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The Chemistry of Photography

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Thesis Summary

People nowadays are used to instant gratification when it comes to taking photographs. They look at a digital display, click a button, and get a perfectly focused and lighted picture that they can see right away. New technologies enable people to have pocket-sized digital cameras, their smart phones, with them at all times, and they're easy convenient, and fast. Behind a single lens reflex (SLR) film camera, the scenario is much different. More time is needed in framing the image and adjusting the aperture and shutter speed to get the correct exposure, and the film must be processed darkroom before the image captured is even visible. Recently, film photography has seen a rise in popularity, and it's cool to own a Polaroid or a SLR. Finding a place to develop film, however, is not so easy.

Photography has been a hobby of mine since high school, and I have always been curious as to how exactly the whole process works. The inspiration for the project came from recipes I found online claiming prints can be developed in coffee ("Caffenol") and wine ("Wineol"), and I had to know how that worked. When you don't understand the process that makes the picture possible, it can seem like magic. When you do understand the process, it is still miraculous.

This thesis project is an exploration of the chemistry of photography through hands on experimentation with the developing process. This project gave me the opportunity to refresh and expand my knowledge of the technical aspects of photography and print making, while applying the chemistry that I have learned through my semesters here at the University of South Carolina. The goal of the project was to recreate the traditional chemicals involved in developing with household alternatives, and to be able to explain why these substitutions work based on their chemical properties. The finished product would be something that any person could create, without accesses to expensive and obscure photography supplies.

After researching the chemical processes and mechanisms in commercial developers, I was able to explain how the DIY recipes worked; which ingredients served which purpose and why not every component had to be included. I designed a recipe of

my own modeled after “Caffenol” and “Wineol” using green tea extract. I also had to find alternatives for some of the other chemicals involved in the development process.

I spent several months in the darkroom testing the online recipes and constructing the correct ratios for my tea recipe (“Teaol”). I used images taken previously to compare the results of each trial. I also tested different methods of fixing, or preserving, the image. Although I was not able to find a common household substitution for the fixing chemical, I did not have to turn to a photography store. I was able to find the main chemical from a pool supply store and make a simplistic fixing solution out of it with no other additions. With all other substitutions made, I started on planning the photographs I wanted to produce.

I finally decided on portraits of my best friends in the Honors College. The portraits are a way of summing up my time here at USC. The subject of the images is representative of my family and home here, and the process by which the prints were made highlights the skills and knowledge I have gained. The final product from this project is a creative expression of my time here at the university.

Introduction

The first photograph is accredited to Joseph Niépce in 1820 a French amateur scientist and inventor. Made with bitumen of Judea it was a contact printing method called heliographing or sun writing. Prior to this effort in the late 1700's chemist Carl Schulze experimented with silver nitrate and its reaction to light and the stabilizing effects of ammonia on this reaction. Physicist Thomas Wedgwood and chemist Humphry Davy attempted the first negative and positive printing method using the same silver nitrate Schulze had been testing, but was unable to preserve the image. Scientists and wealthy inventors alike were trying to solve the problem of capturing an image from light. An artist Louis-Jacques-Mandé Daguerre continued Niépce's work and was able to capture images with silver nitrate, enhance them further, and to fix them for a short while with salt solutions.

What these scientists and inventors had in common was an imaginative and curious mind. Man's understanding of general chemistry was not as developed as it is today, let alone the specific chemistry of the processes they were working with. These men were pioneers of photographic chemistry, piecing together reactions that they did not understand to create something revolutionary. As chemical information has been developed over time, the photographic process has been refined and optimized to the point where these early discoveries are often taken for granted.

The chemistry of photography is based on photosensitivity and reactions with light. The chemical processes that create a traditional photograph start inside the camera with the absorption of photons. However, photochemistry alone is not able to produce an image. Development is continued in the darkroom through chemical reactions involving organic and acid and base chemistry principles. The structures of the chemicals involved are extremely important to the reactions that take place as well as the acidity or basicity of the solutions.

Photographic film and paper are made up of photosensitive grains of silver and halides. These grains react with light to create a latent image that is invisible to the eye. In the darkroom, the alkaline, or basic, developing solution reduces the silver halide molecules to atomic metal silver. This creates the dark areas that constitute the visible

image. An acidic stop bath is used to halt the developing process and a fixing solution to preserve the image by dissolving the leftover silver halides that could still react with light.

To develop an image that was captured in the camera, the film is transferred in the dark to a light-tight container. To this container the developer solution is added and the container is agitated; this is the longest step for film developing. This solution is dumped out and the stop bath is added with more agitation. The fixing solution is next step and is the longest step when developing prints. All of the residual chemicals are then washed off in a long rinse and the film is dried. The same steps are used in the darkroom when making prints from the film negatives. Light is shown through the negative image and enlarged and projected onto photosensitive paper, inverting the light and dark parts of the picture. The print is then agitated in trays of the same chemicals used on the film.

This paper describes in detail the chemistry involved in capturing and developing an image, a process born from the minds of Niépce, Schulze, Wedgwood, Davy, Daguerre, and Talbot. Unlike these scientific experimenters, this project benefits from a familiarity with chemical principals. These topics are reviewed in order to explain why the household recipes “Caffenol”, “Wineol”, and “Teaol” are able to produce an image and how these images are preserved against degradation over time. Using the discoveries of centuries ago and now fundamental knowledge of molecules and reactions, the photographic process can be reversed engineered to create something new, with the same experimental spirit of the early photographers.

Photographic Film and Paper

Photographic paper and film consist of a gelatin emulsion with silver halide grains layered onto either paper or film base. The halides that are often used are chlorine, bromine and iodine, although bromine is the most common. The silver halide grains are crystalline structures of silver ions and halide ions in a lattice structure, shown in figure one. Even though the grains are held together by chemical bonds and are very stable, there is some movement allowed of atoms and electrons throughout the structure.

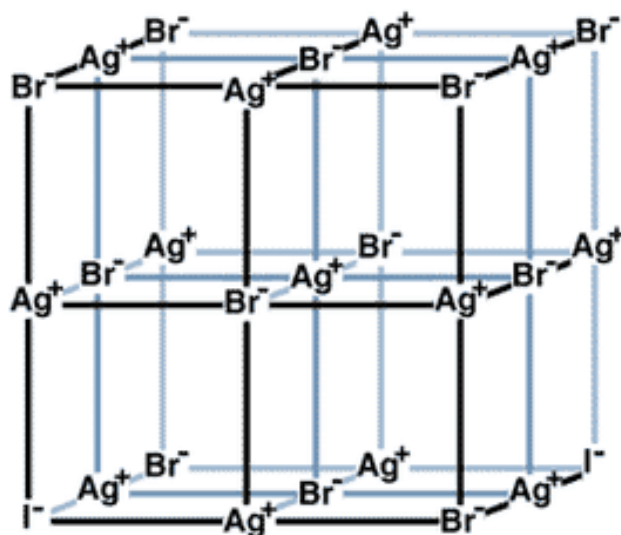


Figure 1

Electronically, there are different energy levels in the grain: the valence band and the conduction band. Electrons in the valence band are localized around the atom to which they belong. Those in the conduction band are free to move through the grain. When photons from light come into contact with a grain, an electron is ejected from the valence band of the halide into the conducting band of the crystal. This electron will then combine with a moving silver ion forming atomic silver. The place where this occurs is the latent image center. When three or four of these events occur at the same location, an aggregate or clump of silver metal is produced. Three or four atoms are necessary for the latent image center to be stable. Each grain has thousands of silver ions, so there are thousands of chances for this to happen. Figure 2 on the following page shows the process by which the first silver atom is produced.

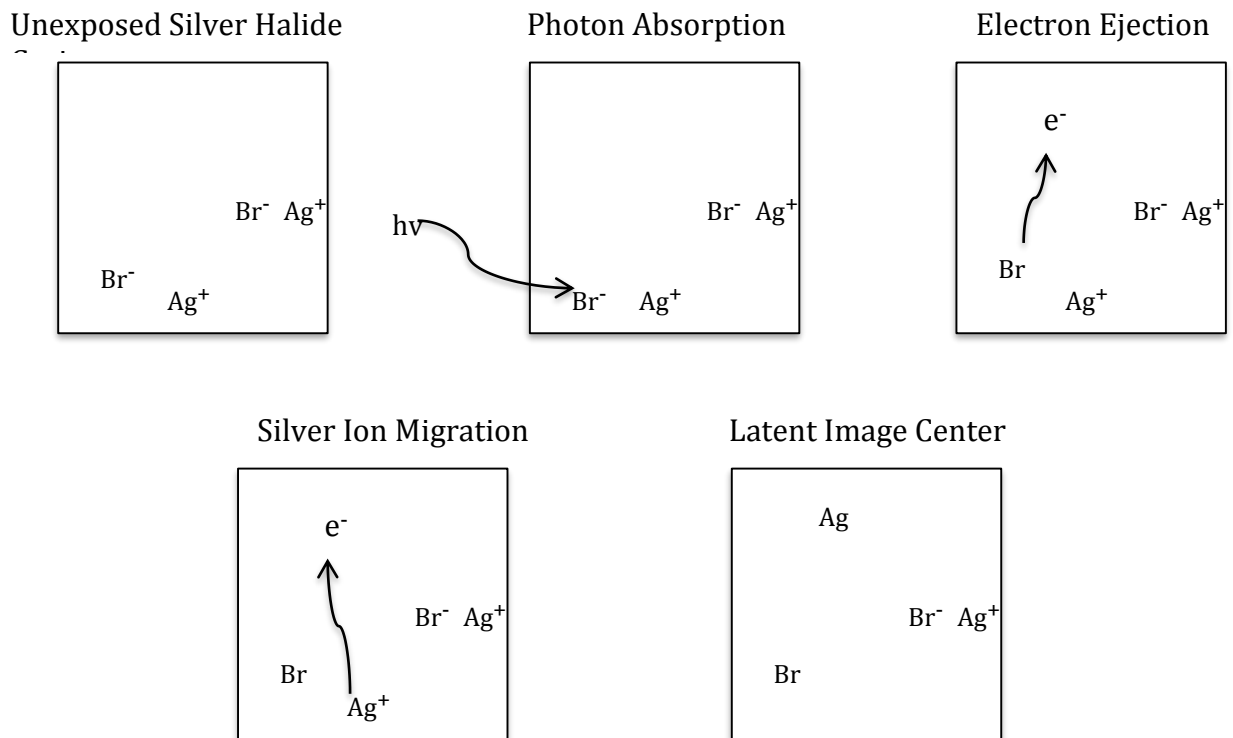


Figure 2

The latent image is invisible to the eye, but after further development, the atomic silver will create dark areas due to its color. The latent center serves as a catalyst for the development in the darkroom. The formation of silver metal is logarithmically proportional to the intensity of light. Therefore places where more light hits the emulsion will have more latent image centers and appear darker on the film. In creating the print, light is shown through the negative, so areas that were originally dark then receive less light and appear brighter.

Developer and Stop

Typical developer is made up of four different components: the developing agent, the accelerator, the restrainer, and the preservative. The developing agent is a reducing agent; this means that it reduces the silver halides to metallic silver. Reducing agents in the developer donate electrons to the silver halide grains. The electrons enter the conduction band of the compound and reduce more ionic silver to atomic silver. This occurs more rapidly and more completely in grains where photons already initiated this process. This is how the development is chemically accelerated at places in the photo that are brighter and avoided in places that received little to no light stimulation.

Reduction always occurs with oxidation; they are a paired reaction. As the reducing agent donates electrons, it loses electrons and becomes oxidized. It can also become oxidized by oxygen in the air and subsequently become less effective. When the reducing agent has no more electrons to donate, the developing process cannot occur. To help slow this process, a preservative is added. It is a chemical that protects the reducing agent from being oxidized.

The purpose of the accelerator is evident from the name, as well as the restrainer. The balance between the two is important to the developer. The accelerator helps create a chemical environment favorable to the reducing agent. A basic solution deprotonates the reducing agent, freeing up electrons to be donated. So the accelerator is a chemical that makes the developing solution more basic or alkaline. The restrainer has an opposing affect; it stops the developing agent from developing an image too quickly. If this were to happen, areas that were not exposed to much light, where there is not already a latent image center, would get developed.

Homemade Developers:

Caffenol:

- 450 ml water
- 6 tsp. instant coffee
- 3 tsp. washing soda
- 1½ tsp. vitamin C

Wineol:

- 400 ml red wine
- 5 tsp. washing soda
- 5 tsp. vitamin C

*Recipes from Caffenol.org

Teaol:

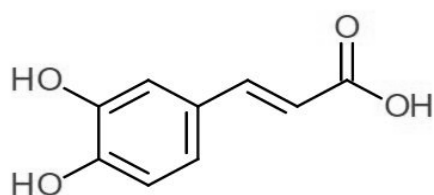
- 400 ml water
- 3 tsp. green tea extract
- 3 tsp. washing soda
- 3 tsp. vitamin C

*Experimental recipe

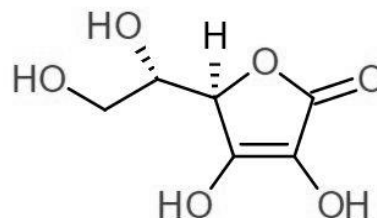
These homemade developers are extremely simplistic in that they are only comprised of the reducing agent and the accelerator; in fact they contain two reducing agents. In Caffenol and Wineol, caffeic acid is the primary reducing agent. Vitamin C or ascorbic acid acts as a secondary reducing agent.

Many commercial developers utilize two reducing agents because the combination results in superadditivity. The reduction potential or activity of two developers is greater than just the sum of the two. This effect will speed up the developing time without compromising tonality. Fast developers develop low contrast with high mid-tone detail. This is due to the high activity of the developer. If the reducing agent is very active then it can reduce grains that did not have latent image centers. This causes low contrast and less detail in the final image. Slow developers on the other hand, create more contrast. These reducing agents are less active and there is more discrimination between grains with latent centers and those without. The pairing of two reducing agents compromises these effects; the speed and the contrast.

These developers, along with two typical commercial developing agents, are shown below.



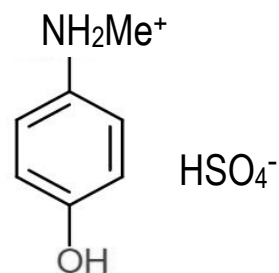
Caffeic acid



Ascorbic acid (Vitamin C)



Hydroquinone



Metol

Figure 3

Common features in the structures are the benzene rings and —OH groups. In the alkaline environment that the accelerator provides, the hydrogen atoms on the —OH groups come off of the molecule. This is due to the electronegativity of the oxygen atom. It holds the electrons in the OH bond much tighter, so the hydrogen is more easily removed. As a result the molecule holds an extra electron from the broken bond and a negative charge. This extra electron is what is donated to the silver ions. The aromatic ring structure is important because it stabilizes this negative charge through p-orbitals. The electrons of each atom in the ring have p-orbitals that are further away from the nucleus of the atom and extend above and below the ring. All atoms of the ring share the electrons in these orbitals and this stabilizes any charge on the molecule. The mechanism of the reduction is shown with hydroquinone but is similar to all the reducing agents.

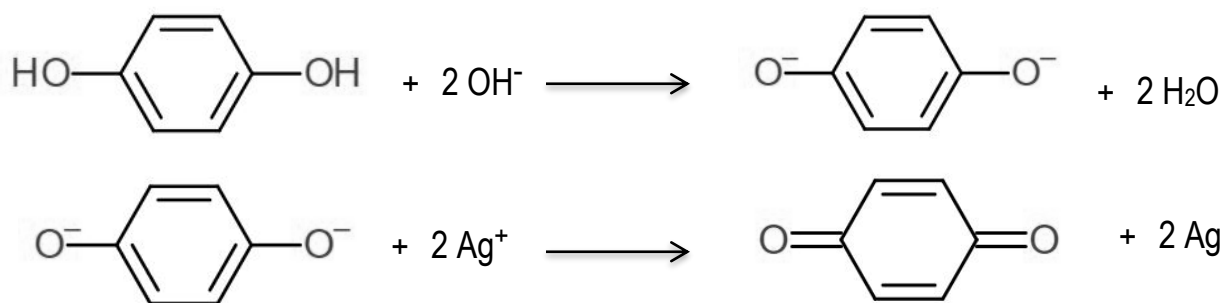
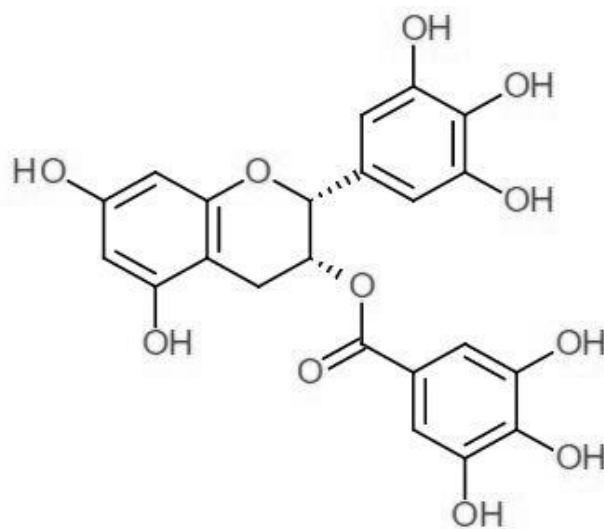


Figure 4

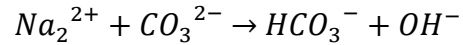
In Teaol, the primary reducing agent is epigallocatechin galate (EGCG), a derivative of epicatechin and one of four green tea catechins (GTC). There are three other epicatechin derivatives in green tea extract, but EGCG makes up 50% of the mixture. It has the same structural features as the previous reducing agents, but much larger. The other GTCs differ in how many –OH groups are present on the rings. EGCG has the most –OH groups, so it should be the most active reducing agent of the four.



Epigallocatechin galate (EGCG)

Figure 5

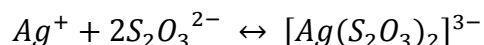
The washing soda acts as the accelerator by making the solution basic. Washing soda, or sodium carbonate (Na_2CO_3), is used in tie dying and as a water softener in laundry. In water, the sodium and carbonate dissociate, and the carbonate ion removes a hydrogen atom from water. This leaves a hydroxide ion behind, lowering the pH of the solution.



The next step in the darkroom is the stop bath. The stop bath halts the developing process to prevent the developing agent from reducing all the grains of silver halide, even those where no latent image formed. Since developing agents work best under alkaline conditions, an acidic solution is sufficient to stop development. Water, with a pH of 7, is acidic enough in comparison to the developing solution.

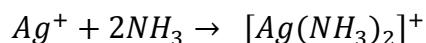
Fixer and Wash

The purpose of the fixer is to dissolve the unreduced silver halide molecules left on the paper after development. This is a way of preserving the image because if these grains are not removed, they can continue to be reduced by sunlight and degrade the image. This degradation causes a purple hue on the image and the loss of fine details. Silver halides alone are insoluble in water, so a reaction must occur in order to remove them. A typical fixer is sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). The reaction with silver halides creates a complex that makes the silver halide dissolve. Although silver halides are practically insoluble, a very small portion of dissociated silver and halide ions will be present. The complex ion that is formed with thiosulfate is more stable than the silver ion, and thus, more of it is created and less ionic silver is left behind. More silver halides will dissociate to maintain equilibrium and eventually most will be dissolved. The reaction equation for this interaction is shown below.



Sodium thiosulfate is an outdated fixer due to its slow fixing time, about five to six minutes. Commercial fixers, called “fast fixers,” add other ingredients to speed up this time. Other additions are sometimes made to have various effects on the prints. Some such additions are hardeners, which prevent the swelling of grains on the paper. This would make the surface softer and more easily damaged. Acids are also added to some fixers. Hardeners perform better in an acidic environment, and this will further halt the development if some developer is carried over from the stop bath.

The only possible household alternative with foundation in chemical properties is ammonia. Silver chloride is soluble in dilute ammonia, and silver bromide is soluble in concentrated ammonia. Silver iodide is not soluble in any concentration of ammonia, but the percentage of iodide in photographic papers is quite small. The solubility is increased for the same reason as above, the complex ion formed between ammonia and silver ions is more stable, causing the formation of more ions and the dissolution of more silver halides. The reaction between silver and ammonia is shown below.



The effects of ammonia fixing and no fixing can be seen in the images below taken seconds, thirty minutes, and a day after exposure to sunlight. These tests used Caffinol as the developer and a two-step bath in 1:1 and then 1:2 dilutions of ammonia.



Left: Ammonia fixing. Right: Un-fixed. Seconds after exposure to sunlight



Left: Ammonia fixing. Right: Un-fixed. Thirty minutes of exposure to sunlight



Left: Ammonia fixing. Right: Un-fixed. One day of exposure to sunlight

A final wash in water is necessary to rinse off the dissolved silver halides as well as residual chemicals on the paper. The thiosulfate fixer makes a compound that is soluble in water, so the leftover silver halides rinse off in the water. The fixer itself also must be removed because it itself can degrade the image. It decomposes to form acid that reacts with the silver to form silver sulfide. This compound makes a yellow-brown staining over time.

Product

For the final product to illustrate the DIY chemical processes, I decided on a series of portraits of my best friends, fellow honors college students from the class of 2016 students. For me, taking portraits can be awkward. Sitting behind the camera trying to get the lighting and focus just right, the subject feels weird, and it can make the picture look awkward. For my photo shoot, I had all my friends together, and they took turns sitting for a photo. With all of us together it was less uncomfortable. Each of their personalities came through, and we had some fun with it. I hope that to observers, the engagement of the sitter camera will be noticeable and that the photographs will show individual personalities instead of forced smiles.

I took the photos around the horseshoe looking for backgrounds that would frame the subject as well as add visual interest. I have lived on the horseshoe for three years now and it feels like home as well as the center of campus. The combination of the subject and setting make the photo series personal to me. They embody my experience at USC.

Results

In the darkroom all three developer recipes were tested, as well as two different fixer solutions. For the final series of photograph, Caffenol and Teaol were used to develop and sodium thiosulfate was used to fix.

Both Caffenol and Wineol have the same chemical components responsible for development, caffeic and ascorbic acid, and therefore produced images of comparable contrast. Wineol however, had a practicality issue. Since the solution is more viscous than the other two, it did not easily come off the paper. Multiple water stop baths had to be used, and replaced, after each photo in order to prevent contamination of the fixer. This process was extremely time consuming and hard to control, and for this reason, it was excluded from use for the final product. Since the goal of the project was to find a simple and cheap home method for developing, coffee is the obvious choice over wine.

Teaol contained a different primary developing agent from Caffenol and Wineol, EGCG instead of caffeic acid. The prints developed in Teaol came out with a flatter appearance with much less contrast in dark and light areas. EGCG is the more active reducing agent, it has more electrons to donate and consequently does not discriminate as well between grains previously reduced by light and those not. For the purposes of this project, all of the settings were kept the same in the darkroom; the same filters, the same exposure time, and the same development time were used in both developers in order to see the differences produced just from the reducing agents. However, if one wanted to use Teaol to develop higher contrast images, a higher contrast filter could be used to balance out the effects of EGCG as a more active reducing agent. Alternatively, one could use Teaol if photos were taken in high contrast settings or Caffenol if not. The different developers would act as a filter would.

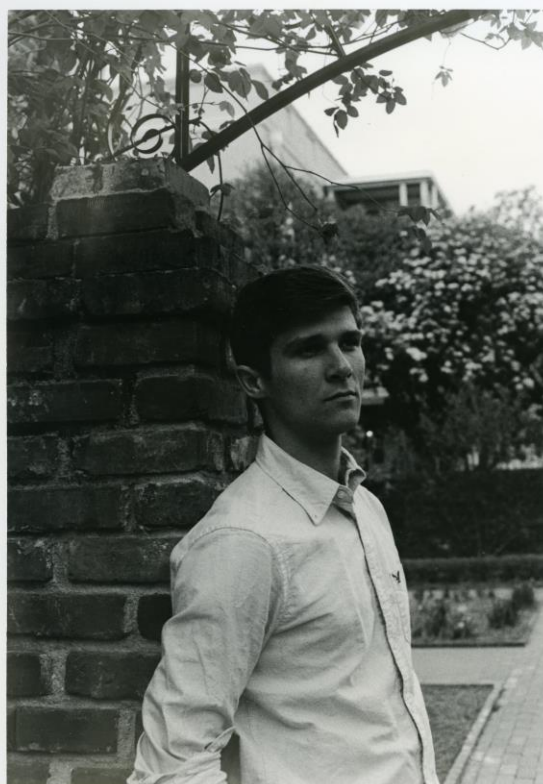
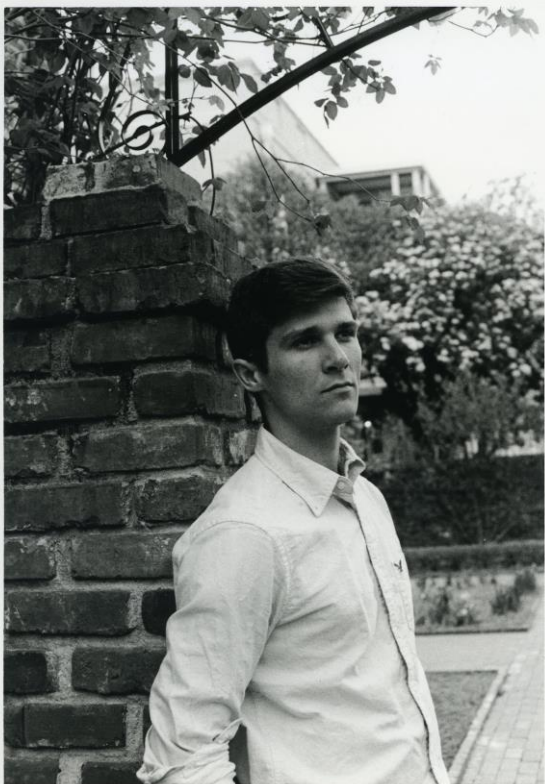
Different methods of fixing with ammonia were tested along with varying concentrations up to a 1:1 dilution with water. Multiple baths were attempted and stronger and strong solutions, but in concentrations that are tolerable to the eyes and nose, ammonia was insufficient to fix the photographs. Over time, the images fixed in ammonia degraded at the same as those that were un-fixed. Additionally, some reaction with the ammonia caused the photos to turn blue after initial exposure to light, although

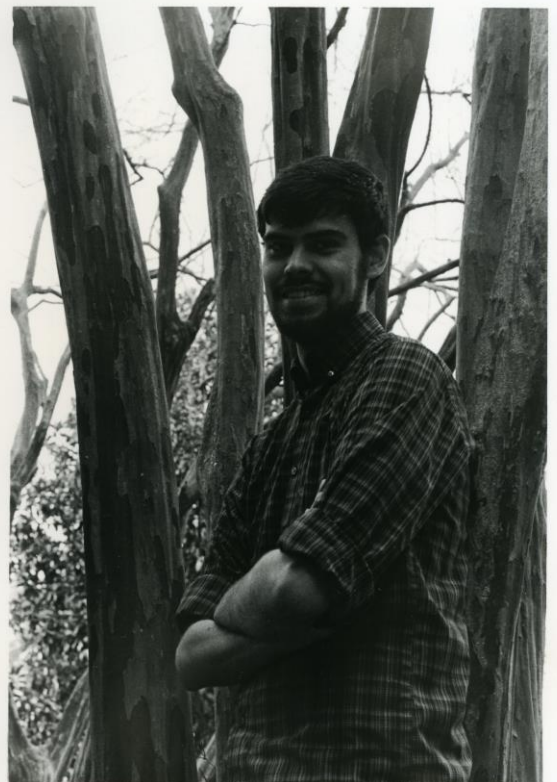
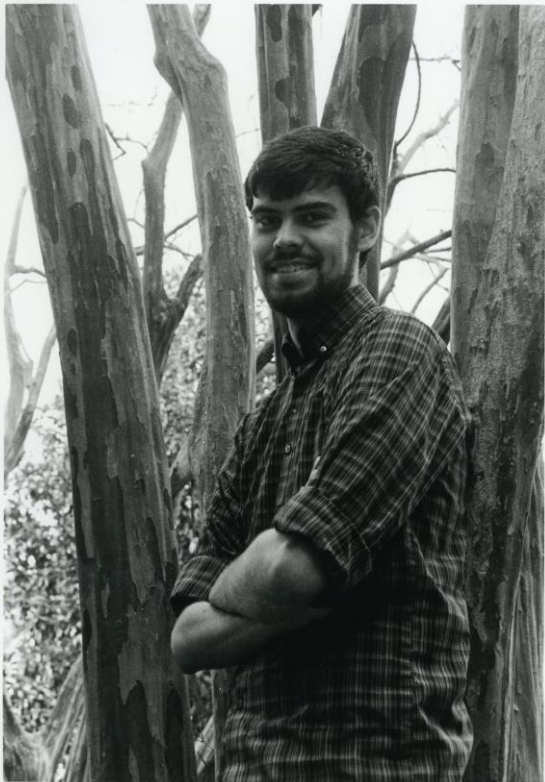
this is over taken by the purple staining, as can be seen in the images from the Fixer and Wash section.

Instead, plain sodium thiosulfate was used as a fixer for this project. As previously discussed, commercial fixer generally has several components, but a solution of sodium thiosulfate is enough on its own to preserve the image. This chemical is also used for controlling the chlorine levels in pools and is available from neighborhood pool supply stores. Therefore, although it is a chemical used in many darkrooms, it can be purchased conveniently and cheaply.

The final series of eight portraits are shown below with the prints developed in Caffenol displayed on the left next to the Teaol prints on the right.











Recipe Book

Caffenol

Ingredients:

- 450 ml water
- 6 tsp. instant coffee
- 3 tsp. washing soda
- 1½ tsp. vitamin C

Directions for mixing: Fill a measuring cup with room temperature. To this, add the instant coffee, washing soda, and vitamin C. Stir until all ingredients have dissolved. Some grounds may still be present at the bottom. Transfer to a 5x7 developing tray. (Double the recipe if 8x10 prints are desired)

Wineol

Ingredients:

- 400 ml red wine
- 5 tsp. washing soda
- 5 tsp. vitamin C

Directions for mixing: Pour the red wine into a measuring cup and add the washing soda and vitamin C. The solution will bubble and foam up, stir to dissolve and keep the solution from overflowing. Transfer to a 5x7 darkroom tray. (Double the recipe if 8x10 prints are desired)

Teaol

Ingredients:

- 400 ml water
- 3 tsp. green tea extract
- 3 tsp. washing soda
- 3 tsp. vitamin C

Directions for mixing: In warm water, dissolve the green tea extract. Remove the large leaves from the water. Add in the washing soda and vitamin C and stir until all the ingredients have dissolved. There will still be smaller leaves floating in the solution. Transfer to a 5x7 darkroom tray. (Double the recipe if 8x10 prints are desired)

Fixer

Ingredients:

- 2 cups of water
- ½ cup of sodium thiosulfate crystals

Directions for mixing: In a glass measuring cup heat the water to 125°F. Pour in the sodium thiosulfate crystals and stir until dissolved. This solution is an irritant to the eyes, skin, respiratory and gastrointestinal tract. Wear gloves and mix in a well-ventilated area. Transfer to a 5x7 developing tray. (Double the recipe if 8x10 prints are desired)

Developing Instructions:

Fill one more 5x7 developing tray with tap water and set up a rinse tray with running water. Place the trays in the following order: developer (caffenol, wineol, or teaol), stop bath (tap water), fixer, and rinse.

Place the exposed paper in the developer and gently agitate for 90 seconds. Using tongs, remove the print and let the excess developer drip back into the tray. Transfer the print to the stop bath and agitate for 15 seconds. Next, move the print to the fixer once again letting the excess liquid drip off of the paper. Agitate constantly in the fixer for 5 minutes. Transfer the finished print to the rinse and leave for at least 10 minutes or until all prints finished developing.

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