	6 g	Sodium citrate	6 g
Ammonium chloride	6 g	Ammonium chloride	6 g

Sensitizing Solution

Distilled water	30 mL
Silver nitrate	4 g

Discussion Questions

Compare the appearance of salted paper prints made with starch versus gelatin salting solution. Which binding agent do you think works best?

Part 3: Design Your Own Experiment

In this portion of the lab, you will choose one of the two photographic methods performed and test one of the variables related to it in an experiment you design. For example, you may be curious about what impact the exposure time has on the salted paper prints; you might ask, will you get a darker print with longer exposure time? How would you design an experiment to answer this question? Other examples include:

- How much binder is ideal? Run a series of experiments while you change the amount of binder used in the salted paper process.
- Can you make a print using metal or glass? Test different support substances.
- Does the temperature of the wash steps have an impact on image quality?

Work with your instructor to choose a question of interest to you and plan an experiment before coming to class. Be sure to consider what you will use as your control and how you will evaluate your results.

References

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