Ammonium Citrates for Stain Removal in Paper

Staining in paper is varied and complicated. It can be local or overall, can be caused by degradation of cellulose, or be initiated by pollution, grime, or paper additives. Because of this complexity, conservators need numerous materials and procedures which can be used as far as possible to selectively treat stains without causing further complications.

There are many concerns to be taken into consideration. For instance, using oxidation (hydrogen peroxide or light) or reduction (sodium borohydride) agents might not remove the stain and might also contribute to degradation reactions, or an alkaline bath combined with light exposure might catalyze irreversible reactions of photo sensitive optical brighteners.

Another variable is metals in paper, either as contaminants brought in environmentally or intentionally included in the paper pulp.[1] Metals can be problematic if initially processed with light, hydrogen peroxide, or sodium borohydride treatments. Or having a high alkaline pH or oxidative process in the initial wash might change soluble metal contaminants into insoluble metal oxides. In some cases, recurrance of staining may be observed.

Portion of a light-bleached drawing 10 years after treatment.

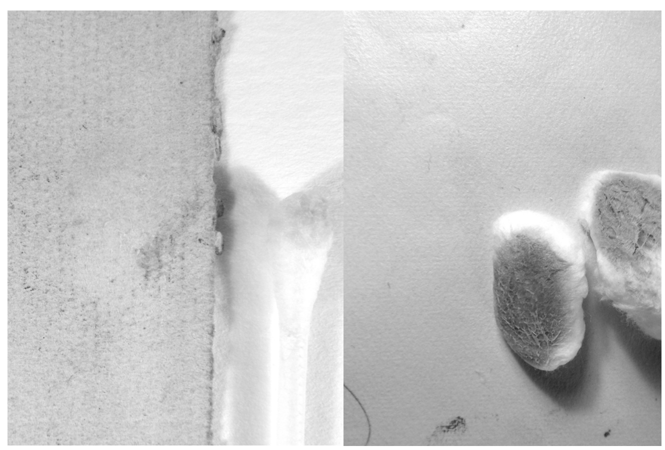
A different approach for addressing metal-related stains in paper is to consider ammonium citrate in dibasic or tribasic form. Ammonium dibasic and tribasic are mild chelating agents. They can capture and sequester staining material and create a favorable environment for stabilizing artifacts. Their use provides a logical starting point in the sequence of stain-diminishing options.

Ammonium citrate has been used in object, textile, and painting conservation specialties for over twenty-five years, and its properties are well known to the profession. The following introductory articles will familiarize paper conservators with the basic concepts. Leslie Carlyle's et al. 1990 article describes how the ammonium citrate tribasic at low pH and low concentrations compares to other surface cleaning systems for paintings. [2] Rachel Morrison's et al. article of 2008 shows that any potential residue is easily removed with a damp swab. [3] The textile article by Timar-Balazsy and Eastop describes in more detail the possible mechanisms and interactions with stains or grime. [4]

With some accommodations, this useful reagent can be adapted to the requirements of paper artifacts and their media. In general, this means using either the ammonium citrate dibasic or tribasic at a pH in the neutral range and at a 1% concentration. The solution is prepared in demineralized water. The pH is adjusted with drops of ammonium hydroxide.

Ammonium citrate dibasic is more readily available through conservation suppliers and is economical for bathing. The ammonium citrate tribasic can be obtained through chemical suppliers, but in smaller and pricier quantities. The ammonium citrate dibasic as prepared has a pH of 6.0 and for paper artifacts should be adjusted into the neutral range for most uses. Ammonium citrate tribasic as prepared has a pH of 7.0 and can be adjusted as determined best for specific stains. You can also make your own citrate solutions, either ammonium or sodium citrates, as described by Chris Stavroudis.[5]

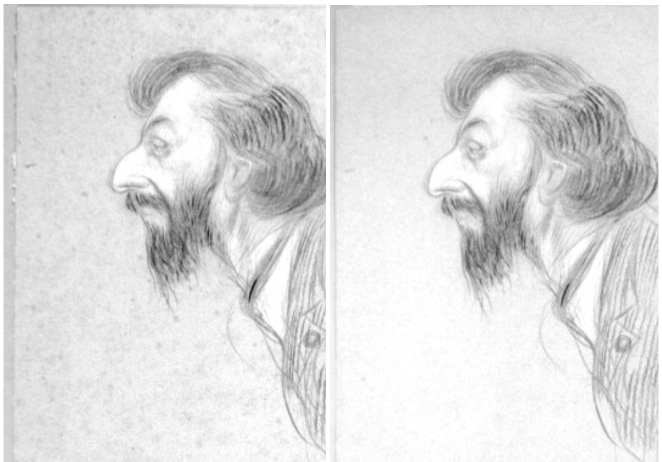
Ammonium citrate can be substituted for more traditional dry-cleaning techniques. On sized papers, it can be applied on a swab to lift grime, followed with a damp swab as a rinse. Whenever rinsing, adding some calcium to the rinse solution is a good practice. For large areas, such as the reverse of an oversize artifact, it can be applied with cotton balls followed by rinsing. This is a very effective and non-abrasive method. On non-sized papers, overall immersion is a better option for grime removal.



One of the outstanding advantages of using ammonium citrate dibasic or tribasic is the ability to remove stains without lightening paper support color which typically happens with bleaches. This is especially important on toned papers where the media and the paper color were closely designed by the artist.

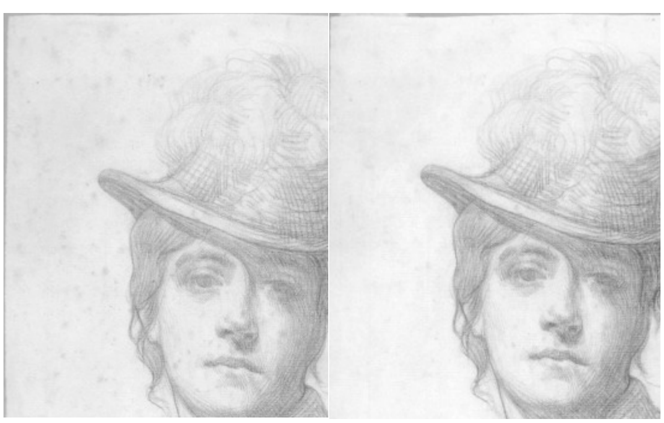
Overall foxing stains have been successfully eliminated from a drawing on pink paper, and mat burns have been removed from brown papers without altering the support paper color. Often, all staining can be removed without any additional bleaching agents. Because the ammonium citrate solutions are used at a neutral pH and low concentrations, generally media is not adversely affected.

by Antoinette Dwan



Michel Manzi, overall foxing on pink paper. Float washed, followed by float application of ammonium citrate 1 and 2 % at pH 7.0 with rinsing and drying between applications. Before and after photographs. (Unfortunately, the image is not able to show the distinct pink color of the paper. Editor.)

Manet, overall foxing on brown paper. Bathing and drying followed by 1, 2% ammonium citrate bathing at pH 7.0 with rinsing and drying between applications. Before and after photographs.

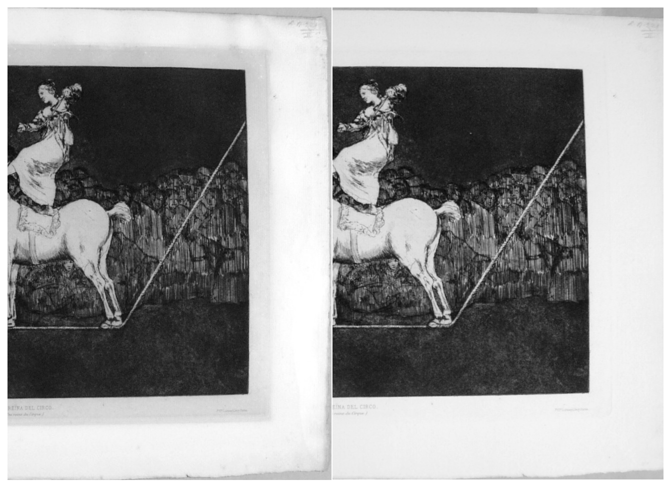


Anonymous red chalk drawing, overall foxing. Float bathing and drying followed by 1,3% ammonium citrate baths at pH 7-8 with rinsing and drying between applications. Before and after photographs.

Always test on media for stability. Always test media when changing concentration. Stability at 1% does not mean stability in 2%.

If the media is stable, bathing follows typical paper conservation practices. First bathe the artifact (float, suction, blotter, etc.) in water baths to remove any water-soluble degradation products. Dry the artifact and prepare the ammonium citrate solution. If the ammonium citrate is going to effectively remove stains, it will be obvious as the solution pulls out degraded material, similar to regular water bathing. Change the exhausted solution for a fresh 1% solution, and continue the exchange until no more color is observed in the solution. Follow by rinsing with some calcium added to the rinse water, and dry the artifact for observation.

At this point, if stains persist, a 2% concentration of ammonium citrate can be tested and the sequence repeated. Again, it will be obvious if staining is being pulled into the solution or not.



Goya, overall discoloration, foxing, mat burn. Bathing and drying followed by 1,2,3% ammonium citrate baths at pH 7-8 with rinsing and drying between applications. Before and after photographs.

Curtis, severe foxing overall. Bathing and drying followed by 1,3, 5% ammonium citrate baths at pH 7-8 with rinsing and drying between applications. Before and after photographs.

Ammonium Citrates for Stain Removal in Paper, continued

Alternatively, ammonium citrate can be considered a pre-treatment step for other stain removal processes. After an initial treatment with ammonium citrate, often only a dilute (0.01 – 0.1) sodium borohydride treatment is needed to completely remove residual staining. Remember that a condition for most bleaching options is to remove metal impurities prior to either oxidative or reducing bleaches, and the ammonium citrate fulfills this requirement. In some instances the reducing agent, sodium borohydride, can change Fe^{3+} to Fe^{2+} so that it is more soluble. The washing process may require a back and forth sequence between citrate and sodium borohydride. However, for iron or copper particles or metal oxides, a chelating agent such as DPTA or EDTA may be necessary. [6]

Gericault, overall discoloration, foxing, mat burn. Float wash and drying followed by float application of 1 (2x), 2 (2x), 4 (2x)% ammonium citrate baths at pH 7 with rinsing and drying between applications. Followed by .01% sodium borohydride applied by spray on verso. Before and after photographs.

Ammonium citrate also works very well when used locally. Often mat burns can be removed with local application, followed by rinsing. In general, keeping the solution at a neutral pH and varying concentration works well. However, for some stains it works best to stabilize the concentration and work up and down pH range. Another successful local application method is to use sodium citrate prepared in a 5% agarose gel and placed along a mat burn or other stain, followed by rinsing. The sodium doesn't evaporate like the ammonium citrate so the pH is stable when making gels.

The effectiveness of ammonium citrate solutions seems to implicate some metallic contribution to many stains in paper. It also suggests that metallic particles can be more soluble at lower pH concentrations, and that using high alkaline solutions on paper artifacts can form insoluble metal oxides that will continue to stain and degrade the artifact. When viewing artifacts in ultra violet light before and after treatment there is often no change noted, even though the stain has disappeared from the visible range. Our profession would benefit from scientific research into this area.

After some practice and experimentation on expendable items, ammonium citrate may become a useful tool to add to your repertoire in treating paper artifacts. It may also change your standard of practice and view on the mechanisms of staining in paper.

This material was first presented in February 2013 as a workshop at the National Gallery Paper Conservation Department and at the Winterthur Paper Conservation lab and as a talk at the annual WAAC meeting, September 2013. The author wishes to thank Dr. Galen George, Head of Chemistry Department, Santa Rosa Junior College for his contributions.

Notes

1. Sarah Bertalan. 2015. Foxing and reverse foxing: condition problems in modern papers and the role of inorganic additives, Miami AIC presentation.

2. Leslie Carlyle, Joyce Townsend and Stephen Hackney. 1990. Triammonium Citrate: An investigation into its application for surface cleaning. In *Dirt and Pictures Separated*. United Kingdom Institute for Conservation of Historic and Artistic Works, 44 - 48.

3. Rachel Morrison, Abigail Bagley-Young, Aviva Burnstock, Klaas Jan van den Berg, and Henk Van Keulen. 2008. An investigation of parameters for the use of citrate solutions for surface cleaning unvarnished paintings. *Studies in Conservation*. 52 (4): 255-270.

4. Agnes Timar-Balazsy and Dinah Eastop. 1998. "12.2 Sequestering agents" in *Chemical Principles of Textile Conservation*. Butterworth Heinemann, 221-225.

5. Chris Stavroudis. 2015. A tale of two citrates. *WAAC Newsletter, 37(2)*.

6. Helen Burgess. 1991. The use of chelating agents in conservation treatments (CCI).