Experiment 35
BLACK AND WHITE PHOTOGRAPHY

MATERIALS:  Pin-hole camera, black and white photographic paper, safe-lights, developer bath, stop bath, fixer, water bath, development trays and tongs.

PURPOSE:  The purpose of this experiment is to understand the chemistry involved in producing a black and white photographic print.

LEARNING OBJECTIVES:  By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Describe the formation of a “latent image” on black and white photographic film/paper.
2. Explain the development process and the role of the silver atoms in developing the image.
3. Explain the effect that the pH of the “stop bath” solution has on the developer and the developing process.
4. Describe how the “fixer” (the complexing agent, thiosulfate ion) fixes the image.

INTRODUCTION:

The roots of photography can be traced back to the 10th century A.D. An Arabian scholar of that time, Hassan ibn Hassan, described the use of the “camera obscura” for his observations of a solar eclipse. The camera obscura (Latin for ‘dark room’) was a dark box or room with a small hole at one end. When light from a scene passed through the hole, an inverted image of the scene was projected onto the opposite wall. This is essentially the principle governing the pin-hole camera used in this laboratory. Using a camera obscura, an artist could trace the projected image to produce a very accurate depiction of the scene. Unfortunately, a chemical method for permanently capturing the image would not arise for eight more centuries.

It had been known since the early 1600's that silver salts were sensitive to light. In 1725, Johann Schulze demonstrated that a sheet of paper soaked with silver nitrate would turn black upon exposure to
light. This “light sensitivity” was due to the reduction of silver ions to silver metal. In the late 1700's Sir Humphry Davy and Thomas Wedgwood employed the light sensitivity of silver salts to capture images of static objects. Unfortunately, these images were not made permanent (fixed) and they eventually turned completely black with further exposure to light. The first successful photographic process was developed by Louis Daguerre in 1839. These “daguerreotypes” used copper plates coated with a thin layer of silver iodide. Upon exposure of these plates to light, silver ions were reduced to silver metal to produce an image. This image was enhanced by the further reduction of silver ions using mercury vapor. The image was fixed by removing unexposed silver ions with sodium sulfite.

From these primitive beginnings, the chemistry of photography has progressed significantly. However, the essential elements of the process have not changed. In this experiment you will take a picture on photographic paper using a simple pin-hole camera, then develop and fix this picture to give a “negative” image of the object you photographed.

BACKGROUND:

The Pin-Hole Camera: The optics of a pin-hole camera are quite simple. Unlike a typical 35 mm camera that employs a lens to focus the image onto the film, the pin-hole camera has a small hole that allows light to enter and expose the film (Figure 1). The optics of the pin-hole camera produce an image which is reversed horizontally and inverted vertically. The amount of light entering the pin-hole camera is determined by the size of the hole and the length of time the hole is open.

Photographic Paper: Photographic paper consists of a layer of silver bromide bound to a plastic support, while photographic film consists of the silver bromide bound to a clear film support. The silver bromide is in the form of a very fine powder. This powder is bound to the surface of the support using a transparent material called gelatin. Gelatin is sufficiently rigid to prevent movement of particles that could cause image blurring, but it is flexible enough so that it does not crack when the film is flexed. Most importantly, gelatin is permeable to the developing solutions.

Gelatin, the same substance used in “Jell-O”, is a colloidal protein obtained from animal tissue. The gelatin protein consists of a long chain of 100 to 300 amino acids. The basic structure of gelatin is shown in Figure 2. The symbol R represents a group of carbon atoms of unspecified length or structure. In proteins these R groups may contain occasional atoms of nitrogen, oxygen, sulfur, or phosphorous. The composition of these R groups has a profound effect on the properties of the film.

![Figure 1. Optics of the Pin-hole Camera.](image1)

![Figure 2. The Structure of Gelatin.](image2)
**Latent Image Formation**: The basic process of photography is the focusing of light onto photographic paper containing silver bromide. The light forms an invisible image on the paper called a “latent image.” The latent image formation results from a light-initiated oxidation-reduction reaction of the silver bromide. Bromide ions absorb photons of light ($h\nu$) and are oxidized. The electron from this oxidation reduces silver ions to silver atoms. As the photographic paper is exposed, small clusters of silver atoms are formed (e.g. $Ag_2, Ag_3, Ag_4$). These clusters of silver atoms make up the latent image.

\[
\text{Oxidation: } \quad Br^- + h\nu \rightarrow Br + e^- \\
\text{Reduction: } \quad Ag^+ + e^- \rightarrow Ag
\]

The latent image is enhanced during the developing process by the reduction of additional silver ions.

**Developing the Latent Image**: In order to produce a visible image from the latent image, additional silver must be deposited in the vicinity of each silver atom cluster. This can be done using a variety of reducing agents. The original *daguerreotypes* employed mercury as the reducing agent. The oxidation-reduction reaction was as follows:

\[
\text{Hg (l)} + \text{AgBr (s)} \rightarrow \text{HgBr (s)} + \text{Ag (s)}
\]

This developing process was quite hazardous due to the toxic nature of mercury. Fortunately, mercury has been replaced by less toxic reducing reagents. Today, the most widely used reducing agent is the dianion of hydroquinone. Hydroquinone, $C_6H_4O_2$, is a water soluble weak acid that dissociates according to the following equilibrium equation:

\[
\text{Since this equilibrium lies far to the left, a strong base, hydroxide ion, must be added to hydroquinone to form the dianion. Hydroxide ion removes two protons from hydroquinone to form the hydroquinone dianion.}
\]

\[
\text{In the presence of silver ions, the hydroquinone dianion acts as a reducing agent and becomes oxidized to quinone. The oxidation and reduction half-reactions are:}
\]
Oxidation:

\[
\text{Reduction: } 2 \text{Ag}^+ + 2 \text{e}^- \rightarrow 2 \text{Ag}
\]

The overall oxidation-reduction reaction is:

The developer solution is maintained in the pH range of 10-12. This pH ensures that sufficient hydroquinone dianion is present to develop the latent image.

Up to this point we have ignored several obvious questions regarding the development reaction. Why does the reduction of silver ions only occur in the vicinity of the silver atoms of the latent image? Why doesn’t the hydroquinone dianion reduce all the silver ions in the photographic paper? The key to these questions lies in the fact that the silver atoms of the latent image greatly enhance the rate of reduction of additional silver ions. In essence, the silver atoms of the latent image act as catalysts for the reduction of silver ions with which they are in contact. The developer can and will reduce all the silver ions in the film if development is extended for too long. Consequently, the photographic paper is developed until the image sufficiently darkens, but the development is stopped before all the silver ions are reduced.

The resulting image is a negative of the original image. The negative image appears dark where the object was light and appears light where the object was dark. The silver atoms on the paper seem dark because the reduced silver on the photographic paper is formed into very small, evenly dispersed particles. When light hits the surface of the developed photographic paper, the silver particles diffract light and appear dark.

**The Stop Bath:** When the development process is completed (i.e. when sufficient silver has been reduced to give the desired image density), the film is placed into a stop bath. The purpose of the stop bath is to prevent any further reduction of silver ions. Since the developer solution is only active above pH = 7, the development process can be stopped by washing the photographic paper in a dilute acid solution. The acid converts the hydroquinone dianion back to hydroquinone, thus stopping further reduction of silver ions. In this experiment, a dilute solution of acetic acid is used as the stop bath. It is important that the film is removed from the developer just before it is fully developed because the gelatin holds some of the hydroquinone dianion and it takes time for the acid in the stop bath to diffuse into the gelatin layer to protonate the trapped developer.
The Fixer: After the developing reaction is stopped, what remains is a silver image superimposed on a background of pale yellow silver bromide. This silver bromide was not reduced in the development process and it must be removed or the image will ultimately darken due to gradual reduction of the silver ions by exposure to light (as with Davy and Wedgwood’s original photographic images). In order to remove the silver bromide from the photographic paper it must be converted into a soluble substance. This can be accomplished by addition of a substance which will form a strong complex with silver ions. There are many substances that form soluble complexes of silver ions. In this experiment, the thiosulfate ion, $S_2O_3^{2-}$, is used to dissolve silver bromide by forming the $Ag(S_2O_3)_2^{3-}$ complex ion. The overall dissolution reaction is:

$$AgBr (s) + 2 S_2O_3^{2-} (aq) \rightarrow Ag(S_2O_3)_2^{3-} (aq) + Br^- (aq)$$

The Final Rinse: After the photographic paper has sequentially passed through the developer, the stop bath, and the fixer, it must be thoroughly rinsed with water. This is done to help preserve the image because residual thiosulfate ions will turn the photo yellow and cause the image to fade.

Obtaining a Positive: In this experiment, you will obtain a negative image on photographic paper. To produce a positive image from this negative you could either take a picture of the negative or scan it into a computer and produce the image digitally. This negative of a negative would be a positive image (Figure 3). This, in essence, is how positive photographs are produced. Modern photographic film, when developed, produces a negative image on a transparent background. A positive is produced by shining light through the negative onto a piece of photographic paper. This is termed “exposing” the photographic paper and gives an “exposed” photographic paper with a positive latent image. Developing the film will result in a positive image on the paper.

![Figure 3. Negative and Positive images.](image-url)
PROCEDURE:

1. **Load the pin-hole camera.** Prior to turning off the lights, make sure the top of your pin-hole camera is open and the rails inside are clear of obstructions. Under safe-light conditions, insert the photographic paper into the rails inside the camera box. The sides of the photographic paper are different. The shiny side of the photographic paper **must** face the pin-hole! The dull side must face the back of the box. Do not touch the shiny side of the paper. When the camera is loaded, carefully close and seal the top. Make sure the pin-hole is covered and there are no gaps where light can enter.

2. **Go outside and take a picture.** Point the camera (pin-hole towards the subject) and peel back the tape covering the pin-hole. Exposure times will vary depending upon conditions. The exposure time can be as short as 6 seconds on bright sunny days and as long as to 2 minutes on dark overcast days. The subject and the camera **must** remain stationary during the exposure. Because the exposure times for the pin-hole cameras are so long, the clearest images are obtained when the camera is supported on a very stable surface and the subject is stationary. If the camera or subject moves, multiple images or blurring may result.

3. **Develop the image.** Under safe-light conditions open the camera and remove the photographic paper. Do not touch the shiny surface of the paper.

   a. **The Developer.** Using tongs, place the photographic paper into the developer. Since a quick, even wetting of the gelatin is necessary, the paper should be slid into the solution from an edge with the face (shiny side) down. Use the tongs to gently agitate the paper while it is submerged in the developer and turn the paper over after approximately 5 seconds. Continue to agitate the paper until the image begins to appear then remove the paper from the bath using the tongs. The paper will continue to develop after the paper has been removed from the developer, so it is necessary to “lead your image” a little. Normally the image will appear in **15 to 20 seconds**, at which time you should be ready to put it into the stop bath.

   b. **The Stop Bath.** Next, use the tongs to place the paper in the stop bath using the procedure above. The paper should remain in the stop bath for approximately **1 minute**.

   c. **The Fixer.** Following the stop bath, use the tongs to place the paper in the fixer. The paper should remain in the fixer for approximately **1 minute**.

   d. **Permawash.** Following the fixer bath, use the tongs to place the paper in the Permawash. The paper should remain in the Permawash for **1 minute** before being rinsed thoroughly with distilled water and allowed to dry on paper towels.

4. **Look at the picture and try again.** You will take two pictures during this lab. Use your experience with the first picture (exposure time, developing time, etc.) to improve your second picture.

REFERENCES:

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1. How does exposure time affect the photographs?

2. Why are your photographs known as “negatives”?

3. What could you have done to improve your photographs? List at least two corrections.

4. Attach your best photograph below.