
The Use of Chelating Agents in Paper Conservation

A Workshop Review

Introduction

The workshop “The Use of Chelating Agents in Paper Conservation” took place at Stanford University, March 27-29, 2018, which the author attended thanks to the generous support of the FAIC/NEH individual professional development scholarship grant and the Colonial Williamsburg Foundation. The group of attendees was composed of 22 paper conservators, mostly mid-career, with a variety of experience regarding chelating agents.

Antoinette Dwan and Chris Stavroudis were the instructors of this program. Dwan is a senior conservator of works of art on paper, who graduated from the University of Delaware and has been working in private practice for more than 25 years in Sebastopol, CA. Chris Stavroudis is a paintings conservator in private practice based in Los Angeles, CA. He also graduated from the University of Delaware, and since 2002 Stavroudis has been developing the Modular Cleaning Program (MCP).

This article is intended to provide a review of the workshop and to give some research perspectives on the subject. Prior to the start of the program, spectrophotometry and XRF were performed on samples to be used during the workshop, in order to evaluate any correlation between the amount of metal ions removed and visual changes. While results presented here cannot provide definitive conclusions, the hope is to contribute to a broader discussion about chelating agents and their use during the treatment of paper objects.

The Theoretical Approach of the Use of Chelating Agents in Paper Conservation

Chelating agents – “chela” coming from Greek meaning “claw of the lobster” - are chemical compounds that sequester metal ions (Burgess 1991, 36). These compounds, also called ligands or complexing agents, contain two or more electron donor atoms that can form coordinate bonds to a metal atom. Each successive donor atom that binds creates a ring around the metal atom, resulting in the formation of a chelation complex (Howard and Wilson 1992).

Although they still are not widely used in paper conservation, chelating agents have been integrated in conservation treatments for paintings, objects, and textile since the 1980s (Dupré 2010). Dwan has been using them in her private practice for the past fifteen years, and chelating agents play an important part in the MCP developed by Stavroudis.

Their chemistry in regard to paper conservation was first stated by Burgess in the 1990s (Burgess 1991). Initially seen as a necessary first step prior to chemical bleaching - as well as removing metal ions detrimental to the long-term stability of paper - they have also been shown to be an aid to the removal of discoloration and stains during aqueous treatment.

The complexity of these chemicals, combined with the inherent fragility of paper, may partially explain why they still are not commonly used in paper labs. This highlights the importance of workshops taught by Dwan and Stavroudis, specifically developed for experienced paper conservators. The lecture part of the workshop was divided between the two instructors. Stavroudis' presentations were dedicated to the chemistry of chelating agents, whereas Dwan presented the applications for paper conservation.

Because chelating agents act as multifunctional weak acids when dissolved in water, the acid-base theories were presented by Stavroudis. These included explanations of strong acids/bases versus weak acids/bases, and the pH concept. Ionic strength, as well as conductivity were discussed. Following this introduction to aqueous chemistry, Stavroudis detailed the theory of chelating agents and focused specifically on citrates, EDTA (ethylenediaminetetraacetic acid), and DTPA (diethylenetriaminepentaacetic acid).

Chelating agents are effective only in an aqueous environment, with water as the exchange medium. The metal ion must dissolve into water for the chelating agent to bind it in its cage, promoting the dissolution of more metal ions. The appropriate use of chelating agents is dependent upon several parameters such as the pH of the solution, the formation constant (pK_f), and the solubility product of a metal salt in water (pK_{sp}).

Chelating agents are most effective when they are completely ionized, which occurs under alkaline conditions. Because they are weak acids, each ionization stage has a specific pK_a (dissociation constant). The degree of ionization also has an influence on the form of the chelate complex (Timar-Balazsi and Eastop 1998).

The formation constant (pK_f) is the equilibrium constant for the formation of the chelate complex, with the metal ion and the ligand in its fully dissociated form. The pH also has an influence on the formation constant, since hydroxide ions can interact with the metal ion and affect its ability to form a complex. For example, iron will form iron hydroxide, which is very insoluble and does not complex easily, under alkaline conditions (Burgess 1991).

How a particular metal ion dissolves in water is defined by the dissociation constant of its metal salt (pK_{sp}). Therefore, the pK_f of a given metal ion for a chelator must be larger than the pK_{sp} of the concomitant metal salt for the chelation to take place.

Citric acid, considered a mild chelating agent, can be prepared with either ammonium hydroxide or sodium hydroxide to add the counter ion. If ammonium citrate has been predominantly used in the past, both Wolbers and Stavroudis have been advocating for a switch to sodium citrate. In case there are residues of ammonium citrate left

in the paper, the ammonium counter ion will eventually evaporate, leaving citric acid behind that could potentially be harmful to cellulose.

EDTA was first recommended as an aid to remove transition metals from paper before bleaching with sodium borohydride (Burgess 1991; Lehtaru and Ilomets 1997). DTPA, which can be described as an enhanced version of EDTA, has been progressively replacing the latter. DTPA has higher formation constants for all metal ions than those of EDTA and is viewed as more effective.

Sodium citrate, EDTA, and DTPA are prepared by progressively adding 10% sodium hydroxide to the solution until reaching the desired pH. All of these chelating agents were used at 0.05M to 0.1M concentrations. Most conservators are still preparing their solutions in weight per volume, which is not advisable if one wants to evaluate the efficacy of each chemical and compare them. For example, a 0.05M solution of citrate is 0.96%; of EDTA is 1.46%; and of DTPA is 1.97% (w/v).

Stavroudis gave examples of chelation scenarios relating to paper. One of the drawbacks of using chelating agents on paper is that calcium ions will be chelated and removed from the substrate. According to Dwan and Stavroudis, the theory behind using chelating agents as an aid to remove discoloration/stains is that the removal of calcium opens up degradation clusters. Indeed, soil particles tend to stick to calcium ions.

Cellulosic fibers and soil particles are usually negatively charged when they are immersed in water. Calcium ions, that are positively charged, create a linking bridge between the two negatively charged items, making soil more difficult to remove (Daniels 2011, 293). This notion is well-known by textile conservators and is the principal reason why chelating agents are often found in laundry detergent.

However, Stavroudis presented an option to preserve the calcium ions in paper, by adding an equal molar concentration of calcium hydroxide to the DTPA solution. This solution would be able to target more specifically iron II ions, without stripping calcium ions out of the paper.

Introduced as an “improved Seth Irwin’s method” (Irwin 2011), Stavroudis also presented a solution containing DTPA, calcium hydroxide, and a reducing agent, such as sodium metabisulfate. He described briefly some of the reducing agents used in paper conservation, such as sodium borohydride, sodium dithionite, and sodium metabisulfite.

These can be used in conjugation with chelating agents, in order to transform very slightly soluble iron III into more soluble iron II. Then iron II can be chelated, which is not the case with iron III. However, reducing agents have a bleaching effect and the concentration and type of reducing agent should be considered.

Integrating Chelating Agents in Treatment Protocols

Dwan’s presentation focused on her extensive experience using chelating agents. Several parameters should be considered in designing a successful treatment with chelating agents.

First, if possible, the artwork should be bathed to remove as much of the discoloration products as possible. Then, media should be tested with the chelating solution. Dwan insists on the need to repeat testing each time the concentration of the chelating agent solution is increased or the pH changed (Dwan 2015, 11).

The artwork can be immersed, floated, or treated locally for stain reduction with the appropriate solution. For objects that tolerate only minimal amounts of water, the solution can also be applied locally with swabs or cotton balls. However, this surface cleaning method is recommended only for hard sized papers, as cotton can be abrasive.

When possible, Dwan uses float washing, particularly for sensitive media, and has been having great success with this method. Chelating agents can be successful in removing pronounced mat burns without using any bleach. Dwan also uses chelating agents in combination with reducing agents with a personal preference for sodium borohydride. Another technique involves spraying the reducing agent with an airbrush in order to obtain a very soft transition, particularly for mat burn reduction.

Chelating agents can be used alternately with reducing agents with a rinsing step in between. Indeed, a critical step in treatment with chelating agents is the rinsing. The artwork must be rinsed after every application of chelating agents and reducing agents. This step is critical in order to leave as few chelating agent residues as possible in the substrate, as well as to remove additional discoloration. Dwan has been using calcium hydroxide at pH 8.5 as a final rinsing solution in order to reintroduce calcium in the paper after treatment.

The practice session was organized around a series of exercises. Each workshop participant brought their own samples. The exercises included a comparison of chelating agents at similar concentrations, comparison of one chelator at different pH levels, a comparison of various reducing agents, and finally variation in combinations of reducing agents and chelating agents. The practical session included a demonstration of how to use pH meters and how to prepare each solution.

Further Research and Development

In preparation for the workshop, spectrophotometry measurements and XRF were performed on samples of papers. These were selected from a cache of expendable papers available in the Colonial Williamsburg Foundation’s paper lab.

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Spectrophotometry measurements were performed with a spectrophotometer Konica Minolta CM-2600d (using D65 illuminant, 10° observer, and CIELAB 1976 color space) before and after the workshop. XRF was performed by Kirsten Moffitt, materials analyst at the Colonial Williamsburg Foundation with a Bruker Tracer III-V+ portable XRF device with a rhodium (Rh) target and a silicon PIN (Si-PIN) Diode detector. Parameters both before and after treatment were 15kV, 28uA, vacuum, no filter, 120 second duration. Measurements were acquired on blank areas of the papers.

All samples were washed, prior to treatment with chelating agents, with ammonium hydroxide (pH 8). They were rinsed, after treatment with chelating agents, with a calcium hydroxide solution (pH 8.5). This project is by no means a rigorous research and only intends to provide a few

comments and avenues for further investigation. There are many parameters at play, such as the time constraint of the workshop, and this should be considered while reading our observations.

Not all papers could be treated with all chelating agent solutions provided. If time allowed, it would have been interesting to compare the four papers with equivalent solutions.

XRF results (Fig. 1) appear different for each paper. However, the results for the metal ions removed from a particular paper were consistent for all treatments. For instance, paper #2 shows a decrease in calcium following all treatments and paper #3 shows a decrease in calcium, iron, and silicon. Paper #4 shows mostly a decrease in calcium and iron.

Fig. 1. XRF results for four different papers. The Xs indicate that the paper did not receive a particular treatment and that no analysis was performed. XRF results are qualitative and not quantitative. Quantitative XRF demands elaborate and time consuming calibration that was beyond the scope of this project (Barrett et al. 2012).

XRF results (comparison before and after treatment)				
Type of treatment	Paper #1	Paper #2	Paper #3	Paper #4
0.5M sodium citrate (pH 6.5), 1 bath 15-20min	No significant change	Decrease in Ca	X	X
0.1M sodium citrate (pH 6.5), 1 bath 15-20min	No significant change	Decrease in Ca	X	Decrease in Fe, small decrease in Ca
0.05M DTPA (pH 6.5), 1 bath 15-20min	No significant change	X	X	X
0.1M DTPA (pH 6.5), 1 bath 15-20min	No significant change	Decrease in Ca	X	Decrease in Fe
0.1M DTPA (pH 8.5), 1 bath 15-20min	No significant change	X	Decrease in Si, Ca, and Fe	X
0.1M DTPA (pH6.5), 2 baths 20min each	No significant change	X	X	X
0.1M DTPA buffered with citrate (pH 6.5), 1 bath 15-20min	X	X	Decrease in Fe, Ca, and Si	Decrease in Ca, Fe
0.1M DTPA and calcium hydroxide buffered with citrate (pH6.5), 2 baths 20min each	No significant change	Decrease in Ca	X	X
0.1M DTPA and calcium hydroxide buffered with citrate and 2% sodium metabisulfite (pH6.5), 2 baths 20min each	No significant change	X	Decrease in Ca, small decrease in Si and Fe	X

Paper 1: machine-made blue laid paper, early 20th century. Blank areas contain Al, Si, Ca, Cr, Mn, and Fe.

Paper 2: machine-made thick wove paper, early 20th century. Blank areas contain Ca, Al, Si, Fe, and Ba/Ti.

Paper 3: machine-made thick wove paper, early 20th century. Contains small amounts of Al, Ca, Fe, Zn, and Si.

Paper 4: machine-made moderately thick wove paper, early 20th century. Small amounts of Al, Ca, Ba/Ti, and Fe detected.

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Interestingly, calcium appears to be the most frequent ion removed, and this does not seem to be affected by the type of solution used. This may indicate that the rinsing step with calcium hydroxide did not compensate for the calcium removed by the treatment.

Paper #1 presents no significant change detected in metal content, for all treatments.

Spectrophotometry results (Fig. 2) were utilized only for paper #1 since this set of samples was the one consistently treated with most of the solutions. On this set of samples, there is no visual difference between the use of sodium citrate and DTPA at 0.05M. These delta E* also reflect that the difference before and after treatment cannot be detected visually, since the human eye starts perceiving a difference in color around a Delta E* of 2 (Macadam 1942).

When the sodium citrate concentration was doubled (0.1M), the cleaning efficiency was doubled as well and a visual difference can be observed.

However, this wasn't the case for DTPA, with a Delta E* of similar values at concentrations 0.05M and 0.1M. An increase in pH for the DTPA solution also did not increase the Delta E* for paper #1. But a second bath with DTPA

improved the cleaning efficiency considerably, when compared to a single bath with DTPA.

Two washing steps with a solution containing DTPA, calcium hydroxide, and citrate had a similar visual effect.

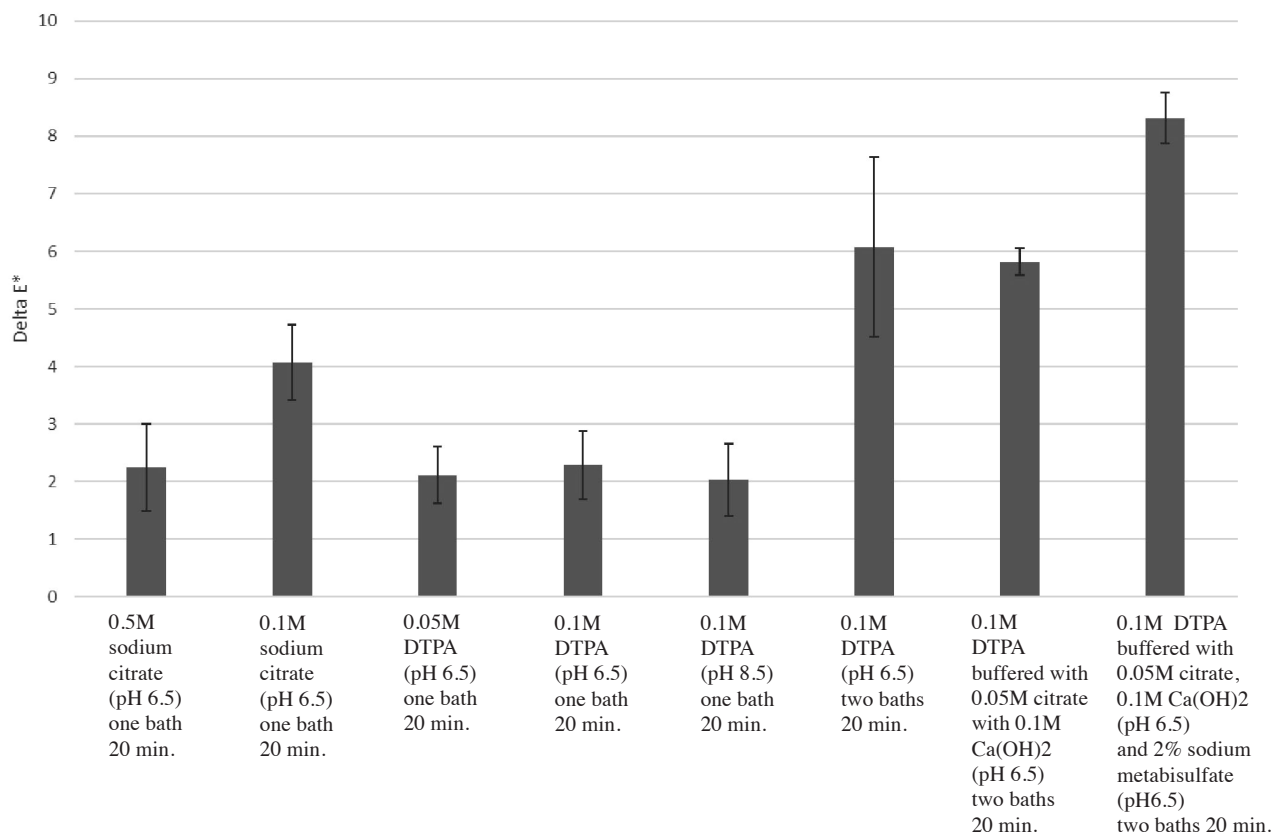
Finally, the solution containing DTPA, calcium hydroxide, citrate, and 2% metabisulfite caused the biggest difference before/after treatment. This is not surprising since sodium metabisulfite also acts as a mild bleaching agent.

When compared with the XRF results (fig. 1), the lack of change in metal content after treatment, throughout all types of treatment, seems surprising. One may intuitively correlate a greater removal of metal ions with greater removal of discoloration.

The amount of metal ions removed may not be significant enough to be detected by the instrument, but still translated in very different visual impacts. This shows the discrepancy that conservators often observe between theory and practice.

DTPA, considered a stronger chelating agent, can sometimes be less successful at removing discoloration than sodium citrate, considered a weaker chelating agent. This underlines the importance of testing solutions before treatment.

Fig. 2. Comparison of Delta E* values (CIELAB 1976, D65 illuminant, 10° observer) for paper #1, after treatment with various chelating agent solutions. Three measurements per sample were performed, with a spectrophotometer Konica Minolta CM-2600d.



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Further research is needed to understand the specific mechanisms behind the removal of discoloration with chelating agents. Future investigations should also include an evaluation of the rinsing step efficacy to determine how much rinsing is necessary.

Consequently, there is a need to evaluate how much calcium and magnesium need to be reintroduced into paper after treatment with chelating agents. At the end of her presentation, Dwan suggested that further investigation should be performed on metallic components in paper as well as their origins. Dwan further advised that additional experimentation should be done with sodium metabisulfite, a relatively new reducing agent.

Conclusion

Despite the fact that chelating agents have been used on paper for the past 20 years, some research is still needed to understand the long-term consequences of their use as well as the mechanisms behind their efficacy. Conservation literature provides some studies in which aging tests were performed on samples treated with ammonium citrate tribasic (Hashimoto 2015) and EDTA (Lehtaru and Ilomets 1997). Used appropriately, both appear to be safe for paper. DTPA and EDTA have been used increasingly by the paper industry since the 1990s to prevent the transition metal ions such as manganese, iron, and copper from catalyzing the decomposition of peroxide during the bleaching of chemical and mechanical pulps (Virtapohja 1996).

Dwan and Stavroudis' workshop is key to gaining a better understanding of the use of chelating agents in paper conservation and how to safely integrate them in a treatment protocol. Using chelating agents can present a steep learning curve, and each workshop participant will have to do the individual work of experimenting further.

These chemicals, when properly used, can provide some incredible results and are a wonderful addition to the tool set of a paper conservator. While these solutions can sometimes be challenging to prepare, it is worth spending the time to understand the chemistry behind them. When other methods fail, they may provide an efficient tool and a great alternative to bleaching.

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