
Chelating Agents in Paper Conservation

Even in normal times, not everyone can take part in the chelating workshops that Antoinette and Chris have offered. So, in the interest of sharing with a much larger group, we're presenting the core material here in the *Newsletter*.

To supplement this article with many recipes and protocols, a power point presentation, "The Use of Chelating Agents in Paper Conservation," is available on the WAAC website at www.waac-us.org/chelatingagents, password: WAAC-Dwan. A short video is also available at www.waac-us.org/citratelutions.

In the simplest model to describe aging in paper, light and oxygen cause the oxidation of the cellulose. The paper discolors because the oxidized molecules absorb blue light causing the paper to reflect everything but the blue light, thus becoming yellow. This discoloration is something that a paper conservator may want to minimize with treatment.

The gentlest treatment, but not without consequences, is to wash the paper. Water can solubilize some of the degraded/oxidized components of aged paper. When immersed, a lot of discoloration products can be seen diffusing into the wash water. It is also possible to modify the wash water by altering its pH and conductivity to control and enhance the process.

If the decrease in discoloration is deemed insufficient, the more aggressive treatment previously has been to bleach the paper. There are two broad classes of bleach: oxidative bleaches and reducing bleaches. Oxidative bleach further oxidizes degradation products that were not water soluble, rendering them water soluble so they can be washed away. Reducing bleaches can be thought of as repairing the damage done by natural oxidation. They reduce the structure that absorbs blue light eliminating the discoloration.

However, there is a treatment between the extremes of simply washing and that of bleaching. That is the subject of this article.

Chelation

As has been found in paintings conservation, we can posit that calcium and magnesium ions (and possibly others) form a bridge between oxidized sites on the cellulose fibers and oxidized degradation products. These ions "cement" the otherwise soluble oxidized and discolored degradation products onto the mechanically sound cellulose. Without these ions the degradation products would wash away, but now they are essentially glued in place. It is reasonable to assume that, in addition to degraded cellulose species, general impurities and absorbed grime are likewise adhered onto the cellulose fibers

Enter chelating agents. Chelation comes from the Greek word *χηλή*, *chēlē*, meaning claw as in "to grab." A chelating agent or polydentate ligand is a water-soluble substance whose molecules can form multiple coordination bonds to a single metal ion.

Or to describe it graphically, these are molecules that possess a three-dimensional structure that forms a water-soluble cage. The acid and other functional groups on the chelator molecules will abstract and hold ions in the cage structure.

The ions that cement the degraded, discolored, and otherwise insoluble components onto the paper fibers are pulled into and held in the cage-like structure of the chelating agent freeing the degraded material to be washed away.

There is, of course, more to the chemistry and physics than this, but it does serve as a model of how a chelating agent can aid in the washing of discolored paper.

The efficacy of using a chelating agent can easily be observed by first washing a degraded paper until no more degradation products are washed out. If the paper is then immersed into a chelating solution, often more discoloration will be released from the paper into the bath. No bleaching was used so there was no alteration of the paper's chemistry. The "cemented" discolored material was released and allowed to wash away.

Another useful function of chelating agents is the removal of metal ions. Metal ions (iron, copper, lead, tin, aluminum) can cause active catalytic degradation of the paper structure. This is often the cause of foxing. These metal ions can be removed by treatment with chelating agents, often locally applied or overall. Rust stains can also be ameliorated by treatment with a chelating agent, although a reducing agent is also needed.

Citric Acid, EDTA, and DTPA

There are three commonly used chelating agents in conservation: citric acid (citrate); ethylenediaminetetraacetic acid (EDTA); and diethylenetriaminepentaacetic acid (DTPA). Citrate is the mildest, in that its formation constant for the calcium ion is 4.68 while that for EDTA is 10.61 and DTPA, 10.75.

The formation constant, a thermodynamic constant, is a measurement of how strongly a given ion will be held in the chelator's cage. The higher the formation constant, the more strongly that ion will be held by the chelator. We can compare the formation constant of an ion in a given chelator with the solubility parameter of the slightly-soluble salt source of the metal ion. If the formation constant is roughly equal to or greater than the solubility product, the ion will be taken up by the chelating agent. If the solubility parameter is greater than the formation constant, the ion will not dissolve sufficiently to be accessible to the chelator.

All three chelating agents start as free acids; that is, their carboxylic acid groups (three for citrate, four for EDTA, and five for DTPA) are protonated – the acid groups are in their less-soluble, acid form. Citric acid is freely soluble in water, but the free acid forms of EDTA and DTPA are a little harder to dissolve.

As the acid groups are reacted with a base, the carboxylic acid groups are transformed into charged carboxylate groups. The charge renders the chelator molecule more water-soluble. The nature of the counter ion, the base, added is not particularly significant although sodium and ammonium ions are most common – meaning that sodium hydroxide or ammonium hydroxide was added to the acid

form of the chelator molecule to make the solution. In practice, citrate solutions can be either ammonium-citrates or sodium-citrates and can be used interchangeably. Prepared ammonium citrate dibasic or tribasic (also called diammonium or triammonium citrate) are citric acid with either two (di) or three (tri) ammonium ions added to give a pH of 6.5 for the “di” or pH of 7.0 for the “tri”.

You can also make your own solutions beginning with citric acid and adding ammonia or sodium hydroxide to the desired pH using a pH meter. Ready-made products from conservation or chemical suppliers are convenient, but it is cheaper and very easy to make your own. 10% ammonium hydroxide or 10% sodium hydroxide is used to adjust pH in the citric acid.

The ammonia can evaporate from ammonium citrate solutions, so it is important to use freshly made solutions (they are stable for weeks but not months). They are also not a good choice for gels for the same reason: the ammonia evaporates. In comparison tests, ammonium and sodium citrates performed identically.

Some Chemistry

Each carboxylic acid group on a chelator will have a separate acid dissociation constant, K_a . We normally use the ‘p’ notation (negative base-10 logarithm) and refer to the dissociation constants by their pKa values. Citric acid, having three acid groups, has three dissociation constants, pK_1 , pK_2 , and pK_3 ; EDTA has four; and DTPA, five. The values of the dissociation constants can be found in Table 1.

Table 1

Chelator	pK_{a_1}	pK_{a_2}	pK_{a_3}	pK_{a_4}	pK_{a_5}	pH when fully deprotonated
Citric acid	3.13	4.76	6.40			7.3
EDTA	2.00	2.67	6.16	10.26		11.2
DTPA	2.30	2.60	4.17	8.26	9.48	10.4

There is an important distinction between the formula of a powder in a reagent bottle and the behavior of that powder when it is dissolved in water. The bottle can say diammonium citrate or disodium citrate on the label, and that’s completely correct. Each molecule contains one citrate ion, one hydrogen ion, and two ammonium or sodium ions.

However, when dissolved in water, the ions separate, and there will be ammonium or sodium ions; hydrogen ions (pH); and a mixture of citric acid (which we could call trihydrogen citrate which is uncharged); dihydrogen citrate with one negative charge, hydrogen citrate with two negative charges; and citrate ion with three negative charges.

All four species are always present in solution. Some may be at vanishingly low concentrations, but there will always be some of each present. In the case of diammonium citrate or disodium citrate, calculations show that the pH of the solution should be about 5.5. This means that the concentrations will be:

Citric acid	$H_3Citrate$	0.01%
Dihydrogen citrate	$H_2Citrate^-$	4.06%
Hydrogen citrate	$HCitrate^{2-}$	69.02%
Citrate	$Citrate^{3-}$	26.92%

This tells us that at the pH of 5.5, one fourth of the citrate in solution will be in the most active chelation form, $Citrate^{3-}$, while two-thirds will be in the form that matches the name on the bottle.

Each of the forms of a chelating agent will hold ions. How well a specific form of a chelating agent can hold a particular ion is very difficult for chemists to determine. The tabulated formation constants are a measurement of how strongly an ion is held in the fully ionized (deprotonated) form of the chelator. The free acid, hydrogen, dihydrogen, etc. forms will each hold an ion with less force than the fully deprotonated chelator.

The pH of each chelating agent when fully deprotonated is listed in Table 1. At pHs below the fully deprotonated form, as the solution pH increases, a greater proportion of the chelating agent will be in the fully deprotonated form, and therefore the solution will have a stronger chelating action. This increase in effective strength of the chelator with increase in solution pH is in addition to any effects of the pH change on treatment materials.

So, we see that citric acid is at its maximum efficiency above a pH of 7.3. Using EDTA at a pH of 11 or higher will be most effective for most metal ions. In the case of DTPA, the chelator molecule is fully deprotonated at a pH of just over 10, and will be most effective for most ions.

That is unless you are trying to remove iron salts. At high pHs, iron ions form insoluble salts with the hydroxide ion. Striking a balance between the formation of iron hydroxides at high pH and having the less active forms of DTPA or EDTA in solution at lower pHs, the maximum efficacy of both DTPA and EDTA to complex iron ions is around pH 5.0.

Chelators and Alkaline Reserve

As mentioned previously, calcium, magnesium, and other ions can hold degradation products in the paper structure, but calcium carbonate and magnesium carbonate also function as alkaline reserves and historically have been considered to improve the stability of paper dramatically.

If EDTA or DTPA are used to remove the calcium and magnesium ions that are holding discoloring color bodies onto the cellulose structure, the chelators will also remove any alkaline reserve from the paper structure.

However, something interesting (and something that needs more research) happens with citrate solutions. Calcium citrate is only sparingly soluble in water. If you add citrate ions to a solution of calcium hydroxide, after a few minutes a white precipitate of tricalcium dicitrate tetrahydrate will form. The solubility of the precipitate is 0.85g/L.

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(For reference, calcium carbonate's solubility is 0.013g/L and calcium sulfate's, 0.24g/L.) One could speculate that lone calcium ions "cementing" degradation products are taken up by the citrate ion efficiently. Small deposits of calcium carbonate might form a skin of calcium citrate on the surface of the deposits that slowly is washed away in rinsing, perhaps not stripping away all the alkaline reserve.

The potential to remove calcium or magnesium, is anathema to paper conservators. However, at the end of a treatment, calcium or magnesium can easily be added back into the paper structure. Some chelating formulas are designed specifically not to remove calcium but target other degradation-causing metal ions.

A strategy that can be exploited to preserve the alkaline reserve in paper is to use the calcium salt of EDTA or DTPA. By adding the stoichiometric amount of calcium hydroxide to the EDTA or DTPA – one calcium ion per chelator molecule – the chelator will not alter the alkaline reserve. In this case, the EDTA's or DTPA's cage already is holding a calcium ion so no additional calcium ions will be extracted from the paper.

However, metal ions will be pulled into the cage, and a calcium ion will be released. This is because metal ions, Fe^{++} , Fe^{+++} , Cu^{++} , etc. have higher formation constants than the calcium ion and will be preferentially complexed, releasing the calcium ion into the surrounding solution. An example of this formulation is in the Stock Solutions (Table 3).

Anecdotally, several conservators have noted that the presence of the calcium has hindered stain removal. They were more successful when they switched to the formulation without the calcium.

Sources of Metallic Components in Paper

Sarah Bertalan wrote an excellent paper¹ describing the many instances in which inorganic and metallic components might be present in paper artifacts. These include: barium sulfate, calcium sulfate, clay, satin white (coatings), zinc sulfide, calcium carbonate, titanium dioxide, zinc oxide, diatomaceous earth, and earth pigments (iron oxides/hydroxides). Aluminum ions can come from aluminum sulfate used in alum-rosin sizes.

In addition to those mentioned in her work, it is also probable that air-borne pollutants carry metals (such as lead) in the grime deposited on the surface of artifacts. Grime can also be held near the artifact by metal-ion "cement" mentioned above. The paper industry notes that heavy metals are contained in wood pulp itself, especially iron, copper, and manganese. In paper manufacture, DTPA is used to remove metals from pulp so that hydrogen peroxide bleaches are not degraded by the metals. Coatings, fillers, sizing, and dyes, that can contain contaminants are then added back into the paper-making process.

Soyeon Choi in her 2007 publication summarizes the role of metals in foxing: "Metals found in foxing spots

include iron, tin, copper, copper-mercury, or copper-zinc (brass). Metals were typically identified using scanning electron microscopy and energy dispersive x-ray or x-ray fluorescence. It is interesting to note that copper contamination is more potent in foxing formation since copper ions can have higher catalytic effect than iron ions. A copper-induced foxing spot was reported to have the same appearance as an iron-induced foxing spot."²

XRF on a number of papers showed metallic content:

G. Bauman: Zanders Bergisch Gladbach 1917:
iron, chromium, sulphur, aluminum, calcium

Beckett wove, tan, paper made in Ohio:
iron (more than Bergisch), sulphur, aluminum,
silicon, (titanium possible)

Ansbach:
iron (more than other samples), aluminum, silicon,
calcium, barium

Charcoal Newsprint:
iron (large amount), aluminum, chromium,
titanium, calcium

Arches (no other description), new not aged:
iron, calcium, sulphur, aluminum, titanium

Rives (no other description), new not aged:
calcium, sulphur, aluminum, titanium

Iron Is Special

A reducing agent is principally used when iron needs to be complexed and removed. It is difficult to know when iron in one of its many forms might be present as a coloring material, additive, or an accidental ingredient. If iron is suspected then a reducing agent is required in addition to a chelating agent to change any $Fe(III)$ which is insoluble, into $Fe(II)$ which is only slightly soluble but soluble enough to be complexed by DTPA or EDTA.

Although both the reducing agent and chelator can be combined in the same solution, treating an area first with a reducing agent followed by the chelator, going back and forth as needed, can also be successful.

The iron-gall ink study group introduced a non-bleeding indicator test for iron ions (bathophenanthroline indicator paper) that turns magenta in the presence of soluble Fe^{++} (Iron(II) or ferrous) ions. The indicator paper can be used to test for the presence of Fe^{++} ions. To test for both Fe^{++} and Fe^{+++} , a small amount of reducing agent (1% ascorbic acid – vitamin C) is applied to the test strip to reduce the Fe^{+++} ions to Fe^{++} causing the indicator to turn magenta. Further information and instructions can be found on their website: https://irongallink.org/igi_indexff9d.html.

Reducing Agents

Sodium metabisulfite, introduced to the conservation community by Seth Irwin, has an initial pH of 4.1 so 10% NaOH is needed to adjust to the desired pH. It is considered a mild reducing agent. It is soluble in water and slightly

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soluble in alcohols. It is easy to obtain (Amazon) and is not considered hazardous. It mixes easily and can be disposed of simply. It is used in food production (“...metabisulfite solution concentrations between 1.25% and 12% in shrimp during storage”) and common laundry products.

For use with DTPA, 2% sodium metabisulfite was selected because the recommended ranges in conservation literature for reducing agents have been between 2% – 5%. In the authors' tests, 2% seems to be a suitable concentration, however further experimentation is encouraged.

Sodium dithionite has an initial pH 7, and both Helen Burgess and Season Tse recommend using it at 0.1 M concentration. However, it can be tricky to use: it has to be made immediately before use; if not buffered, it quickly degrades, forming acidic by-products, turns yellow, and smells bad. Since there are other options, it was not selected for the workshops, but can be used successfully if desired. It is the primary reducing agent in the paper conservation literature.

In "The Chemistry of Sodium Dithionite and its Use in Conservation,"³ Lyndsie Selwyn and Season Tse reported on their many tests that showed using a reducing agent alone followed by rigorous rinsing can change Fe (III) to Fe (II). The Fe (II), which is soluble, is removed during the rinsing. However, using only a chelating agent did not remove Fe (III).

They further tested two methods, combining the reducing with chelating agents in the same solution or using the reducing agent followed by the chelating agent. Both were successful.

The chelator was used to remove any remaining Fe (II) ions. “The iron (II) ions can also react with residual rust to form a gray stain that might be magnetite, or with dithionite decomposition products, such as hydrogen sulfide to form black iron sulfide.” “Re-staining (color reversion) occurs when the remaining iron (II) ions are oxidized back to rust colored iron (III) oxyhydroxides.”⁴ The chelator is a type of insurance that there will be no further reactions from colorless Fe (II) in the future.

Sodium borohydride has an initial pH 9 -10. It is widely used by paper conservators, and it can be both incorporated into chelating systems and used as a separate first application. For iron stains, the authors find that the sodium borohydride at 0.1- 0.15% is needed for adequate reducing prior to use of a chelator. (Table 2)

All reducing agents have the potential to “bleach” the paper, so keeping track of the reducing agent and the color of the artifact is important. A reducing agent removes conjugated double bonds implicated in discoloration. As such it has a dual function as a stain remover for cellulose and to convert iron to a soluble form. A solution can always be repeated to approach the color tone and to remove the stain slowly.

Table 2

Sodium Metabisulfite 190.1g/mol pH 4.0			
1M	190.1 g/L	19 g/to 100 ml	19%
0.25M	47.5 g/L	4.7 g/to100 ml	~ 5%
0.1M	19 g/L	1.9 g/to100 ml (Seth Irwin)	~ 2%

Sodium Dithionite 174.1g/mol pH 7.0			
1M	174.1 g/L	17.4 g/to 100 ml	~17%
0.25M	43.5 g/L	4.4 g/to 100 ml (Seasan Tse)	~ 4%
0.1M	17.4 g/L	1.7g/to 100 ml (Helen Burgess)	~ 2%

Sodium borohydride 37.83 g/mol, pH 9.0			
0.1M	3.78 g/ L	0.37g/to 100 ml or	
0.05M	1.8 g/L	0.18g/to100 ml	
0.03M	13 g/L	0.11g/to100 ml typical stain removal	
		used for 2-step procedure	

Buffers

DTPA is self-buffering between pH 1.4 – 6.1 and pH 7.5 – 10.4. Citrate solutions are buffers between pH 2.2 – 7.3. If you add some citric acid to the DTPA, you have an effective buffer range of pH 1.4 – 10.4.

Antoinette's Notes on Treatment Guidelines

Chelating agents generally are used at the earlier stages of a treatment. A generic sequence might be using a citrate solution to surface clean followed by initial bathing to remove water soluble degradation products, then drying.

If any degradations stains remain, test various chelator solutions for effectiveness. For example, a 2% sodium citrate at pH 8.5 might be more effective than the same solution at a lower pH. Remember to always test media at any change of concentration or pH. When testing, check under UV light to see effectiveness of tests or treatment. Sometimes results can be seen under U.V. before they become obvious in normal light.

To break up staining clusters, a mild chelation treatment (bath, local, brush, or spray application) can be tried prior to any further stain removal, alkalization, or bleaching treatments. Often no other stain removal procedure will be needed.

One consideration is whether the stain has metallic components, since often a stain will have several components. The chelator will remove the metallic contribution to the stain, opening up and releasing degradation products. Since it is generally not known which metals might be contributing to the stain or in what quantity, switching pH or adding a reducing agent will often make a difference in the success of the treatment.

Refer to the solutions chart in Table 3. It is divided into the top section where solutions are made at 6.5 pH and the lower section where solutions are made at 8.5 pH. The formulations come from the MCP. It is necessary to have a calibrated pH meter, as paper strips are not accurate enough. (See supply list.)

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Surface clean sized paper with 1% ammonium or sodium citrate pH 7.0 followed by rinsing. Use a swab and a gentle rolling procedure. You can add some calcium to the rinse and use a swab, as in application. Unsized paper will be abraded, so this is not recommended. Overall bathing may be a substitute for local surface cleaning.

Bathing. After initial bathing, test and use a 1% - 4% ammonium or sodium citrate pH 7.0 - 8.5 bath followed by rinsing to break up stain and degradation components. Test between changes of concentration or pH. Multiple baths at the same concentration and pH may be needed to remove degradation for that setting. When the bath water is clear, move on to another concentration or pH and repeat the process. Rinsing, drying, and testing between changes is recommended. Most metal ions except iron will be removed in the 7-8.5 pH range.

Concentration is significant. At too low a concentration you may not get results. It is advised to start with a 1% solution and work up to stronger concentrations as needed. Working locally may be needed if media is sensitive. Note that if media is, for example, sensitive at 3%, it may not be sensitive at 1% repeated three times.

I have found instances where a mat-burn is removed with a sodium citrate, except one area which needed a DTPA solution.

Gels. Instead of using water to make the gel, use the sodium citrate solutions. Ammonia in the ammonium-citrate solutions may evaporate, leaving an uncertain pH.

Test for iron for stronger chelator use. For suspected iron, use the bathophenanthroline indicator paper. If confirmed, use a reducing agent followed by chelator. If not confirmed, use chelator at higher pH or concentration to capture non-iron metals contributing to stains. Follow by rinsing.

There are advantages to either the one-step or two-step process. When iron is detected and, for example, makes a brown toned paper darker, it may be best to mix the reducing agent, sodium metabisulfite, and the chelator. I don't do this one-step method personally because it may be too surprising due to limitations of testing. However, it is a valid method.

I also don't find that sodium metabisulfite significantly reduces iron at the 2% concentration. More experimentation is encouraged with this reducing agent. Its advantage is that it can be easily mixed to a pH of 6.5, unlike the sodium borohydride.

When iron is found overall, it can be necessary to use a stronger reducing agent such as sodium borohydride which cannot be mixed with the lower pH of DTPA of 6.5 for iron. In that instance use the two-step method. This is my personal approach, perhaps because I am very familiar and comfortable with sodium borohydride.

To make a one-step solution with both the reducing agent and chelating agent together:

Make 100 mL of pH 6.5 DTPA buffered with citrate / 10% sodium hydroxide:

Measure 7.86 grams of DTPA, 1.92 grams citric acid, and 1.48 grams calcium hydroxide into 50 mL distilled water. (The DTPA will not dissolve until some sodium is added.)

Slowly add approximately 30 mL of 10% sodium hydroxide to bring the pH to 6.5 while stirring and monitoring the pH.

Bring the final volume to 100mL.

Add 4 grams of sodium metabisulfite to 75 mL distilled water and adjust with 10% sodium hydroxide to pH 6.5.

Add DTPA and sodium metabisulfite solutions together and bring final solution to 200mL.

To make a two-step solution:

Add 0.15 grams of sodium borohydride to 100mL of distilled water.

Treat either locally or overall (I prefer a spray application rather than a bath) followed by rinsing but not drying.

Use blotters to remove excess moisture.

Apply the sodium citrate solution at pH 6.5 or the DTPA solution at pH 6.5 either locally or overall.

It may be necessary to repeat the procedure for significant results.

Make 100 mL of pH 6.5 DTPA buffered with citrate / 10% sodium hydroxide :

Measure 3.93 grams of DTPA, 0.96 grams citric acid and 0.74 grams calcium hydroxide into 75mL distilled water. (The DTPA will not dissolve until some sodium hydroxide has been added.)

Slowly add approximately 15.45mL of 10% sodium hydroxide to bring the pH to 6.5 while stirring and monitoring the pH.

Bring the final volume to 100mL.

After any treatment, rinsing is very important. You may not see changes until the area is rinsed and dried.

Making Solutions

Some basic recipes for chelating agents are listed in Table 3.

These solutions are intended either as stock solutions to be diluted when used or can be used at these higher concentrations as is. The stock solutions are 0.1M in concentration. This translates to approximately 2% citric acid and 4% DTPA. To use a solution at 0.05M (1% in the case of citrate), simply dilute the concentrate with an equal part of distilled or deionized water.

We haven't given recipes for EDTA-based solutions but you would replace the 3.93 grams of DTPA in the recipes with 2.92 grams of EDTA (the free acid not disodium EDTA),

Table 3 Stock Solutions

0.1M pH 6.5 Citric Acid / NaOH (self-buffered)	To make 100 mL of pH 6.5 citric acid / sodium hydroxide :
1.92 g citric acid	Adjust the pH to 6.5 by slowly adding approximately 9.19 mL or 10.2 grams of 10% NaOH while stirring and monitoring the pH.
~9.2 mL 10% NaOH to adjust pH to 6.5	Bring the final volume to 100mL.
100 mL final volume with distilled water	
0.1M pH 6.5 DTPA / NaOH (unbuffered)	To make 100 mL of pH 6.5 DTPA / sodium hydroxide :
3.93 g DTPA	Measure 3.93 grams of DTPA in 80mL distilled water. (The DTPA will not dissolve until some NaOH has been added.)
~10.9 mL 10% NaOH to adjust pH to 6.5	Slowly add approximately 10.85 mL or 12.04 grams of 10% NaOH to bring the pH to 6.5 while stirring and monitoring the pH.
100 mL final volume with distilled water	Bring the final volume to 100mL.
0.1M pH 6.5 DTPA / 0.05M citric acid (as buffer) / NaOH (buffered)	To make 100 mL of pH 6.5 DTPA buffered with citrate / sodium hydroxide:
3.93 g DTPA	Measure 3.93 grams of DTPA and 0.96 grams citric acid into 75mL distilled water. (The DTPA will not dissolve until some NaOH has been added.)
0.96 g citric acid	Slowly add approximately 15.45mL of 10% NaOH to bring the pH to 6.5 while stirring and monitoring the pH.
~15.5 mL 10% NaOH to adjust pH to 6.5	Bring the final volume to 100mL.
100 mL final volume with distilled water	
0.1M pH 6.5 DTPA / 0.05M citric acid (as buffer) / CaOH / NaOH (buffered)	To make 100 mL of pH 6.5 DTPA loaded with calcium ions, buffered with citrate / sodium hydroxide :
3.93 g DTPA	Measure 3.93 grams of DTPA, 0.96 grams citric acid, and 0.74 grams calcium hydroxide into 75mL distilled water. (The DTPA will not dissolve until some NaOH has been added.)
0.96 g citric acid	Slowly add approximately 9.3mL of 10% NaOH to bring the pH to 6.5 while stirring and monitoring the pH.
0.74 g calcium hydroxide Ca(OH) ₂	Bring the final volume to 100mL.
~9.3 mL 10% NaOH to adjust pH to 6.5	
100 mL final volume with distilled water	
0.1M pH 8.5 Citric Acid / NaOH (unbuffered)	To make 100 mL of pH 8.5 citric acid / sodium hydroxide :
1.92 g citric acid	Measure 1.92 grams of citric acid in 83mL distilled water.
~10.8 mL 10% NaOH to adjust pH to 6.5	Adjust the pH to 8.5 by slowly adding approximately 10.77 mL or 11.96 grams of 10%NaOH while stirring and monitoring the pH.
100 mL final volume with distilled water	Bring the final volume to 100mL.
0.1M pH 8.5 DTPA / NaOH (self-buffered)	To make 100 mL of pH 8.5 DTPA / sodium hydroxide :
3.93 g DTPA	Measure 3.93 grams of DTPA in 78mL distilled water. (The DTPA will not dissolve until some NaOH has been added.)
~13.2 mL 10% NaOH to adjust pH to 6.5	Adjust the pH to 8.5 by slowly adding approximately 13.19 mL or 14.64 grams of 10% NaOH while stirring and monitoring the pH.
100 mL final volume with distilled water	Bring the final volume to 100mL.
0.1M pH 8.5 DTPA / CaOH / NaOH (self-buffered)	To make 100 mL of pH 8.5 DTPA loaded with calcium ions / sodium hydroxide :
3.93 g DTPA	Measure 3.93 grams of DTPA and 0.74 grams of calcium hydroxide into 80mL distilled water. (The DTPA will not dissolve until some NaOH has been added.)
0.74 g calcium hydroxide Ca(OH) ₂	Adjust the pH to 8.5 by slowly adding approximately 7.9mL of 10% NaOH while stirring and monitoring the pH.
~7.9 mL 10% NaOH to adjust pH to 6.5	Bring the final volume to 100mL.
100 mL final volume with distilled water	
0.1M pH 8.5 DTPA / 0.05M citric acid / CaOH / NaOH (self-buffered)	To make 100 mL of pH 8.5 DTPA citrate / sodium hydroxide:
3.93 g DTPA	Measure 3.93 grams of DTPA, 0.96 grams citric acid, and 0.74 grams calcium hydroxide into 75mL distilled water. (The DTPA will not dissolve until some NaOH has been added.)
0.96 g citric acid	Slowly add approximately 9.3mL of 10% NaOH to bring the pH to 6.5 while stirring and monitoring the pH.
0.74 g calcium hydroxide Ca(OH) ₂	Bring the final volume to 100mL.
~9.3 mL 10% NaOH to adjust pH to 6.5	
100 mL final volume with distilled water	
4% sodium metabisulfite (not buffered)	To make 100 mL of sodium metabisulfite / sodium hydroxide:
4.00 g sodium metabisulfite	Measure 4.00 grams of sodium metabisulfite into 75mL distilled water.
? mL 10% NaOH to adjust pH to desired pH	Slowly add 10% NaOH to bring the pH to the target value while stirring and monitoring the pH.
	Bring the final volume to 100mL.

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and use less 10% sodium hydroxide. (Note that the pH 6.5 solution would be self-buffered but the pH 8.5 solution would be unbuffered.)

To make a 10% sodium hydroxide solution:

Be very careful and wear protective equipment.

Always add the sodium hydroxide slowly to the water, as it lets off heat. It's best to use a polyethylene container.

To 500 mL of distilled or deionized water add 50 grams of sodium hydroxide. Store as a stock solution in a plastic container.

Long Term Stability

From a recent publication by Madison Brockman on the testing of paper treated with chelators:

“The results of the microfade testing and the three accelerated aging experiments show that citrate solutions do not appear to cause any deleterious effects to paper supports over time.

Paper samples, regardless of fiber composition or treatment with the citrate solution, appear to age at the same rates and are overall much less prone to change than the Blue Wool standards we rely on for indicating light sensitivity. In conclusion, citrate solutions, when used in normal conditions, appear to be safe for continued use in paper conservation treatments.”⁵

Useful Supplies Available from Amazon.com

Oakton EcoTestr pH 2 Waterproof pH Tester, 0.0 to 14.0 pH range

Apera Instruments SX620 pH Pen Tester Kit with 0.01 pH Accuracy, 3-point auto calibration

Innovating Science - pH Buffer Calibration Kit - 16.9oz (500mL) of each pH 4, 7, 10 and 4oz. (120mL)

G2PLUS 100PCS 3ml Disposable Plastic Graduated Transfer Pipettes

2 of 1 Oz. Plastic Medicine Cups Medline 1fl. Oz. Polypropylene Plastic Medicine Cups, Sleeve of 100

Digital Pocket Scale: Next-shine Digital Gram Pocket Grain Jewelry Weigh Scale by 200 X 0.01g, Black

BIPEE SH-2 Laboratory Magnetic Stirrer Hot Plate, 12x12cm Aluminum Panel, 0~1600RPM, 1L Volume, Heating & Stirring Type

Intllab Magnetic stirrer with stir bar (No Heating). Max stirring capacity 3000mL
Sodium metabisulfite: Duda-Energy

Sodium Hydroxide: Red Hot Devil Lye

Footnotes

1. "Foxing and Reverse Foxing: Condition Problems in Modern Papers and the Role of Inorganic Additives." Sarah Bertalan. *The Book and Paper Group Annual*, 34 (2015).

2. "Foxing on Paper: A Literature Review." Soyeon Choi. *JAIC* 46:2 (2007).

3. "The Chemistry of Sodium Dithionite and its Use in Conservation." Lyndsie Selwyn and Season Tse. *Reviews in Conservation*, 9, 2008.

4. Ibid. 69. "After treatment with SDT (sodium dithionite), it is important to rinse objects well to remove residual soluble compounds such as iron ions, SDT, and its sulfur-containing decomposition products.

Although SDT alone can be effective at changing the color of an iron stain from rust-colored to colorless, the effect may be temporary if the iron (II) ions are not removed by thorough rinsing. Re-staining (color reversion) occurs when the remaining iron (II) ions are oxidized back to rust colored iron (III) oxyhydroxides.

The iron (II) ions can also react with residual rust to form a gray stain that might be magnetite, or with dithionite decomposition products, such as hydrogen sulfide to form black iron sulfide."

5. "Accelerated Aging Study of Papers Treated with Citrate Solutions." Madison Brockman. *WAAC Newsletter*, 42:1 (January 2020).

Additional references

"The Use of Chelating Agents in Conservation Treatments." Helen Burgess *The Paper Conservator*, 15:1 (1991) 36-44.

"Triammonium Citrate: An Investigation into its Application for Surface Cleaning." Leslie Carlyle, Joyce Townsend, and Stephen Hackney. *Dirt and Pictures Separated*. United Kingdom Institute for Conservation of Historic and Artistic Works. (1990).

"Ammonium Citrates for Stain Removal in Paper." Antoinette Dwan. *WAAC Newsletter*, 37:3, 10-12. (September 2015).

"An Investigation of Parameters for the Use of Citrate Solutions for Surface Cleaning Unvarnished Paintings." Rachel Morrison, Abigail Bagley-Young, Aviva Burnstock, Klaas Jan van den Berg, and Henk Van Keulen. *Studies in Conservation*, 52:4 (2008).

"A Tale of Two Citrates (actually four)." Chris Stavroudis. *WAAC Newsletter*, 37:2 (May 2015).

If you want a refresher on the calibration of pH meters and other subjects, go to the GCI UTube channel and you'll find a series of short videos done by the GCI featuring Chris. Scroll down to find one, and then click the Cleaning of Acrylic Painted Surfaces link to find them all.