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What Is It: Empirical Research into the Art of Bleaching Crayon Enlargements

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Abstract

As Robert Feller wrote in 1982, "One of the first things that one should ask in any bleaching problem is: What is it—what is the chemical substance that you are trying to bleach?" (Feller 1982) Three decades later, this question is still valid. The technologies of paper manufacture, chemical structure of cellulose, and various agents of deterioration impact what the conservator encounters at the bench. Heugh-Edmondson Conservation Services, LLC, like many private practices and regional centers, is frequently asked to treat crayon enlargements. These objects are usually in very poor condition, requiring an extensive treatment that often involves washing and some type of bleaching. These treatments have proven to be successful, leading conservators to question the established belief that papers used for crayon enlargements are of poor quality and to ask themselves anew, "What is it?" This paper will present examples of crayon portrait treatments, describe the premise and organization of the project, provide some preliminary results, and discuss directions for further inquiry.

Introduction

Crayon enlargements, or crayon portraits, were the first commercially produced photographic enlargement and was printed on artist papers, processed to remove light sensitive chemistry, and then enhanced with media. The photographic image was faint and was thus a guide for hand coloring: some were heavily colored using artist's pencils, pastels and/or various airbrushing techniques while others were simply enhanced with charcoal and white chalk. The practice of crayon enlargement portraiture was widespread in late 19th century/early 20th century America, and many examples we see today are severely deteriorated. Common condition issues are embrittlement of primary and secondary supports, discoloration, localized staining from exposure to water, mold and/or foxing, or even fire, and physical damage frequently with associated image loss.

Although many conservators prefer to design their treatments with minimum intervention, a multi-faceted treatment, designed to address both aesthetic and structural issues is the preferred approach at Heugh-Edmondson Conservation Services, LLC (H-E). Brittle secondary supports are removed, the primary supports are washed to remove readily soluble contaminants, stains are removed or reduced as much as possible, the primary supports are lined with Japanese paper (usually Hiromi MM1 that is a mix of Thai kozo, sulfide pulp, and Manila Hemp, 65%/25%/10% respectively), losses are filled with a suitable paper or paper pulp, the lined primary supports are dry-mounted to archival boards, and image losses are inpainted. Bleaching techniques are utilized to return the portrait to some degree of its original appearance. This thorough treatment protocol produces a significantly brighter and uniform sheet tone, and sometimes a rejuvenated handle. Loss of applied media is prevented by the airbrush application of a 5%-7% solution of Acryloid B72 in toluene.

Paper quality

The widespread belief among conservators has been that crayon enlargements are executed on poor-quality paper containing lignin. The darkening of the paper support was assumed to be caused by a derivative of oxidized ligneous components within the paper structure. However, a history of highly successful crayon portrait treatment projects has led H-E to question these suppositions.

Washing and bleaching is one of the best methods for treating crayon portraits: the aqueous nature of the treatment appears to strengthen the paper by washing out damaging acid-based degradation products. Bleaching with oxidative and reductive bleaches, solo and in sequences, greatly enhances the sheet tone while appearing to not affect the media. Effectiveness in bleaching techniques alludes to a better quality paper, one without lignin. It is hypothesized that the darkening is not a function of lignin content, but is caused by inadequate washing during production of the photographic image, an unusually high sugar/hemicellulose content within the paper, or a darkened resinous paper sizing.

The authors have been conducting ongoing fiber analysis of crayon portrait primary support papers. At the time of publication, seventeen crayon enlargement papers from across a nearly 20 year spread (and a wide geographic spread as well) have been sampled. All samples from this representative group appear to contain good quality fiber, mostly bast with some possible cotton fibers. Some wood or grass was also noted, but only in some rare samples. Lignin has not been found as a component of any of the seventeen papers.

Further evidence of the use of good quality papers was a Steinbach & Co. of Malmedy (Prussia) watermark found in an enlargement treated at H-E in 2008 (H-E #07-09-043). Steinbach & Co. papers appear in many ads and treatises in 19th century photographic journals, which state that the papers were good quality, made from flax (linen), and suitable for photographic solar pictures (Photographic Times 1901). Treatises also praise Steinbach & Co. for the excellent linen content of their paper (Vogel 1895).

Bleaching

This good quality paper allows for the use of a variety of bleaching techniques, if desired by the conservator. The treatment steps often undertaken at H-E rotate between various types of bleaches and application techniques to reduce staining more effectively. For example: a treatment may start with light bleaching and then progress to adding a drop of hydrogen peroxide (H_2O_2) to the bath. Certain types of stains may be reduced with sodium borohydride ($NaBH_4$) in between light bleaching campaigns. Bleaching with a sequence of oxidizing and reducing steps is not redundant, and the bleaches do not negate each other, providing real benefits to this approach. H-E conservators have found, contrary to popular belief, that these bleaches do not cause significant changes to the image material or applied media.

Methods

A historic crayon enlargement was purchased and subjected to a series of treatment procedures. The ultimate goal was two-fold. 1: study the bleaching treatment procedures at H-E and

determine if any led to color reversion. 2: test various toggling sequences of bleaches to determine if one was more stable overtime than another.

All bleaching techniques used at H-E on works on paper were considered as options for this project. Feller states that color reversion from post irradiation darkening after light bleaching is only correlated with lignin content (Lee 1989). As the sample crayon enlargement did not appear to contain lignin, light bleaching was also considered a viable option for testing.

The concept of toggling oxidative and reductive bleaches was of special interest. Certain pathways may prove to be more or less apt to cause darkening overtime. Feller had discussed the role of sodium borohydride in papermaking and that it could, at high enough concentrations, tie-up the damaged cellulose chains. (Feller 1985) Once tied-up, they might not be as susceptible to acid hydrolysis in aging and slow the deterioration reactions. The concentrations of sodium borohydride in conservation treatment protocols are much lower than papermaking so it might prove negligible, but bleach sequences ending in a borohydride step were explored for possible beneficial outcomes.

Aging was carried out at ambient temperatures and in a natural environment to make empirical observations. All actions were taken to reproduce an actual scenario of treatment by the conservator and display by a client. No accelerated aging was done. Feller's research on cellulose concludes that the components of paper that are sugar in nature – i.e. the hemicellulose and byproducts – darken in the presence of heat. (Lee 1994) Although accelerated aging is expedient, the heat component of the test might prove to darken these sugar components and skew results. It would be hard to determine if the damage was due to the bleaching technique versus the heat from the aging test.

Treatment procedure: Washing and bleaching

The sample crayon enlargement was surface cleaned with grated erasers and then a 1/16 section was removed as the unchanged control. A mist fixative of 5% Paraloid B-72 in toluene was applied to the surface with a Binks Wren B airbrush. (The mist is very effective at stabilizing enlargements with black and white colorants. Enlargements that are more heavily colored may need additional fixatives or a more conservative washing approach to assure that media stays in place during washing.) The primary support was unmounted from the majority of the board mount with a Caselli spatula and washed in a series of filtered tap water baths (naturally pH 9.0 in Kansas City). The papers were originally mounted together with water sensitive adhesives so aqueous treatments were successful for unmounting. The first bath was hot (46°C/115°F) and included two tablespoons of a saturated solution of Orvus WA paste. The soap acted to cut the surface tension of the water and allow better water absorption. A final backing removal was carried out to remove the rest of the board and board facing paper, exposing the reverse of the primary support.

After washing was completed, the sample was cut into sixteen sections and subjected to various oxidative and reductive bleaches, including combinations. Bleaching concentrations were chosen through empirical use in the H-E studio. (The concentrations are presented here in percentages, but all powder-based bleaches are measured with a "recipe" format within the H-E

studio using tablespoons to mL of water.) Sodium borohydride was purchased in the pellet form and cut into pieces using a pill cutter.

Oxidative Bleaches	Reductive Bleaches
▪ Light ▪ Light & 0.18% reagent grade H_2O_2 ▪ 0.18% reagent grade H_2O_2	▪ 0.025% $NaBH_4$ (w/ 1 hour sit-time before use) ▪ 0.3% Super Iron Out (proprietary mixture of sodium hydrosulfite and sodium bisulfite)

Fig. 1. List of oxidative and reductive bleaches used

Oxidative bleaches
The source for light bleaching was a Sun System 2 lamp by Sunlight Supply with a 400W metal halide bulb. The light bank was hung 21.5" above the sink. Filtered tap water (pH 9) was used in all baths. Each light bleaching session lasted three hours on recto and verso. Hydrogen peroxide was added directly to certain baths in order to determine its efficacy.

Reductive bleaches
Sodium borohydride and Super Iron Out bleaching baths were both thirty minutes in length. All bleaches were applied by immersion, and none was applied locally.

Rinsing, Lining, and Display
Extensive rinsing was done in all cases. All bleaching treatments were followed by a series of four rinsing baths, lasting two hours in length with deionized water. After rinsing, the samples were blotted with blotter paper before final drying between felts. The sixteen pieces were lined together on mulberry paper with cooked wheat starch paste, and then dry mounted to a rag board with Buffermount dry mount tissue. The lined and mounted enlargement was over-matted with a mat that also covered the entire section of the control. It was framed behind UV filtering OP3 Plexiglas. The framed photograph was hung on a wall near a south-facing window to assimilate display conditions in a private home. Visible and UV light and weather condition readings were gathered on the enlargement (weekly for 3 times per day) by H-E technicians throughout the 2012 and 2013 seasons.

1 Control. Nothing done except mounting
2 Sequence (Light w/ H_2O_2 and $NaBH_4$)
3 Sequence (Light w/ H_2O_2 and Iron Out)
4 Light w/H_2O_2
5 $NaBH_4$
6 Sequence ($NaBH_4$ and Light w/ H_2O_2)
7 Sequence ($NaBH_4$ and Light and $NaBH_4$)
8 Sequence ($NaBH_4$ and Light)
9 Sequence (Iron Out and Light)
10 Sequence (Iron Out and Light w/ H_2O_2)
11 Iron Out
12 Washed and mount removed only
13 Light
14 Sequence (Light and Iron Out)
15 Sequence (Light and $NaBH_4$)
16 Sequence (Light and $NaBH_4$ and Light)

Fig. 2. Test sample was cut into sixteen sections, and each section was subjected to a bleaching treatment described above.

Color monitoring

Color reversion was monitored by spectrometry. Spectrophotometric readings were taken to monitor change in sheet tone over time and CIEDE2000 (ΔE_{00}) was calculated to quantify the change. Just Noticeable Difference (JND) for ΔE_{00} is 1.5 to 1.6 (Sharma 2005). Due to limited access to the instrument, two sets of readings were taken over 2011 to 2013 and 2015 to 2016 periods, using different instruments and procedures, therefore each set of data was treated independently. For the latter period of monitoring, a margin of error was established as ΔE_{00}=+/- 0.4.

Over the course of five years on display, no significant change to sections under the window mat was observed. Color monitoring showed that during the years 2011 to 2013 period, all sections exposed to light showed slight brightening. During 2015 to 2016 time period, all sections but one (#6 $NaBH_4$ & Light w/H_2O_2) showed additional brightening. The degree of brightening was imperceptible to the human eye, falling well below ΔE_{00}=1.0; however consistent among majority of the samples.

There were a couple of samples that were over ΔE_{00}=1.0 and possibly noticeable to the naked eye. One of the samples, that received sequence of sodium borohydride, then light bleaching with hydrogen peroxide was at ΔE_{00}=1.59. The L* value of this sample changed from 71.18 to 69.97, indicating darkening. At this time additional testing is needed to determine if this is a strange outlier or the first signs of color reversion.

The piece that received a sequence of light bleaching, $NaBH_4$, then light bleaching had a ΔE_{00} of 1.3. The change in this sample was an increase in L* value, from 67.4 to 69, indicating minute brightening. This was not quite at JND, but if +/- 0.4 margin of error is factored in, it might be reaching the point it could be perceived by the eye.

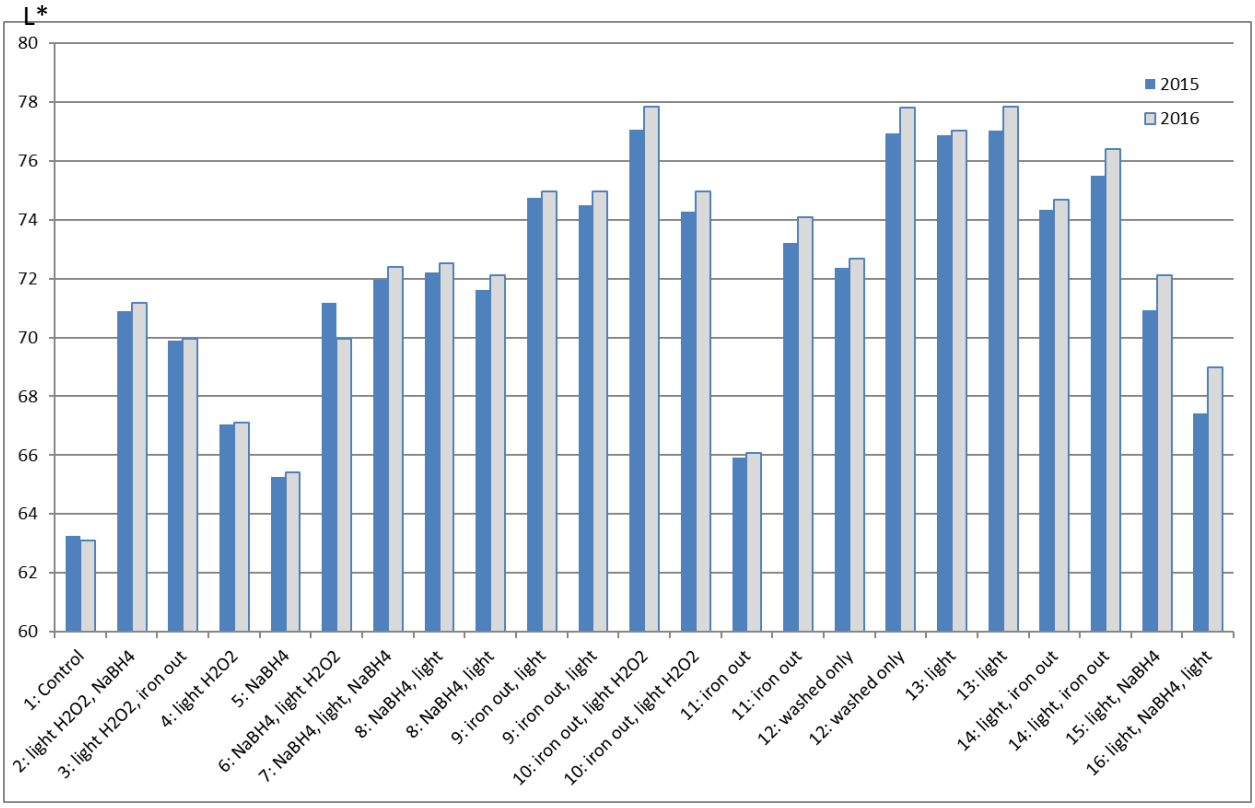

Fig. 3. L* values in 2015 and 2016

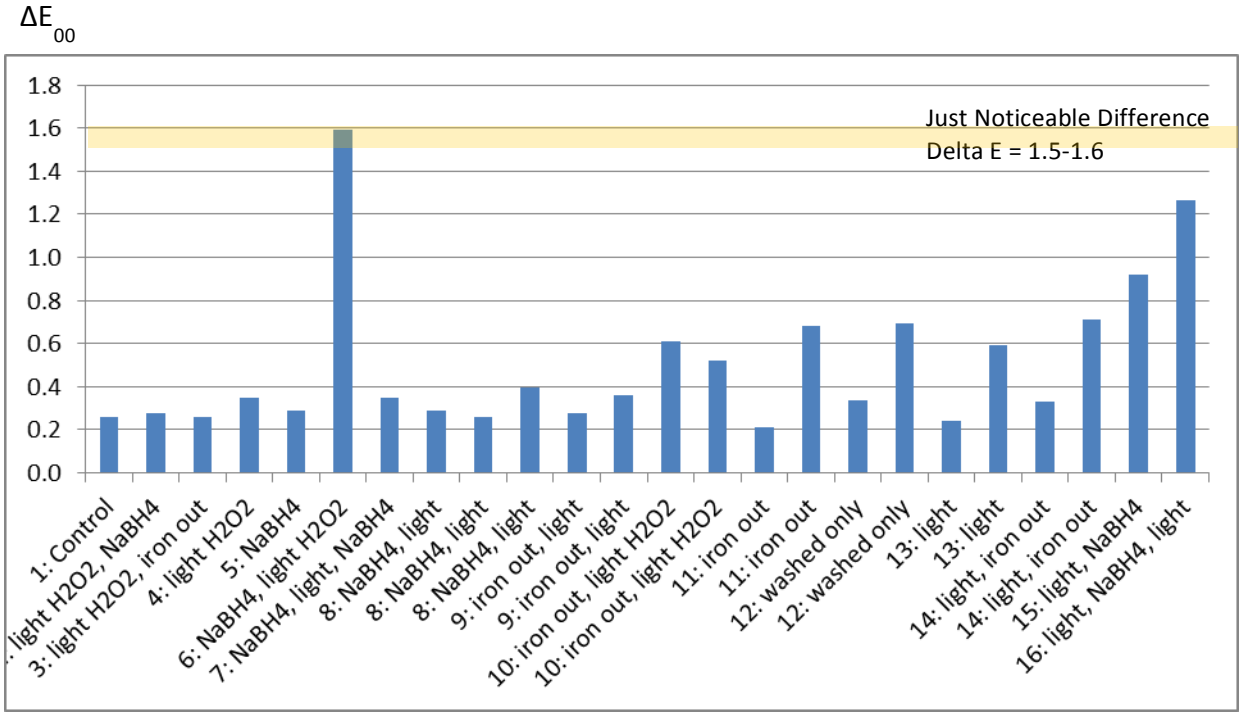

Fig.4. ΔE_{00} of spectrophotometric measurements over 2015-2016

Preliminary Results and Observations

All bleaching treatments resulted in improvement of paper tone, but by varying degrees. In general, sections that received sequenced bleaching brightened more than a single-step bleaching procedure (#5, #11, #12, and #13). Hydrogen peroxide seemed to accelerate bleaching in most of the procedures whenever it was used. Sample pairs #4 (Light w/ H_2O_2) and #13 (Light), #6 ($NaBH_4$ and Light w/ H_2O_2) and #8 ($NaBH_4$ and Light), and #2 (Light w/ H_2O_2 and $NaBH_4$) and #15 (Light and $NaBH_4$) are such examples.

At the time of this reporting, most of the samples are in a brightening stage of the cycle after being exposed to fairly high level of ambient light while on display. This is to be expected with paper of higher quality. The sugar component or Hemi-cellulose is also continuing to brighten under the current display conditions in most cases. We aren't seeing the effects of any color reversion yet– unless the one outlier is the beginning of change. Readings with a pH pen showed that all samples are running acidic, at a pH 6.8 or lower, but no change toward color reversion is trending.

Although testing focused on the paper, no visible or significant changes to the image material were noted in any samples. Sodium borohydride is known to reduce silver in some types of photographs, but no change was noted after bleaching. The silver is not reactive to the concentrations used in treatment and/ or some enlargements may prove to be platinum based image particles.

The crayon enlargement has been off view for a year. Another round of readings will be taken in the near future to determine if a "sleep cycle" has changed anything. Subsequent papers or presentations will cover anything interesting or noteworthy.

Future Work

Color monitoring of the samples is ongoing. The sample has been kept in dark storage after color measurements were taken in 2016. An additional round of testing will determine if there was any color reversion without light. It will be interesting to see if a sleep cycle after excessive display effects results.

H-E hopes to study rinsing procedures in more detail. It might prove valuable to know how much rinsing is needed to effectively remove acidic degradation products and also bleaching chemicals from the paper. There is much to study with crayon enlargements in the future and the authors welcome all to study them. Any curious conservation scientists can contact the authors with questions or further directions of study.

Conclusions

This experiment proved the immediate benefit of extensive treatment on crayon enlargement photographs. They tolerate and respond well to extended washing and bleaching treatments and come out with much improved sheet tone without any sign of loss in image density. Sequencing of oxidative and reductive bleaches generally resulted more satisfactory results than single-step procedure. While on display, the areas exposed to light, beyond the window mat, have continued to brighten. Various questions surrounding treatment of severely discolored crayon enlargements are still unanswered; however, a viable monitoring protocol has been established

during this study, and it is hoped that continued monitoring will provide meaningful data to address some of the questions.

Materials

Super Iron Out: Proprietary chemical made of sodium hydrosulfite and sodium bisulfite
Iron Out, Inc.
2417 Spy Run Ave.
Fort Wayne, Ind. 46805

Hydrogen peroxide: Certified 30%. Stabilized with Sodium Stannate. 500 mL bottle. # h323-500. Formula weight: 34.01

Sodium borohydride: Acros Organics 98% (12-13mm) pellets, 7/16" MW=37.83

Paraloid/ Acryloid B-72: Lot # 038710

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