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A Photographic Process Using Easily Available Reagents

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ABSTRACT: A photographic process that employs inexpensive and easy to find reagents [ascorbic acid, copper sulfate ($CuSO_4$), and sodium hydrogen carbonate ($NaHCO_3$)] is presented. As with other photographic processes, it can be used to demonstrate the effects light can have on chemical reactions in an entertaining manner, allowing students to exercise their creativity. The main advantage of the presented process, compared to many other photographic processes, is its accessibility in circumstances when specialized chemicals are unavailable or undesirable.

KEYWORDS: *Demonstrations, Interdisciplinary/Multidisciplinary, Laboratory Instruction, Oxidation/Reduction, Photochemistry, General Public, Hands-On Learning/Manipulatives*

INTRODUCTION

Experiments and demonstrations involving photographic processes are an engaging and entertaining way to show the effects of light on chemical reactions and tackle other chemical concepts. While there are plenty of photographic processes that can be used in such a context,[1] the vast majority of them require reagents that are not easy to come by outside of a laboratory and often have associated health hazards.

For example, silver halide processes require costly and corrosive silver salts,[2] and the relatively safe and simple cyanotype process needs ammonium ferric citrate and potassium ferricyanide,[3] which may be difficult to obtain. In fact, of the commonly listed alternative photographic processes, only the anthotype process functions without specialized chemicals.[4]

The anthotype process, in turn, is based on nonspecific bleaching of plant pigments and requires long exposure times. Although exposure times can be reduced from days to hours,[5] the chemistry of the process diverges too far from that of the majority of photographic processes for this process to be used as a substitute for more traditional photographic processes in chemistry education.

A process which can be performed with only fairly pedestrian chemicals, readily available in pharmacies and hardware stores, would lower the threshold for entry into the chemistry of photography. This may be helpful in a homeschooling setting,[6] as well as in other situations where access to laboratory chemicals is limited.

Upon examination of the light sensitivities of several reactions between such reagents, the reaction between copper sulfate and ascorbic acid with the addition of a small quantity of alkali appeared to have fitting properties for a photographic process. On the basis of this reaction, a photographic process with the name "svinotype" was developed. This paper describes the process, some of its properties and limitations.

EXPERIMENTAL SECTION

Ascorbic acid is known to be able to efficiently reduce Cu(II). At temperatures from 10 to 80 °C, Cu(II) can be reduced to Cu_2O.[7] At temperatures above 50 °C and a pH of about 5−7, Cu(II) can be reduced to metallic copper Cu(0).[8]

In both cases, the first stage is the formation of $Cu(OH)_2$:

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2$$

$Cu(OH)_2$ is then reduced by ascorbic acid $C_6H_8O_6$ either to Cu_2O

$$2Cu(OH)_2 + C_6H_8O_6 \rightarrow Cu_2O + C_6H_6O_6 \text{ (dehydroascorbic acid)} + 3H_2O$$

or to Cu(0)

$$Cu(OH)_2 + C_6H_8O_6 \rightarrow Cu(0) + C_6H_6O_6 + 2H_2O$$

At room temperature and a pH around 4−5, the reaction takes the former route in the dark, while the latter prevails under the influence of light. The light sensitivity of the reactions allows for their use as a basis for a photographic process.

The reactants for the process were chosen mostly for their accessibility. Pure ascorbic acid is not uncommon in pharmacies; $CuSO_4$ is an accessible source of Cu(II) ions, and $NaHCO_3$ is a mild and easily available basic salt, which can be used to adjust pH. The amounts and concentrations were selected on the basis of the quality of the resulting prints and their stability over time.

All of the reagents used in the experiments were reagent grade: 99.8% copper sulfate pentahydrate $CuSO_4{\cdot}5H_2O$, 99.9% sodium hydrogen carbonate $NaHCO_3$, and 99.2% ascorbic acid.

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All of the solutions were freshly prepared using distilled water. The amounts or reagents required for an A6 print are listed in Table 1. The pH measurements were made using a calibrated Milwaukee pH600 household pH tester.

Table 1. Amounts of Reagents for the Sensitizing Solution for an A6 Print

Aqueous Solution	Per 100 mL[a]	Volume: Sensitizing Solution	Volume: Paper Treatment
1 M $CuSO_4$	25 g of $CuSO_4 \cdot 5H_2O$	0.5 mL	
1 M ascorbic acid	17.5 g of ascorbic acid	2.5 mL	
1 M $NaHCO_3$	8.5 g of $NaHCO_3$	0.25 mL	≈100 mL

[a]Rounded to the nearest 0.5 g.

The same procedures were also successfully followed using exclusively consumer products: $CuSO_4 \cdot 5H_2O$ from a local hardware store, regular baking soda for $NaHCO_3$, ascorbic acid from a local pharmacy, and tap water.

In addition to the reagents, several different items were required. Thick watercolor paper, a sheet of glass, and a tray for paper treatment posed no problem to obtain. Transparent film for a laser printer was purchased in an office supply store. Producing a black and white negative image using graphics software and printing it on such a film was straightforward and resulted in a decent quality negative film. As negative images produced this way let a lot of light through even their darkest areas, two identical films were glued together to ensure good contrast; however, this was not strictly necessary. A 75 W incandescent light bulb was used as a light source due to the consistency of the spectrum of this type of bulb. Other types of light bulbs and direct sunlight were tested as well and proved to work just fine.

Paper Treatment

A sheet of watercolor or drawing paper is treated with a 1 M solution of $NaHCO_3$. This is needed to raise the pH of the sensitizing solution when it is applied to the paper. Although a 1 M solution is a good starting point, the optimal concentration may differ depending on the type of paper and the method of application.

The easiest way to treat the paper is to pour the $NaHCO_3$ solution into a tray and place a sheet of paper on the solution's surface for several seconds. Other methods, such as swabbing the paper with a dental cotton roll, a cotton disk, or a similar product moistened with the solution of $NaHCO_3$, also work.

The paper is then left to dry. It helps to let the paper dry under a weight to prevent it from deformation.

Some acid-free paper, e.g., ISO9706 paper, may not need any treatment since it already contains carbonates.[9] This may suffice to achieve the needed pH level for the reaction, but the results tend to vary from batch to batch, and more often than not, acid-free paper does not work very well or at all. Treating acid-free paper with $NaHCO_3$ solution yields unpredictable results.

Image Printing

Moderate indoor lighting does not noticeably affect the contrast and the quality of the prints if everything is done reasonably quickly; however, it is advisible to dim the lights to the lowest comfortable level.

To make the sensitizing solution, 0.25 mL of 1 M $NaHCO_3$ solution is combined with 2.5 mL of 1 M ascorbic acid. After the bubbling stops, 0.5 mL of 1 M $CuSO_4$ solution is added. Adding

Figure 1. Print with dimensions 14.5 × 11 cm^2 (5.7 × 4.3 in^2). Light source: 75 W incandescent light bulb. Exposure time: 5 min.

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$NaHCO_3$ raises the pH of the solution from 1.8 to 2.6. This is not strictly necessary, since the pH is mostly raised by the $NaHCO_3$ in the paper, but it usually results in an image with higher contrast. Contrast can also be improved by adding more $NaHCO_3$ to the paper during the paper treatment step, but this can cause excessive bubbling during exposure.

Approximately 3 mL of the solution per 150 cm^2 or $23\frac{1}{4}$ in^2 (approximately an A6 sheet or a 4R photo) is poured onto the treated paper, which is then quickly covered with a negative film. The negative film is then pressed down with a sheet of glass to improve contact. Once applied to the treated paper, the solution seemingly loses its light sensitivity on contact with air, so it is important to apply the negative film quickly in order to protect the solution from the air. For this reason, it is inadvisible to spend any appreciable amount of time brushing or otherwise dispersing the sensitizing solution on the paper; practice has shown that its natural spread caused by pressure from the film/glass "sandwich" and surface tension is sufficient to create a good quality print.

The exposure time under a 75 W incandescent light bulb at 15 cm distance from the paper is approximately 3−5 min. Further testing revealed that a 7 W 2700 K LED lamp requires approximately 1.5× longer exposure times on average; a 20 W blacklight CFL requires slightly shorter exposure times, and under direct sunlight, exposure time can be as short as 5−10 s.

After exposure, the paper is rinsed with water for approximately 30 s to remove the unreacted chemicals. The print is then covered with filter paper or a paper towel and left to dry in a dark place. The resulting print is stable if kept dry and does not require any further treatment (see Figure 1). However, it is advisible to coat with transparent varnish to guard the print from moisture and/or slight risks associated with contact with copper compounds.

Test Tube Experiments

The same reaction was performed in a test tube to confirm that nothing in the paper was crucial to the process.

A solution was prepared as follows: 10 mL of 1 M ascorbic acid solution and 0.4 g of $NaHCO_3$ were added to 2 mL of 1 M $CuSO_4$ solution, resulting in a solution with a pH of 4.2. It is worth noting that thoroughly mixing the solution on the surface of the paper is not feasible, and consequently, this pH value can only roughly represent the conditions occurring in the actual printing process. After the bubbling stopped, the mixture was poured into two test tubes. One tube was wrapped in aluminum foil, and the other was left uncovered. Both were placed under a 75 W incandescent light bulb.

After 15 min of exposure, the tube exposed to light was covered with a thin, lustrous layer of copper on the illuminated side, and a thick brown precipitate had formed. The brown precipitate was filtered out and washed with water, and then with 96% ethanol, and it was left overnight. When completely dry, the precipitate displayed a pronounced metallic luster after being pressed with a hard object. The dry precipitate also displayed fairly low electrical resistance as shown by a multimeter. Both of these findings are consistent with this precipitate being metallic copper. As this precipitate appeared in the illuminated test tube, the brown color of the exposed areas of the printed images can also be attributed to metallic copper.

The tube wrapped in foil had no copper on its walls and only a thin orange-yellow precipitate suspended in the solution. Under these conditions, the expected product is Cu_2O.[7] Indeed, this precipitate was visually similar to the Cu_2O precipitate that appears in Benedict's test for reducing sugars. As Benedict's test employs a similar set of reagents and is known to give false positives with ascorbic acid,[10] it is safe to assume that the precipitate was indeed Cu_2O. As it appeared in the non-illuminated test tube, this precipitate can be held responsible for the yellow staining on the unexposed areas of the printed images.

■ HAZARDS

Ascorbic acid and sodium hydrogen carbonate are generally considered safe. Copper salts and oxides, as well as fine copper particles, are toxic if ingested or inhaled and can cause skin and eye irritation. To avoid unnecessary contact with the copper compounds present in the printed image, it is advisible to cover the image with a transparent varnish.

■ DISCUSSION

When assessing the properties of the presented process, it is convenient to compare it to a similar and more widely known and used process. Cyanotype fits this role well, being primarily a contact-printing method and being relatively easy to perform.

Svinotype requires no special skills, and even younger students can perform it with not much more difficulty than cyanotype. The accessibility and relative safety of the reagents needed for the presented process make this approach suitable for a wide range of situations in which laboratory chemicals are unavailable or inappropriate.

Although the observed variation in exposure time under different light sources suggests that, not unlike cyanotype, svinotype is most sensitive to light somewhere in the UV region; it shows fairly reasonable exposure times with generic indoor light sources. In general, svinotype seems to be more light sensitive than cyanotype and its variants, which usually require minutes of exposure under sunlight.[4,11] Greater light sensitivity is advantageous for indoor use.

However, this process also has some drawbacks. For one, the necessity of applying the sensitizing solution right before printing is limiting, as it does not allow the experimenter to easily position the sheet in any way other than horizontally. This can be worked around, however, by affixing the paper/negative/glass "sandwich" to a plywood support using binder clips.

Some kinds of paper, especially larger sheets, tend to wrinkle when wetted from one side more than they do with cyanotype, which affects the quality of the prints. To mitigate this problem, thicker paper can be used, and glycerol can be added to the sensitizing solution.

The sensitivity to air of the sensitizing solution once applied to paper makes it more difficult to distribute the solution evenly on larger sheets of paper and renders preparing the sensitized paper in advance nearly impossible. This limitation is most likely caused by the oxidation of reduced copper species by oxygen in the air, resulting in the catalytic oxidation of ascorbic acid[12] which leaves no visible traces on the paper. The cyanotype process has no such impediments.

Another issue is that the images are prone to bleaching as they dry. This is most likely caused by oxidation of copper Cu(0) in the image either by leftover Cu^{2+} and/or by the oxygen in the air. The former can happen in the presence of chlorides.[13] More thorough rinsing can help remove the excess Cu^{2+}, and applying a solution of $NaHCO_3$ to the print before letting it dry considerably reduces bleaching, presumably because the resulting rise in the pH reduces the rate of corrosion of copper.[14]

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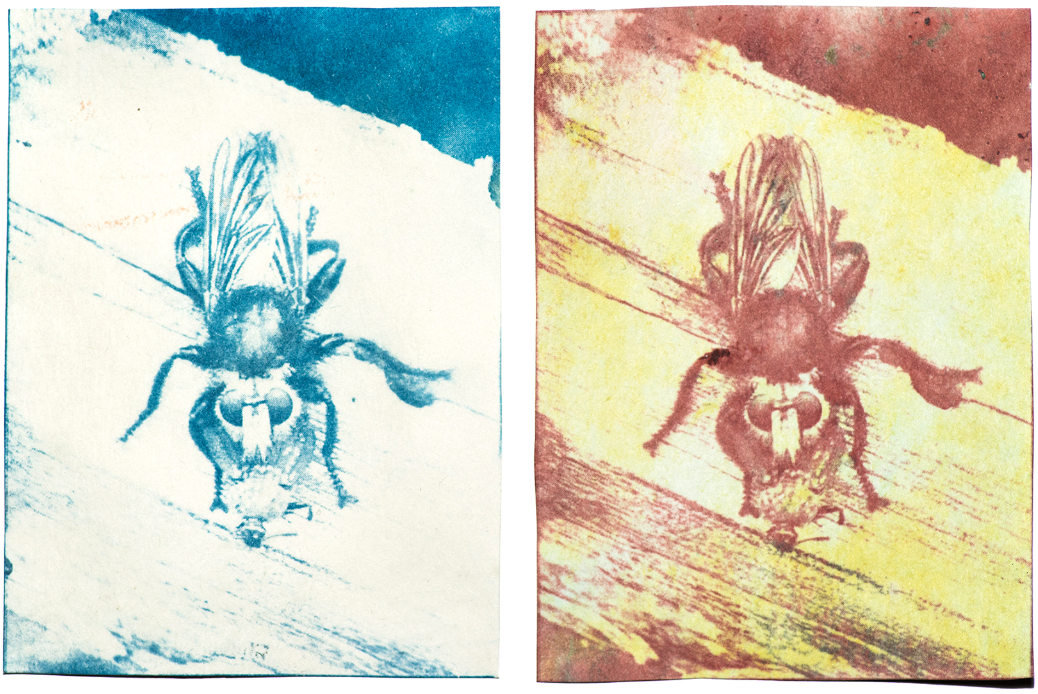

Figure 2. Cyanotype print with dimensions 8 × 11 cm^2 (3.15 × 4.33 in^2) (light source, 20 W blacklight CFL; exposure time, approximately 1.5 h) compared to a svinotype print (light source, 75 W incandescent light bulb; exposure time, 5 min) from the same negative image.

In terms of quality, the prints are comparable to cyanotypes (see Figure 2). They fall slightly short when it comes to image contrast and are prone to defects caused by the bubbling of the decomposing carbonate.

Another common defect is the color of the background, which is sometimes unevenly stained yellow.

Printing photographs is just one way to demonstrate the reactions employed in this process. For example, just as with silver halide photography,[15] the reaction can be performed in a vessel, allowing the experimenter to draw with light.

This account leaves some important questions for further investigation. What is the mechanism responsible for light sensitivity? What are the precise sensitivities at different parts of the spectrum? What exact conditions are optimal for light sensitivity?

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.0c00467.

Graphical instructions (PDF)

Video instructions (MP4)

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Notes

The author declares no competing financial interest.

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