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Spectroscopic Analysis of the Traditional Cyanotype Process and its Impact on Art

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Spectroscopic Analysis of the Traditional Cyanotype Process and its Impact on Art

A Thesis

Presented to the Department of Chemistry and Biochemistry

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Butler University

In Partial Fulfillment

of the Requirements for Graduation Honors

Jacob Applegarth

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Introduction

The cyanotype process, developed in 1842, was originally used by photographers and art enthusiasts to create images (*1*). "The cyanotype process, also known as the blueprint process, was first introduced by John Herschel (1792 – 1871) in 1842. Sir John was an astronomer, trying to find a way of copying his notes." (*2*). The process involves the photo catalyzed formation of the Prussian blue pigment, iron(III) ferrocyanide. Over time Herschel and others made improvements on his process. Herschel himself responds to the works of others and shares the improvements he made to the process (*3*). After a short time the process was used commercially, given that the process is cheap, easily performed, and nontoxic.

Architects and others involved in the printing of building plans began to use the process to make copies of their floor plans. The term "blue print" was actually derived from the cyanotype process because the end result is a blue photograph, produced from a negative. Lois Price, in conjunction with the American Institute for Conservation of Historic & Artistic Works, wrote that "The introduction of the blueprinting process, originally called the ferro-prussiate or cyanotype process, in the late 1870's, however, revolutionized the production of architectural drawings and significantly affected the practice of architecture by facilitating the coordination of increasingly large and complex projects" (*4*).

Herschel's traditional cyanotype process was the first ever successful non-silver printing process. Formation of a solid, water-insoluble, blue pigment results from the photo catalyzed reaction between ammonium iron(III) citrate and potassium ferricyanide. When suitable ultraviolet radiation shines on a mixture of these two reagents, photo oxidation of the citrate is accompanied by a concurrent photo reduction of the ferric ion.

$$
UV + Fe^{+3} + C_6H_5O_7^{-3} \to Fe^{+2} + CO_2 + C_5H_5O_5^{-2}
$$
 (Eq. 1)

Immediately thereafter, an electron moves from the iron(II) to the ferricyanide to make iron(III) ferrocyanide, which is the Prussian blue pigment. *(6)*

$$
\text{Fe}^{+2} + \text{Fe(CN)}_6{}^{3-} \rightarrow \text{Fe}^{+3} + \text{Fe(CN)}_6{}^{4-} \rightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 \text{ (s)}
$$
(Eq.2)

In 1995, Mike Ware made improvements upon Herschel's process, altering the formulation to create better looking images with more stable reagents. This process involved the use of ammonium iron(III) oxalate as a reagent (*5*).

Glen Lawrence from Long Island University informs readers that the process is not just popular with photographers and artists (*7*). Many studies have been done on the process, including Lawrence's experiment on UV catalysts. He explains a small part of the reaction and the current state of affairs surrounding it when he states, "The chemical reactions taking place in the cyanotype process are not well understood, beginning with the uncertain structure for ammonium ferric citrate. The structure of insoluble Prussian blue is not known in detail…" (*7*). Other details of the reaction, including the mechanism by which electrons move and intermediates involved, are still not understood.

Since 1999, when Lawrence claimed the structure was not well understood, it has been discovered Prussian blue has a fairly common solid state structure. The pigment has a face centered cubic unit cell with alternating iron(II) and iron(III) ions. The lattice is arranged in such a way that the iron(III) ions can coordinate to six nitrogen atoms (*9*).

Figure 1: Prussian Blue face centered cubic lattice from Keggin and Miles; (●)Fe3,(○)Fe2. (*8*)(*9*)

Ware made significant attempts to further understand the traditional cyanotype process. He hoped to produce a pigment that was produced more quickly, did not produce mold when stored in solution, did not precipitate off the image, and was more readily absorbed by media such as paper. Ware developed his own "New Cyanotype Process" (*5*) that is allegedly more sensitive and produces a higher quality print. Ware offers suggestions, such as the use of ammonium ferricyanide, but he did not quantify the effect that the change in reagent had on the print. In an online publication Ware cites ammonium ferricyanide as the answer to problems associated with traditional process stating, "A 'gritty' sensitizer is useless, and if this happens within the sensitized paper it can cause quite pretty, but totally unwanted fern-like patterns. The answer to the problem would be simply to use ammonium ferricyanide instead of the potassium salt, but this still seems to be unobtainable commercially (so far as I know) and is rather troublesome to make."(*5*) However, ammonium ferricyanide is commercially available and was used in our studies.

In 2009, students at Buffalo State College made cyanotypes using the traditional iron(III) citrate and potassium ferricyanide recipe and compared them to those created by Mike Ware's modification that uses iron(III) oxalate and potassium ferricyanide (*10*). However, they did not prepare the solution of iron(III) oxalate and ammonium ferricyanide. They showed that Ware's solution produced a much more vibrant print (Image 1).

Image 1: Cyanotypes produced by students at Buffalo State College. From left to right: traditional cyanotype and Ware cyanotype (*10*).

Our initial studies have showed that other factors may impact print quality. The rate for formation of the print is a function of the reagents used, the intensity of the UV light, and the reagent formulation. Also, it was observed that an initial time period must pass before the Prussian blue sticks to the paper. This may affect the quality of the prints produced, especially for prints with fine detail.

Another significant knowledge gap In the Prussian blue print to be addressed is the apparent deterioration of the prints. Under certain reaction conditions, the print will develop Prussian blue and then convert it to Prussian white with continued exposure.

Studies have shown that Prussian white is a further reduced form of Prussian blue and may be produced through a common redox reaction that is light dependent (*11*). This is potentially a problem for a piece of art that could be on display in a well-lit room. Understanding how and why this byproduct is produced could help explain or guide conservation effort.

Cyanotype print preservation and conservation is an increasingly complex topic. According to Barandiaran, cyanotypes are some of the most sensitive pieces of art (*12*). Barandiaran has shown that mechanical cleaning, solvent cleaning, wet cleaning, bleaching and deacidification have varying degrees of efficacy. Ware has also discussed how understanding the formation and stability of Prussian white could lead to better conservation of cyanotype prints (*13*). Understanding the chemistry behind the conservation treatments of these prints could be of vital use to finding the best course of action for preserving the art.

Our study used reflectance spectroscopy to determine how various reagents and reagent concentrations impact the color of the print. Four hypotheses were made concerning the cyanotype process and Prussian blue formation.

• **Hypothesis 1: the use of oxalate as the reductive species will increase the rate of Prussian blue formation compared to citrate.**

This hypothesis was examined by comparing solutions made with ammonium iron(III) citrate to those made with ammonium iron(III) oxalate of a comparable concentration. Concentrations were altered to determine a rate order for each

reducing agent. Results demonstrated which species was a better electron donor based on how quickly they donated an electron.

• **Hypothesis 2: the use of ammonium ferricyanide rather than potassium ferricyanide will give a different counter ion in solution that will also impact the rate of pigment formation.**

Concentrations of either potassium or ammonium ferricyanide were altered while either the citrate or oxalate concentration was held constant. Rate of Prussian blue formation was determined. These results demonstrated whether potassium or ammonium cations in solution have any impact on the formation of pigment.

• **Hypothesis 3: the media to which the photo reactive solution is applied will impact the rate of formation of Prussian Blue.**

Various sensitizer solutions were applied to two different types of paper. The effect of each on the rate was observed. It was predicted that a paper produced for wet media would absorb more solution and therefore produce pigment more quickly.

• **Hypothesis 4: the rate of formation of blue pigment will show some correlation with how individuals perceive the artwork.**

Images were made, and participants were surveyed to determine whether or not faster or slower reactions were perceived as more colorful or artistically appealing. These results demonstrated how the research can be applied to an artistic setting.

Material and Methods

Formation of Prussian Blue:

Four different solutions of varying concentrations were examined throughout the course of this study. Each solution contained either potassium ferricyanide, $K_3Fe(CN)_6$, (Fisher Scientific Company) or ammonium ferricyanide, (NH_4) ₃Fe(CN)₆, (MP) Biomedicals LLP) and either ammonium iron(III) citrate, $C_6H_{5+4}yFexNyO_7$, (Sigma Aldrich) or ammonium iron(III) oxalate, $(NH_4)_3Fe(C_2O_4)_3$, (Alfa Aesar, 98% purity). The four solutions prepared were potassium ferricyanide and iron(III) citrate, potassium ferricyanide and iron(III) oxalate, ammonium ferricyanide and iron(III) citrate, and ammonium ferricyanide and iron(III) oxalate. Throughout the rest of this document, these solutions will be referred to as Solution A, B, C, and D, respectively. Each concentration was produced using a certain mass of reagent per 1.5mL of deionized water. Each compound was added to 1.5mL of water. The two components of the solution were then combined prior to coating. This allowed the solutions to be kept for longer periods of time without worry that they might react in the presence of light. Each total solution (A-D) of 3mL was equally applied to two types of paper. Different papers were tested to determine whether or not the media used impacted Prussian blue formation.

Two papers were used in this study, Strathmore Bristol and Strathmore Watercolor. Bristol is a vellum surface paper used for finished artwork with dry media. Vellum surface papers have ridges and grooves that collect media better than a smooth surface. This gives artwork on vellum surfaces a varied texture. Watercolor is a cold press paper for use with wet media. Similar to the vellum surface of the Bristol paper, the cold press surface of the water color paper provides texture to the image and implements

bumps and grooves that soak up the water based media. Both papers are acid free, and gloves were worn when handling to prevent residue transfer. Solutions were applied equally to a 1x5 inch strip of each type of paper.

Approximately 1.5mL were applied to each of the two types of paper. The solution was deposited on the paper using a 1mL plastic pipette and then spread using a soft paint brush. Each paper was then kept in the dark and allowed to dry for one week. After one week, the samples were analyzed using percent reflection spectroscopy for data collection while the paper was exposed to light within a light box.

 Data were gathered every minute for thirty minutes using an Ocean Optics, Inc. ST2000 fiber optic spectrometer and color detection software. Color data were plotted in three dimensional space using CIE values and their axis (Image 2). Only the b* axis was considered due to the fact that the pigment formed is blue. A negative b* value indicates a movement in the blue direction away from white; therefore, the larger the negative b* the more blue a pigment.

Image 2: L*a*b* axis for CIE values representing color in three dimensional space

Image 3: Data collection setup with fiber optic spectrometer

The rate was determined by the absolute value of the slope of the b^{*} values in the first five minutes of data collection. Rates were determined by calculating the slope of the first five data points in a b* vs Time (minutes) graph (Figure 2).

Figure 2: Potassium ferricyanide at 0.25M with 0.46M ammonium oxalate to illustrate how rate was determined.

Using this data collection method, rates of pigment formation and the rate laws with respect to potassium or ammonium ferricyanide concentration and oxalate in solution were determined by varying the concentrations of reagents (Tables 1, 2, and 3).

Formation of Prussian White:

Solutions B and D were applied to 1x5 inch pieces of paper following the same procedure utilized for formation of Prussian blue. However, these samples were exposed to light for a total of one hour, as opposed to typical thirty minutes for Prussian blue. Data collection for determining a rate of Prussian white formation did not begin until fifteen minutes after exposure had started. After that point in time, rate data were calculated by the absolute value of the slope of the b* values given by the data collection over time 15-20 minutes. Rates were determined by calculating the slope of the first five data points in a b^* vs Time (minutes) graph (Figure 2).

Prussian Blue Formation

Over the last three years extensive work was done with the formation of Prussian blue pigments. The primary focus of our study was the kinetics of the photo oxidation and reduction process involved in the formation of the pigment. It was hypothesized that the rate of the reaction could be altered in two ways, by changing the concentration of the reagents and substituting compounds with similar reactivity to potassium ferricyanide and iron(III) citrate into the reaction. Ammonium ferricyanide and iron(III) oxalate were selected as suitable substitutes. Ammonium has the same charge as potassium, but it provides a different counter ion in solution. Similarly, oxalate has a very similar structure and identical charge to citrate, but differs slightly in the overall composition and connectivity of the compound.

The reactions performed appear to be first order with respect to ammonium oxalate when either potassium or ammonium ferricyanide was in solution (Table 1 and Table 2).

Potassium Ferricyanide (M)	Citrate (M)	Oxalate (M)	Rate (P1) b*/minute	Rate (P2) b*/minute
0.2025	0.3		0.516	0.564
0.2025	0.644		0.876	0.824
0.2025	0.76		1.666	1.4
0.2025		0.33	2.25	2.668
0.2025		0.4672	3.218	3.673333
0.2025		0.6293	3.394	2.93

Table 1: Rate of Prussian blue formation when changing citrate and oxalate concentration with potassium ferricyanide held constant

Table 2: Rate of Prussian blue formation when changing citrate and oxalate concentration with ammonium ferricyanide held constant

Potassium Ferricyanide (M)	Citrate (M)	Oxalate (M)	Rate (P1) b*/minute	Rate (P2) b*/minute
0.25	0.3		0.68	0.826
0.25	0.644		1.032	1.134
0.25	0.76		1.02	1.042
0.25		0.33	2.374	1.624
0.25		0.4672	2.574	2.576
0.25		0.6293	2.623	2.796
0.25		1.2586	3.874	

Unfortunately, rates could only be measured within a narrow concentration range due to difficulties with saturation of the media with solution. This made determining the rate laws more difficult. Data collection near the upper limit of the concentration range gave data that did not follow the same trend observed at lower concentrations. This can be seen in the highest concentration trials for each solution (Table 3).

Table 3: Rate of Prussian Blue Formation when oxalate concentration is held constant for both the Bristol (P1) and Watercolor (P2) papers.

A second consequence of greatly increasing the concentration was a distinct, qualitative difference between the two prints. Compared to a 0.63M, 1.20 M solution D produced a print that was somewhat grainy and displayed pinpoint variation in color, compared to the first two concentrations which produced solid, deep blue prints (Image 4). This could be due to the amount of ammonium iron(III) oxalate needed to reach the 1.2 M concentration. The solution likely reached a critical mass prior to that needed to produce the desired concentration.

Image 4: 1.2M versus 0.6293M. The print on the left was made from a 1.2 M ammonium iron(III) oxalate solution, whereas the print on the right was made using a 0.6293 M solution

Data were also collected to determine the rate order with respect to potassium and ammonium ferricyanide when reacted with iron(III) oxalate (Table 3). The data showed that increasing the concentration of either potassium or ammonium ferricyanide caused a decrease in the rate of formation of blue pigment. The general trend appeared to show that the rate order for the reaction was negative one. This indicates that as the concentration of either ammonium or potassium ferricyanide increases, the rate of the reaction decreases. As of now, we propose no logical reason why this should occur. The expectation was that rate would increase with the increase in concentration. However, it would even be possible for the rate to saturate and level off if the concentration of

ferricyanide reached a point where the rate of photon absorption and subsequent photooxidation became the rate-limiting step.

Unfortunately, the work performed concerning the rate of formation of Prussian blue when citrate was used as the reducing agent gave data that did not demonstrate a clear trend or concentration dependent rate law. This could be attributed to several factors and is best seen when citrate reacted with a high concentration of either counter ion (Table 2).

The theoretical mechanism of the formation of Prussian blue via potassium ferricyanide and iron(III) citrate is as follows:

$$
UV + Fe^{+3} + C_6H_5O_7^{-3} \to Fe^{+2} + CO_2 + C_5H_5O_5^{-2}
$$
 (Eq. 3)

$$
Fe^{+2} + Fe(CN)_6^{3} \to Fe^{+3} + Fe(CN)_6^{4} \to Fe4[Fe(CN)_6]_3
$$
 (Eq. 4)

This mechanism gives the potential for oxidation of the citrate anion at two different locations. These locations are identified below (Figure 3). The availability of two different oxidation sites could be responsible for the inconsistency seen in the rate data. This inconsistency was not seen with reactions using oxalate as the reducing agent. It was hypothesized that this was due to the fact that oxalate has only one unique site where oxidation would occur (Figure 4). When the citrate is oxidized at the different sites it would produce different ions. These ions could interact with the ferrocyanide differently and thus affect the rate. Also, comparing the reduction potentials of citrate (E° = -0.180V) and oxalate ($E^{\circ} = -0.49V$) shows that oxalate is a better oxidizing agent than citrate (*14*)(*15*). When the cell potentials of both the citrate and oxalate systems are calculated, E° _{cell} for citrate and ferricyanide was -0.18V and the E° _{cell} for oxalate was

0.13V. This could also contribute to the increased rate of pigment formation for oxalate containing solutions because the electrochemical process is more spontaneous.

Figure 3: The chemical structure of citrate in solution.

A study by Abrahamson et. al. showed that differences in pH could also affect the quantity of iron(III) carboxylate complexes, which is another possible explanation for the varied rates (*16*).The pH of the solution could also potentially be used to explain the difference caused by changing the iron(III) salt. The researchers showed that increasing the pH of the reaction solution from 2.7 to 4 lead to a 50% increase in quantum yields for many carboxylates (*16*). However, increasing the pH decreased the yield of the iron(III) oxalate complex. The article also states that ligand ratios could affect the production of Prussian blue. The researchers showed that these reactions were most efficient at lower ligand to metal ratio. When production was measured at 0.0015M carboxylate and 0.3mM Fe(III), oxalate produced the most product.

Applying the work from Abrahamson et. al. to the work done at Butler, it can be seen that the ratio of citrate to Fe(III) was substantially different. This, combined with the unpredictable nature of two sites of oxidation, could have contributed to the inefficient, unsteady rate of formation of Prussian blue seen in Table 2. Further work should be done to specifically detect the pH of various reaction solutions and their effect on Prussian blue formation.

Prussian White Formation

During data collection of some solutions, it was observed that certain solutions began to fade and produce a less negative b value as exposure time approached thirty minutes. This was especially true for solution B, which contained oxalate. This change in color could be due to the production of Prussian white. The conversion from Prussian blue to Prussian white has been studied using cyclic voltammetry, and the proposed reaction is as follows (*9*):

$$
Fe_4(III)[Fe(II)(CN)_6]_3(s) + 4e^+ + 4K^+ \leftrightarrow K_4Fe_4(II)[Fe(II)(CN)_6]_3(s) \qquad (Eq. 5).
$$

The four electron process converts Fe^{3+} in Prussian blue to Fe^{2+} in Prussian white. In order to determine the extent of Prussian white formation, solutions B and D were applied to paper following normal procedure but were exposed to light for one hour rather than thirty minutes. The first reaction performed was solution B with a concentration of 0.25M ammonium ferricyanide and 0.46M ammonium oxalate (Figure 5). This reaction illustrated the need to study Prussian white formation further. The reaction also displayed at what time Prussian white data collection should begin.

Based on this preliminary finding, it was decided to record CIE values every five minutes for the first fifteen minutes of exposure and then every minute after that point up until one hour. Measurements taken from minute 15 to 19 were used to calculate the rate of formation of Prussian white. This was done for both solution B on both types of paper. The data showed that generally the samples made with the Watercolor paper started Prussian white production prior to those samples made with Bristol paper. This is most likely due to the amount of solution absorbed by the wet media paper compared to that of the dry media Bristol paper.

Difference in Media

The two papers used in this study were Strathmore Bristol and Strathmore Watercolor. Bristol is a vellum surface paper used for finished artwork with dry media. Watercolor is a cold press paper for use with wet media. Each of the papers were used with samples of the same solutions in hopes of determining the effect the paper can have on the pigment formed.

The Strathmore Bristol paper is marketed as a vellum surface paper. According to the manufacturer, "Bristol generally describes a drawing paper that is pasted to form multi-ply sheets. Bristol sheets provide a stiff, strong surface to work on without the need for mounting. The term Bristol derives from the early days of European papermaking when mills would send their finest papers to Bristol, England to be pasted together" (*17*). The difference between vellum and smooth Bristol is that vellum surface paper have ridges and grooves that collect media better than the smooth surface. This gives artwork on vellum surfaces a varied texture.

Strathmore Watercolor is marketed as a light weight watercolor paper that has a cold press surface good for water based media. Similar to the vellum surface of the Bristol paper, the cold press surface of the water color provides texture to the image and implements bumps and grooves that soak up the water based media. However, this increase in texture and absorbance often leads to dull color (*18*).

After Prussian blue formation was compared between the two papers, one key difference was determined. Based on CIE data, the Strathmore Watercolor paper was

generally shown to produce a greater rate of formation of Prussian blue, especially in citrate trials (Table 2).

Qualitative Analysis

In order to determine the combined effects of the various combinations of reagents with different media on the artistic quality of the prints, a qualitative survey was taken. The survey asked participants to rank characteristics of the images from 1-5 with a value of 5 designating the highest quality. The characteristics asked about were as follows: color, consistency, clarity, artistic appeal, and texture. Participants were shown a total of eight different pigments with each image produced in triplicate in order to observe consistency. Results of the study were gathered using Qualtrics.com in conjunction with Butler University. There were 109 participants in the survey. Participants in the survey were recruited through the Butler University Honors Program and The Department of Chemistry and Biochemistry email accounts. The survey was IRB approved, and all eight images from the survey can be found in the appendix (Survey 1).

From the results of the survey, participants ranked the pigments in terms of color and artistic appeal as shown below:

Figure 6: Color (shown in blue) and artistic appeal (shown in black) ratings determined by an anonymous survey of 109 subjects. These rankings were determined out of a maximum of 5 points. The images studied where made on Strathmore Watercolor paper.

Figure 7: Color (shown in blue) and artistic appeal (shown in black) ratings determined by an anonymous survey of 109 subjects. These rankings were determined out of a maximum of 5 points. The images studied where made on Strathmore Bristol paper.

Generally, participants found pigments made with ammonium iron(III) oxalate and potassium ferricyanide to have better color than those that contained either ammonium iron(III) citrate or ammonium ferricyanide. Also, participants generally found images that contain oxalate and were made on the Bristol dry media paper to be more artistically appealing. The results were inconsistent with respect to the potassium versus ammonium ferricyanide. Further work could be done to understand what changes could be made to the solutions to make them more artistic appealing.

Another variable to consider when taking into account the qualitative data is the method of data collection. Participants were asked to make qualitative judgments from a photograph of a produced image. It is possible that had participants judged and examined the original prints, then they would have assigned different values for the characteristics being studied. The digital photographs may have been poor representations of the artistic quality of each print.

Conclusion

In conclusion, it was determined that increasing the concentration of either potassium or ammonium ferricyanide caused a decrease in the rate of formation of blue pigment. The general trend appeared to show that the rate order for the reaction was negative one. Also, the reactions performed appear to be first order with respect to ammonium oxalate when either potassium or ammonium ferricyanide was in solution. Strathmore Watercolor appears to produce Prussian blue at a higher rate than Strathmore Bristol. As far as artistic qualities, participants surveyed found pigments containing oxalate and produced on Bristol paper to have the best color. They also ranked these images highest in artistic appeal. Further work should be done to understand the mechanism of Prussian white formation and to understand why as the concentration of either ammonium or potassium ferricyanide increases, the rate of the reaction decreases.

Apendix

Survey 1

Q3 This survey should take approximately 10 minutes to complete. The data collected will be used as part of an honors thesis. Participation is voluntary. All responses are anonymous and will be kept confidential.Q2 Please rank the set of images below based on the qualities of the prints provided (5 being the highest)

Q1

Q23

Q24

Q25

Q26

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