

A preliminary investigation into three aids to washing paper: XRF elemental analysis of paper treated with EDTA, TAC and ammonia

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ABSTRACT

This paper explores three additives that were observed to generally enhance the removal of discolouration from paper during washing. The additives included two chelating agents; ethylene diamine tetra acetic acid (EDTA) and triammonium citrate (TAC); and ammonia solution. The investigation explores the possible mechanisms for the enhanced washing as well as the potential impacts that these solutions might have on paper. A literature review and preliminary testing with X-ray fluorescence (XRF) spectroscopy were undertaken in order to begin addressing these points. The XRF analysis identified that the two chelating agents were removing significant quantities of calcium and inhibiting the re-uptake of calcium during a buffered wash. Further analysis revealed that a deionised water rinse after the use of either of the chelating agents allowed calcium to be redeposited in the paper in a subsequent buffered wash.

KEYWORDS

paper, EDTA, TAC, ammonia, washing, XRF

INTRODUCTION

Aqueous treatment of paper-based material has a long tradition in paper conservation. The use of water with various additives to remove soluble acidic material and impurities has been extensively explored in the conservation literature. This paper outlines a preliminary investigation into the chemical interaction of three additives to the washing process that have been observed to have a wider effect on the removal of discolouration than had been previously noted. It explores the chemistry of paper treated with ethylenediamine tetra acetic acid (EDTA), triammonium citrate (TAC) and ammonia with the aim of determining what substances are removed, what residues are left, and the efficacy of attempts to replace potentially lost buffering material. The elemental surface chemistry is examined with x-ray fluorescence spectroscopy (XRF), and the possible chemical pathways for the process of their actions are explored. The results of this analysis suggest that significant quantities of calcium are removed by EDTA and TAC and this may be contributing to the increased solubilisation of discolouration.

Traditionally purified water has been used to extract discolouration from paper, with aids such as ethanol to improve wetting and alkaline buffers to solubilise and extract more acidic products. It is often the case that these solutions stop being effective before the yellowing and staining have been sufficiently reduced to be considered not disfiguring. If it is deemed necessary to continue reducing staining or discolouration, for example if the work must function as an aesthetic object, then the conservator may resort to bleaching. While bleaching can be very effective, it can also be difficult to control and can have adverse affects on the paper through further oxidative degradation or the evolution of gas bubbles.

Recently at the Centre for Cultural Materials Conservation (CCMC), paper conservation has been exploring a number of alternative washing aids: ammonia solution and two chelating agents: TAC and EDTA. These have been observed in some circumstances to provide greater stain reduction or enhance the extraction of overall discolouration in paper than occurred with deionised or calcium-buffered water alone. The significance of these observations is that they occurred consistently, and in the case of the chelating agents, they occurred with discolouration not traditionally associated with metal ions – the primary area of chemical interaction of these two reagents.

These observations initiated two lines of inquiry:

1. Why are these solutions drawing out more discolouration and staining?
2. Are they safe to use on paper and media?

This paper presents the preliminary investigations into answering these two questions.

In order to approach these questions it was necessary to review the mechanisms of yellowing in paper and to establish what is being removed at an elemental and molecular level when paper is washed. It was anticipated that this information would inform the question: what part of the discolouration is being accessed by the three solutions that water alone cannot reach? Similarly, it was hoped that a review of the available literature on ammonia, EDTA and TAC and would contribute towards answers to these questions, offer recommendations for how they should be used, and identify problems that have been encountered by conservators with their usage.

The final part of this paper presents the results of preliminary testing using XRF, which was carried out to examine elementally the changes to a series of papers treated with the three substances examined.

LITERATURE REVIEW

Yellowing in paper

Discolouration of paper is a natural consequence of oxidation on aging. Through acid and alkali-catalysed degradation chromophores are formed which absorb blue/violet light (Daniels 1996, p.181). Daniels states that discolouration products can be obtained from any of the ingredients that make up paper and the range of chromophores that can be expected is correspondingly large.

The major component of paper, cellulose, forms chromophores when it undergoes oxidation as hydroxyl groups are converted first to carbonyl and finally carboxyl groups. Carbonyl and carboxyl groups contain double bonds which cause a yellow appearance in paper. The oxidation reaction can be catalysed by the presence of metals in the paper especially copper and iron. Such reactive metals can bond with lignin to cause highly coloured compounds (Hart 1981, p.43).

Metal ions may find their way into paper during manufacture in the water used or from the breakdown of processing equipment. Wood fibres can also contain trace metals from the soil. All papers are said to contain iron and copper, as well as other trace metals depending on the location and period of their manufacture (Hey 1979, p.77). Lignin on its own is a source of discolouration

as described in a paper by Hon: 'The phenolic groups in lignin molecules are associated closely with its oxidation to coloured quinonoid products' (Hon 1981, p.130). In addition to these oxidation and metal/lignin reactions, organic acids may be formed in the paper during ageing through the uptake of nitrogen and sulphur and these can also contribute to colour production (Daniels 1988, p.93).

The types of chromophores expected in paper include furans, quinones, methides and stilbenes, with furans evidently producing most of the discolouration (Hon 1979; Lewin 1965). Furan derivatives are described as 'volatile non-acidic organic degradation products' and include furfural, which is formed from the pentose sugar residues in the hemicelluloses and 5-(hydroxymethyl) furfural, which is formed from the glucose units of the cellulose (Anders & Bredereck 1996, p.482).

Foxing

Foxing in paper is a specific form of discolouration, the cited causes of which include fungi, metal particles or a combination of both. There is general agreement that the sites of foxing spots have a greater degree of oxidation than in the surrounding paper (Bicchieri et al 2001). The foxing spot itself therefore, is chemically not unlike a sheet of paper that has suffered overall oxidation as a result of natural ageing. So if foxing is oxidised paper, then presumably the same reactions have occurred as described above.

The reported presence of iron in foxing is what prompted conservators at CCMC to start exploring the use of EDTA given its ability to chelate metals and thus facilitate their removal from paper. It was during these treatments that the property of EDTA to reduce general discolouration in paper was observed. When EDTA was applied locally to a foxing spot during a general wash, over-cleaning around the staining was sometimes observed. This led to the wider application of EDTA, first to more wide-ranging stains including mount burn, and finally to reduce general discolouration.

Previous research by CCMC Masters student Nola Orr (2007), suggested that an alternative chelating agent, triammonium citrate (TAC) may also be safely used on paper. Triammonium citrate is used widely by painting and objects conservators. Earlier ad hoc experiments had suggested that TAC may prove affective at reducing staining and discolouration when EDTA did not, and vice versa.

Washing paper

According to the literature, the coloured substances that are removed during washing are the products of paper degradation such as soluble acidity. Sulphuric acid is mentioned as one of the types of soluble acidity (Hey 1979, p.66). Other substances washed out are short chain cellulose degradation products. An analysis of 'paper extract' (a substance used for paper toning obtained by extracting and reducing the highly-coloured water-soluble material from old degraded mount and back boards) showed it was composed of monosaccharides - the most basic units of carbohydrates (Ormsby 2001). This suggests that the soluble component of paper discolouration is simply broken down cellulose and other components. The monosaccharides detected included mostly arabinose, xylose, rhamnose and galactose, with smaller components of glucose and mannose. This supports Haverman and Dafour's statement that 'the majority of the soluble fraction of degradation products is composed of neutral sugars' (1997, p.107).

Washing in water alone will not remove carboxylic acid groups from the cellulose molecules or partially hydrolysed aluminium sulphate. However, if these acid groups are neutralised with an alkaline material such as calcium hydroxide, they can be made more soluble and more able to be extracted (Hey 1979 p.70; Burgess 1988, p.15). This implies that a portion of the degraded cellulose and the alum sizing agent are being washed out during aqueous treatment with calcium-buffered water.

Ammonia

The application of ammonia to the conservation treatment of paper is not a recent adaptation, but seems to have not been the focus of much attention in recent years. In the 1980's Keiko Keyes suggested it as a safe alternative to bleaching paper and Koura & Krause (1987) identified high concentrations of ammonia in liquid and gaseous phases for the mass treatment of embrittled paper. The useful action of ammonia is its ability to break the cross-links between cellulose molecules in the crystalline regions of highly hydrolysed papers, which then appear to be re-established as amorphous areas, thereby increasing fold strength and flexibility. The highly basic nature of ammonia permits it to break hydrogen bonds between cellulose molecules which are not accessible to water. This action is well established in textile conservation and manufacture where ammonia is an alternative to sodium hydroxide for the mercerisation of cotton (Rouette 2001).

Keiko Keyes (1987) identified ammonia as being suitable for use in the washing of paper in solutions of up to 0.05% and indicated that it yielded a brighter paper after washing than solutions of either calcium hydroxide or magnesium bicarbonate. The mechanism for the increase in solubilisation of the discolouration is not addressed, but it could be extrapolated that increasing the accessibility of washing to regions of the paper to which they had previously been excluded would allow a greater quantity soluble material to be accessed. Florian's (1996) analysis of foxing would give a potential explanation as to why ammonia would work on this type of stain, because she found that 'an alkaline [she used sodium hydroxide] solution dissolved all the protein-stained fungal structures, which suggests they had become soluble due to the chemical environment in the stained area'.

One of the perceived benefits of ammonia over other cleaning agents, is its volatile nature which suggests that it would not leave residues in the paper. Research by Koura and Krause indicated that evaporation is the most efficient method for the elimination of ammonia from paper (1987, p32).

Anders, Bredereck and Heberditzl (1996) state that ammonia is not suitable for use in paper conservation since it causes shrinkage of between 10 and 20%, but the basis for this assertion is not clarified. Feindt notes an average shrinkage of 5% for samples treated in pure ammonia and 85% ammonia with higher shrinkage for machine-made paper compared to hand-made papers. Ammonia solutions used at CCMC are at pH 9, which is less than 0.05% vol/vol. They have been used locally and generally and no evidence of shrinkage has been observed.

Ammonia has the potential to interfere with pH sensitive media and some mention has been made of the possibility of alkaline solutions to saponify oil based inks including some printing inks (Book and Paper Group 1990, p.18).

Experimentation with ammonia at CCMC began as a result of two projects. The first involved testing the viability of treating a series of badly mould stained but physically intact works on paper. A solution of ammonia at pH 9.5 was tested in an attempt to increase solubility by altering pH, and proved the most successful of all washing treatments tested. The second treatment involved a series of works badly stained by aged cat urine. Research into the chemistry of urine and urea as they age indicated that solubility decreased coinciding with the off-gassing of ammonia. Preliminary testing involved reintroducing ammonia in an attempt to revert the urea to a soluble state. Treatment with ammonia increased the solubility of the stains, though no testing has been carried out to see if the effect is the result of the original hypothesis or a by product of the general increase in cleaning observed with ammonia solutions.

Chelating agents

A chelating agent is a negatively charged compound capable of forming a strong ring structure that incorporates a metal ion.

This caged ring structure alters the reactivity of the metal ion and prevents it from entering into a reaction (Hart 1981, p.43). Because of this ability, chelating agents are used in conservation to reduce metal-based staining or dirt. They work best when the chelating agent and the metal to be chelated are both present in solution. It is therefore often recommended to first use a reducing agent, for example to reduce coloured, insoluble ferric iron (III) to the more water-soluble, colourless, ferrous form (II). Most iron stains in paper will be in ferric form. Any ferrous iron would probably be removed by simple water washing, although a chelating agent would speed up the process and potentially prevent redeposition.

EDTA (ethylenediamine tetra acetic acid)

The most familiar chelating agent to paper conservators is EDTA, due to its recommended use as a rust-removal treatment (Suryawanshi & Bisaria 2005; Burgess 1991). EDTA, the salts of ethylenediamine tetra acetic acid, has been commercially available since the mid-1930s. It may be in an acidic or alkaline form in aqueous solution depending on cations present, and complexes nearly all metal ions in their full range of oxidation states as well as alkali earth metals like magnesium and calcium which exist only in one oxidation state (Burgess 1991 p.39; Book and Paper Group 1990, p.18). In addition to its use for metallic stains such as rust, it is also suggested as a way to remove transition metals in paper before bleaching with hydrogen peroxide or sodium borohydride and to enhance the removal of oily or greasy stains in paper¹ (Burgess 1991, p.42). No article was found that mentioned the use of EDTA for the reduction of overall yellowing in paper.

To use EDTA safely on paper, the recommendation is to make up a 0.1 molar EDTA solution that is adjusted to a pH of 7 to 8 (Burgess 1991, p.40). To achieve this, 32.7 grams of EDTA is dissolved in 1 litre of deionised water, with the addition of 5-10% sodium hydroxide until desired pH is reached. The potential dangers of EDTA are the presence of high concentrations of sodium ions and the removal of magnesium and calcium from the paper. The work should therefore be washed extensively in water after treatment to flush out the excess sodium², and enough calcium or magnesium should be returned to the paper to replenish what has been lost (Burgess 1991, pp.40-41). Part of the experimental process of this research project was to determine the quantities of calcium required to achieve the latter.

The effects of EDTA on paper and pigment stability have been examined previously. One study found that a selection of papers treated with 1% EDTA tended to yellow on storage and colour change occurred with a number of pigments (Norville-Day et al 1997, pp.142-148). While these results are not encouraging, the EDTA solution does not appear to have been buffered to improve its working pH, and the amount of washing time after treatment to remove damaging sodium ions was not mentioned. Furthermore, there was no mention of replacing lost calcium and magnesium. All of these factors could have contributed to the yellowing of the papers. It is accepted however that EDTA needs to be used very cautiously on media. In addition to the findings of this study, it is known that EDTA, among other chelating agents, has been used in the paper recycling industry to aid in the removal of ink and ink binders (Hart 1981, p.44).

Another study looked at iron stain removal using different concentrations of EDTA, alone, with buffering agents, and with sodium dithionite (Suryawanshi & Bisaria, 2005, p.284). The study concluded that EDTA alone is too damaging to the paper and that it should be used with alkalis to protect the physical strength properties of the treated paper. In terms of removing iron stains, it was found that sodium dithionite in combination with EDTA was the most effective.

TAC (Triammonium citrate)

Triammonium Citrate, the salts of citric acid, is commercially available as a white crystalline powder. It is soluble in water and

can achieve a neutral pH (of 7) at 5% solution concentration. It is used by painting conservators at between 1-5% to remove surface grime from paintings. The mechanism for TAC's ability to remove dirt, which is generally a combination of organic and inorganic material, is not fully understood. A recent theory is that calcium ions are present in the dirt from the accumulation of building dust, so when the TAC chelates these metals, it also solubilises the attached dirt (C Stavroudis, pers. comm., 15 February 2010).

Triammonium citrate does not have a documented history of use in paper conservation, which in part prompted CCMC Masters student Nola Orr to investigate its potential. In Orr's study (2007), four papers were treated with TAC at three different concentrations; 1%, 2% & 5%, all solutions showing a pH of just under 7. All papers were pre-wet with ethanol and deionised water (50/50), immersed in the TAC solution for 20 mins, then rinsed twice in deionised water for 20 mins each time. Papers were analysed before and after ageing using colourimetry, pH testing and tensile testing. Results showed that in terms of strength, colour and pH stability, the use of triammonium citrate did not produce any detrimental changes in the papers tested. There was an indication from the pH testing that calcium and magnesium were lost during treatment of one of the papers and it was acknowledged by the author that this might be countered by following the treatment with an alkaline-buffered wash. Microscope analysis indicated that no crystalline material was left on the surface of the papers after treatment.

METHOD

The paper chosen for testing was a 1963 copy of the book *The Children's Treasury of Classics* printed on a highly lignified paper that is likely to contain alum rosin size³. A book was chosen for testing so as to allow a large number of samples of relatively uniform composition, which had undergone the same natural aging process. It was known that this book had been stored for most of its life in a subtropical environment, without artificial heating or cooling and in close proximity to the beach.

A preliminary testing cycle was carried out to confirm the observation that solutions were drawing out additional discolouration. This involved five pages being immersion washed in a deionised water bath for two cycles of 30 minutes. The pages were then transferred to wet blotting paper. The test pages were brushed into close contact with the blotting paper, and individual sheets were brushed out with the following solutions:

1. Deionised water
2. Saturated calcium hydroxide in deionised water applied drop-wise to pH 8
3. Ammonia in deionised water applied drop-wise to pH 9.5
4. EDTA 0.1M with NaOH to pH 8.5 in deionised water
5. TAC 5% wt/vol in deionised water

Further mobilisation of discolouration was able to be observed as transferred impression on the blotting paper. Results of these preliminary tests showed additional discolouration was solubilised by the three test solutions, with minimal further movement from the page re-washed with deionised water and the calcium hydroxide solution.

The pages selected for formal testing were adjacent pages which were taken from the centre of the book to reduce the likelihood of disproportionate soiling from handling or deposition. Samples were prepared as outlined in Table 1. All samples were pre-wet with ethanol applied with a dahlia sprayer and air dried after treatment.

SAMPLE	PRE-WASH	WASHING AID	RINSE/ BUFFER	RINSE/ BUFFER
1	Control			
2	DI H ₂ O 30 min x 2			
3	H ₂ O/CaOH pH 8.5 x 30 min x 2			
4	DI H ₂ O 30 min x 2	H ₂ O/NH ₃ pH 9.5 x 30 min		
5	DI H ₂ O 30 min x 2	H ₂ O/NH ₃ pH 9.5 x 30 min	H ₂ O/CaOH pH 8.5 x 30 min	
6	DI H ₂ O 30 min x 2	H ₂ O/EDTA 0.1M x 30 min		
7	DI H ₂ O 30 min x 2	H ₂ O/EDTA 0.1M x 30 min	H ₂ O/CaOH pH 8.5 x 30 min	
8	DI H ₂ O 30 min x 2	H ₂ O/TAC 5% x 30 min		
9	DI H ₂ O 30 min x 2	H ₂ O/TAC 5% x 30 min	H ₂ O/CaOH pH 8.5 x 30 min	
10	DI H ₂ O 30 min x 2	H ₂ O/TAC 5% x 30 min	DIH ₂ O x 30 min	H ₂ O/CaOH pH 8.5 x 30 min
11	DI H ₂ O 30 min x 2	H ₂ O/EDTA 0.1M x 30 min	DIH ₂ O x 30 min	H ₂ O/CaOH pH 8.5 x 30 min
12	DI H ₂ O 30 min x 2	H ₂ O/EDTA 0.1M x 30 min	DIH ₂ O x 30 min	1:1 H ₂ O: sat. CaOH pH 10 x 30 min
13	DI H ₂ O 30 min x 3	H ₂ O/TAC 5% x 30 min	DIH ₂ O x 30 min	1:1 H ₂ O: sat. CaOH pH 10 x 30 min

Table 1.

Testing was carried out on test pages with Brucker Tracer III-V handheld X-ray fluorescence analyser courtesy of Museum Victoria⁴. Proprietary Bruker AXS software was used for semi-quantitative comparison⁵.

Small samples were cut from test pages avoiding ink where possible and placed on the sensor of the XRF. Three locations were tested per sheet. These were taken from from each page at the fore-edge, the gutter and the centre to allow consistency for comparison between samples.

RESULTS

Spectra obtained indicated peaks for the following elements: silicon, aluminium, chlorine, potassium, calcium, iron, and magnesium. These were considered individually with regard to their potential impact on the paper chemistry and their comparative behaviour between samples.

Silicon and aluminium appeared unaffected by all the washing treatments tested. Their presence may be indicative of fillers or sizes. They were not considered further in this research. Magnesium peaks were too small for meaningful comparison so were not further considered within this project.

Chlorine was affected uniformly by all treatments, being largely removed. Its presence may be the result of the air-born salts from the book's close proximity to the beach or as residues from a manufacturing process. Chlorides are potentially harmful to paper through the formation of hydrochloric acid and encouragingly analysis showed a significant reduction through all washing treatments tested.

The remaining elements presented recognisable trends. Potassium is potentially present as part of a potassium aluminium sulphate size, and is perhaps the least significant of the identified elements in regard to the permanence of paper. It presented inconsistent results, or appeared to be unaffected by washing with deionised water or the ammonia solution. It was consistently

reduced with all other washing methods though not significantly. The inclusion of a buffered wash did not appear to have any effect on the potassium levels.

The results showed that significant levels of iron were reduced consistently by all washing techniques. Surprisingly EDTA and TAC removed no more iron than washing with ammonia and calcium water. This is interesting since EDTA and TAC theoretically chelate metals including iron, in all oxidation states. All solutions removed more iron than deionised water alone.

Clear trends were presented with regard to the effect of the various washing treatments on calcium present in the samples. All of the washing processes, with the exception of the calcium hydroxide buffered solution, removed measurable quantities of calcium. The least amount of calcium was removed by the deionised water and pure ammonia solutions. The greatest amount was removed by the two chelating agents. Not surprisingly, there was an increase in the calcium content of the paper after the calcium hydroxide buffered water wash.

When the ammonia solution was followed by a calcium hydroxide buffered wash, the uptake of calcium was to levels equivalent or slightly higher than before treatment. When the chelating agents were followed by a calcium hydroxide buffered wash there was no measurable uptake of calcium. If the chelating agents were followed by a deionised water wash, then a calcium hydroxide wash, calcium uptake reached levels equivalent to pre-treatment. If the calcium level in final buffered wash was increased to 50% saturated calcium hydroxide solution as described by Margaret Hey, calcium levels were significantly higher than pre-treatment levels (Hey 1979 p.74).

DISCUSSION

Iron has a destabilising effect on paper, contributing to oxidative degradation. Any removal of iron has a positive impact on the stability and longevity of paper. In this way, the reduction of iron found with most washing techniques was encouraging. The failure of the chelating agents to further reduce iron in comparison to buffered washing alone may be explained by that fact that they are simply not able to access the residual iron. Two suggested mechanisms for this trend are: if the iron exists in an insoluble state (FeIII) then it may not have been pulled into solution thus preventing the chelation; alternatively, if the iron is bound in an inaccessible part of the cellulose macro-molecule, the chelation similarly could not occur.

In the first instance, chelation may be enhanced by reducing the iron to its soluble state (FeII). Sodium dithionite has been mentioned in the literature for this express purpose. In the second instance the addition of ammonia as precursor or addition to the chelating solution may increase the amorphous regions of the paper and permit the chelation of previously inaccessible iron. Both these hypotheses present areas for further research.

The failure of pure deionised water to remove as much iron as the buffered solutions may result from a lack of available ions in the wash solution for ion exchange.

As demonstrated by the first stage of testing, further discolouration was able to be extracted from the sheets with the addition of EDTA and TAC. Since only minor quantities of iron were removed with chelating agents, these results suggest that when chelating agents reduce yellowing in paper, this is not related to the extraction of iron.

The failure of calcium to be re-adsorbed by the paper when a chelating solution is followed by a calcium hydroxide buffered wash suggests that residues of the chelating solution remain in the paper and are preventing the calcium being deposited. The cleansing action of the pure deionised water rinse appeared sufficient to reduce residues and allow calcium levels to be replenished. Washing with ammonia solutions reduced the calcium in similar fashion to deionised water alone, but did not

inhibit the uptake of calcium in the same way as the chelating agents did.

The only treatments which left significant additional buffering material in the paper were those that included the highly concentrated calcium solution. The analysis indicated that washing with lower concentrations of calcium hydroxide deposits smaller quantities of calcium within the paper, suggesting that cycles at lower concentrations may eventually provide enough of a residual buffer.

As significant quantities of calcium were removed in all washing treatments except the calcium hydroxide buffered wash, and significant yellowing was extracted in the first phase of testing with all solutions except the calcium hydroxide buffered wash, the hypothesis that the solubilisation of yellowing in paper is connected to the removal of calcium has not been disproved, opening avenues for further research in this area. For example it is possible that chelating agents are breaking cross-linking of the cellulose (to which calcium may be contributing) and making accessible more discoloured components. This is supported by Anders, Bredereck and Heberditzl whose assertion is that "the functional groups in oxidised cellulose represent new reactive centres, which can crosslink the cellulose chains by ionic bonds (with earth alkali cations) and by covalent bonds, such as acetal and ester bonds, making the fibres less flexible and more brittle" (1996, p.483).

The potential for EDTA to leave harmful sodium residues in the paper remains of concern, however XRF is not able to detect sodium, so levels could not be assessed as part of this study.

CONCLUSIONS

In conclusion, a review of conservation and wider literature on the ageing of paper failed to provide clear explanations for why the solutions examined improved general washing in paper. There are conflicting studies with regard to their safe use on paper, and of particular concern is their interaction with media, but in the majority and within defined parameters, they are considered safe.

This preliminary investigation suggested that iron removed from the paper during washing did not represent a significant factor in the further solubilisation of discolouration. Conversely the relationship between calcium and discolouration in paper is an area of further research.

Recommendations

As a result of this investigation, the authors can make the following recommendations for the safe use of the solutions examined:

1. As chelating agents remove beneficial calcium from the paper, buffering material will need to be replaced
2. Residues of chelating agents appear to prevent the uptake of calcium re-buffering solutions. This study indicated that a deionised water rinse after the use of chelating agents significantly improved the uptake of calcium into the paper.

Several further potential areas for research have been identified:

1. Exploration of the use of lower concentrations of EDTA and TAC to prevent residues remaining in the paper
2. Evaluation of the viability of buffering EDTA with ammonia to potentially facilitate the chelating agent's ability to access previously un-accessible regions of the cellulose macromolecule
3. Quantification of residual sodium levels in the paper after treatment
4. Assessment using colorimetry of changes in the brightness of the paper treated with washing solutions
5. Assess physical and chemical properties of papers treated, before and after ageing

Statistical validity

The testing has been designed as a preliminary process only, with the aim of identifying trends which may become the target of further and more in-depth research. The authors acknowledge that the results are limited in the statistical relevance due to the limited number and variety of samples tested. The use of leaves from a single book allowed the use of a naturally aged paper, and permitted the comparison of wide variety of washing scenarios, but limited the results to a single and highly specific paper type, and one not most frequently the subject of intensive washing treatment.

ENDNOTES

- ¹ EDTA may work on these stains because they will be present as fatty acid salts of calcium, iron, or copper
- ² Sodium residues can produce acidity in paper, which is why they need to be flushed out after treatment (Hey, 1979, p.77).
- ³ The highly lignified nature of the paper was determined using phloroglucinol spot test which gave a strong positive result. Iodine-potassium iodide test for starch was negative. The suggestion of an alum rosin size is based on the inexpensive and functional nature of the paper, the absence of a starch sizing, and the presence of potassium and aluminium as detected using XRF
- ⁴ Settings were as recommended by Bruker Consultant Dr Bruce Kaiser for the testing of paper: blue filter, 15KeV, 15µamp, 180 sec assay
- ⁵ Bruker XRF Handheld Inc. S1PXRF version 3.8.24

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Suryawanshi, D & Bisaria S 2005, 'Removing metallic stains from paper objects using chelating agent EDTA', *Restaurator*, pp. 276-285

MATERIALS

Disodium ethylene diamine tetraacetic acid (EDTA)

APS Ajax Finechem
Crown Scientific (distributor) PO Box 6032 Minto BC NSW 2566
T: 1300 727 696
F: 1300 135 123
E: sales@crownsoci.com.au
W: www.crownsoci.com.au

Triammonium citrate (TAC)

Chem-Supply Pty Ltd PO Box 201 Bedford Street Port Adelaide, SA 5015
T: (08) 8440 2000
F: (08) 8440 2001
E: info@chemsupply.com.au
W: www.chemsupply.com.au

Ammonia 30% solution

Chem-Supply Pty Ltd

Sodium hydroxide pellets

Chem-Supply Pty Ltd

Calcium hydroxide

Chem-Supply Pty Ltd

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BIOGRAPHIES

Briony Pemberton has been working as a paper conservator since 2000, undertaking positions at the Tate Gallery in London, The State Libraries in Victoria and New South Wales, and the National Gallery of Victoria. She has been at the Centre for Cultural Materials Conservation since 2007 working primarily on the consultancy program, where she treats works on paper for a wide variety of clients. Briony also delivers lectures and practical sessions for the Masters Course in Cultural Material Conservation at the University of Melbourne. She has a Bachelor of Arts in Fine Art History and History from the University of Melbourne (1995) and a Masters in Paper Conservation from Camberwell College of Arts, London (1999). She has presented papers on the history of the graphite pencil, pressure-sensitive tape, and the treatment of an 18th century mezzotint. She has undertaken research into efflorescence found on leather bindings and published the findings in the 2008 AICCM Bulletin. In 2001 she co-curated an exhibition on drawing materials at Tate Britain.

Libby Melzer graduated from the University of Canberra with a Bachelor of Applied Science in Conservation of Cultural Materials specialising in paper conservation. She was the Ian Potter Art Conservation Centre paper conservation intern in 2002. In 2004 she completed a seven-month Australian Youth Ambassadors for Development Project surveying and developing a management plan for a collection of Spanish colonial Church archives in the provincial centre of Bohol in the Philippines.

Supported by an Australian Postgraduate Award, Libby is currently undertaking her Masters by Research into the Materials and Techniques of French and Flemish Illuminated Manuscripts in Australian Collections. She has previously been employed as a Paper Conservator by the National Archives of Australia in Canberra and Melbourne. She is the current treasurer of the Victorian Division of the Australian Institute for the Conservation of Cultural Materials.

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