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An investigation into the use of the chelating agent tri-sodium citrate in Laponite and methylcellulose gel formulations for the removal of metallic staining.

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ABSTRACT

This study investigates whether Laponite and methylcellulose gels can be effective carriers for the chelating agent tri-sodium citrate with the purpose of removing metallic staining from textiles. Whereas chelating agents are often used in immersion treatments, this is not always a suitable option for some textile substrates, so localised treatments provide an alternative solution. The gel/tri-sodium citrate formulations were tested on undyed cotton and silk samples to determine the most effective gel/chelating agent concentrations, investigate their working properties, how effectively they rinse from the fabric, and whether any residues remain. Following this, the chelation abilities of the gel/tri-sodium citrate formulations were tested on alum-mordanted dyed silk samples, where the aim was to draw the dye from the fabric into the gel through the tri-sodium citrate chelating with the aluminium in the mordant. Methods to deposit metallic soiling onto fabric, in this instance copper corrosion, were also examined. The results were mixed: the gels were easy to combine and apply to the fabric, but left residues. Chelation was ineffective, and a negligible amount of dye was removed from the test samples. The dissertation concludes with a comparison of the two gels, with the aim of providing guidance for textile conservators exploring this method of treatment.

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Introduction

Chelating agents are compounds that are able to form complexes with metal ions through wrapping themselves around the ion so that it becomes inactive and unable to take part in reactions. They have been used in the conservation profession to facilitate the removal of metallic soiling and staining, and besides their addition to immersion treatments, have also been used for localised cleaning to limit the area of treatment, through combining the chelating agent with a gel. Gels are commonly used across the conservation disciplines to remove soiling and staining, and can be mixed with active agents such as detergents, chelating agents and enzymes.

Using gels with chelating agents to remove metallic soiling found on textiles can be useful for a number of reasons: metallic soiling can catalyse degradation and is visually disfiguring, some textiles have metallic surface embellishments, dyes mordanted with metal ions, or metal threads that can restrict the use of immersion cleaning with a chelating agent, and metallic staining may only feature on regions of the fabric rather than spread more uniformly throughout, so a localised treatment may be more desirable than immersion. In addition, gels are quick, cheap, and easy to prepare, their viscosity can help to limit and control the area of application, and their transparency can facilitate the monitoring of stain removal.

The aim of this investigation was to examine the efficacy of combining gels with a chelating agent for the purpose of performing localised cleaning treatments on textiles, to facilitate the removal of metallic soiling. The following research objectives were identified:

- Review the existing literature to identify which chelating agent and gels would be appropriate for testing
- Identify a method to deposit metal ions onto fabric for the purpose of testing the chelation abilities of the gel/chelating agent
- Design experiments to test the workability of the gels on fabric samples, their chelation abilities, and whether any residues are left on the fibres
- Make recommendations for textile conservators based on the findings of these experiments

The dissertation is divided into eight chapters. Chapters One and Two help to contextualise the project; Chapter One is a review of the literature that helped to design the experiments, and Chapter Two provides an overview of chelating agents. Chapter Three synthesises the findings of the literature review to provide the rationale for the experiments and identifies a series of research questions to provide a focus for the testing. Chapter Four introduces the gels tested in the experiments and evaluates the preparation process with the aim of determining the optimum concentrations of the gels to combine with the chelating agent. Chapter Five presents a series of experiments to analyse the effect of applying the gel/chelating agent formulations to undyed fabric samples for the purpose of examining the gels' workability, and any residues remaining on the fabric following treatment. Through analysing the gels' working properties, an optimum gel/chelating agent was selected for further, more rigorous testing on dyed fabric samples to assess the gels' chelation abilities, as described in Chapter Six. Following this, one of the more successful gel/chelating agent combinations was tested in a case study of an historic textile featuring possible copper corrosion deposits, with the results discussed in Chapter Seven. Methods for depositing metal ions, in this case, copper staining, were identified in the literature review, with the methods tested and evaluated in Chapter Eight. The dissertation is concluded in Chapter Nine with an evaluation of the research questions identified in Chapter Three, to provide recommendations for textile conservators wishing to approach this method of treatment.

Chapter One

LITERATURE REVIEW

1.1 Introduction

This review examines and evaluates published and unpublished literature that has informed the experiments in this dissertation. It primarily focuses on the use of chelating agents and gels in textile conservation, plus a review of relevant literature from other conservation disciplines where a chelating agent has been used for a localised cleaning treatment.

1.2 Chelating agents in textile conservation wet cleaning systems

Over the last two decades, articles have been published reporting effective results when using chelating agents for soiling and metallic stain removal in wet cleaning systems.

<u>Soil removal</u>

The ability of chelating agents to remove soiling is an important factor in their addition to the wash bath, especially where the soiling features metallic elements, indicating the chelating agent's affinity to metal ions.

Timar-Balázsy and Eastop, Whelan, and Chapman have all reported increased success when adding a chelating agent to the wash bath alongside a surfactant to improve its soil removal capabilities, rather than using a surfactant alone.[1, 2, 3] Although the soiled tapestries described in a report by Cartright et al. does not specifically highlight any metal content, it is interesting that EDTA was used as a sequestering agent in the wash bath where metal threads were present. The threads contained a high proportion of copper, and the decision to use EDTA was based on the concept that there is less affinity

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[1] Á. Timar-Balázsy and D. Eastop, *Chemical Principles of Textile Conservation* (Oxford, 1998), 255-257.

[2] V. Whelan, *A Comparison of the Effectiveness of a Chelator, a Surfactant, and a Chelator/Surfactant Solution in the Removal of Artificially Aged Soil on Cotton*, Unpublished report, Winterthur/University of Delaware, Delaware, 1996, 5.

[3] V. Chapman, 'The Conservation of a Painted Silk Tambourine – and Tri-ammonium Citrate', in *Painted Textiles. Postprints of the UKIC Textile Section Forum held at the Museum of London, 21 April 1997,* V. Lockhead ed., (London, 1997).

of EDTA to copper, thus reducing the risk of the threads corroding.[4] These sources have all been useful in reinforcing the concept that chelating agents have an impact on the removal of soiling featuring metal ions.

Corrosion removal

Whereas many of the aforementioned articles illustrate the use of chelating agents to remove soiling, there are also reports describing experiments that determine the efficacy of chelating agents at removing corrosion products from textiles. Margariti's dissertation and subsequent abridged publication are very thorough in describing the experimental process and results of testing three different chelating agents: tri-ammonium citrate, tri-sodium citrate, and EDTA on cotton samples artificially stained with iron and copper corrosion. Her report has greatly informed this dissertation and of particular value is the 'Recommendations for Textile Conservation' section at the end of both reports, which summarised her findings.[5, 6] Whereas Margariti has tested on cotton, the chelating agents were not tested on protein fibres, indicating a gap in this research.

The aim of Margariti's, Timar-Balázsy and Györk's articles are similar in that they test fabric samples in immersion treatments featuring a chelating agent. Both describe two different processes for artificially staining cotton and silk fabric with copper corrosion,[7] with Timar-Balázsy and Györk's being the only authors who have tested on silk fibres.[8]

Dye removal

Three studies in successive years test the application of chelating agents on dyed fabrics. These are informative experiments in that they highlight the risk of using chelating agents on dyed fabrics, as the presence of a mordant with metal content such as alum can cause the dye to be released due to the affinity of the chelating agent to the metal ion. Potter's unpublished study tested tri-ammonium citrate in Laponite gel on dyed

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[4] H. Cartwright and A. Colombini, 'Detergent Monitoring During the Washing Process at the Textile Conservation Studios, Hampton Court Palace', in *Preprints of the ICOM CC 10th Triennial Meeting, Washington DC, USA 22-27 August 1993*, J. Bridgland ed., (London, 1993), 295.

[5] C. Margariti, *The Use of Chelating Agents in Textile Conservation - An Investigation into the Efficiency and Effects of Three Chelating Agents Used for the Removal of Copper and Iron Staining from Cotton Textiles,* Masters dissertation, University of Southampton, Southampton, 2002, 91.

[6] C. Margariti, 'The Use of Chelating Agents in Textile Conservation - An Investigation into the Efficiency and Effects of Three Chelating Agents Used for the Removal of Copper and Iron Staining from Cotton Textiles', In *Dust, Sweat and Tears: Recent Advances in Cleaning Techniques,* L. Dawson and M. Berkouwer eds., (London, 2003) 28-38.

[7] Margariti 2002, 26.

[8] Á. Timar-Balázsy and M. Györk, 'Effects of Stains and Stain Removal on Historical Textiles', in *Preprints of the ICOM CC 10th Triennial Meeting, Washington DC, USA 22-27 August 1993*, J. Bridgland ed., (London, 1993), 331.

fabric mordanted with alum, to assess the reaction. She wished to avoid dye removal as much as possible as the textile requiring localised treatment to remove rust stains was dyed and she only wanted to remove the rust.[9] Adler and Eaton found that using tri-sodium citrate in an immersion treatment did affect the dyes, with some dye appearing in the wash bath after treatment.[10] Hackett builds on this study through testing the ability of tri-sodium citrate to positively remove dye bleed from textiles through various *in-situ* treatment methods, where the proposed treatment areas were masked off from the untreated areas to limit the region of treatment. Although her experiments were not considered successful enough to recommend as a potential conservation treatment, some removal of dye was observed on the treated areas of fabric, indicating not only the ability of a chelating agent to remove dye from textiles, but also its potential for *in-situ* treatments in the form of a poultice.[11] These studies are all useful in highlighting the reaction of metal mordants with chelating agents.

1.3 Chelating agents in gel formulations

Textile conservation

There are scant articles that describe the use of chelating agents in gel formulations for treating textiles. Two articles largely informed this dissertation, the choices of chelating agent and gels, and the experimental design: one by Jenny Potter and a later article by Deborah Bede. The reports focus on the removal of rust using *in-situ* gel treatments, where immersion was not possible due to the complex composition of the objects. Potter's report of the experimental process to arrive at her choice of chelating agent and gel to treat a textile with rust stains is very useful but hard to obtain as it is unpublished,[12] however an abridged version of these experiments was published almost a decade after the original study.[13] Bede's article is less thorough, but the process of combining methylcellulose with a chelating agent is well explained.[14] Of particular

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[9] J. E. Potter, *A New Method of Removing Rust Stains from Indian Chintz,* Masters project report, Royal College of Art/Victoria and Albert Museum, London, 1994, 35-38.

[10] S. Adler and L. Eaton, 'Chelating Agents in Wet Cleaning Systems', In *AIC Textile Specialty Group, 23rd Annual Meeting, June 1995, 5,* P. Eures and B. McLoughlin eds., (Washington DC, 1995), 76-77.

[11] J. Hackett, *The Use of Chelating Agents for the Selective Removal of Dye,* Unpublished report, Winterthur/University of Delaware, Delaware, 1997.

[12] Potter, 1994.

[13] J. Potter, 'Experiments in Rust Removal on a Painted Indian Chintz', in *Dust, Sweat and Tears: Recent Advances in Cleaning Techniques*, L. Dawson and M. Berkouwer eds., (London, 2003), 39-57.

[14] D. Bede, 'Conservation of the Wright Flyer III: Serendipity and Substantiation', In *Strengthening the Bond: Science and Textiles. Preprints of the NATCC 2002, April 5 and 6,* V. J. Whelan ed., (Delaware, 2002), 21-23.

interest is the explanation of the decisions behind their choice of gel, with both authors citing the transparency of the gels and their easy removal from the fabric, plus the speed of preparation to be defining factors for their use; [15, 16] these attributes were factors for the inclusion of these two gels for testing in this dissertation. Applying the gels to rust-stained cotton, not protein fibres or on any other form of metal corrosion, or testing tri-sodium citrate in a gel formulation indicates the limitations of these experiments.

It is worth highlighting two unpublished student dissertations that have helped to inform this dissertation through their use of gels on textiles: Collinge, who experimented with combining methylcellulose and Laponite with enzymes,[17] and Da Silveria, who mixed Laponite with a detergent and solvent to clean feathers.[18] Like Potter's report, these dissertations were particularly beneficial in informing the design of the experiments, especially the process of applying, monitoring and removing the gels from the textile, but also in highlighting the possibility of using a barrier method to prevent residues transferring to the fabric.[19, 20] This contrasts with Potter and Bede's experiments where barrier layers were not recommended for testing, so provided an alternative angle on the use of gels on textiles that was worth consideration.

Other conservation disciplines

As there are relatively few published sources on the use of chelating agents in gels in textile conservation, it was important to research literature from other disciplines to help to inform the experiments in this dissertation, and various articles are worth mentioning.

Three articles describe the effect of combining a chelating agent with a gel to apply as a localised treatment. Of particular note is the use of tri-ammonium citrate in hydroxypropyl cellulose gel, which was applied to a bronze sculpture to remove copper corrosion. The method for mixing the gel is briefly described and reports positive results, suggesting the efficacy of this method of corrosion removal, and citing the

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[15] Potter 1994, 31.

[16] Bede 2002, 22.

[17] R. Collinge, *A Preliminary Investigation into the Use of Enzymes for Localised Treatments on Textiles*, Masters dissertation, University of Southampton, Southampton, 2004.

[18] L. Silveria, *An Evaluation of a Poultice Treatment for Cleaning Feathers Using Laponite Gel as an Absorbent,* Unpublished diploma report, Textile Conservation Centre/Courtauld Institute of Art, 1995.

[19] Collinge 2004, 64-65.

[20] Silveria 1995, 27.

practicality of limiting the treatment area as the defining reason for using this method.[21] Similarly, Wolbers also supports the use of chelating agents in methylcellulose to clean soiled painted surfaces.[22] In contrast, Ankersmit attempted to combine five different chelating agents (including citrates) respectively with sodium carboxymethylcellulose, but found that the gel was too difficult to remove from the surface of corroded iron rods on an item of contemporary artwork.[23] These articles present the concept that it is possible to easily combine chelating agents with gels for corrosion and soiling removal in a localised treatment.

1.4 Choices of chelating agent and gels for textile conservators

No articles have been published on the use of chelating agents in textile conservation since Margariti's article in 2003, which is very thorough in examining the wide range of chelating agents available for use in a literature review from the preceding decades,[24] and recommend tri-ammonium citrate and tri-sodium citrate above other chelating agents for use on copper and iron corrosion. Since Potter and Bede's articles, also published in 2002 and 2003 respectively, no further studies could be found to recommend any other gels besides Laponite and methylcellulose. Therefore, these three sources above others have been useful for explaining the chelating agent, gel, and concentrations used, which has helped to inform these experiments in this dissertation.

1.5 Conclusion

This review of the literature has identified a number of gaps in the use of chelating agents in textile conservation. Various articles have tested chelating agents within a wash bath to remove iron or copper staining, however it is apparent that few studies exist describing the effective use of chelating agents in gels to treat textiles. No research has been conducted into localised copper stain removal using gels, should an immersion treatment be problematic. Only one has been published on the effects of using chelating agents on silk, albeit as an immersion treatment, whereas most are focused on testing on cellulosic textiles, through both immersion and with localised cleaning. Whereas tri-

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[21] J. Heuman, 'Removing Corrosion on a Painted Outdoor Bronze Sculpture with Mild Chelating Agents', *The Conservator,* 16:1 (1992), 16.

[22] R. Wolbers, *Cleaning Painted Surfaces, Aqueous Methods* (London, 2000), 122.

[23] H. Ankersmit, R. Timmermans and S. Weerdenburg, 'Conservation of a Work by Soto: Treatment of Iron Corrosion on Paint', In *Modern art, new museums: contributions to the IIC Bilbao Congress 13-17 September 2004* , A. Roy and P. Smith eds., (London, 2004), 60-61.

[24] Margariti 2002, 4-10.

sodium citrate is a commonly used chelating agent in the textile conservation studio, it has not been tested in a gel formulation. The removal of dyes featuring a metal mordant is mentioned, whether incidentally as a consequence of immersion, or purposefully to remove dye bleed, but the articles report unconvincing or inconclusive results. It would be judicious to address these gaps in the research with further testing to provide more options to textile conservators when considering the use of chelating agents.

Chapter Two

AN INTRODUCTION TO CHELATING AGENTS

The aim of this chapter is to provide background information on the science behind chelating agents. With this information in mind, it is possible to understand how chelating agents affect textiles.

2.1 What are chelating agents?

Chelating agents are compounds that are able to form complexes with metal ions through coordinate bonds. A complex is defined by the presence of coordinate bonds, which form in the structure alongside primary bonds.[25] The chelating agent is often a large molecule that wraps itself around the metal ion so that it becomes inactive and unable to take part in reactions.[26] The word 'chelate', pronounced *key-late* derives from the Greek word for 'claw of a lobster', reflecting the chelating agent's ability to wrap itself around a metal ion like a claw.[27]

Burgess describes the classification of a chelating agent:

> 'In order to be called a chelating agent, a molecule must have two appropriate functional groups, each having a donor atom which is capable of combining with a metal atom by donating a pair of electrons.'[28]

The chelation molecule will consist of a negative charge that is able to bond with the positively charged metal. This can happen in two ways: through the loss of a proton from an acidic compound, thus creating a negatively charged molecule able to bind with a positively charged metal, or through the donation of two electrons to create a negatively charged molecule capable of complexing with the positive metal centre, as is the case with basic compounds. This reaction can be exemplified by the loss of a proton from a carboxylic acid group: $\text{-COOH} \rightarrow \text{-COO} \rightarrow \text{-COOM}^{+}$ or through the donation of

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[25] Á. Timar-Balázsy, and D. Eastop, *Chemical Principles of Textile Conservation* (Oxford, 1998), 221.

[26] A. Phenix and A. Burnstock, 'The Removal of Surface Dirt on Paintings with Chelating Agents', *The Conservator*, 16:1 (1992), 28.

[27] H. Burgess, 'The Use of Chelating Agents in Conservation Treatments', *The Paper Conservator*, 15: 1 (1991), 36.

[28] Burgess 1991, 36.

electrons from a basic hydroxyl group: H-O: → H-O:M, to provide some typical examples.[29]

Chelating agents also require the ability to create a four- or five-ringed structure through the complexing of the metal ion with the functional groups. They must be oriented in such a way that they are able to produce a ring with a metal centre, as exemplified below, with the dotted line representing the coordinate bond:

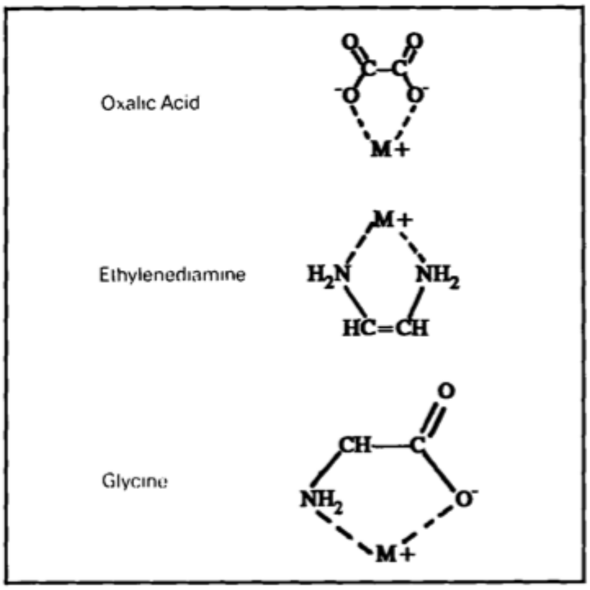

Fig. 1 The formation of a ring structure when oxalic acid, ethylenediamine, or glycine complex a metal centre.[30]

2.2 Types of chelating agents used in conservation

Citrates such as tri-sodium citrate and tri-ammonium citrate are commonly used as chelating agents across the conservation disciplines, due to their ability to complex with metal ions through dissociated carboxylic acid groups (fig. 2[31]).[32]

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[29] Burgess 1991, 36.

[30] Burgess 1991, 36.

[31] C. Margariti, 'The Use of Chelating Agents in Textile Conservation. An Investigation into the Efficiency and Effects of Three Chelating Agents Used for the Removal of Copper and Iron Staining from Cotton Textiles', In *Dust, Sweat and Tears: Recent Advances in Cleaning Techniques,* L. Dawson and M. Berkouwer eds., (London, 2003), 30.

[32] Alan Phenix and Aviva Burnstock, 'The Removal of Surface Dirt on Paintings with Chelating Agents', *The Conservator*, 16:1, (1992), 28.

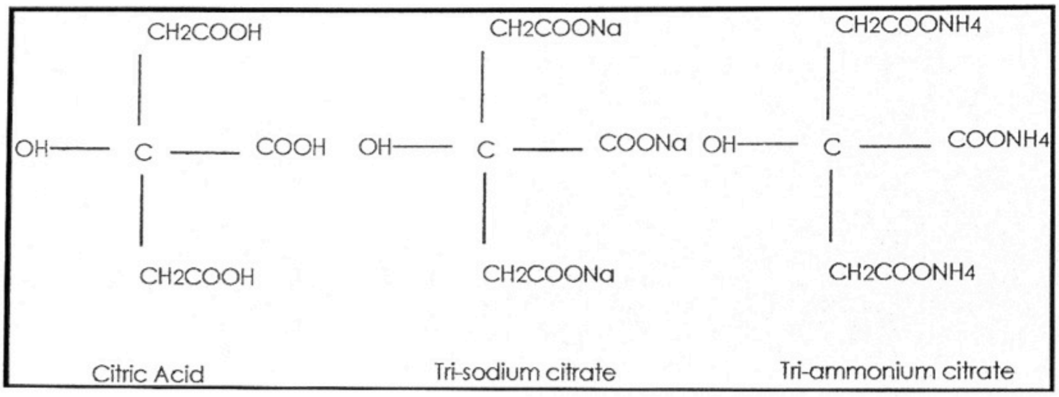

Fig. 2 Molecular structure of citric acid and the two citrates.

2.3 Uses in conservation

Chelating agents are generally found to be effective at removing metallic soiling deposits and are used across the conservation disciplines in numerous ways. Paintings conservators will often use chelating agents with swabs to clean the surface of paintings,[33] whereas corroded metalwork and sculptures can be cleaned with a poultice.[34] Paper and textile conservators will commonly use chelating agents as an additive to the wash bath to remove soiling and metallic staining.[35,36]

2.4 Stability constants

Stability constants represent the thermodynamic stability of the complex and the equilibrium of the reaction. The stability of the complex is dependant on the metal involved in the reaction, and through a series of calculations based on the chelation of citric acid with various metals carried out by Phenix and Burnstock, it is possible to determine the value of the stability constant, with the greater the value, the more stable the complex. Some common metals encountered in conservation cleaning are iron (Fe^{3+}), copper (Cu^{2+}), aluminium (Al^{+}) and lead (Pb^{2+}). This table shows their stability values:[37]

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[33] Phenix and Burnstock 1992, 30.

[34] J. Heuman, 'Removing Corrosion on a Painted Outdoor Bronze Sculpture with Mild Chelating Agents,' *The Conservator*, 16:1 (1992), 16.

[35] Burgess 1991, 39.

[36] Timar-Balázsy and Eastop 1998, 255-257.

[37] Phenix and Burnstock 1992, 29.

Metal Ion	Stability constant value
Fe^{3+}	11.85
Cu^{2+}	14.21
Al^{+}	7.0
Pb^{2+}	6.5

Based on these calculations, it is possible to arrange the metals in an order of preference for chelation with citrates. The following sequence has been identified, describing the chelation ability of citrates:[38]

$Cu^{2+}>Fe^{3+}>Al^{3+}>Pb^{2+}>Zn^{2+}>Ni^{2+}$, $Co^{2+}>Cd^{2+}>Mn^{2+}>Mg^{2+}>Ca^{2+}>Fe^{2+}>Sr^{2+}>Ba^{2+}$

This sequence shows the greater affinity of citrates to copper, compared with lead or magnesium, and thus dictates that when a chelating agent is used in a wet cleaning system featuring these metal ions, it will first complex with the ions in this order of preference. To reinforce this concept, Timar-Balázsy and Eastop make the pertinent observation that when citrates are used to soften water, they are more effective when copper and iron are not present, due to the preferences of the chelating agent to these metal ions.[39]

2.5 Influence of pH

Citrates such as tri-sodium citrate are regularly used as buffers in wet cleaning systems in the textile conservation profession. Chelating agents are generally most effective when they are completely ionised and in their most negatively charged form, to provide greater affinity to the positively charged metal ion, which is most likely to occur with conditions at the highest pH possible. Extremes of pH are undesirable when wet cleaning textiles, thus the chelating agents commonly used by conservators, tri-ammonium citrate and tri-sodium citrate, feature pH ranges of 6.0-7.5 and 7.5-9.0 respectively at 5% solutions.[40]

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[38] Phenix and Burnstock 1992, 29.
[39] Timar-Balázsy and Eastop 1998, 224.
[40] Phenix and Burnstock 1992, 29.

Chapter Three

EXPERIMENT RATIONALE

The literature review was helpful in identifying potential gels and chelating agents to test based on reported successful experimentation, plus methods for depositing metal ions onto the fabrics, and designing the experiments themselves.

Based on the findings from the literature review, the following chapter describes the rationale behind the experiments, and defines the factors and variables that influenced the results of the experiments. A series of research questions is identified at the end of this chapter, to help keep the experiments on track.

3.1 Chelating agent

Tri-sodium citrate (TSC) was selected as the chelating agent to test for a number of reasons:

- TSC is recommended for the removal of metallic staining[41]
- It is considerably cheaper than buying tri-ammonium citrate (another recommended chelating agent),[42] and as it is commonly used in the wash bath as a buffer, would mean that it is likely to be available in conservation studios and therefore readily accessible

3.2 Concentration of chelating agent

The ratio of TSC to chelating agent is unknown, but based on Potter's recipes of using tri-ammonium citrate in its solid form,[43] and Margariti's previous evaluation of the literature, both 2.5% w/v and 5% w/v tri-sodium citrate to chelating agent were tested.[44]

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[41] C. Margariti, *The Use of Chelating Agents in Textile Conservation - An Investigation into the Efficiency and Effects of Three Chelating Agents Used for the Removal of Copper and Iron Staining from Cotton Textiles,* Masters dissertation, University of Southampton, Southampton, 2002, 91.

[42] Margariti 2002, 92.

[43] J. E. Potter, *A New Method of Removing Rust Stains from Indian Chintz,* Masters project report, Royal College of Art/Victoria and Albert Museum, London, 1994, 90-91.

[44] Margariti 2002, 10.

3.3 Gels

Due to success described in the literature review of previous experiments using Laponite and methylcellulose (MC) respectively to mix with a chelating agent, these two gels were selected for testing. Both gels are considered to be quick, cheap and easy to prepare and require minimal mechanical action on removal.[45, 46] Both mix to form a transparent gel, which facilitates monitoring of stain removal.

3.4 Concentration of gels

The existing literature suggested that a concentration of between 5-10% w/v of Laponite and MC in de-ionised water is sufficient to form a stiff, controllable gel to hold the chelating agent.[47, 48]

3.5 Fabric

Undyed and dyed fabric samples were tested on. Silk and cotton fabrics were selected to analyse the effects of the gel/chelating agent on different types of fibres.

3.5.1 Undyed

Samples of plain weave, undyed, bleached cotton lawn and undyed heavy-weight silk habutai, cut to 120mm x 120mm were tested on for the preliminary experiments to determine the optimum working properties of the two gels.

3.5.2 Dyed

Initially, it was proposed to stain the aforementioned cotton and silk samples with copper corrosion, however this was unsuccessful, as described in Chapter Eight. Alternatively, plain weave, alum-mordanted dyed fabric was provided for the final tests,

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[45] Potter 1994, 53.
[46] Bede 2002, 23.
[47] Potter 1994, 77.
[48] R. Collinge, *A Preliminary Investigation into the Use of Enzymes for Localised Treatments on Textiles*, Masters dissertation, University of Southampton, Southampton, 2004, 55.

where aluminium within the mordant replaced copper as the metal ion to test the chelation ability of TSC in a gel formulation.

3.6 Time

Potter and Bede found that stain removal could be monitored due to the transparency of the gels, with up to 1 hour to be the maximum amount of time required to remove rust deposits effectively, with Potter citing twenty minutes as sufficient.[49, 50] Therefore, these parameters were used as a guide, and where one hour appeared to be insufficient time for discernible stain removal, the time was increased accordingly.

3.7 Application and removal of gel

Throughout the experiments, two methods of application were tested, as described in Potter and Bede's experiments, to compare their efficacy in the conclusion. Potter applied the gel directly onto the top surface of the stained fabric using a Melinex® template. The template consisted of a hole cut to the shape of the stain requiring treatment, with the Melinex® masking the surrounding areas to limit application.[51] Bede applied the gel directly to the stained area of fabric with a spatula.[52]

For every method of application, 1.5g of each gel was measured and applied to a one penny-sized circle defined by a pencil line to an area of 31.4mm$^{2;}$ keeping the shape of the treatment area regular provided facilitated analysis. For consistency, the depth of each gel was controlled to 5mm ± 0.5 mm as measured by a ruler. Each gel was applied with a microspatula.

Potter and Bede did not recommend a barrier layer between the gel and fabric to prevent potential residues occurring, so the gel was applied directly to the fabric in these experiments too.

The results were monitored every five minutes and observations were recorded over the period of one hour. Removal of the gel with a spatula is recommended by Potter and

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[49] Potter 1994, 40.
[50] Bede 2002, 22.
[51] Potter 1994, 18.
[52] Bede 2002, 22.

Bede, and the area rinsed with a small paintbrush moistened with de-ionised water, then blotted dry with sheets of blotter.[53, 54]

3.8 Research questions

To help keep the experiments on track, a series of research questions were identified:

1. Do the existing gel/chelating agent formulation recipes provided by Potter and Bede prove to be effective carriers for tri-sodium citrate and if not, can they be modified accordingly to provide effective results
2. Is it possible to control the area of application of the gels through working with their viscosity to prevent spreading to other regions of the fabric
3. Are the gel/chelating agent formulations equally effective on cotton and silk, or is there a difference in the workability of the gels or level of residues remaining on the fabric following treatment
4. Does the application and removal of the gels/chelating agent formulations damage the fibres
5. Are the selected gel/chelating agent formulations effective at chelation
6. Is one gel/chelating agent formulation more workable and effective at chelation than the other

These questions were evaluated throughout the dissertation, and summarised in the conclusion, to fulfil the aim of making recommendations for textile conservators based on the findings of these experiments.

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[53] Potter 1994, 39.

[54] Bede 2002, 22.

Chapter Four

EVALUATION OF LAPONITE AND METHYLCELLULOSE FOR PRACTICAL APPLICATION

4.1 Introduction

The aim of this chapter is to describe the series of experiments designed to determine the optimum concentration of both Laponite and methylcellulose gels to combine with tri-sodium citrate in Chapter Five. The working properties of the gels were unknown, therefore a large amount of this practical work was experimental in order to obtain an ideal working concentration to hold the tri-sodium citrate, as well as fulfill the qualities required to perform as an effective working gel treatment.

Aims and objectives

- Provide background information about Laponite and methylcellulose
- Evaluate the process for preparing the gels and comment on their working properties
- Determine the optimum concentration of each gel to enable it to retain its shape as well as prove easy to remove when applied to undyed cotton lawn and heavy-weight silk habutai

4.2 What is a gel?

Gels are colloidal substances consisting of large molecules that are held together through electrostatic forces when dispersed in another substance, such as water; these properties can provide useful workability through the suspension of the active agents within the solution to help to control the area of application.[55] The two gels used in these experiments, Laponite and methylcellulose, are commonly found across the conservation disciplines and are favoured due to their transparency, and tests show that they are easy to remove from fabric.[56, 57]

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[55] J. Potter, 'Experiments in Rust Removal on a Painted Indian Chintz', In *Dust, Sweat and Tears: Recent Advances in Cleaning Techniques,* L. Dawson and M. Berkouwer eds. (London, 2003), 40.
[56] Potter 2003, 53.

4.2.1 Laponite RD

Laponite RD is a synthetic, inorganic fine white powder that mixes with water to form a transparent gel. One unit cell of Laponite has the empirical formula $Na_{0.7}^{+}$ $[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{0.7-}$ A single Laponite crystal is disc-shaped (fig. 3), which consists of around 2000 of the repeating unit cells. Laponite crystals are stacked together and held through electrostatic forces by shared sodium ions that are present between adjacent crystals. When Laponite crystals are dissolved in water, the sodium ions are released into the solution where their positive charge repels the positive charge of adjacent particles, resulting in a stabilised, low viscosity structure. When adding an additional polar compound to the structure, such as a salt, a layered 'house of cards' structure ensues, which is a combination of flocculated particles held together through weak electrostatic forces to create a highly thixotropic gel (fig. 4).[58] Laponite forms a gel at 2% concentration and has a pH of 9.8.[59]

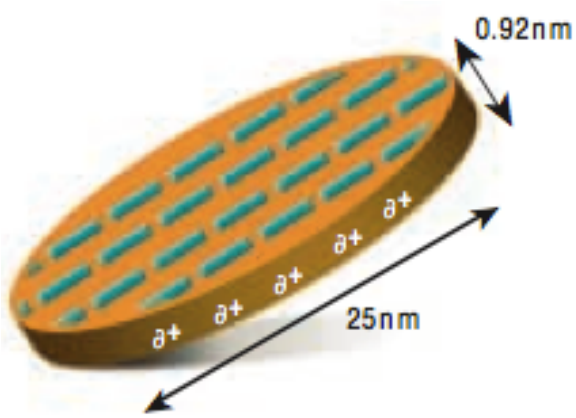

Fig. 3 A single Laponite crystal[60]

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[57] D. Bede, 'Conservation of the Wright Flyer III: Serendipity and Substantiation', *Strengthening the Bond: Science and Textiles. Preprints of the NATCC 2002, April 5 and 6,* V. J. Whelan ed., (Delaware, 2002), 21-23.
[58] Rockwood Additives, *Laponite Performance Additives,* Rockwood Additives Ltd, http://www.scprod.com/pdfs/LaponiteBrochureE.pdf (accessed 27th August 2012), 17-19.
[59] Conservation Resources, *Laponite RD*, Conservation Resources, http://www.conservation-resources.co.uk/index.php?main_page=product_info&products_id=615 (accessed April 19, 2012).
[60] Rockwood Additives, 17.

Fig. 4 Gel formation – house of cards[61]

Concerns have been expressed that buffering Laponite to a more neutral pH for use on historic textiles can modify its transparency and viscosity, although it does not appear to alter its performance.[62]

4.2.2 Methylcellulose

Methylcellulose (MC) is an inert, water-soluble anionic polymer derived from cellulose and is pH neutral (fig. 5). It is typically supplied as a fine white powder that is mixed with cold water to form a gel. It is used as a thickener and binder, and is commonly used in the pharmaceutical, food, cosmetic and paper industries, amongst others.[63]

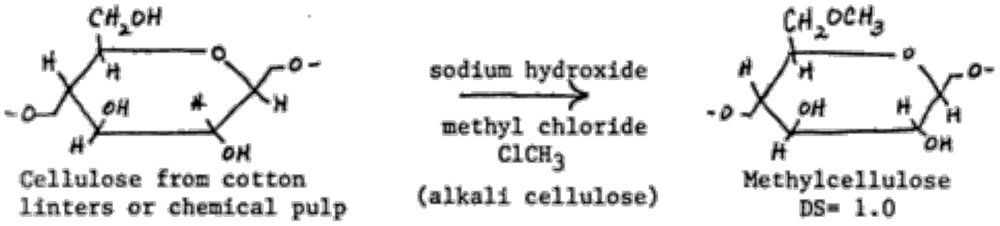

Fig. 5 The Chemical process to create methylcellulose from the glucose unit of the cellulose polymer[64]

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[61] Rockwood Additives, 19.

[62] R. Collinge, 'A Preliminary Investigation into the Use of Enzymes for Localised Treatments on Textiles', Masters dissertation, University of Southampton, 2004, 57.

[63] C. Baker, 'Methylcellulose & Sodium Carboxymethylcellulose: Uses in Paper Conservation', In *The Book and Paper Group Annual,* 1 (1982), http://cool.conservation-us.org/coolaic/sg/bpg/annual/v01/bp01-04.html (accessed 27th August 2012).

[64] Baker 1982.

4.3 Preparation of gels

4.3.1 Laponite

The following concentrations of Laponite gel were prepared:

- 5% w/v Laponite (5g Laponite dissolved in 100ml de-ionised water)
- 7.5% w/v Laponite
- 10% w/v Laponite

The Laponite powder was sprinkled into a beaker of 100ml de-ionised water and mixed with a glass stirring rod. After starting off as a cloudy solution, each gel began to thicken within five minutes of continuous stirring and a clear gel of varying degrees of viscosity depending on the concentration was formed after ten minutes. Each gel was left overnight at room temperature (20°C) in a beaker covered with Clingfilm. By the following morning, the gels were and clear and viscous (fig. 6).

Fig. 6 Left to right: 5%, 7.5% and 10% Laponite gels left overnight

4.3.2 Methylcellulose

Two quantities of MC were made, to obtain a similar viscosity to the Laponite gels:

- 5% w/v MC
- 7.5% w/v MC

Cold water is specified to mix MC, so 100ml of de-ionised water was measured, with the methylcellulose powder sprinkled on top. The gels were very cloudy and yellow-toned upon mixing, but began to thicken after five minutes of stirring. However they also appeared to contain many bubbles, even after leaving them for an hour at room temperature to thicken. The gels appeared to be at their optimum viscosity after an hour, but were covered with Clingfilm and left overnight at room temperature to settle. The following morning, many bubbles were still apparent in the liquid, although it was transparent, if not slightly yellow-toned (fig. 7). Consultation with staff suggested that the bubbles should not cause any issues concerning the working properties of the gel, and it was not clear why they had formed, so the gel was used in this state.

Fig. 7 Left to right: 5% and 7.5% MC gels left overnight

4.4 Experiments to determine optimum gel concentration

The following table summarises the variables for each fabric sample tested in this chapter, and introduces the sample codes, which are referred to in the tables of results for the testing later in the chapter.

Sample coding interpretation

Example 1
L-CU-7.5
L=Laponite
C=Cotton; U=Uncovered
7.5=7.5% gel concentration

Example 2
MC-SC-5
MC=Methylcellulose
S=Silk; C=Covered
5=5% gel concentration

Table 1: Fabrics and gels tested

Experiment	Sample Code	Gel	Fabric	Gel concentration (%w/v)	Covered or uncovered
4.4.1	L-CC-5	Laponite	Cotton	5	Covered
	L-CC-7.5			7.5	
	L-CC-10			10	
	L-CU-5			5	Uncovered
	L-CU-7.5			7.5	
	L-CU-10			10	
	L-SC-5		Silk	5	Covered
	L-SC-7.5			7.5	
	L-SC-10			10	
	L-SU-5			5	Uncovered
	L-SU-7.5			7.5	
	L-SU-10			10	
4.4.2	MC-CC-5	Methylcellulose	Cotton	5	Covered
	MC-CC-7.5			7.5	
	MC-CU-5			5	Uncovered
	MC-CU-7.5			7.5	

	MC-SC-5		Silk	5	Covered
	MC-SC-7.5			7.5	
	MC-SU-5			5	Uncovered
	MC-SU-7.5			7.5	

Both the Laponite and MC gels were tested on fabric samples of undyed cotton and silk for the purpose of analysing their working properties as a gel. It was possible that the gels may dry whilst applied to the fabric, therefore some samples were covered with a petri dish and the others left uncovered to monitor the effects. The following factors were considered throughout the testing to enable a conclusion to be drawn to determine the ideal working concentration of each gel to combine with tri-sodium citrate:

- Ease of application
- Degree of spreading beyond the treatment boundaries
- Drying of gels
- Ease of removal and rinsing
- Analysis of residues

Refer to Chapter 3.6-3.7 for detailed information concerning applying and removing the gels.

4.4.1 Laponite on cotton and silk

Table 2: Results of testing Laponite on cotton and silk

Temp: 19.6 degrees **RH:** 44.8 %							
Sample code	**Application observations**	**Approximate (~) spread in mm after application** - = no new observations				**Removal observations**	**Rinsing observations**
		5 min	10 min	15 min	15-60 min		
			COTTON				
L-CC-5	Gels clear but fairly viscous. Easy to spread to define treatment area but	~5	~9	~12	-	Both showed no drying. Hardest to remove – required a few attempts at scraping the residues.	Both rinsed fairly easily, fabric felt only slightly crisper to touch but no obvious residues
L-CU-5		~5	~7	~10	-		

	quite runny and both eventually spread beyond treatment boundaries						observed under visual examination
L-CC-7.5	A slightly stiffer, clear gel but holds shape well	~3	~7	~9	-	No drying. Second easiest to remove – slightly stickier than 10%	As above
L-CU-7.5		~3	~5	~7	-		
L-CC-10	The most viscous of the gels. Holds shape well but is least easiest to apply to the fabric and manipulate in place	~3	~6	~6	-	No drying. Easiest to remove	As above
L-CU-10		~3	~4	~4	-		

SILK							
L-SC-5	As above, for cotton samples	~2	-	-	-	Hardest to remove – fabric seemed saturated with gel and had penetrated to the reverse, sticking to the Melinex® backing	Hard to rinse gel. Fabric still felt very stiff on treatment area and a stain appeared where the gel had been.
L-SU-5		~2	-	-	-		
L-SC-7.5		~1	-	-	-	As above, but easier to remove than 5%	
L-SU-7.5		~1	-	-	-		
L-SC-10		~1	-	-	-		
L-SU-10		~1	-	-	-		

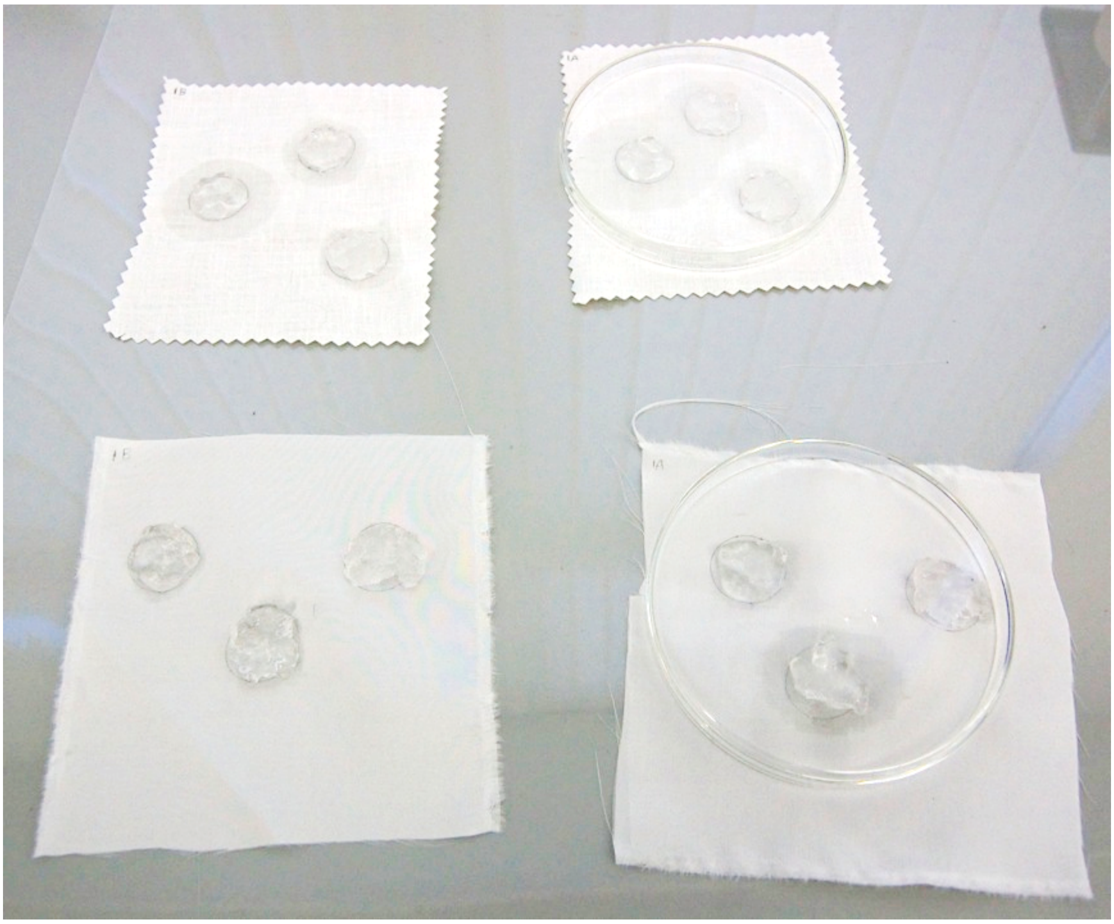


Fig. 8 Monitoring Laponite on cotton and silk. Right side: samples covered with petri dishes

4.4.1.1 Evaluation

Based on a subjective analysis of the working properties of the gels, these series of experiments determined that the 10% w/v concentration of Laponite is preferred to carry forward to the next set of experiments. The 10% concentration was easy enough to apply and manipulate into the designated treatment area of all the samples, and held its shape well. This concentration displayed the least spread when left uncovered; this is beneficial as it resulted in the most control when applying the gel and limiting it to the treatment area. Drying did not appear to be an issue for the uncovered gels. Removal was easy for the cotton samples and after rinsing, only minimal residues appeared to remain but with a refined technique it is felt that this could be reduced further. The cotton was only slightly crisper to touch in the treatment area, compared with untreated areas of fabric. Unfortunately, the silk samples displayed staining where the gel had been applied and was hard to rinse, however no difference was observed for residues or inflexibility of the fabric between each concentration. Adjustments will need to be made if Laponite is to be a feasible treatment option for silk due to the issues with staining and rinsing.

4.4.2 Methylcellulose on cotton and silk

Table 3: Results of testing MC on cotton and silk

Temp: 22. 5 degrees **RH:** 33.8 %							
Sample	**Application obser-vations**	**Approximate (~) spread in mm after application** MC- = no new observations x = no spread				**Removal observations**	**Rinsing observations**
		5-15 min	15-30 min	30-45 min	45-60 min		
COTTON							
MC-CC-5	Left gel overnight but still contained bubbles in the morning. Yellow tinged. Much harder to apply gel to fabric than Laponite – very sticky and hard to control. Does not hold a firm, stiff shape well, but did not spread beyond treatment boundaries on application.	X	-	~1-2	-	Hard to remove as it appeared to saturate the fabric. Very sticky. Required scraping with spatula to remove all residues. Uncovered samples slightly drier than covered	Rinsing was difficult**,** fabric feels stiff to touch as if gel is still within the interstices of the fabric
MC-CU-5		x	Slight drying	-	-		
MC-CC-7.5	A slightly thicker gel than 5%, still very sticky and hard to apply but held shape better on fabric	x	-	~1-2	-	As above, but slightly easier to remove and less residues left following removal	As above
MC-CU-7.5		x	Slight drying	-	-		

SILK							
MC-SC-5	As above, for cotton samples	x	-	~1-2	-	Rinsing was difficult; fabric feels stiff to touch as if gel is still within the interstices of the fabric	Rinsed poorly. Staining is evident and fabric felt very stiff and inflexible
MC-SU-5		x	Slight drying	-	-		
MC-SC-7.5		x	-	~1-2	-		
MC-SU-7.5		x	Slight drying	-	-		

4.4.2.1 Evaluation

Based on a subjective analysis of the working properties of the gels, plus the stereomicroscope analysis, these series of experiments determined that the 7.5% w/v concentration of MC is marginally preferred to carry forward to the next set of experiments. The 7.5% concentration was easy enough to apply and manipulate into the designated treatment area of all the samples, and held its shape well. Only minimal spread was observed on both fabrics. Removal was hard for both cotton and silk samples but it was easier to rinse from cotton, however silk displayed heavy staining. Both fabrics felt more inflexible compared with treated areas. Adjustments will need to be made if MC is to be a feasible treatment option for silk due to the issues with staining and rinsing.

Chapter Five

EVALUATION OF TRI-SODIUM CITRATE IN LAPONITE AND METHYLCELLULOSE GELS

5.1 Introduction

The aim of this chapter is to describe the series of experiments designed to evaluate the effect of combining Laponite and methylcellulose with the chelating agent tri-sodium citrate. The working properties of the two gels were monitored and evaluated, so that the optimum concentration could be determined.

Aims and objectives

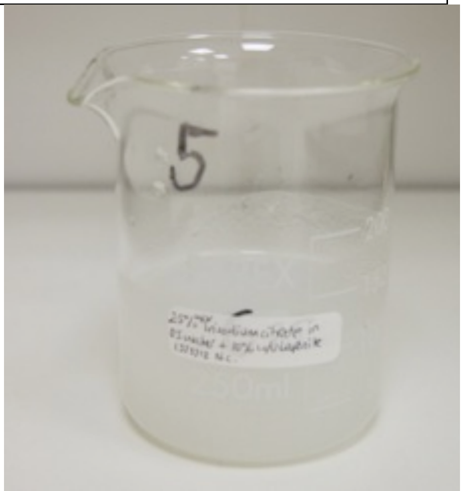
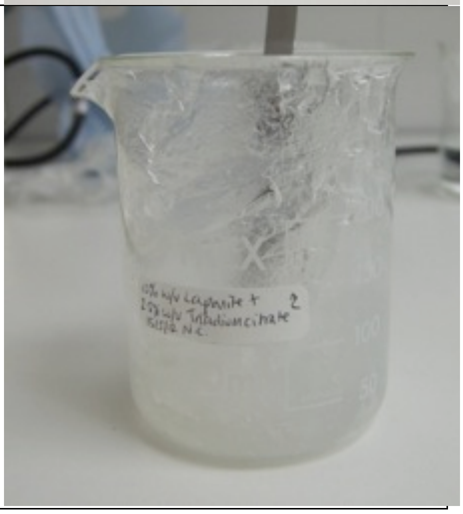
- Experiment with combining the gels with tri-sodium citrate (TSC) to determine an optimum working concentration to apply to undyed cotton and silk
- Monitor the working properties of the gels once combined with TSC on cotton and silk
- Analyse the effect of the gels using visual analysis, microscopy, SEM (scanning electron microscope) and through taking pH readings of the gels and fabric to indicate whether any residues are left following treatment
- Determine the most effective gel/TSC combination for Laponite and methylcellulose (MC) respectively

5.2 Combining gels with tri-sodium citrate

Following the experiments in Chapter Four to determine the ideal concentration of each gel, a method was sought to combine each gel with the chelating agent TSC and evaluate its working properties. TSC is supplied as white granules that resemble granulated sugar. It is often dissolved in water to form a transparent liquid when used as a buffer in wet cleaning systems. It is assumed that Potter used a solid form of tri-ammonium citrate (suppliers list was unavailable) to combine with the 10% w/v Laponite in de-ionised water, so a similar method to combine TSC in Laponite was tested. To mix the two, 20g of 10% w/v Laponite gel was weighed out, then mixed with 1g of tri-ammonium citrate to make a 5% w/w concentration of the gel and chelating agent.[65] For these experiments, three methods were tested for the purpose of combining the gel with TSC to evaluate their working properties:

- **Method 1:** Mix a solution of TSC in de-ionised (DI) water before adding the gel powder to create a gel
- **Method 2:** Mix the gel until it has almost thickened to working consistency, then add TSC
- **Method 3:** Making a w/w ratio of gel:TSC (Potter's method, above) through weighing the solid ingredients and mixing the two together

Table 4: Testing methods to combine TSC with Laponite and MC

LAPONITE *Lap = Laponite			
Method	**Quantities tested**	**Observations**	**Image of gel after mixing**
1	2.5% w/v TSC 10g Lap powder (10% w/v Lap in solution)	Add Lap powder to TSC solution. Milky and cloudy after ten mins stirring. Gel would not form	
2	10% w/v Lap 2.5g TSC (2.5% w/v TSC in solution)	When Lap gel started to form and appear transparent, added TSC. Gel formed after 5 min stirring but still cloudy. Less viscous than 10% Lap with no TSC	

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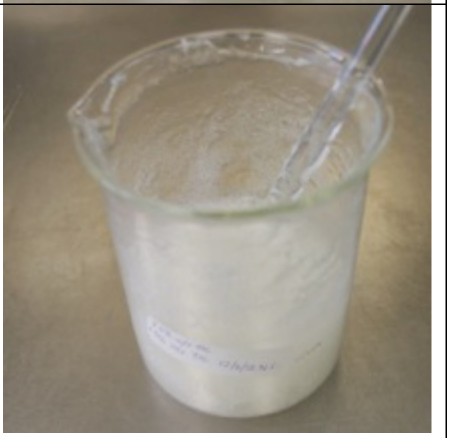
[65] J. E. Potter, *A New Method of Removing Rust Stains from Indian Chintz,* Masters Project Report, Royal College of Art/Victoria and Albert Museum, London, 1994, 90-91.

3	• 20g of 10% w/v Lap in DI water • 1g TSC	Added TSC to readymade 10% gel. Slightly runnier and cloudier, but not as cloudy as 2 and generally still felt like 10% Lap gel	
METHYLCELLULOSE			
1	• 5% w/v TSC • 7.5% w/v MC	As for method 1 Laponite	
2	• 7.5% w/v MC • 5% w/v TSC • 10% w/v MC • 5g TSC (5% w/v TSC in solution)	When MC gel started to form, 5g TSC was added. A gel formed, but less viscous than 7.5% MC alone. Cloudy with bubbles but granules dissolved well. 10% w/v MC gel tried instead. Thicker when adding TSC and like the 7.5% MC gel alone. Heated to break down lumps which helped, but caused the gel to separate, however it reformed when cool	

3	• 20g of 10% w/v MC in de-ionised water • 1g TSC	Added TSC granules to readymade 10% gel. Seemed to break gel to thinner consistency and remained cloudy	

5.2.1 Evaluation

This exercise has been useful to learn about the properties of the gels when mixing with another active agent. The TSC appeared to alter the consistency of the gel and caused it to break down, resulting in a cloudier gel across all three methods. As method 1 did not form either a Laponite or MC gel, it was eliminated from further testing.

Adding solid TSC to the readymade gel appeared to be the best solution (method 3), although it is uncertain whether any TSC granules had dissolved, or were simply suspended in the gel. Combining the gel and TSC midway seemed to help the granules to dissolve better (method 2), however the desirable working properties of the gel (transparency, viscosity) had certainly altered. Between methods 2 and 3, it is uncertain whether or not the TSC is more effective 'dissolved', as in method 2, or suspended in the gel, as in method 3, for which further investigation was required to ascertain its efficacy at stain removal.

5.3 Experiments to determine the effect of gel/tri-sodium citrate on cotton and silk

These series of experiments were designed to analyse the effect of using the combined Laponite/TSC and MC/TSC on undyed cotton lawn and heavy-weight silk habutai. The gels were monitored whilst applied to the fabrics, and the effects on the fabrics analysed through visual examination, microscopy and pH readings to determine how effectively the gels could be removed from the substrate following treatment.

Refer to Chapter 3.6-3.7 for methodology.

The following table summarises the variables for each fabric sample tested in this chapter, and introduces the sample codes, which are referred to in the tables of results for the testing later in the chapter.

Sample coding interpretation

Example 1

L-C-10-5-3
L=Laponite
C=Cotton
10=10% gel concentration
5=5% TSC concentration
3=Method of dissolving (3)

Table 5: Fabrics and gels tested

Experiment	**Sample code**	**Gel**	**Gel concentration (% w/v)**	**Fabric**	**TSC concentration (% w/v)**	**Method of dissolving (see 5.2)**
5.3.1	L-C-10	Lap	10	Cotton	N/A (control)	
	L-C-10-2.5				2.5	2
	L-C-10-5-3				5	3
	L-C-10-5-2				5	2
	L-S-10			Silk	N/A (control)	
	L-S-10-2.5				2.5	2
	L-S-10-5-3				5	3
	L-S-10-5-2				5	2
5.3.2	MC-7.5	MC	7.5	Cotton	N/A/ (control)	
	MC-7.5-5-2				5	2
	MC-7.5-5-3				5	3
	MC-10-5-2		10		5	2

5.3.1 Laponite and tri-sodium citrate on cotton and silk

Table 7: Results of testing Laponite/TSC on cotton and silk

Temperature: 20.2 degrees RH: 32%							
Sample	**Application observations**	**Approximate (~) spread in mm after application** - = no new observations D = drying observed					**Removal observations**
		5 min	10 min	10-30 min	30-45 min	45-60 min	
COTTON							
L-C-10	Fairly easy to apply, very thick but easy to limit to application area	~1	~4	-	-	-	Easy to remove in one scrape
L-C-10-2.5	More viscous than control, spreads quickly	~4	~7	-	D	-	As above, + RINGING
L-C-10-5-3	More like control to apply, stiffer and holds shape well	~1-3	~3-5	-	D	-	
L-C-10-5-2	Similar to L-C-10-2.5	~7	~10-12	-	D	-	
SILK							
L-S-10	Hard to apply gel to silk – sticky. No spread	-	~1	-	D	-	Appears to really saturate fabric, still sticky on surface after removal. RINGING
L-S-10-2.5	As above, 1mm spread immediately observed	~2	~2-3	-	D	-	
L-S-10-3		~0.5	-	-	D	-	
L-S-10-2		~2-3	~4	-	D	-	

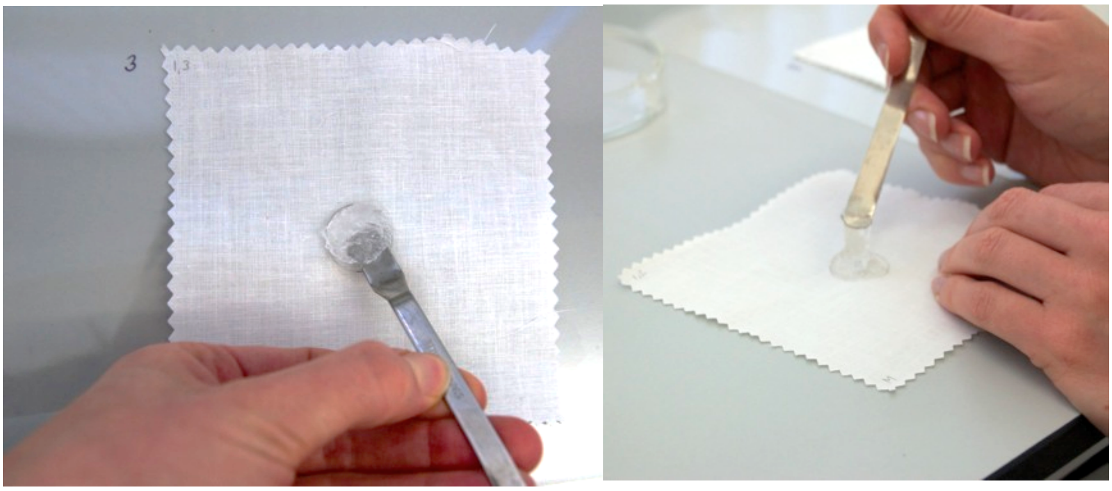


Fig. 9 Removing the gels with a spatula – the Laponite (left) was easier to remove than MC (right)

5.3.1.1 Experiments to reduce ringing

When the gels were rinsed from the cotton and silk and it had dried, ringing was detectable on all samples except the control (fig. 10). It appeared that adding TSC to the gel caused this issue, as the control gel was unaffected. Also, the colour of the Laponite/TSC gels were less transparent than Laponite gel alone, which could have contributed to this stained and ringed effect. If one was using the gels to treat staining on historic textiles, it would be undesirable to have ring marks left on the fabric following treatment, so a method to prevent this problem was sought.

Fig. 10 Ringing on cotton samples

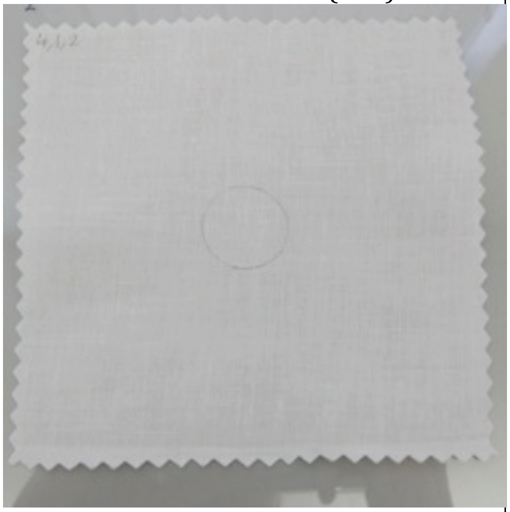
It was possible that the pencil line drawn on the fabric to define the treatment area was mobilised through contact with the gel, so this was investigated first. The following series of methods were designed to attempt to reduce ringing:

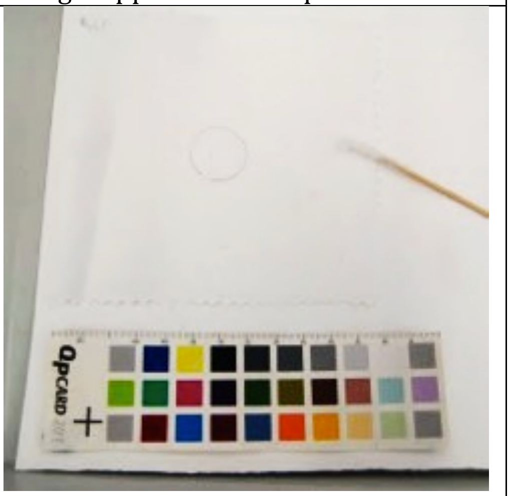
1. Using a pipette, drip a 5% w/v solution of TSC in DI water onto the pencil-marked fabric to discover if the TSC is mobilising the pencil
2. A Melinex® template featuring a hole cut to the one penny-sized treatment area was created, and the gel applied into the hole to negate the need to use pencil on the fabric

3. Using a cotton swab, clean the ring mark using 5% w/v solution TSC in DI water to see if it reduces the effect
4. As above, but clean the ring mark using DI water

The gel applied to the fabric contained 10% w/v Laponite and 5% TSC in DI water (dissolved using method 2). As before, the gel was left on the fabric samples for an hour before removal with a microspatula. The results were as follows:

Table 8: Results of experiments to reduce ringing

Temperature: 20.9 degrees RH: 39.1%			
Method	**Observations**	**Analysis**	**Images**
1	Pencil line did not mobilise	Pencil line does not appear to be causing ringing	 Above: The treated fabric (wet)  Dried fabric displaying no ringing or mobilisation of pencil line

2	Removed template immediately after applying gel to fabric. No more spread observed over whole experiment than applying gel to pencil-lined boundaries and was useful method for limiting gel to treatment area	Ringing still evident using this method of application	 Method of applying the gel with template  The gel applied and template removed
3	Swabbed with TSC when ringing was dry. Successfully removed ring mark	Swabbing reduces ringing after treatment	 Ringing removed through swabbing
4	Swabbed with DI water when ringing was dry. Successfully removed ring mark	Swabbing reduces ringing after treatment	As above

The silk stained much more heavily than the cotton fabric, and the samples were much stiffer. It was considered that allowing the silk samples to dry a little following rinsing of the gel could be causing the gel to become more 'ingrained' (fig. 11), so swabbing immediately versus leaving the fabric to dry was tested. The result for all variations was that some staining and ringing was removed (fig. 12), but considered generally unsuccessful, as the fabric is still inflexible and stained around the treated area.

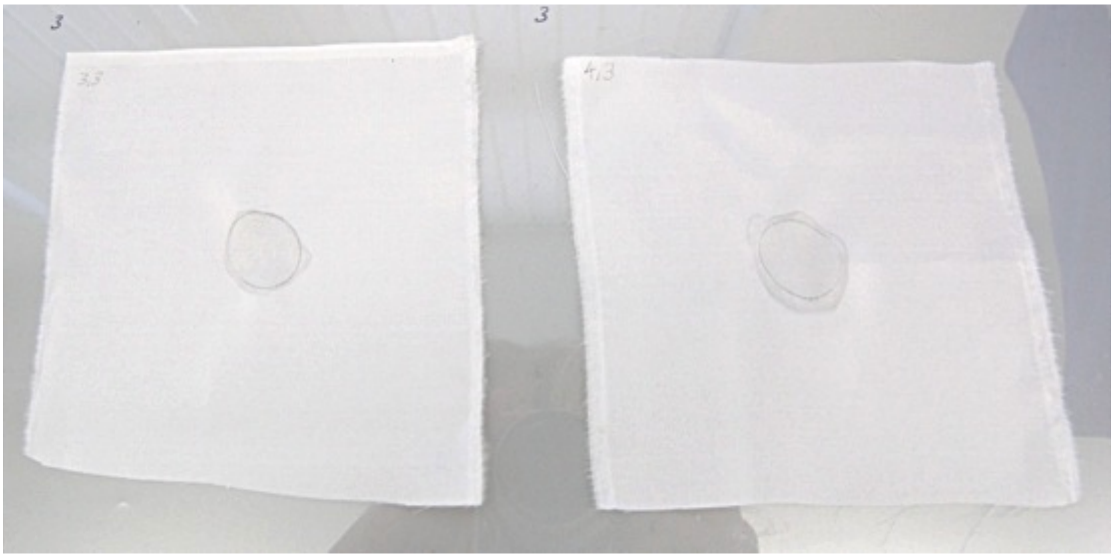


Fig. 11 Stained silk after treatment

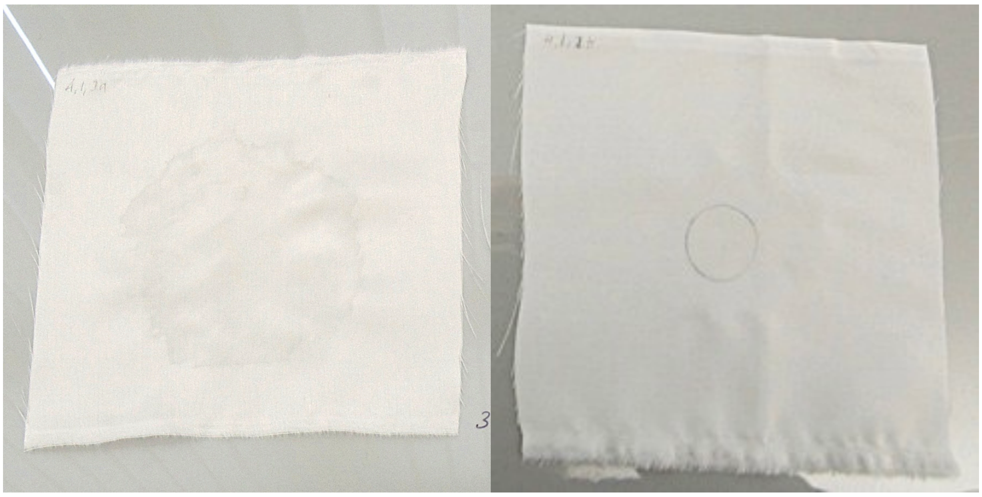


Fig. 12 Effects of reducing ringing on silk

5.3.1.2 Conclusion of reducing ringing

Based on these experiments, it appeared that the pencil lines from the treatment area were not causing the ringing, and the staining and ringing was potentially caused by the TSC dissolved in Laponite, which had discoloured the gel and fabric. Although ringing can be reduced on the cotton samples through swabbing the affected area using DI water alone (as well as with a 5% w/v TSC in DI water), this is not an ideal solution as it involves affecting an area outside the designated treatment boundaries; this could be undesirable if limiting the area of treatment was important on an historic textile.

Swabbing the ringing and staining on silk was generally unsuccessful, although it did reduce the intensity of the stain. If time constraints had allowed, methods to discover an effective barrier layer to reduce the amount of contact of the gel with the fabric would have been an option, although swabbing the cotton fabric is a useful compromise to alleviate this issue for the purpose of these experiments.

5.3.2 Methylcellulose and tri-sodium citrate on cotton

Following the experiments of MC on silk, it was decided that the heavy staining and difficulty rinsing resulted in the silk sample set being eliminated from further testing with TSC. Time constraints meant that refining the application and rinsing techniques were not possible. Therefore, the combinations described in Table 9 were tested on cotton samples only.

Table 9: Results of testing MC/TSC on cotton

Temperature: 22.5 degrees RH: 33.8%						
Sample	**Application observations**	**Approximate (~) spread in mm after application** - = no new observations x = no spread D = drying observed				**Removal observations**
		5 min	10 min	15-45 min	45-60 min	
MC-7.5	Sticky and hard to apply to treatment area. Holds shape well and is transparent and smooth	x	-	-	D	Hard to remove. Very sticky. Had to scrape fabric with spatula

MC-7.5-5-2	More fluid and easier to apply than MC-7.5	x	~1	-	D	Easier to remove than MC-7.5, but still irremovable in one scrape
MC-7.5-5-3	Like jelly, quite lumpy. Not all TSC dissolved but holds shape well	x	-	-	D	Much easier to remove than MC-7.5-5.2 comes off easily with few residues evident
MC-10-5-3	Similar to MC-7.5-5-3, but easier to work with and holds shape well. Lumpy and not all TSC dissolved	x	-	-	D	Easy to remove like MC-7.5-5-3, left some residues but blotchy pattern on fabric suggests insufficient saturation of gel

5.3.3 pH readings

The pH of the gels, untreated and treated fabrics tested in experiments 5.3.1 and 5.3.2 were taken using a flat tip pH electrode (Fisherbrand FB68797). When treating historical textiles, a neutral pH is recommended. Therefore, it is desirable for the treated areas of fabric to remain as close as possible to the pH of the untreated areas, and this method of analysis helped to discover whether the pH of the fabric altered following treatment. Three pH readings were taken at 15, 30 and 45 second intervals to provide an average overall reading (the pH reading fluctuated slightly between intervals). These were taken firstly on a region of untreated fabric, and then repeated on three different areas of the treated fabric after rinsing at the same time intervals, to provide an average pH reading for the treated fabric in case the rinsing of the gel from the sample was irregular. This exercise was repeated in its entirety for all three fabric samples in the set to gain a range of accurate measurements. The entire series of readings can be found in Appendix A.

Laponite

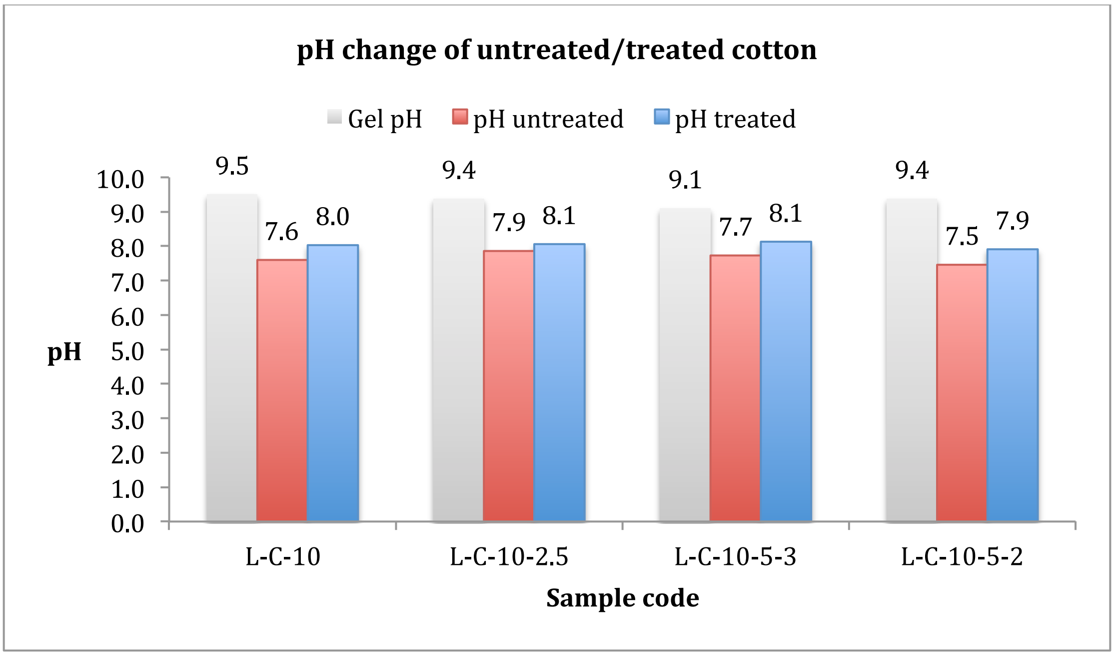


Fig. 13 pH readings for Laponite on cotton

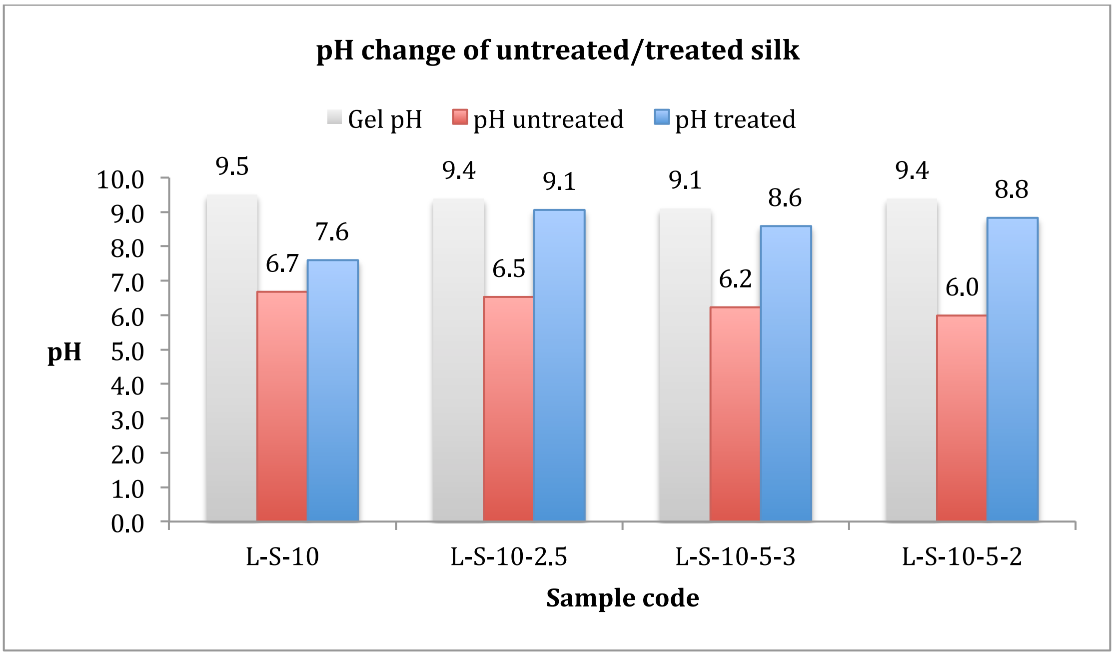


Fig. 14 pH readings for Laponite on silk

These readings demonstrated that Laponite was not completely rinsing out of the silk samples, hence the rise in pH of the treated fabric. Laponite gel is very alkaline, and the increase in alkalinity of the treated samples reflected this. This also corroborated with the observation that it is very difficult to effectively rinse the gel from the fabric. The deviation of pH readings for the treated and untreated areas of cotton was fairly minimal, indicating more effective rinsing, again as observed. The results for the cotton control were similar to the test samples, so in conclusion, there is no significant change in pH on cotton caused by the treatment.

Methylcellulose

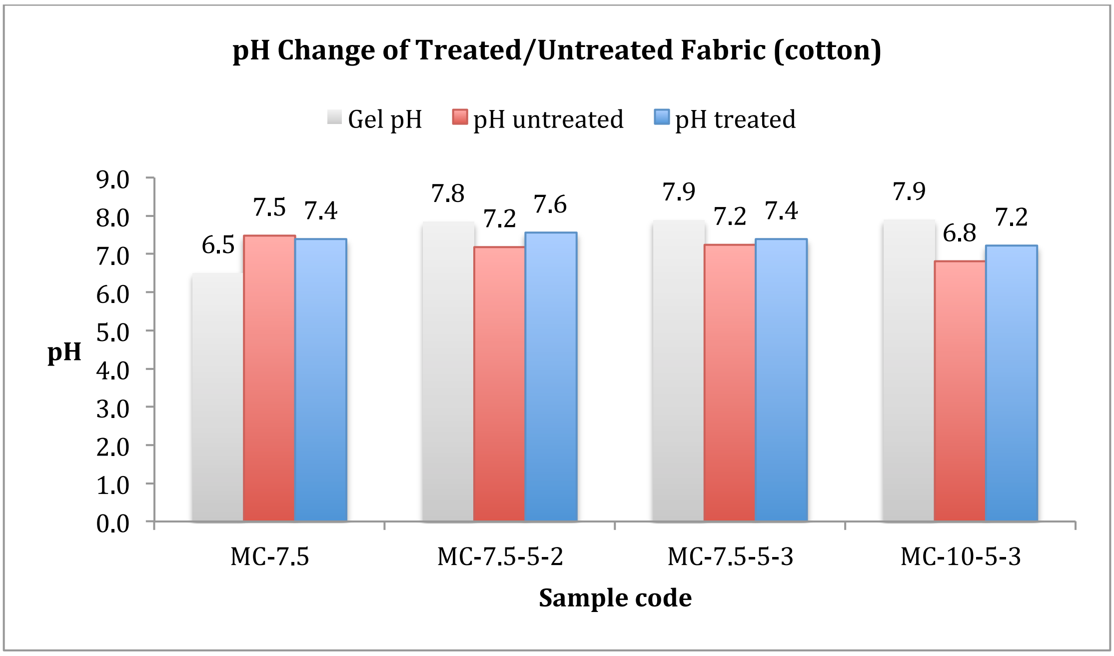


Fig. 15 pH readings for MC on cotton

The pH differences were relatively too small to be significant so the conclusion was there is no indication of a large amount of residue remaining on the fabric. Readings taken of 2.5% and 5% w/v TSC in DI water were both pH 8.2, indicating that the rise in pH of the MC gel was likely to be due to the addition of TSC. However, the pH of the treated areas was still lower than the pH of the gels, so rinsing had been fairly effective. Although gel residues are undesirable when treating historic textiles, the pH of the treated fabric was still around neutral.

5.3.4 Microscopic analysis

Laponite

The first fabric sample of three in the set was examined under 50x magnification using a stereomicroscope and at 500x magnification with a Dino-lite Digital Microscope Premier to obtain images of residues that may be evident on the fabric. Residues were detected for all cotton and silk samples, and all fabrics felt less flexible compared with the untreated samples. Less ringing and more flexibility was observed on sample L-10-5-3 where the solid TSC was mixed with Laponite at a 5% w/w ratio. This could indicate that it had penetrated the fabric less as the gel was generally felt to be more viscous than with the alternative method of dissolving the TSC into the Laponite (method 2).

Residues were evident between the interstices of the weave on all cotton samples as transparent bubbles, and appeared to sit more on the surface of all the silk, creating a stiff, inflexible layer (fig. 16).

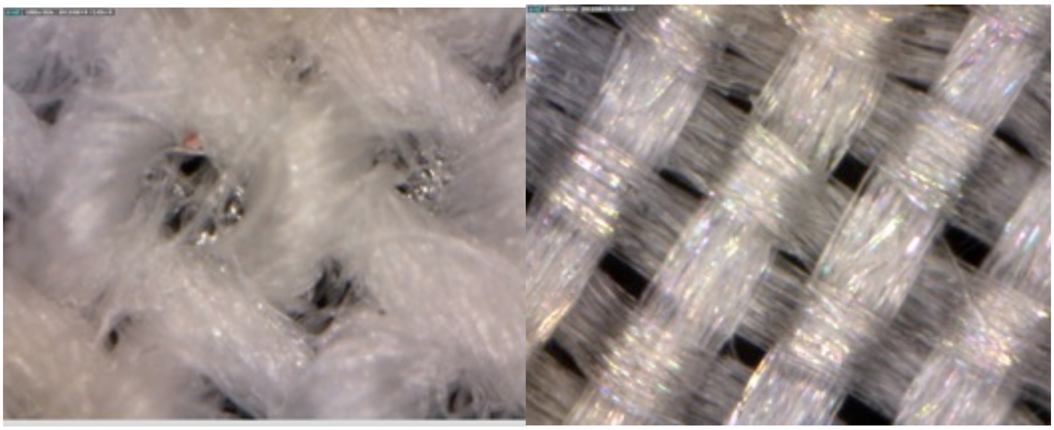


Fig. 16 Typical Laponite residues observed on cotton (left) and silk (right)

It was hard to remove these deposits effectively through the rinsing methods tested, and there was a concern that more aggressive rinsing techniques could damage the fibres. The fibres appeared unaffected by the selected rinsing method, as the untreated regions of fibres resembled the treated fibres with no physical disturbance to their structure. It is unknown what the long-term effects are of Laponite residues, which would require investigation if more analytical time was available.

Methylcellulose

The Dino-lite analysis clearly depicted residues between the interstices of the cotton weave for all samples (fig. 17). However, the fibres appeared undamaged and undisturbed, which was a concern due to the level of mechanical action required to try and remove as much MC from the samples during rinsing. MC did not appear to cause staining and discolouration on any samples, although it did cause each treated area of fabric to feel very inflexible, indicating the difficulty of rinsing the gel.

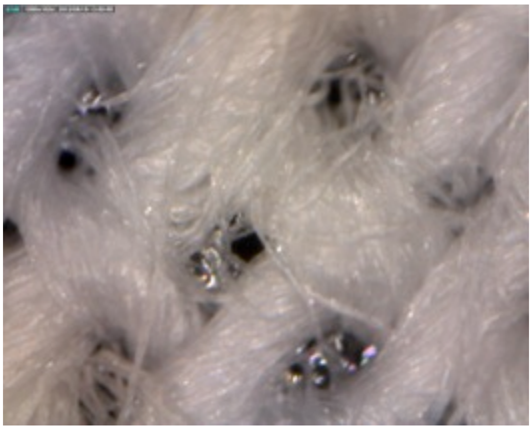


Fig. 17 Typical MC residues observed on cotton

5.3.5 SEM-EDX analysis[66]

The National Museum of Scotland's CamScan MX2500 SEM was used to examine the surface topography of the fabrics under x 10-100 magnification using Backscattered Imaging (BSC) to observe any fibre disturbance or residues invisible under lower magnification or visual analysis. Elemental analysis was undertaken with a Noran Vantage EDX system to display the individual elements present on the samples to help determine whether any gel residues remained on the fibres. SEM analysis was only available after the experiments were completed, so the results could not influence the choice of gel/TSC combination to put forward for testing in the next chapter. Therefore, one sample from set L-C-10-3 and MC-7.5-5-3 were examined, with the treated area compared with an untreated area – these were the two most successful gels used in chapter six. All SEM images not included in this report feature in Appendix C.

L-C-10-5-3

The BSC photomicrograph (figs. 18 & 19) depicted high levels of white residues that was likely to be Laponite/TSC gel between the interstices of the fabric. Likewise, the EDX graph (fig. 20, red graph line) shows increased levels of sodium, silicon, magnesium and potassium on the treated areas of fabric, supporting this theory that residues were remaining.

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[66] All images and results from SEM-EDX analysis were provided in the following document: L. Troalen, *Evaluation of poultice gels for the cleaning of silk and cotton fabrics: SEM-BSC Observation and EDX analysis,* Unpublished report, National Museum of Scotland, Edinburgh, 2012.

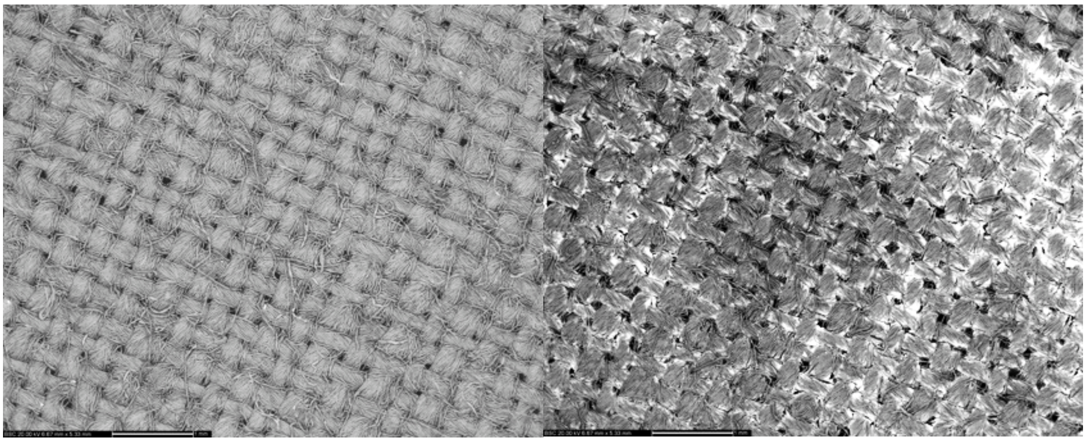

Fig. 18 BSC x 18 micrograph of untreated cotton (left) and cotton treated with Laponite/TSC (right)

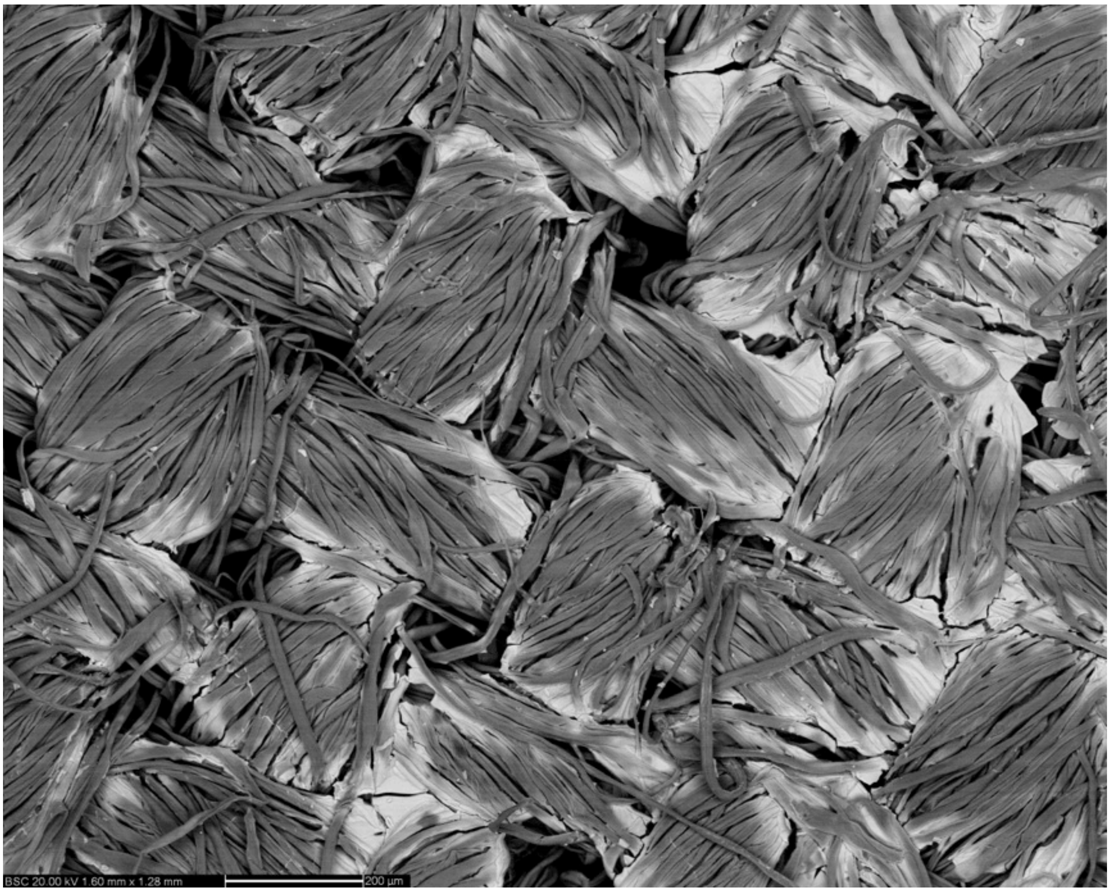

Fig. 19 BSC x 100 micrograph of cotton treated with Laponite/TSC

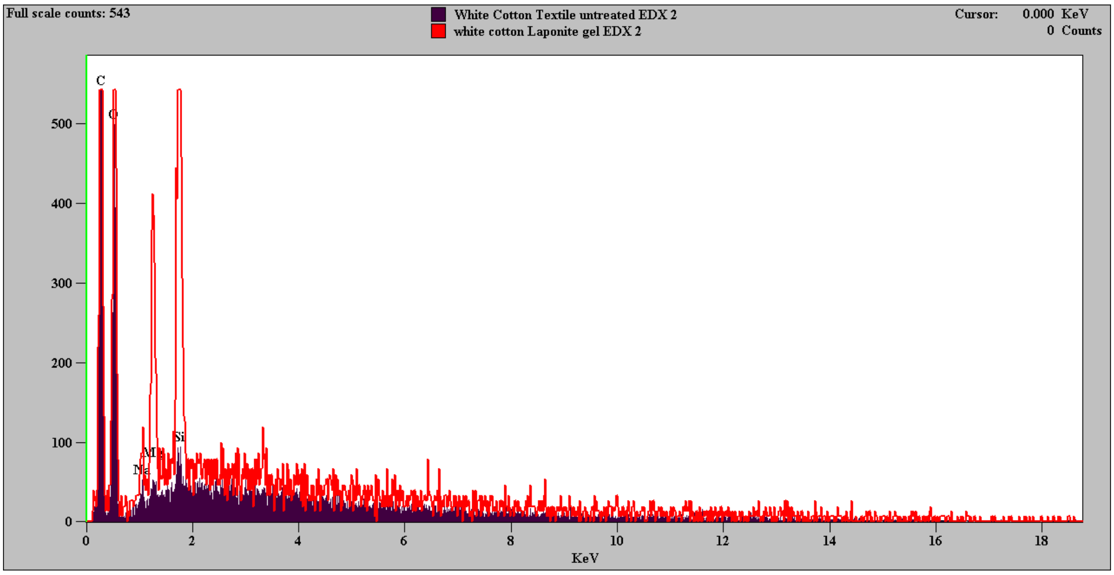

Fig. 20 EDX composition depicting untreated cotton (purple) and cotton treated with Laponite/TSC (red)

<u>MC-7.5-5-3</u>

A comparison of the BSC photomicrographs showed no distinction between the level of residues on the treated and untreated areas of the fabric, and no surface disturbance. This contrasted with the microscopy (5.3.4), which depicted residues between the interstices. It is possible that the MC gel did not saturate the entire treatment area, and the sample area examined with SEM contained no gel residues, rendering the results inconclusive. This is also reflected in the EDX graph, where only an increased level of aluminum is observed on the treated fabric. Cross-contamination could account for this rise in aluminum levels.

5.4 Conclusion to testing Laponite and methylcellulose on cotton and silk

The purpose of these experiments was to select a Laponite/TSC and MC/TSC combination to put forward for testing on the dyed fabric samples based on a subjective analysis of the working properties of the gel, pH readings before and after treatment, and microscopic examination. Subsequently, the following conclusions were made:

1. It was difficult to discern any obvious differences in working properties, pH readings and microscopic examination between any of the combined gels/TSC. Therefore it would appear that dissolving TSC with the gel midway through stirring (method 2), or adding it as a w/w ratio (method 3) did not appear to affect its properties as a gel. With this in mind, the two mixing methods cannot

be distinguished from one another in terms of effectiveness, so both methods were recommended for testing on dyed fabric samples.

2. Residues were evident between the interstices of the weave on cotton, and appeared to sit more on the surface of silk, creating a stiff, inflexible layer. It was hard to remove these deposits effectively through the rinsing methods tested, and there was a concern that more aggressive rinsing techniques could damage the fibres, which appear unaffected by the selected rinsing method. The conclusion is that the gels can be rinsed reasonably effectively from cotton, but less effectively from silk, and were therefore not recommended for silk. As these are new fabrics, further testing would be required on more fragile historical textiles in case of mechanical/chemical damage.
3. Ringing following rinsing of Laponite was an issue, more so on silk than cotton, where it could be reduced through using a cotton swab moistened in DI water. Staining and ringing may be less evident on coloured fabric, but an awareness of this effect of using the gels is important to note.
4. The pH readings demonstrated that both Laponite and MC gels were being rinsed fairly effectively from cotton. However, the high pH readings of Laponite on silk was a concern, and along with issues of ringing and effective rinsing, the technique of applying Laponite to silk needs much refining to make it as effective as on cotton.
5. Applying Laponite or MC gel to silk resulted in visibly detectable residues, and a stiff, inflexible and stained treated area of fabric. Combined with insufficient rinsing detectable through high pH readings of the treated area, it is not recommended that either treatment be used on silk.

Chapter Six

EVALUATION OF THE CHELATION ABILITIES OF TRI-SODIUM CITRATE IN LAPONITE AND METHYLCELLULOSE GELS

6.1 Introduction

The aim of this chapter is to describe a series of experiments that test the Laponite/tri-sodium citrate and methylcellulose/tri-sodium citrate gels selected in Chapter Five on coloured fabric samples, to determine their efficacy at chelation. Originally, fabric samples stained with copper were proposed, however this was unsuccessful (see Chapter Eight), so alternative coloured samples were sought, with the decisions behind the choice explained in this chapter.

Aims and objectives

- Determine the efficacy of using tri-sodium citrate (TSC) in solution on dyed fabric samples to chelate an alum mordant
- Determine the most effective Laponite/TSC and methylcellulose/TSC gel at chelation through testing on dyed fabric samples
- Analyse the efficacy of the selected gels at chelation using visual analysis, colourimetry, microscopy, and taking pH readings of the fabric to indicate whether any residues are left on the fabric following treatment

6.2 Choice of Fabric

Initially, these experiments had been designed so that the gels could be tested on copper-stained cotton and silk samples. However, due to the inefficacy of the researched copper staining method, an alternative was sought so that the gels could still be tested for their chelation abilities.

Dyed fabric that consisted of a mordant (which allows the dye to bind with the fabric) was proposed for a number of reasons. Firstly, the ability of TSC to chelate metals was important to test, so a dyed fabric mordanted with alum was selected. Alum is a chemical compound with the formula $KAl(SO_4)_2 \cdot 12H_2O$.[67] In the chelation series that specifies the ability of citrates to chelate with various metals (explained in Chapter 2.4), aluminum features after iron and copper, which illustrates its affinity to the aluminum ion. It was therefore predicted that applying TSC to an alum-mordanted fabric would allow chelation to occur with the aluminum within the mordant, thus loosening the dye from the fabric. Any resulting colour removal of the dye from the fabric from the treated areas would also facilitate visual analysis of the gels' abilities to prove effective at chelation. The dyed fabric samples were generously provided by National Museums Scotland, obtained from their 'Monitoring of damage to historic tapestries' (MODHT) project, where the samples were dyed using traditional recipes from the sixteenth century.[68]

6.3 Experiments to test the chelation abilities of tri-sodium citrate

It was judicious to test the chelation abilities of TSC on the dyed samples to determine whether it was effective at removing colour from the samples, before testing it in a gel formulation. It was predicted that colour removal would be due to the TSC chelating with the aluminum in the alum mordant, thus loosening the dye from the fabric. Six fabric samples were selected: three silk and three wool, to determine if there was any difference in chelation between the fibre types. These were immersed in three beakers containing different solutions. Simultaneously, the three solutions were also pipetted three times onto six different fabric samples to determine whether this method of application produced any colour removal from the regions treated with the pipette. The results were recorded at five minute intervals for the duration of one hour. The following table summarises the variables for each fabric sample tested in this experiment.

Sample coding interpretation

Example 1
S-2.5-I
S=Silk

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[67] Encyclopaedia Britannica, *Alum,* Encyclopaedia Britannica *http://www.britannica.com/EBchecked/topic/17885/alum* (accessed 29th August 2012).

[68] Historic Royal Palaces, *Monitoring of damage to historic tapestries,* Historic Royal Palaces, http://www.hrp.org.uk/aboutus/whatwedo/collectionscare/monitoringthedamagetohistorictapestries (accessed 29th August 2012).

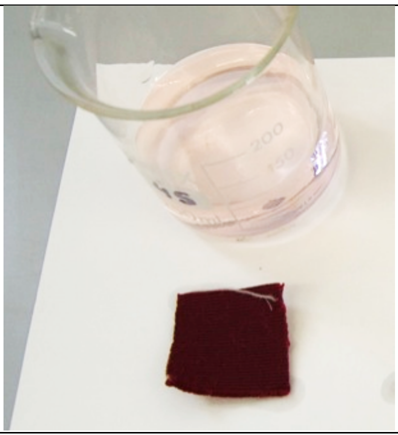
2.5=2.5% concentration TSC

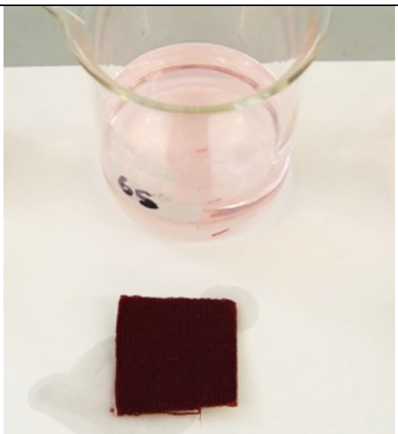
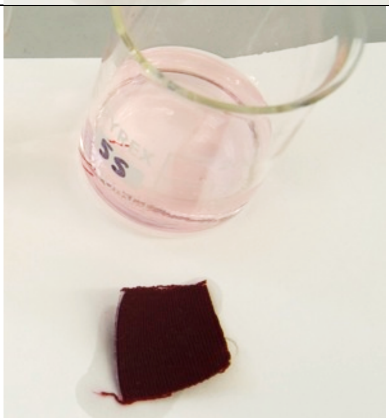
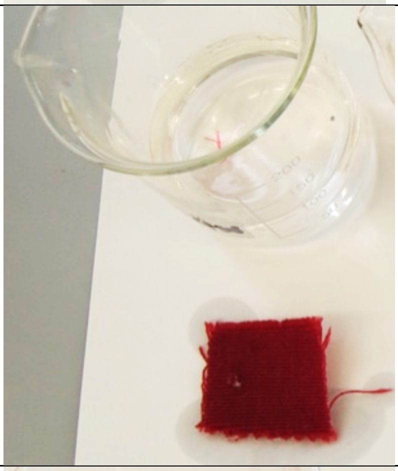
I=Immersion

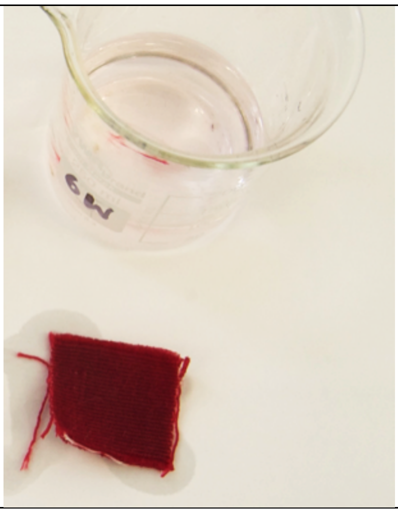
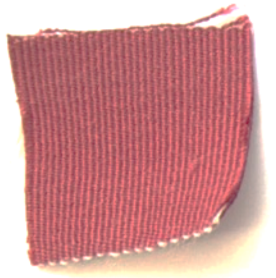
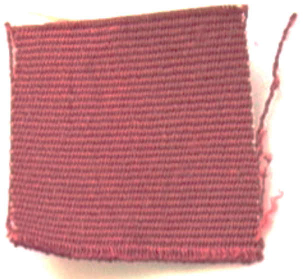
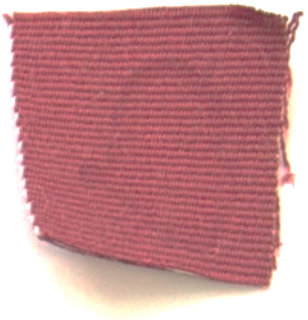
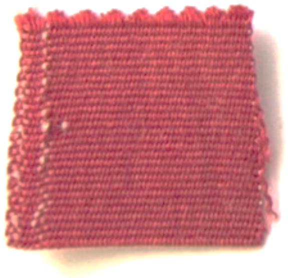
Table 10: Fabrics and concentrations tested

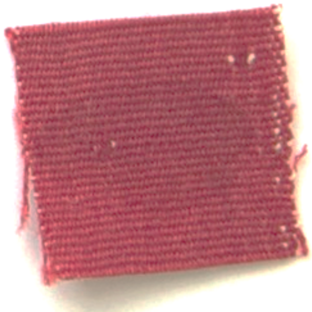
Experiment	**Sample code**	**Fabric & dye**	**TSC concentration (% w/v)**	**Method of application**
6.3	S-I	Silk – weld and woad	N/A (control)	Immersion
	S-2.5-I		2.5	
	S-5-I		5	
	W-I	Wool – weld and woad	N/A (control)	
	W-2.5-I		2.5	
	W-5-I		5	
	S-P	Silk – weld and woad	N/A (control)	Pipette
	S-2.5-P		2.5	
	S-5-P		5	
	W-P	Wool – weld and woad	N/A (control)	
	W-2.5-P		2.5	
	W-5-P		5	

Table 11: Results of experiments to test chelation abilities of TSC

Sample	**Observations** x = no colour removal detected in beaker			**Images of samples after 60 min**
	5-30 min	**30-45 min**	**45-60 min**	
S-I	x	40 min: some colour detected in beaker	Least colour removed of all three	

S-2.5-I		30 min: slight colour removal	More colour removal than S-I	
S-5-I			Most colour removal	
W-I	x	x	x	
W-2.5-I			Most colour removal	

W-5-I			Slight colour removal	
S-P	x	x	x	
S-2.5-P			50 min: Slight colour loss and ringing	
S-5-P			50 min: Slight colour loss and more ringing than S-2.5-P	
W-P	x	x	x	

W-2.5-P			50 min: Slight colour loss and ringing	
W-5-P			50 min: Slight colour loss and more ringing than W-2.5-P	

6.3.1 Experiment conclusions

The amount of colour bleed detected in the beakers from the samples immersed in TSC solution indicated that it did appear to have some effect on loosening the dye from the fabric, compared with the samples immersed in de-ionised water alone. However, colour loss was also detected in the control beakers with no TSC, so it cannot be clear whether water alone was causing the dye to wash out of the fabric. The wool samples displayed much less colour loss; this could be due to the affinity of the dye to the amorphous nature of wool, plus silk is harder to dye than wool so it is possible it is harder to fix the dye to the fabric. The pipetted samples presented the least colour change, but some loss of colour was observed on those treated with TSC, and not on those treated with de-ionised water for both silk and wool. The outcome of this experiment has therefore produced the following conclusions:

1. TSC appeared to have some effect on loosening the dye, so further experiments were undertaken using it in the gel to determine its efficacy in this medium
2. There does not appear to be a marked difference between the chelation abilities of 2.5% and 5% w/v TSC
3. Silk was used for testing the gels over wool, as it presented the most visually detectable results for colour change

4. It was important to test the gels/TSC with a control gel with no TSC to obtain an objective result, as it appeared that water alone was affecting colour loss

6.4 Experiments to test gel/tri-sodium citrate combinations

The aim of these experiments was to test the series of gels used during the testing on unstained fabric (Chapter Five) to determine which Laponite/TSC and MC/TSC gel is most effective at chelation. As there was little difference between the working properties of the gels tested (see Chapter 5.4), or a marked difference between the effect of 2.5% or 5% w/v TSC (see Chapter 6.3.1), a number of gels were put forward for testing to determine their efficacy and ultimately, select the most effective from the range for Laponite and also for MC. The ten selected gels all featured variations of the concentration of TSC and the method of combining the TSC into the gel, as described in Chapter 5.2).

Sample coding interpretation

Example 1
MC-7.5-5-3
MC=Methylcellulose
7.5=7.5% concentration of gel
5=5% concentration of TSC
3=Method of dissolving (explained in Chapter 5.2)

Table 12: Fabrics, gels and concentrations tested

Experiment	Sample code	Fabric & dye	Gel	Gel concentration (% w/v)	TSC concentration (% w/v)	Method of dissolving (see 5.2)
6.4	L-10	Silk: green weld and woad & alum mord-	Lap	10	N/A (control)	
	MC-7.5		MC	7.5		
	L-10-5-3		Lap	10	5	3
	MC-7.5-5-3		MC	7.5		
	L-10-2.5-3		Lap	10	2.5	
	MC-7.5-2.5-3		MC	7.5		

	L-10-5-2	ant	Lap	10	5	2
	MC-7.5-5-2		MC	7.5		
	L-10-2.5-2		Lap	10	2.5	
	MC-10-2.5-2		MC	7.5		

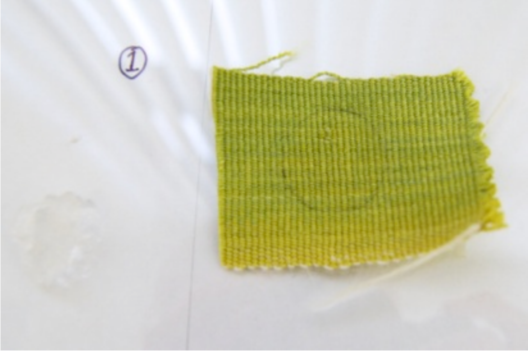
Due to the small size of the fabric samples provided, and the large number of gels to test, only one sample of fabric per set was available for testing to ensure that all samples could be tested on the same swatch of fabric for consistency. As these were considered to be preliminary experiments to determine the optimum Laponite/TSC and MC/TSC gel from the range available, the intention was to repeat the tests again for more rigorous analysis on larger sample sizes and on more samples per set for a more effective comparision of results. For this reason, a subjective visual analysis of the samples was undertaken.

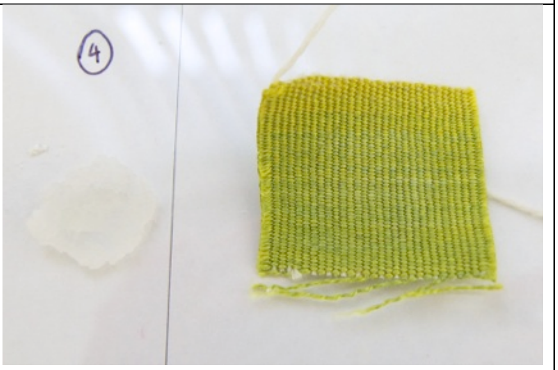
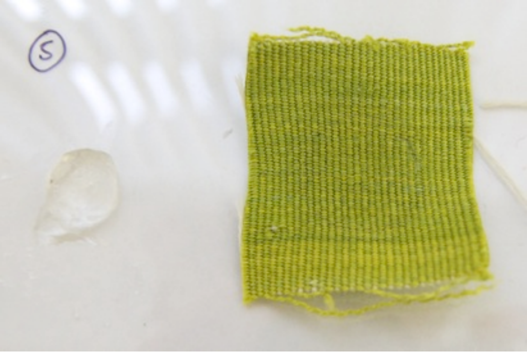
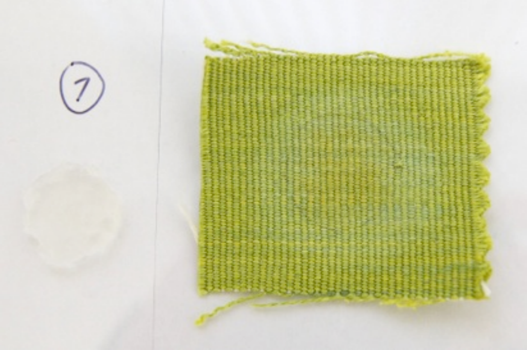
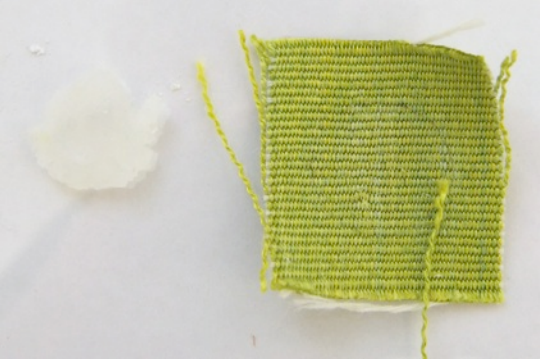
Refer to Chapter 3.6-3.7 for methodology.

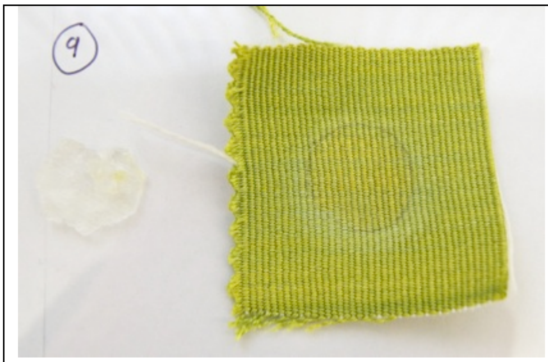
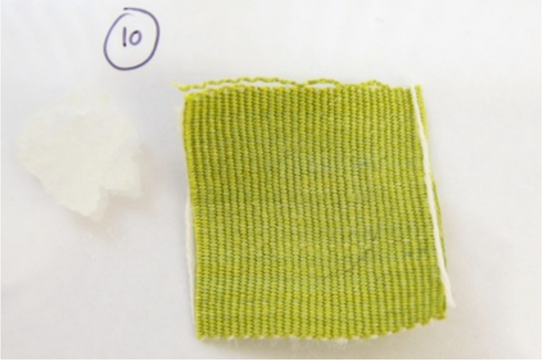
6.4.1 Evaluation

It became evident after an hour that no visible difference in colour had been observed between the treated and untreated areas, although the samples had all started to dry after twenty-five minutes. It was decided that leaving the samples for a further hour would be advantageous, to examine the effects. The samples were covered with a petri dish to prevent further drying. After two hours, the gels were removed with a microspatula and rinsed with a cotton swab dipped in de-ionised water. The samples were retained for visual and microscopic analysis, to compare the efficacy of the gels.

Table 13: Photos of gels and fabrics after two hours of treatment

L-10	**M-7.5**
	

L-10-5-3	**MC-7.5-5-3**
	
L-10-2.5-3	**MC-7.5-2.5-3**
	
L-10-5-2	**MC-7.5-5-2**
	
L-10-2.5-2	**MC-10-2.5-2**

A subjective visual analysis of colour removal from the samples revealed that no gels greatly outperformed the others in terms of their chelation abilities. Generally, all the gels were still the same transparency on application once removed, with only a couple (MC-7.5-5-2 & MC-7.5-2.5-2) displaying a slight green tinge. Some caused staining with a halo effect around the treated area (L-10-5, L-10-5-3 & L-10-2.5-3); this only became apparent following rinsing indicating that the technique was potentially spreading the Laponite gel beyond the treatment boundaries and not thoroughly removing it. This was not an issue for MC and no ringing was detected. Samples L-10-5, MC-7.5-5-2 & MC-7.5-2.5-2 retained their flexibility.

6.4.2 Conclusion

These experiments were designed to select the most effective Laponite/TSC and MC/TSC gel at chelation to put forward for final testing and analysis on dyed fabric samples. It appeared that the method of dissolving TSC into the gel did not affect its chelation abilities as no gels were particularly effective at chelation; likewise, it was not possible to differentiate between a 2.5% or 5% concentration of TSC. Therefore, the decision to select the most effective gel formulations at chelation was based on the working properties of the gels in described in Chapter Five, and any discernible stain removal observed in these experiments. Therefore, the following Laponite and MC combinations were selected:

- (L-10-5-3) 5% w/w TSC in 10% w/v Laponite in de-ionised water
- (MC-7.5-5-3) 5% w/w TSC in 7.5% w/v MC in de-ionised water

6.5 Final experiments with chosen gels

The aim of these experiments was to test the chosen Laponite and MC gels on dyed fabric samples for the purpose of more rigorous scientific analysis using microscopy, pH testing, colourimeter readings, and SEM (scanning electron microscope) to examine their working properties and chelation abilities. Although it is advisable to test on at least three samples per set, due to the limited dyed fabric samples available these tests were repeated on two samples per set, with the control MC and Laponite gels with no TSC tested on a single alternative dyed sample, due to fabric limitations. Both fabric swatches used an alum mordant, and were of a similar weave and colour.

Methodology

A larger test area the size of a two-penny coin (53.1mm^2) was used to allow the Chromameter head to fit onto the test area three times. The amount of gel was increased proportionately to 1.95g per sample based on the amounts tested in the previous experiments. Based on experiences from the earlier experiments, the gels were covered with a petri dish to prevent drying, and were left for two hours, which was the amount of time required for the gels to have an impact on colour removal as discovered above. The gels were applied using the Melinex® template method described in Chapter 3.7; this was to prevent drawing onto the fabric where the colour of the pencil line could adversely influence the Chromameter readings.

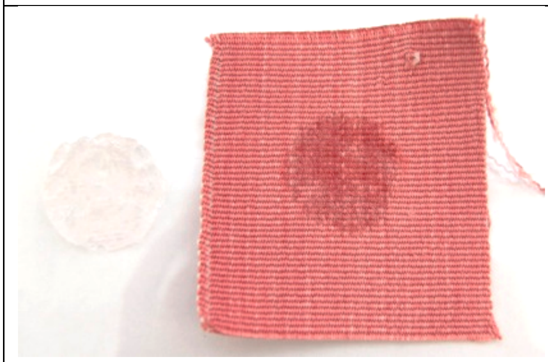
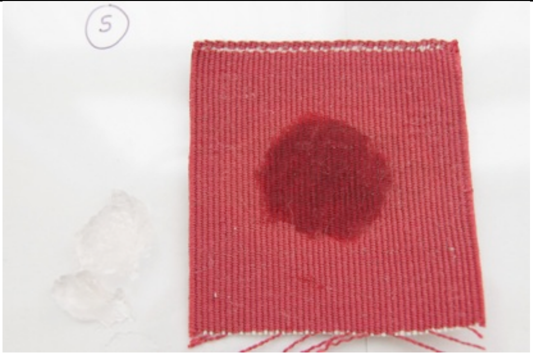
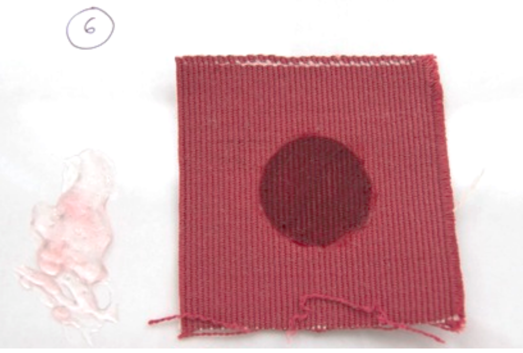
The following gel combinations were tested:

Table 14: Fabrics, gels and concentrations tested

Experiment	Sample code	Fabric & dye	Gel	Gel concentration (% w/v)	TSC concentration (% w/v)	Method of dissolving (see 5.2)
6.5	L-10-5	Silk: Madder & Lye (alum)	Lap	10	5	3
	MC-7.5-5		MC	7.5		
	L-10	Silk: Cochineal (alum)	Lap	10	N/A (control)	
	MC-7.5		MC	7.5		

The gels were applied and removed with a microspatula, and then rinsed using a cotton swab dipped in de-ionised water.

Table 15: Photos of gels and fabrics after two hours of treatment

L-10-5	**MC-7.5-5**
	
L-10	**MC-7.5**
	

6.5.1 Visual analysis

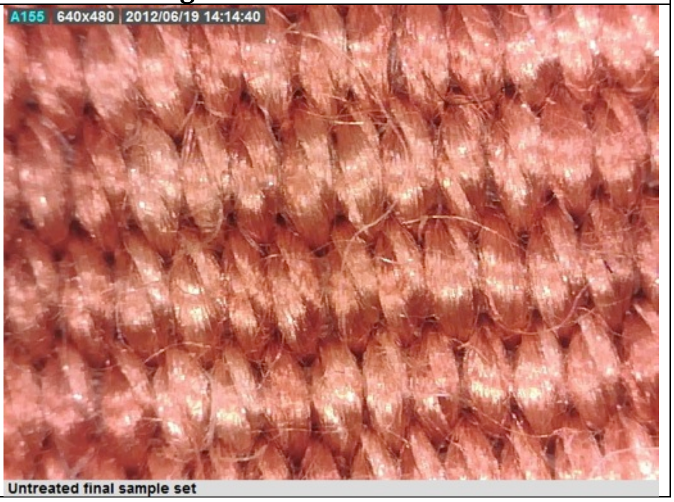
A subjective visual analysis was performed on each sample to judge colour change and examine the effect of the gels on the fabric. All samples appeared to show some slight colour removal, however, the two control gels also appeared to affect colour removal, with MC-7.5 visibly pink-tinged. Rinsing the gels with cotton swabs displayed colour transfer on the swabs themselves (fig. 21); this result, along with the removal of colour from the control gels, which indicated that de-ionised water could be responsible for colour removal. MC-7.5-5 was the least flexible after treatment, and displayed the most residues on visual examination. The other samples all retained their flexibility and displayed fewer residues.

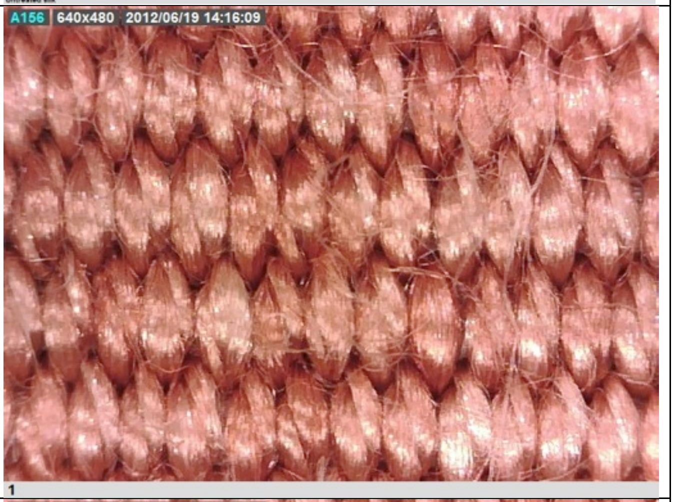
Fig. 21 The pink-tinged cotton swabs used to remove the gel

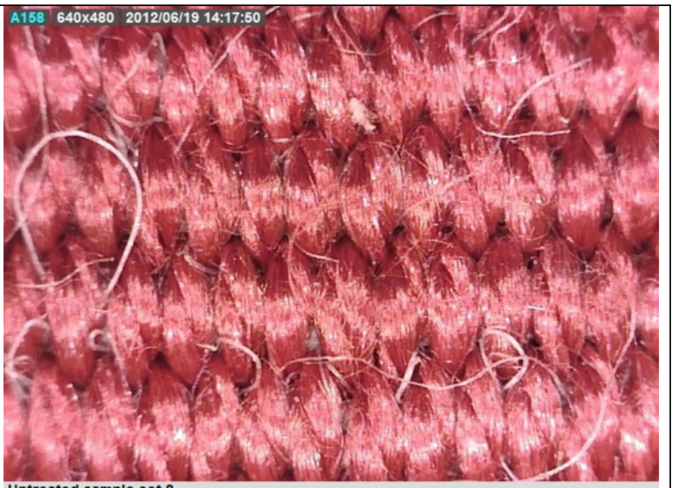
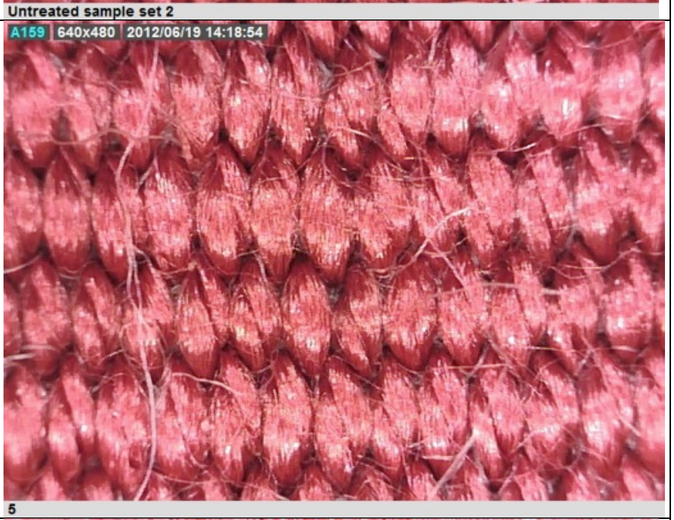
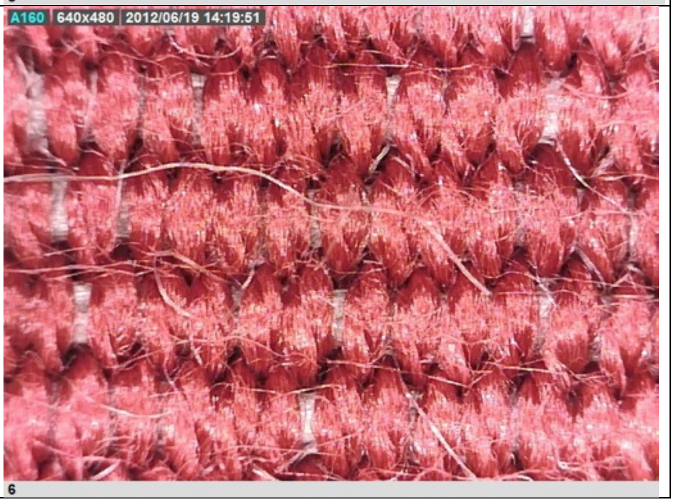
6.5.2 Microscopic analysis

One sample per set was examined under the Dino-lite at 200 x magnification. Images of untreated areas from samples L-10-5 and L-10 were used to compare with the treated areas, however none of the images were particularly revealing concerning any residues left on the fabric.

Table 16: Observations of microscopy of dyed fabric samples

Sample	Observations	Dino-lite images
Untreated silk: Madder & Lye	Small crystals between interstices (indicated by blue arrow) – could be deposits from dye process. Evident on treated and untreated areas – not to be confused with gel deposits.	

		
L-10-5	Crystals – see above. Fibre disturbance appeared minimal. Minimal residues observed.	
MC-7.5-5	Fibre disturbance more evident as horizontal streaks of fibres. Residues appear as whiteish film over fibres.	

Untreated silk: Cochineal	Small crystals between interstices – could be deposits from dye process. Evident on treated and untreated areas – not to be confused with gel deposits.	
L-10	No obvious residues observed. No fibre disturbance.	
MC-7.5	Staining from gel apparent. Residues clearly coated surface of fibres as white film. Fibre disturbance visible as horizontal streaks of fibres.	

6.5.3 pH testing

Refer to Chapter 5.3.3 for methodology

Each gel combination used in these experiments was tested to determine the pH of the gel, and the average pH of the fabric the gel was applied to, before and after treatment.

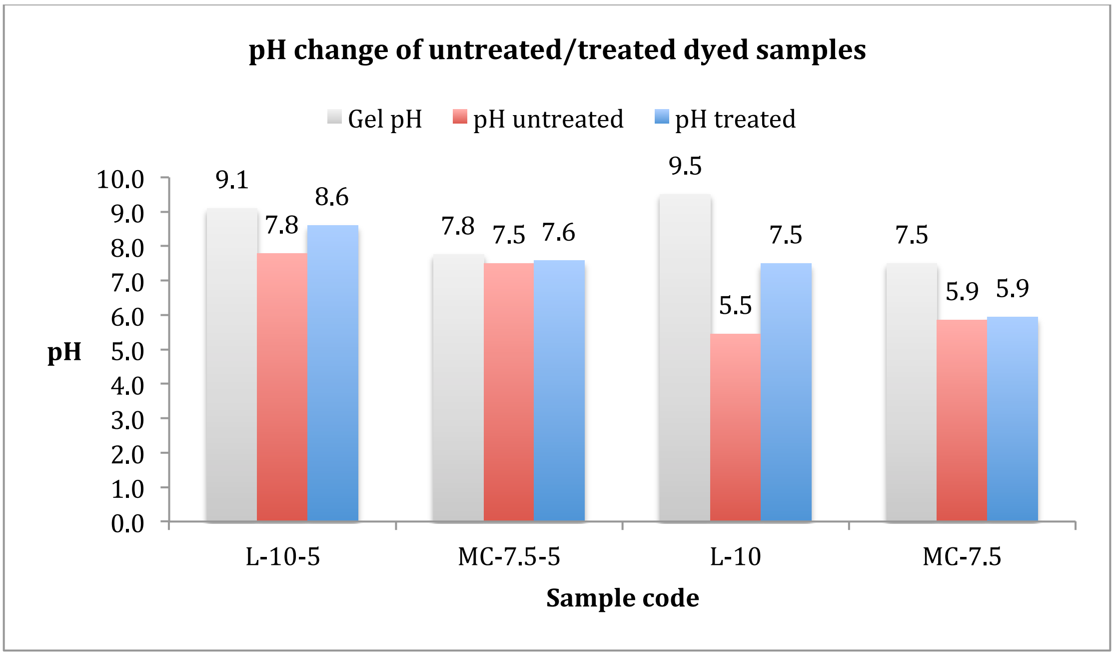


Fig. 22 pH readings for Laponite/TSC and MC/TSC on dyed silk samples

The pH of L-10-5 was closer to alkaline than neutral pH, which could be undesirable for historic textiles, whereas samples from MC-7.5-5 were closer to neutral pH. It is possible that the minimal change in pH of the MC gels was due to insufficient saturation on the fabric, which correlated with images of the patchy regions of fabric once the gel was removed as shown in Chapter 6.5, potentially accounting for the low deviation in pH between the treated and untreated areas.

6.5.4 Chromameter readings

A Minolta CR-210 Chromameter was used to measure whether there was any colour change between the treated and untreated areas of the samples to indicate that the gels were removing dye. This is a more objective method than visual analysis, where the chromameter uses the L*a*b* colour space system to record colour lightness (L*), how red (a* +) or green the colour is (a* -) and how yellow (b* +) or blue the colour is (b* -). Higher L* value indicate paler colour, and higher a* + and b* + values indicate more saturated colour.[69] For each fabric sample, three readings were taken from three different spots on the fabric before and after treatment. To ensure that the same area of fabric was being recorded before and after treatment, a Melinex® template cut to the

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[69] Minolta Camera Co., Ltd, *Precise Color Communication. Color Control from Feeling to Instrumentation* (Osaka: Minolta Camera Co., Ltd, 1993), 18.

size of the sample featuring tracings of the Chromameter head facilitated the exact positioning of the Chromameter (fig. 23). The graphs represent the average L*, a* + and b* + readings of each sample in a set.

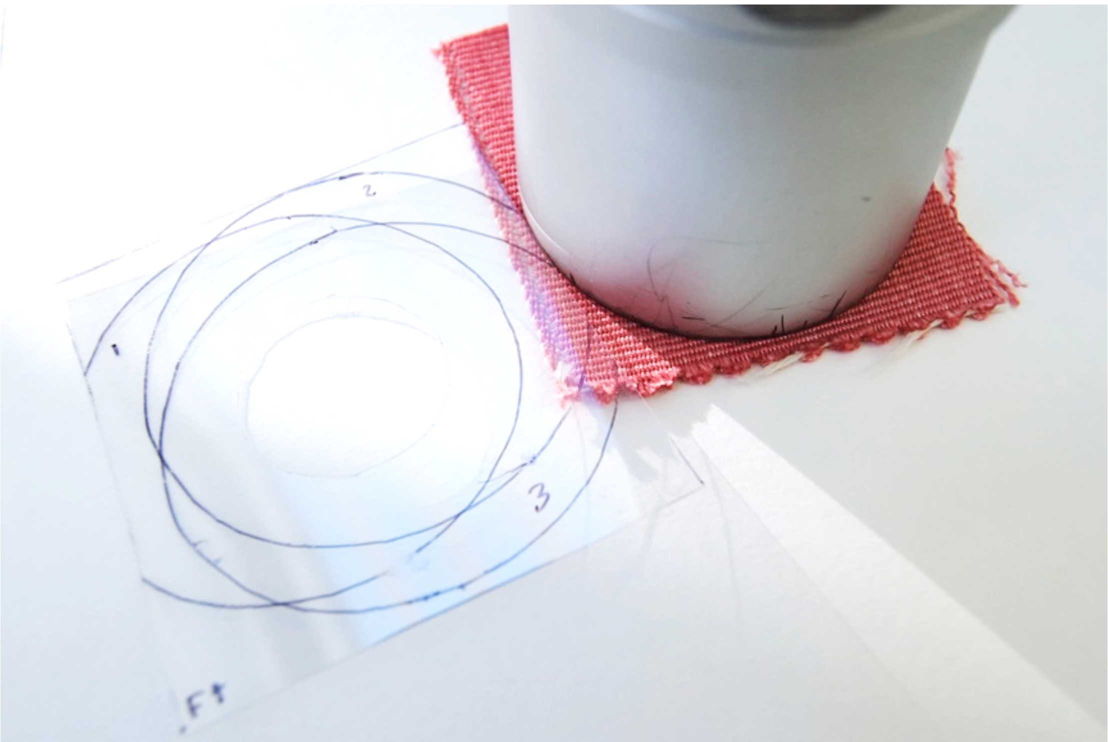

Fig. 23 Melinex® template to facilitate measuring with chromameter

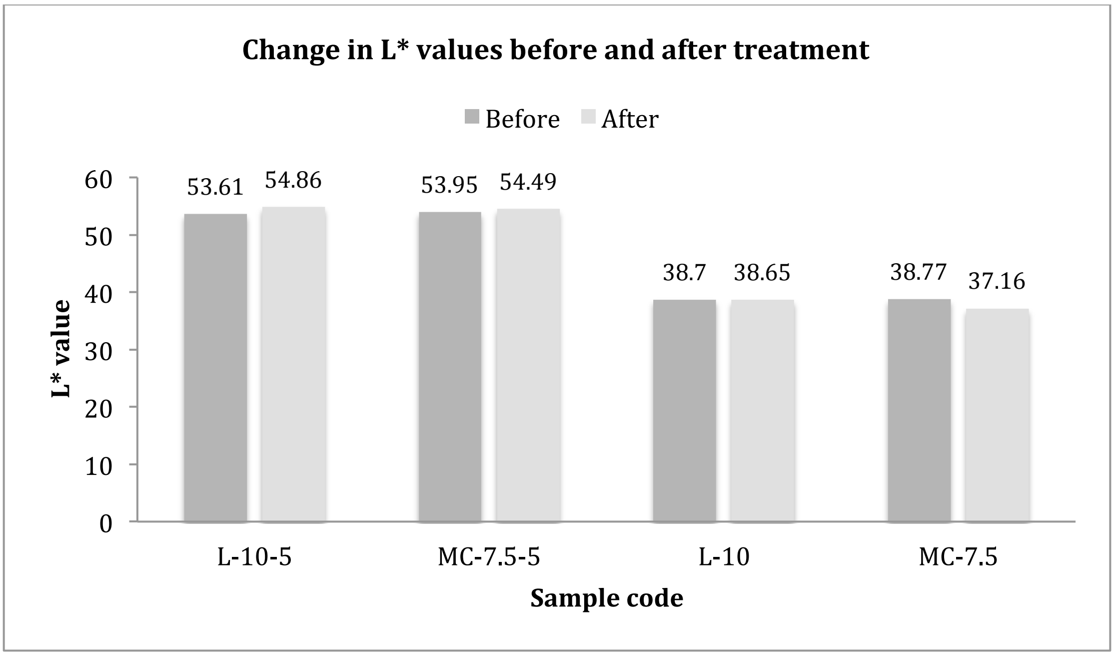

Fig. 24 Change in L* values before and after treatment

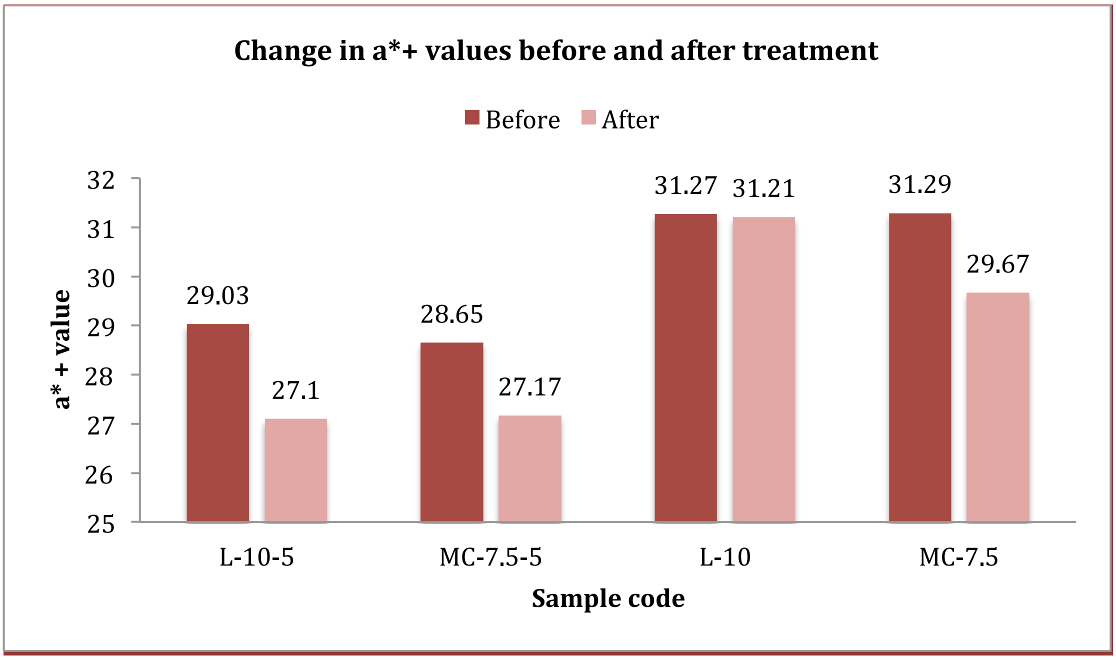

Fig. 25 Change in a* + values before and after treatment

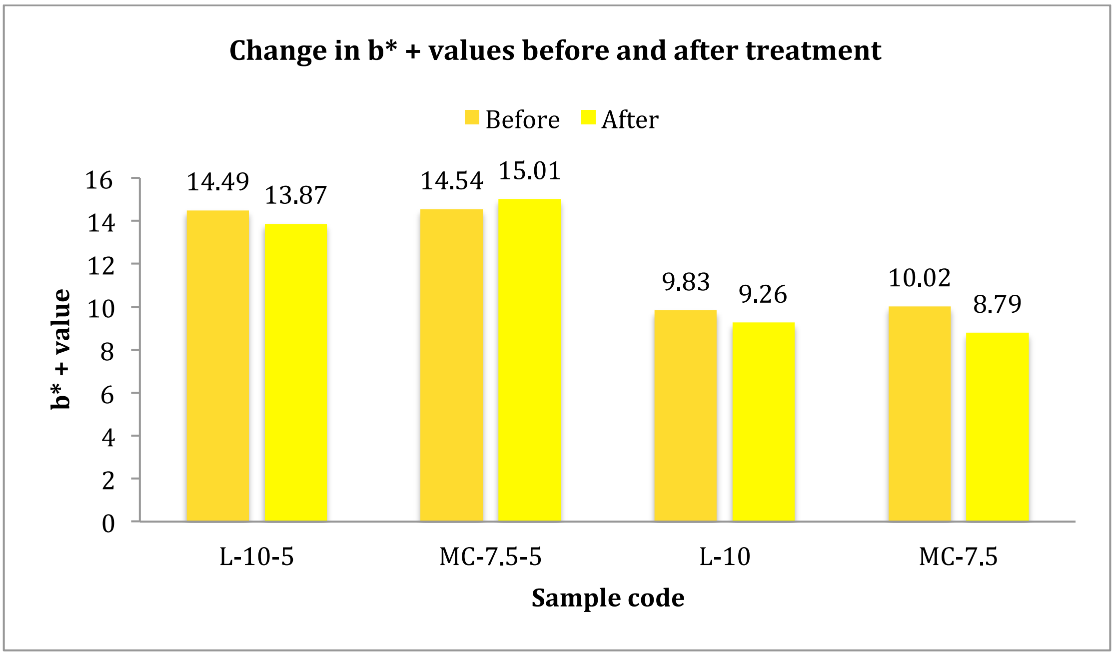

Fig. 26 Change in b* + values before and after treatment

There was a very slight change in lightness values for the samples treated with TSC. The higher readings after treatment indicated that the fabric had become lighter. Likewise, the a*+ readings had reduced slightly following treatment indicating that the colour had become less saturated. Both treated fabrics displayed contradictory results for b* + values: one was slightly more saturated, one slightly less. This could be due to residues from the MC gel residing on the fabric after treatment, as the MC gel had a slight yellow tinge. These readings were not particularly revealing as the change in values are so slight, suggesting that the gels have only removed some colour. However, as the control gels (L-10 and MC-7.5) with no TSC had also displayed a change in L* a* b* values, it cannot be certain whether the TSC is having an effect on removing colour from the samples.

6.5.5 SEM-EDX analysis

SEM was used to examine the surface topography of the fabrics under very high magnification to observe any fibre disturbance or residues invisible under lower magnification or visual analysis. EDX analysis was used to identify the elements present in the fabrics. *Procedure described in Chapter 5.3.5.*

L-10-5

There were few differences between the treated and untreated samples (figs 27 & 28). Small residues were discernible on the treated fabric, and could be associated with the use of Laponite and TSC, as the elements present were sodium and magnesium (which feature in Laponite). It is unknown why there are high levels of calcium on both samples. The untreated sample displayed increased levels of aluminum compared with treated areas; this could suggest that some alum mordant had been removed with the chelating agent (fig. 29 – purple line on graph is untreated). Higher levels of silicon after treatment could indicate the presence of Laponite residues (Laponite consists of silicon). The surface disturbance was minimal comparing untreated and treated samples.

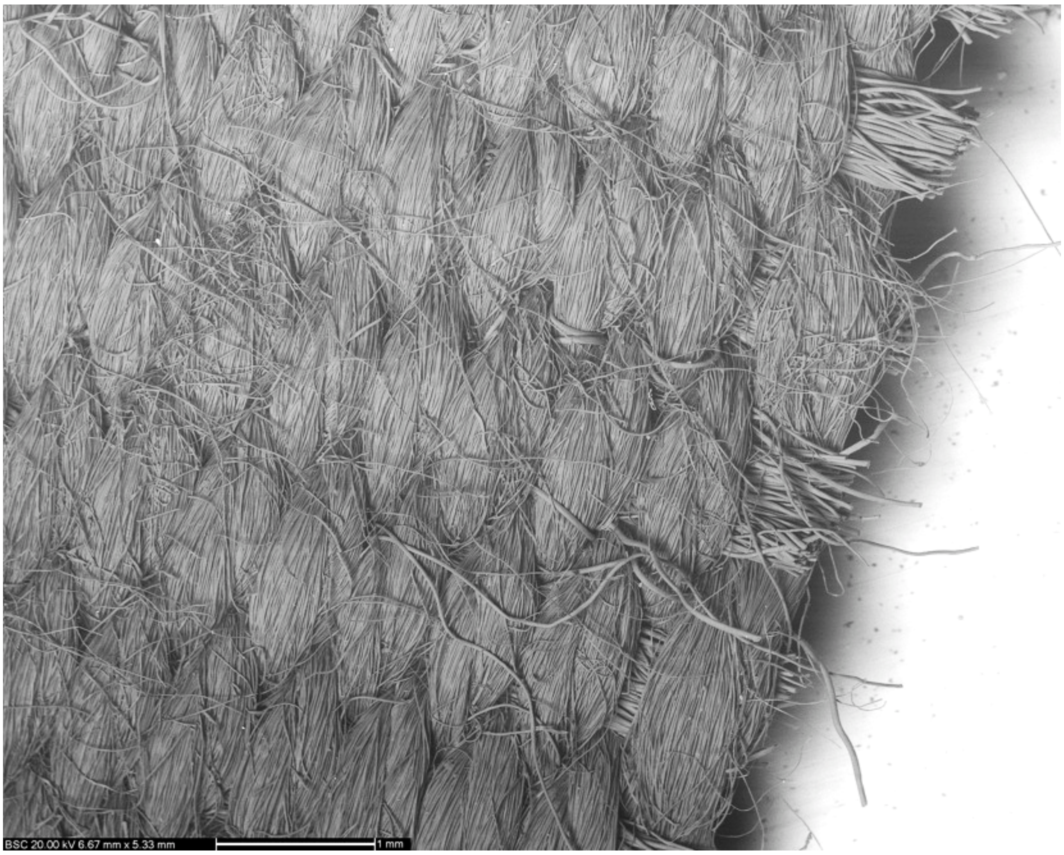

Fig. 27 BSC x 18 micrograph of untreated silk

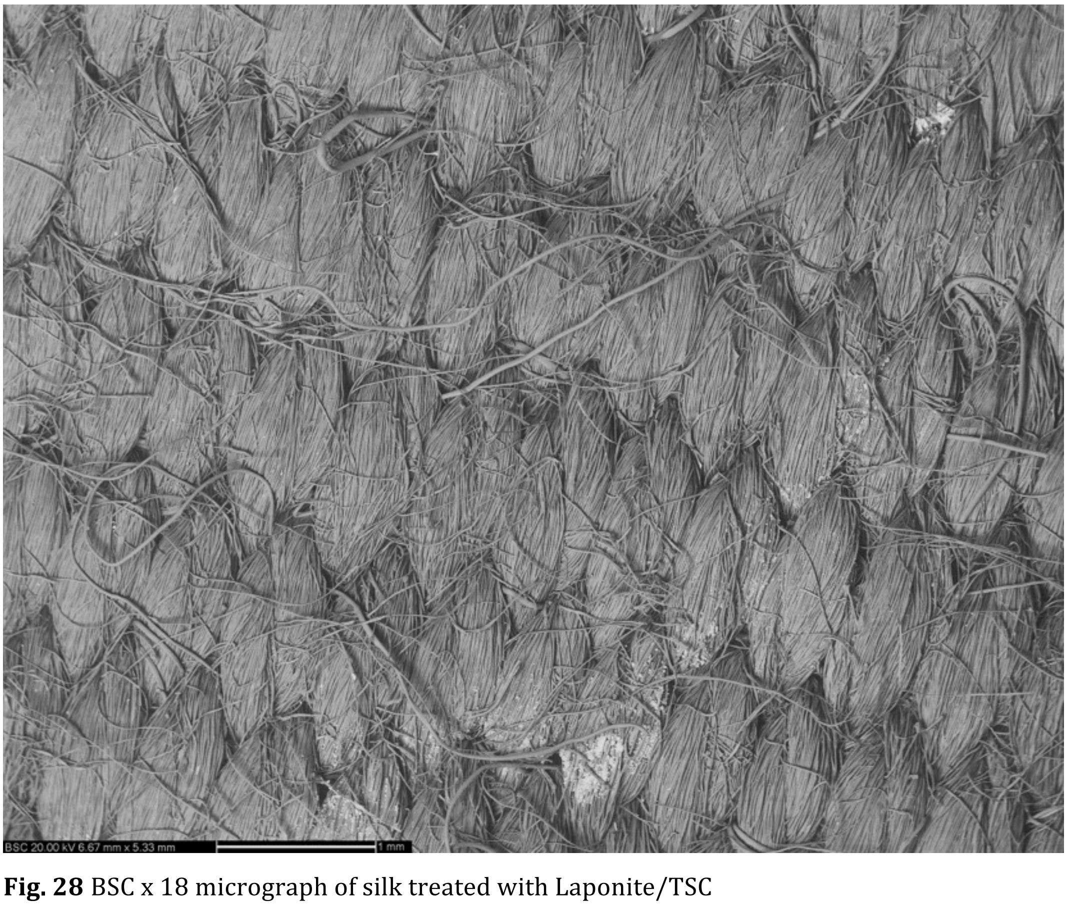

Fig. 28 BSC x 18 micrograph of silk treated with Laponite/TSC

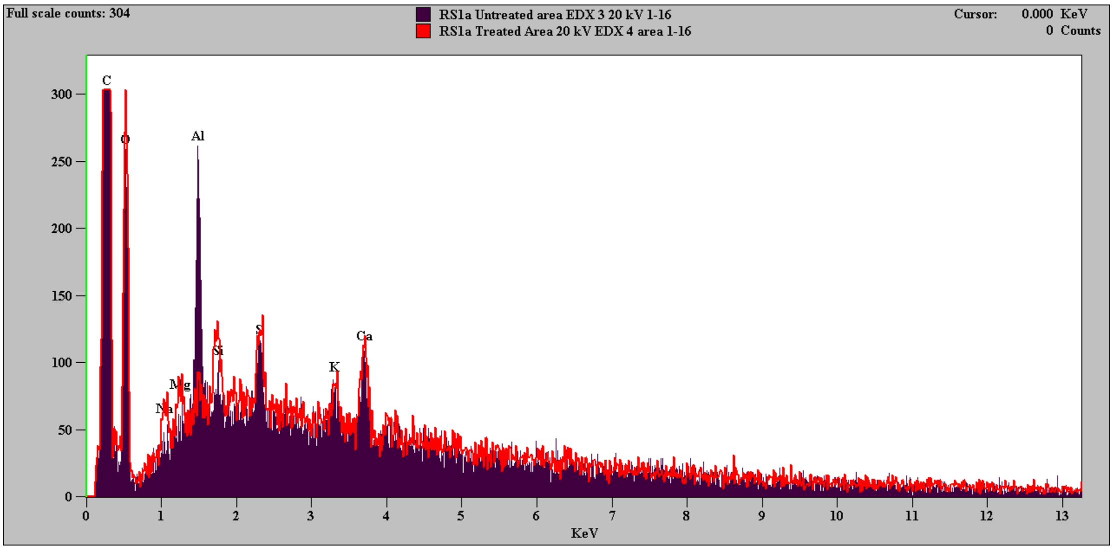

Fig. 29 EDX composition depicting untreated cotton (purple) and cotton treated with Laponite/TSC (red)

<u>MC-7.5-5</u>

The EDX analysis displayed similar results as for sample L-10-5. However, there were less traces of sodium; this could be due to the higher levels of sodium present in the Laponite/TSC gels compared with MC/TSC gel. As with much of the analysis of MC/TSC in this chapter, it is possible that the area of fabric analysed with SEM (fig. 30) was an area where the gel had not adequately saturated the fabric, as highlighted by the patchy regions following gel removal in Chapter 6.5 Once again, there is a disparity between results when comparing the Dino-lite images (Chapter 6.5.2) with these, where fibre disturbance was observed, but is not evident in the photomicrograph.

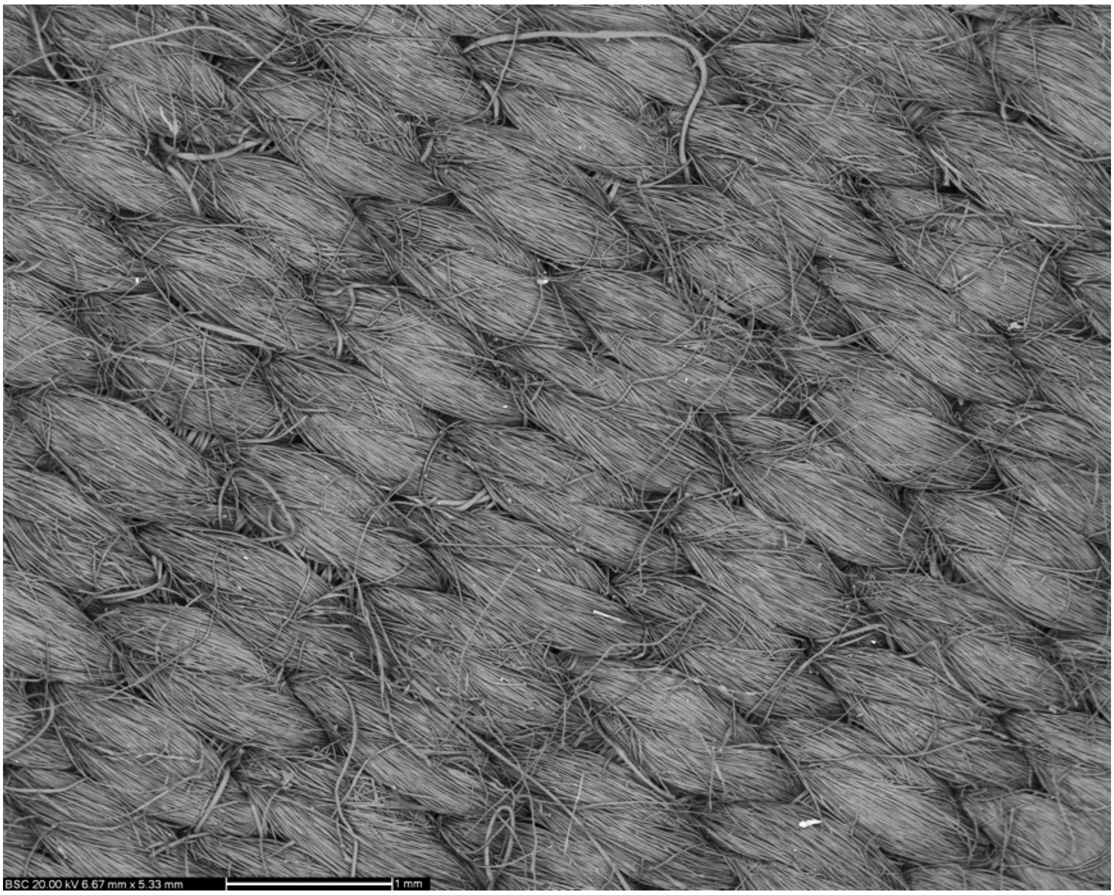

Fig. 30 BSC x 18 micrograph of silk treated with MC/TSC

6.6 Conclusion to testing Laponite/tri-sodium citrate and methylcellulose/tri-sodium citrate on dyed silk

The purpose of these experiments was to select the most effective Laponite/TSC and MC/TSC combination at chelating alum, through a series of experiments and analysis on dyed fabric samples. In summary, the following conclusions were made:

1. Neither selected Laponite/TSC or MC/TSC tested in the final set of experiments were effective at chelation, and neither discernibly outperformed the other. Their chelation abilities were tested on dyed fabric samples mordanted with alum, and it was anticipated that colour loss from the fabric would be observed, due to the chelating agent removing the mordant. As the colour removal was unconvincing when the samples were examined both visually and through colourimetry readings, it was concluded that neither gel combination would be recommended for removing metallic soiling.

2. As the control gels with no TSC caused colour to be removed from the test fabrics, this further indicated the unreliability of the tests to determine the chelation abilities of TSC.
3. It was possible that the MC gels were not adequately saturating the fabric on application, as patchy regions were observed when the gels were removed. This could have impacted on the microscopy and SEM examination, where a disparity between the two methods of examination was highlighted. Whereas microscopy depicted some fibre disturbance, SEM did not. This could be because the area examined under SEM was a region where inadequate saturation was observed.
4. SEM examination showed no physical disturbance to any fabrics from the final set of experiments, however some surface disturbance was observed on the MC samples through microscopy. This disparity between the SEM and microscopy resulted in the conclusion that removing MC could be disturbing the surface of the fibres, although this was inconclusive, however Laponite is not physically disturbing the fibres.
5. The SEM photomicrographs depicted residues of Laponite that remained on the fabrics after treatment, but no MC residues were evident. The lack of MC residues could be attributed to the gel not sufficiently saturating the fabric.

Chapter Seven

CASE STUDY

7.1 Introduction

After the final series of experiments were completed, a textile from the TCC reference collection was discovered that potentially displayed small areas of green staining near metallic fastenings that were characteristic of copper corrosion.[70] Although it was not clear whether the staining was copper corrosion (due to time constraints it was not possible to analyse the staining to confirm its chemical composition), the aim was to conduct a brief experiment to discover whether any of the staining could be removed, to help inform the conclusion of the chelation abilities of the gels/tri-sodium citrate through testing on a different form of potential metallic staining. It was also considered advantageous to transfer the methods of the laboratory experiments to an historic textile, to examine the effects of using the gel on an aged object. Due to time limitations, these tests were rudimentary.

7.2 Brief object description and condition assessment

Description and condition

Plain weave silk(?) and cotton(?) ladies bodice that fastens at back. Painted silk around neck; silk trimmings (fig. 31). Brass(?) hook and eye fastenings on back. Bodice is fragile and the fabric is brittle to touch. General yellowing suggested cellulose degradation. Possible water damage due to regions of staining.

Green staining

The eye fastenings have blackened, suggesting corrosion, with the surrounding area of fabric distinctly green-tinged, also characteristic of copper corrosion deposits (fig. 32). The size of the staining and the proximity to the fastenings does appear to lend weight to the theory that the staining is copper corrosion, as this type of staining does not occur on any other region of the fabric. It also features next to a large stain that is also

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[70] Á. Timar-Balázsy, and D. Eastop, *Chemical Principles of Textile Conservation* (Oxford, 1998), 136.

characteristic of water damage; copper corrosion is often caused through contact with moisture.[71]

Fig. 31 Bodice before treatment. Left: Front, right: back

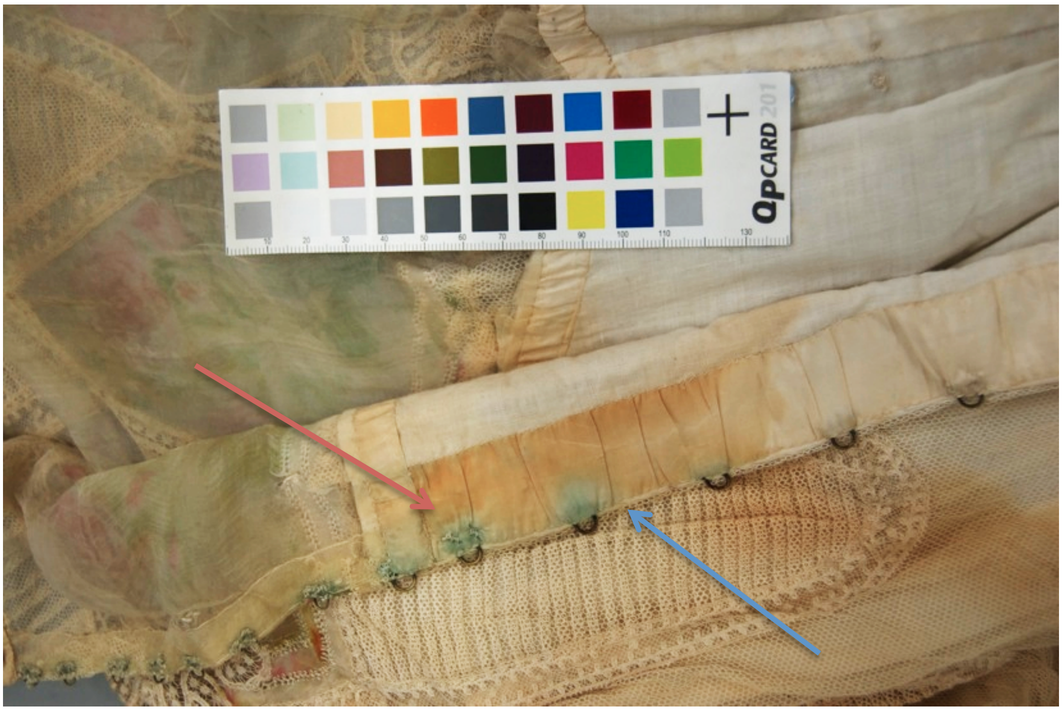

Fig. 32 Bodice before treatment. Red arrow: to be treated with control gel, blue arrow: to be treated with Laponite/TSC

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[71] Timar-Balázsy and Eastop 1998, 136.

7.3 Treatment

A combination of 10% Laponite gel with 5% tri-sodium citrate (TSC) (mixed using method 3 – refer to Chapter 5.2) was selected. This was a gel that had been used in the final set of experiments (Chapter 6.5) and the Laponite was felt to be easier to work with and manipulate onto the treatment area than methylcellulose (Chapter 5.4). A small quantity of the gel (approximately 1g) was applied on top of a fastening surrounded by green staining. The gel covered the entire area of staining (fig. 33). Simultaneously, a control gel of 10% Laponite with no chelating agent was also applied to the adjacent fastening, to help to ascertain whether the TSC was affecting removal of the stain. The gel was left uncovered for one hour. It was removed with a spatula and rinsed using a cotton swab dipped in de-ionised water.

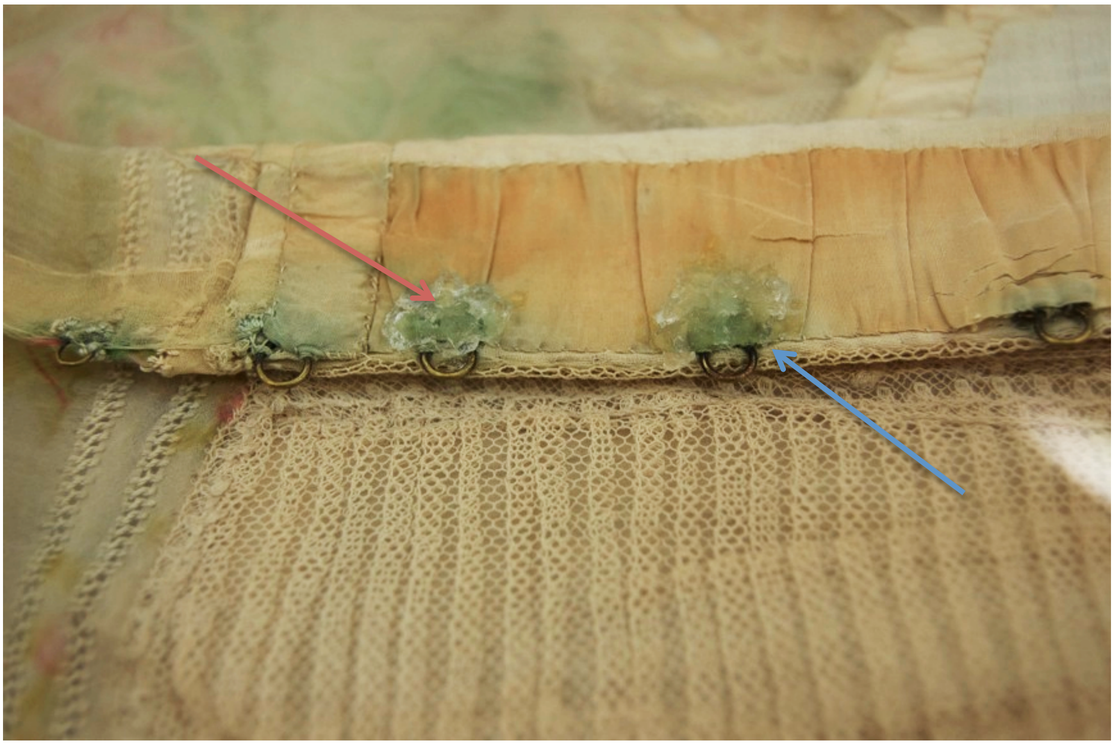

Fig. 33 Treating the bodice. Red arrow: Control gel, blue arrow: Laponite/TSC

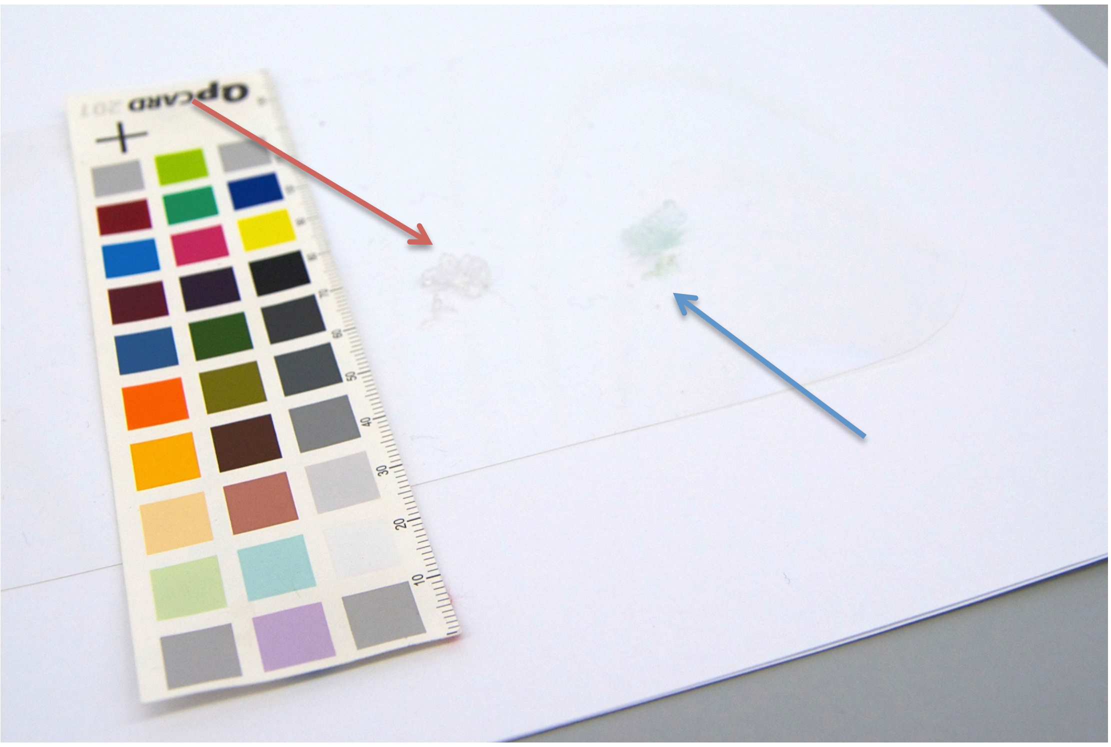

Fig. 34 The gels after treatment. Red arrow: Control gel, blue arrow: Laponite/TSC

7.4 Conclusion

The results were again, inconclusive. Firstly, it cannot be certain whether the staining was copper corrosion, so these tests are only rudimentary. The colour of the gel did not appear to change during treatment to suggest staining was being removed, however the gel with TSC did display a definite green-tinge once removed from the textile, with the control gel remaining transparent (although this is not captured as effectively in fig. 34). It appeared that the region treated with the gel/TSC was somewhat lighter and less stained than it had been before treatment (compare fig. 32 with fig. 35), although the effect is negligible. Rinsing the gel did not appear to cause ringing as it had with the undyed cotton samples (Chapter 5.3.1.1); it is possible that the colour of the bodice has negated this somewhat should ringing be evident. Overall, it was concluded that the gel/TSC could have had a minimal effect on corrosion removal, but further tests would be required to modify the gels to produce more positive results.

Fig. 35 Bodice after treatment. Red arrow: where control gel was applied, blue arrow: where Laponite/TSC was applied

Chapter Eight

RECREATING COPPER CORROSION ON COTTON AND SILK

8.1 Introduction

The aim of this chapter is to describe the process of staining cotton lawn and heavy-weight silk habutai fabric samples with copper salts to replicate copper corrosion, using two different recipes obtained through the literature review. The stained samples would have been used to test the chelating agent/gel combinations so that the efficacy of copper corrosion removal could be analysed. Copper corrosion is typically a greenish-blue colour, and it was hoped that applying the gels/chelating agents would reveal a distinct area of unstained fabric to indicate that they had performed successfully at removing copper corrosion. The issues encountered during the process are described and evaluated, with the intention of providing guidance to others who wish to follow a similar method for artificially staining fabric samples with copper.

Aims and Objectives

- Test published staining methods to determine which is more effective at staining the fabric with copper salts to recreate copper corrosion
- Modify the recipes if required to obtain the desired staining result
- Comment on the process of artificially staining fabric samples for the benefit of other conservators wishing to recreate the effect
- Evaluate the results of the staining to determine whether the samples are suitable for testing the gels on

8.2 Recipes

A literature search produced two recipes that recreated copper corrosion on textiles, which are described as follows:

Table 17: Copper corrosion recipes

Method	Published by	Process described to stain cotton	Notes
1	Margariti[72]	Immerse fabric in 1M aqueous copper sulphate ($CuSO_4$) for 10 minutes. Transfer fabric to 0.05M aqueous sodium hydroxide (NaOH) and immerse for 5 minutes. Rinse fabric with softened water for five minutes	The author said that NaOH was used to form copper hydroxide ($Cu(OH)_2$) which is the salt associated with copper corrosion on textiles
2	Timár-Balázsy and Mátefy[73]	Immerse fabric in a 2% aqueous solution of $CuSO_4$ for thirty minutes	

8.3 Creating the copper solutions

Methods 1 and 2 were made up to ascertain the effect of staining the fabric samples and to deduce whether or not the fabric samples would be suitable for testing. Twenty 120mm x 120mm squares of scoured cotton lawn and heavy-weight silk habutai were selected for staining.

8.3.1 Method 1, first attempt

This recipe was initially made up using anhydrous copper(II) sulphate ($CuSO_4$), indicating that this copper salt contains no water molecules. It has a molecular weight of 159.62g/mol and is supplied as a fine, greyish powder. A 1M solution was prepared by dissolving 78.81g of the powder in a beaker of approximately 200ml of de-ionised water using a magnetic stirrer on the stirring hot plate (no heat used), which took around two to three hours to ensure all the granules had dissolved. The solution was transferred to a 500ml volumetric flask and topped up with the remaining de-ionised water to make a 500ml solution (fig. 36). The flask was stoppered and the contents shaken to mix. The liquid was transparent, and coloured a vivid blue.

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[72] C. Margariti, *The Use of Chelating Agents in Textile Conservation - An Investigation into the Efficiency and Effects of Three Chelating Agents Used for the Removal of Copper and Iron Staining from Cotton Textiles,* Masters dissertation, University of Southampton, Southampton, 2002, 26.
[73] Á. Timar-Balázsy and M. Györk, 'Effects of Stains and Stain Removal on Historical Textiles', In *Preprints of the ICOM CC 10th Triennial Meeting, Washington DC, USA 22-27 August 1993*, J. Bridgland ed., (London, 1993), 331.

A 0.05M solution of sodium hydroxide (NaOH) was also required. This was prepared by dissolving 2g of NaOH in approximately 100ml of de-ionised water using a magnetic stirrer on the stirring hot plate. It dissolved within half an hour. The solution was transferred to a volumetric flask and made up to 500ml with de-ionised water. The flask was stoppered and the contents shaken to mix. The resulting solution was transparent and colourless.

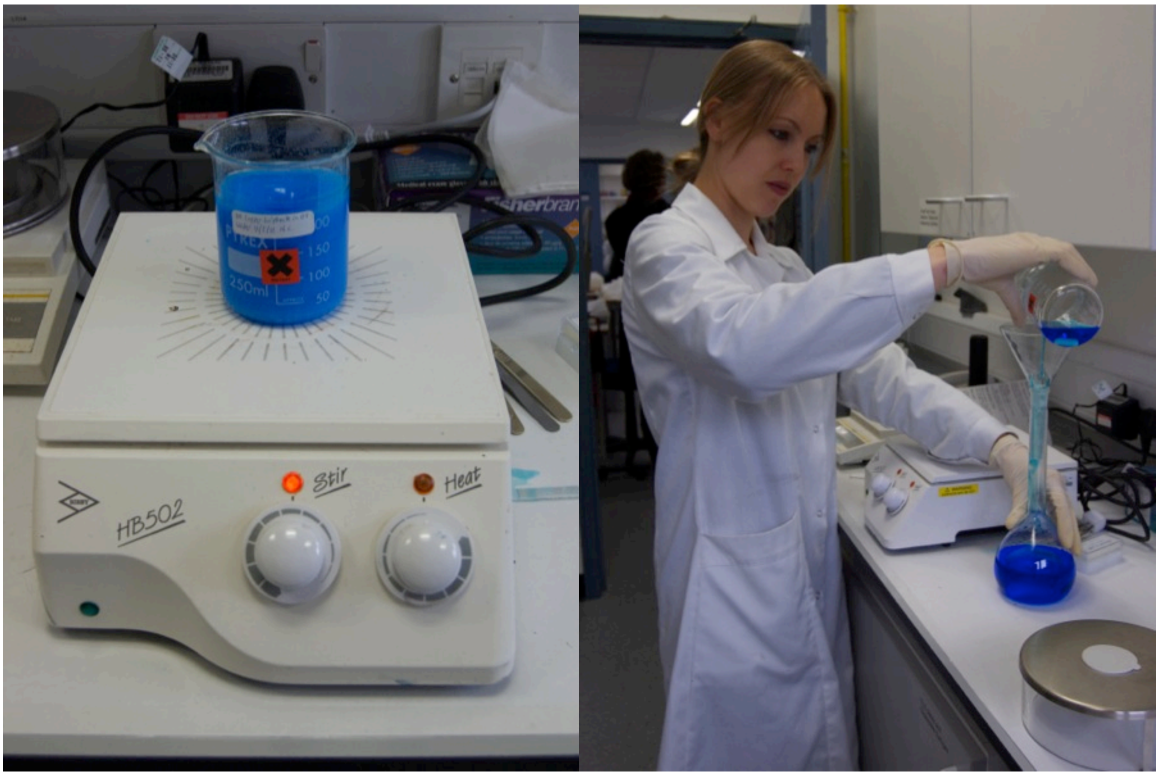

Fig. 36 Creating the copper(II) sulphate solution. Left: On stirring hotplate and right: pouring the contents into a volumetric flask

All the $CuSO_4$ solution was poured into a large beaker and twenty of the cotton samples were immersed for ten minutes in the solution at room temperature (approximately 21^oC).

Upon removing the samples, they appeared to be coloured a light blue. They were not rinsed, and immediately immersed into NaOH solution and left for a further five minutes. It was evident on removal from NaOH that the colour they had absorbed from the $CuSO_4$ had almost all drained off of the samples. A thick layer of sediment, likely to be the $CuSO_4$ remained at the bottom of the beaker of NaOH and the samples were pale and only slightly greenish blue (fig. 37).

Fig. 37 The beakers of solutions after treatment. Left beaker: $CuSO_4$ solution, right beaker: sodium hydroxide solution

The final stage was carried out, and the samples were immersed in softened water for five minutes, however this seemed to rinse out any remaining colour and following drying, the samples were almost as white as they had started out. The experiment was repeated with the silk samples, however the same final result was observed. All of the samples were crisper to touch, so it was likely that they had picked up some copper staining, but they were determined to be unusable for testing as the copper staining was not intense enough.

8.3.2 Method 1, second attempt

Following discussion with Dr Paul Wyeth who was involved in Margariti's experimental work, it transpired that the pentahydrate form of copper(II) sulphate had been used.[74] Pentahydrate has the chemical formula $CuSO_4{\cdot}5H_2O$ and features five water molecules compared with the anhydrous powder. This makes it more water soluble than the anhydrous form – pentahydrate's solubility in water is 316 g/L (0 °C) and anhydrous is 243 g/L (0 °C). It is supplied as a blue powder and has a molecular weight of 249.70g/mol.

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[74] P. Wyeth, *Creating Copper Corrosion,* Personal Communication via Email, 16th May 2012.

The experimental procedure described in Method 1, first attempt, was repeated with 1L of a 1M solution made by dissolving 249.70g of $CuSO_4 \cdot 5H_2O$ in de-ionised water. There was a large quantity of powder to dissolve compared with the anhydrous $CuSO_4$, which had not fully dissolved after a couple of hours stirring, so to accelerate the dissolution, heat was employed (fig. 38). This had an immediate effect and the powder had successfully dissolved after half an hour. The solution appeared a much deeper blue than the anhydrous solution. The scoured cotton samples were immersed in the various solutions as before, however the colour loss observed during the first attempt at staining the samples became evident again and very little copper colouring remained on the samples after the final immersion (figs. 39 & 40). As a result, the silk samples were not immersed due to the lack of success with cotton. In conclusion, the samples were deemed to be unsuitable as the copper staining was not intense enough to be feasible to test on.

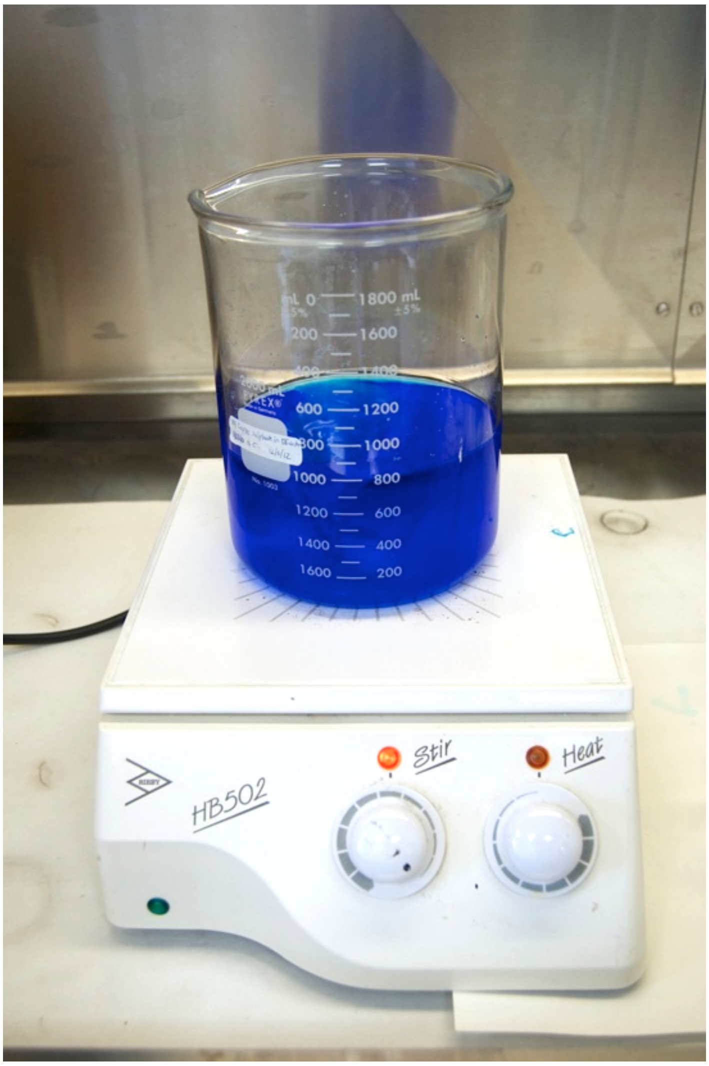

Fig. 38 Dissolving the $CuSO_4$ (pentahydrate) on a stirring hot plate

Fig. 39 Removing the cotton samples from the $CuSO_4$ solution (pentahydrate)

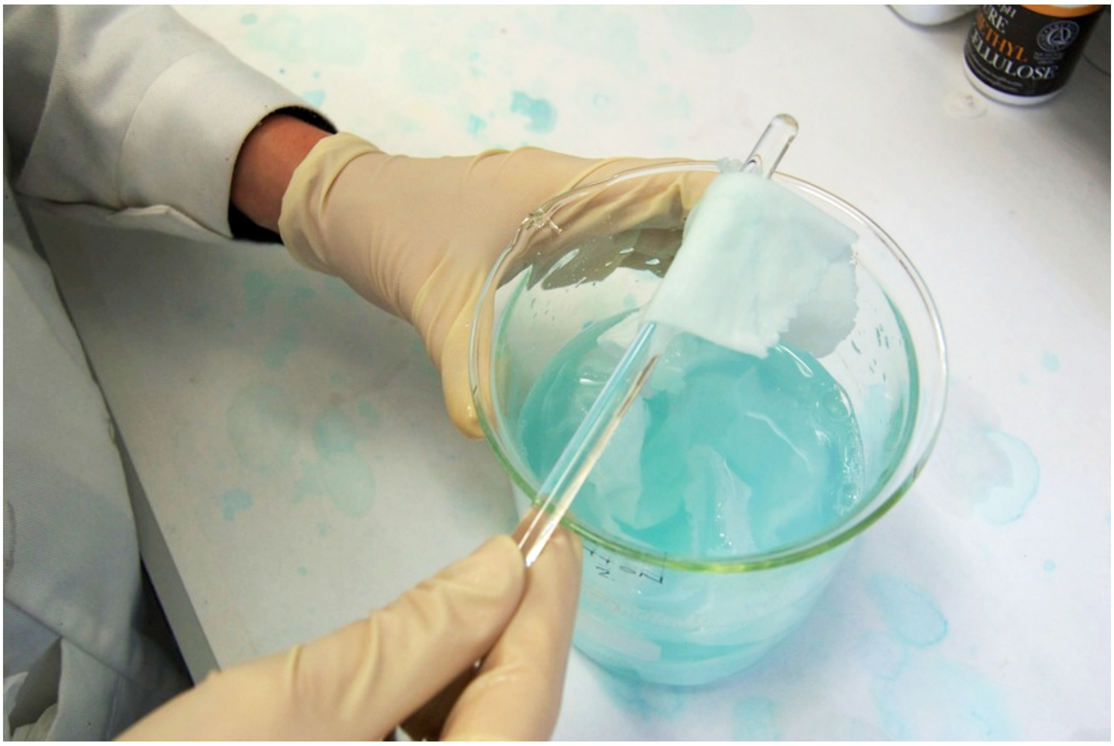

Fig. 40 Removing the cotton samples from the sodium hydroxide solution

8.3.3 Method 2

The instructions to create this method were not described in detail in the authors' paper, and simply stated that a 2% copper solution was required to stain the samples. Therefore, 10g of $CuSO_4$ (anhydrous) was measured out and dissolved in 500ml of de-ionised water in a volumetric flask to create a 2% w/v solution (fig. 41). The scoured cotton and silk samples were immersed for thirty minutes, removed, and left to dry at room temperature. Initial observations were that the silk samples appeared a deeper blue compared to the cotton samples, which had not absorbed much copper at all. This alone determined that the samples were not viable for testing due to the lack of intensity of copper staining.

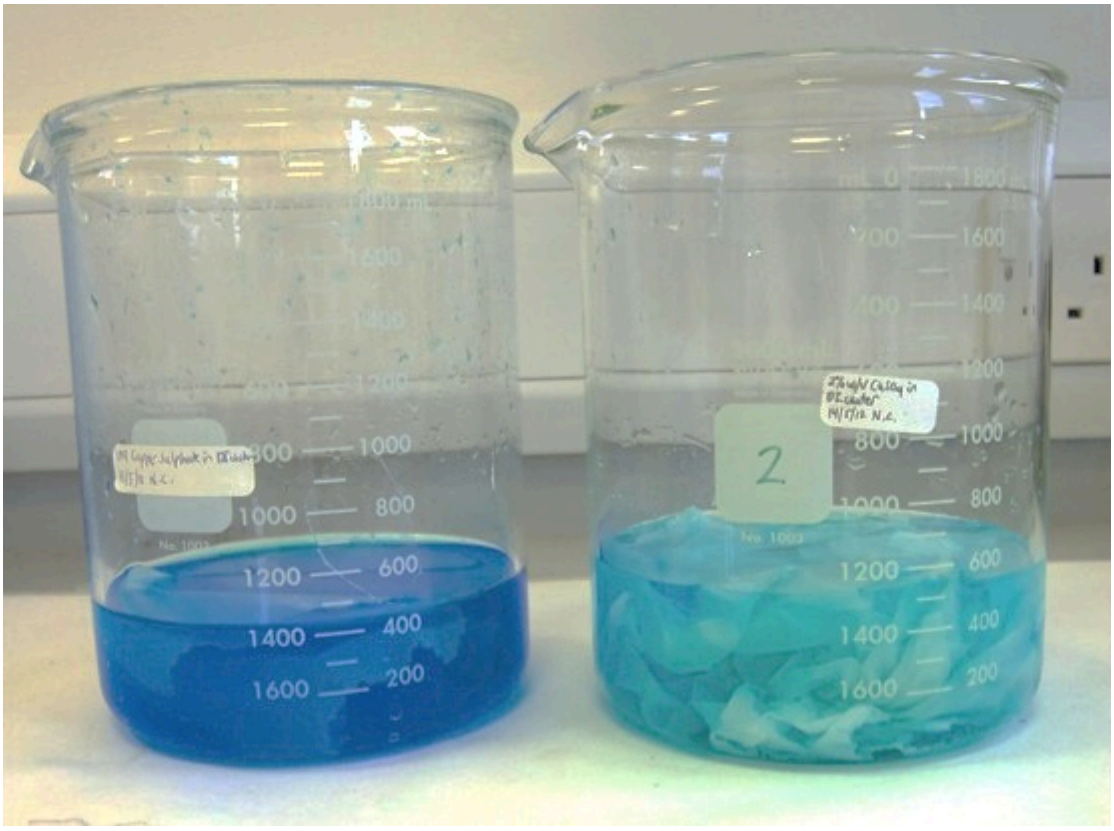

Fig. 41 A comparison of the colour of the $CuSO_4$ solutions from methods 1 (left beaker) and 2 (right beaker)

8.3.4 Discussion

As the samples were not stained with enough copper corrosion, it would not be evident whether the corrosion was removable with the gel/chelating agent combinations. Various methods were tested to remedy this, including soaking the fabric samples in

Method 1 $CuSO_4$ solution alone, leaving to dry, which resulted in a mid-blue shade. However it was evident that the copper corrosion was only loosely deposited on the surface, and dripping water onto the sample resulted in obvious colour loss. This would not produce a consistent reproducible experiment as one could not be certain whether water alone, or the chelating agent and gel were having an effect on the stain removal as the stain was obviously soluble in de-ionised water.

In discussion with Dr Wyeth, he commented that whereas some copper ions may bind directly to the cotton from the $CuSO_4$ solution, the aim is to deposit copper hydroxide between the interstices of the weave and on the fibres themselves, formed during immersion in the NaOH solution, so that the copper ions are mechanically affixed.[75] Examination of samples prepared by Margariti revealed two differences to the samples made in this study. Firstly, the deposited copper ions on Margariti's fabrics were in patches of varying shades of green-brown rather than uniform pale blue, and secondly, the deposits appeared well fixed to the fabric. Despite following Margiriti's method very carefully, it was not possible to reproduce the copper deposition that she had achieved. It was therefore decided not to test the chelating agent/gels on the faintly stained fabrics because the copper ions were too weakly bound, so one could not be certain whether or not the copper staining is removable with water, or if the chelating agent is having a positive effect on stain removal.

8.4 Conclusion

It would appear that it is possible to artificially stain fabric samples with $CuSO_4$ to deposit copper, however it is evident that $CuSO_4$ is only mechanically affixed to the fabric, and can therefore be washed out with minimum agitation and immersion in water. Whereas this method of artificially staining fabric samples could be a useful experiment should the desired result be to obtain a copper-blue coloured sample, it is not appropriate for immersion treatments or for the purpose of the testing proposed in this dissertation.

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[75] Wyeth, 2012.

Chapter Nine

CONCLUSION

9.1 Evaluation of research questions

The literature review indicated that few studies existed describing the successful use of gels and chelating agents on textiles, particularly on fabric other than cotton or on metallic staining other than rust. It was also discovered that although tri-sodium citrate is a commonly used chelating agent in the textile conservation studio, it has not been combined with a gel in a localised treatment. The experiments in this dissertation aimed to address these gaps in the research through testing the efficacy of tri-sodium citrate in Laponite and methylcellulose gels, on both cellulosic and protein fabrics.

It was initially proposed that cotton and silk artificially stained with copper corrosion would be tested on, but due to a lack of success with staining the fabrics with copper corrosion, undyed cotton and silk, and dyed silk mordanted with alum were used instead. This modification to the original research proposal still allowed the gaps in the existing research to be addressed.

In order to meet the aims of the experiments, it was important to identify a series of research questions to help design the experiments, which were introduced in Chapter Three. To conclude this dissertation, an evaluation of each research question is provided.

1. Do the existing gel/chelating agent formulation recipes provided by Potter and Bede prove to be effective carriers for tri-sodium citrate and if not, can they be modified accordingly to provide effective results

Mixing the gels proved to be straightforward, however combing the gels with tri-sodium citrate (TSC) presented some difficulties. It was discovered that creating the gel, adding the TSC granules then mixing appeared to be the most effective method for combing the two, although it was uncertain whether the TSC granules dissolved, or were simply suspended in the solution. This method of mixing facilitated the application and removal of the gels from the fabric as it retained a desirable, thick viscosity, and appeared to be marginally more effective at chelation compared with mixing the gel and TSC together before the gel had fully dissolved. The ratio of gel to chelating agent may require modification, as it was apparent that the methylcellulose (MC) gels did not penetrate the fabric as well as Laponite, as on removal the treated fabric appeared patchy where the gel had been. A lower viscosity MC gel could be more effective. In conclusion, the gels can carry TSC, but how effective they are at chelation is inconclusive, as explained in (3) below.

2. Is it possible to control the area of application of the gels through working with their viscosity to prevent spreading to other regions of the fabric

Two methods of application were tested: applying the gel directly to the fabric with a microspatula to a circular treatment area defined with a pencil line, and through using Potter's Melinex® template method, where the gel was applied through a circular hole in the template to limit the area of application. Both methods were equally effective at limiting the treatment area and would be recommended for use when applying gels to textiles. It should be highlighted that the application methods did not affect the spread of the gels on the fabric and the subsequent issues with ringing as described in Chapter 5.3.1.1, which were a result of the gel and fibre tested on.

3. Are the gel/chelating agent formulations equally effective on cotton and silk, or is there a difference in the workability of the gels or level of residues remaining on the fabric following treatment

The gel/chelating agents were not equally effective on cotton and silk, and numerous issues were encountered.

Ringing was an issue when Laponite/TSC was applied to undyed cotton samples, which was likely to be due to the addition of TSC causing the gel to discolour and stain the fabric. Although the ring mark could be removed through swabbing with de-ionised water, this could be problematic if limiting the treatment area is important. This was not an issue with MC/TSC.

It appeared that the weave of the silk affected penetration of the gels. The undyed silk habutai displayed heavy staining following removal of Laponite (as a consequence MC was not tested on undyed silk due to the lack of success with Laponite/TSC), and the pH levels (Chapter 5.3.3) of untreated and treated areas of undyed silk also depicted a large deviation between the two, reinforcing the concept that it was inadequately rinsing from the fabric and leaving residues. These effects were observed less on the dyed samples, perhaps owing to the denser weave structure and therefore lesser penetration of the gels. Alongside this, removal of the gels from the undyed silk displayed heavy staining and discolouration, reinforcing the unsuitability of this method of localised cleaning on finely woven silks, such as habutai.

One indication that Laponite and MC left residues on all test fabrics following rinsing is the observation that they all generally felt more stiff and less flexible when comparing the treated areas of fabric with treated. Further scientific analysis revealed that it is highly likely that using Laponite caused residues to remain on the undyed cotton and dyed silk fabrics following treatment, but using MC proved less conclusive. These observations can be explained through microscopy (Chapters 5.3.4 & 6.5.2) and SEM imaging (Chapters 5.3.5 & 6.5.5), which illustrated the Laponite residues more visually than the results of pH testing, which only depicted slight deviations between the readings for treated and untreated areas. Whereas MC gel was observed on cotton through microscopy as gluey deposits between the interstices of the weave, pH testing and SEM-EDX did not conclusively highlight residues. This could be explained due to insufficient saturation of the gel on the fabric – the fabric also felt dry and appeared patchy after removal, so it is possible that the area examined under SEM was not an area where the gel had made sufficient contact with the fabric.

4. Does the application and removal of the gels/chelating agent formulations damage the fibres

It was more difficult to remove MC from the test fabrics, which was much stickier to apply and remove, than Laponite, and thus more scraping with the microspatula was required. Laponite was generally easy to remove in one scrape, and microscopy and SEM did not highlight any major inconsistencies between the treated and untreated areas of all test fabrics when using Laponite, indicating minimal fibre disturbance. Slight disturbance to the fibres in the shape of horizontal stray fibres was only observed through microscopy (Chapter 6.5) of the dyed silk treated with MC/TSC; the gel appeared to sit within the dense weave structure after application and was noticeably harder to remove than Laponite. Therefore it can be concluded that the mechanical action of removing the gels from the fabrics was more of an issue with MC due to its stickiness, so refinement of removal techniques may be required.

5. Are the selected gel/chelating agent formulations effective at chelation

Neither Laponite nor MC gel combinations were effective at chelation. No visible dye removal was observed on the silk test samples for either gel, and the chromameter readings (Chapter 6.5.4) only showed minimal deviations of colour change comparing the treated and untreated areas – also evident from the control samples, which contained no TSC.

Although the case study was brief and the copper corrosion unverified, these tests displayed the most positive results for chelation, due to the green discolouration of the Laponite/TSC on removal when compared with the control gel. Likewise, it appeared that some of the stain had diminished, although the effect was minimal. In conclusion, the addition of TSC to the gels had a negligible effect at chelation, so as there are also questions about the long-term effects of gel residues remaining on the fabric after treatment, the benefits of applying the gels to historic textiles to remove metallic staining are doubtful.

6. Is one gel/chelating agent formulation more workable and effective at chelation than the other

One of the aims of this testing was to compare Laponite/TSC with MC/TSC to determine whether one gel formulation was more effective than the other, to allow conservators to make a choice between the two for their own treatments. As the analysis concluded that neither gel was particularly effective at chelation and both presented numerous issues, the following table summaries the two based on attributes that were considered desirable for the gels to perform effectively.

Table 18: A comparison of Laponite/TSC and MC/TSC

	Laponite/TSC	**Methylcellulose /TSC**	**Notes**
Cost of gel	1kg = £24.65[76]	1kg = £49.95[77]	10% w/v =10g in 100ml DI water
Cost of TSC	1kg = £33.31[78]		5% w/v = 5g in 100ml DI water
Ease of mixing	Dissolved within one hour, but left overnight	Dissolved within one hour, but left overnight	Both stored at room temperature (21 degrees)
Preferred concen-trations	Laponite 10% TSC 5%*	MC 7.5% TSC 5%*	* Ineffective at chelation
Transparency	Very transparent	Slightly yellow-tinged but still clear. Bubbles evident	
Gel pH (with TSC)	9.1-9.5	6.5-7.9	There is a concern that the extreme alkalinity of Laponite could damage the fibres if residues remain
Viscosity	Held shape well at 10% w/v	Sticky, but held shape well at 7.5% w/v	
Drying	Slight drying after 30 min uncovered	Slight drying after 45 min uncovered	Covering with petri dish negates effects of drying
Application	Easy to apply and manipulate with microspatula	Harder to apply and manipulate with microsptaula – sticky	
Monitoring	Transparent, so easy to monitor stain removal	Yellow-tinged, but transparent enough to monitor stain removal	
Removal	Generally easy to remove in one scrape with microspatula. Minimal swabbing required to remove residues	Harder to remove in one scrape with microspatula, sticks to fabric more. More swabbing required to remove residues	
Staining	Stained habutai silk.	None observed	MC not tested on silk

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[76] Conservation Resources UK Ltd., *Laponite RD,* Conservation Resources, http://www.conservation-resources.co.uk/index.php?main_page=product_info&products_id=615 (accessed 23rd August 2012).

[77] Preservation Equipment Ltd., *Methylcellulose,* Preservation Equipment Ltd., http://www.preservationequipment.com/Store/Products/Conservation-Materials/Mounting-$4-Framing/Methyl-Cellulose (accessed 23rd August 2012).

[78] Fisher Scientific, *S/3280/60 - tri-Sodium citrate 99+% SpeciFied, Fisher Scientific,* https://extranet.fisher.co.uk/insight2_uk/getProduct.do;jsessionid=4A992925924E38612B55CFB3A52E23DB.uklbhja34p?productCode=S/3280/60&resultSetPosition=1 (accessed 23rd August 2012).

/ringing	Ringing on cotton.		
Residues	Very evident on habutai silk. Evident under microscopy on cotton and dyed silk	Evident under microscopy on cotton and dyed silk	MC not tested on silk
Fabric flexibility	All test fabrics were less flexible after treatment	All test fabrics were less flexible after treatment	
Chelation	Ineffective*	Ineffective	*Potentially more effective than MC, as some staining was removed on object in case study

9.2 Lessons learned

It was disappointing to not obtain effective results from the gel/TSC formulations, as previous success was reported using other chelating agents by Potter and Bede. It was possible that the TSC was not dissolving sufficiently in the gels, thus affecting chelation, and further testing with the methods of combing the two could be useful. TSC is readily available in conservation labs, compared with tri-ammonium citrate, so pursuing the combination of a gel and TSC could be beneficial to textile conservators. Likewise, staining the fabrics with copper proved problematic and frustrating and could be investigated further to obtain effective results for further testing. It became evident that the experiments quickly deviated from the original proposal due to unexpected results, such as the issues with staining the fabrics, combining the gels and TSC, and ringing. Perhaps focusing on refining and resolving some of these issues one-by-one would be useful to provide a more thorough overall investigation of this form of localised treatment.

9.3 Future research

Progressing through this dissertation from the literature review to the experiments highlighted a series of future research questions that could warrant investigation to refine this method of localised treatment.

1. <u>Creating copper corrosion</u>

Improving the technique to deposit copper corrosion onto the fabrics could facilitate future testing

2. Experimenting with barrier layers
   This could prevent residues, but could also inhibit saturation of the gel on the fabric

3. Artificial ageing and tensile strength testing
   Artificially ageing in an ageing oven, then examining the tensile strength of the fibres following treatment could determine the longer-term effects of the gels on the fibres. Larger fabric samples would be required for tensile strength testing than those tested in these experiments

4. Testing gel/TSC formulations on rust
   It is possible that the gel would work more effectively on iron corrosion

5. Examining gel residues
   The high pH of Laponite could cause the fibres to degrade more quickly following treatment, as residues were shown to remain on the fabric. The residues for both gels could be analysed to determine their long-term effects on the fabrics.

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APPENDIX A

pH Readings of Laponite/TSC on undyed cotton (3 fabric samples per set)
Refer to Chapter 5.3.3 for data analysis

Sample set: L-C-10 (Control)

1				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.29	7.10	7.21	7.20
Spot 1	8.45	8.47	8.50	8.47
Spot 2	8.42	8.49	8.49	8.47
Spot 3	7.70	7.73	7.74	7.72
Average pH reading of Spots 1-3:				**8.22**

2				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.50	7.50	7.51	7.50
Spot 1	7.51	7.69	7.76	7.65
Spot 2	7.77	7.79	7.86	7.81
Spot 3	8.06	8.14	8.18	8.13
Average pH reading of Spots 1-3:				**7.86**

3				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	8.10	8.11	8.11	8.11
Spot 1	8.41	8.38	8.42	8.40
Spot 2	7.72	7.76	7.72	7.73
Spot 3	7.84	7.92	7.96	7.91
Average pH reading of Spots 1-3:				**8.01**

Average pH reading across all sample set from all spots of treated fabric: 8.03

Sample set: L-C-10-2.5

1				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.94	7.85	7.83	7.87
Spot 1	8.69	8.60	8.69	8.66
Spot 2	7.79	7.80	7.86	7.82
Spot 3	7.84	7.91	7.91	7.89
Average pH reading of Spots 1-3:				**8.12**

2				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.53	7.54	7.45	7.51
Spot 1	7.40	7.56	7.63	7.53
Spot 2	7.84	7.88	7.89	7.87
Spot 3	8.26	8.26	8.28	8.27
Average pH reading of Spots 1-3:				**7.89**

3				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	8.16	8.21	8.23	8.20
Spot 1	8.09	8.13	8.15	8.12
Spot 2	8.16	8.19	8.14	8.16
Spot 3	8.19	8.25	8.25	8.23
Average pH reading of Spots 1-3:				**8.17**

Average pH reading across all sample set from all spots of treated fabric: 8.06

Sample set: L-C-10-5-3

1				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.47	7.46	7.43	7.45
Spot 1	8.31	8.33	8.34	8.33
Spot 2	8.08	8.13	8.13	8.11
Spot 3	8.08	8.06	8.17	8.10
Average pH reading of Spots 1-3:				**8.18**

2				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.51	7.70	7.61	7.61
Spot 1	7.73	7.84	8.03	7.87
Spot 2	8.52	8.58	8.59	8.56
Spot 3	8.06	8.12	8.16	8.11
Average pH reading of Spots 1-3:				**8.18**

3				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	8.16	8.12	8.08	8.12
Spot 1	7.84	7.88	7.93	7.88
Spot 2	7.88	7.93	7.97	7.93
Spot 3	8.24	8.29	8.31	8.28
Average pH reading of Spots 1-3:				**8.03**

Average pH reading across all sample set from all spots of treated fabric: 8.13

Sample set: L-C-10-5-2

1				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.77	7.70	7.65	7.71
Spot 1	8.05	8.06	8.11	8.07
Spot 2	8.48	8.52	8.55	8.52
Spot 3	8.24	8.24	8.27	8.25
Average pH reading of Spots 1-3:				**8.28**

2				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.37	7.40	7.40	7.39
Spot 1	7.27	7.38	7.46	7.37
Spot 2	7.76	7.80	7.98	7.85
Spot 3	7.92	7.96	8.12	8.00
Average pH reading of Spots 1-3:				**7.74**

3				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	7.32	7.28	7.28	7.29
Spot 1	7.30	7.54	7.59	7.48
Spot 2	7.91	7.99	8.01	7.97
Spot 3	7.67	7.72	7.77	7.72
Average pH reading of Spots 1-3:				**7.72**

Average pH reading across all sample set from all spots of treated fabric: 7.91

pH Readings of Laponite/TSC on undyed silk (3 fabric samples per set)

Refer to Chapter 5.3.3 for data analysis

Sample set: L-S-10 (Control)

1				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	**pH**			
Untreated	7.70	7.35	7.00	7.35
Spot 1	7.42	7.73	8.11	7.75
Spot 2	7.94	7.92	7.87	7.91
Spot 3	7.84	7.87	7.87	7.86
Average pH reading of Spots 1-3:				**7.84**

2				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	**pH**			
Untreated	6.25	6.05	6.00	6.10
Spot 1	6.48	6.46	6.47	6.47
Spot 2	6.76	6.77	6.77	6.77
Spot 3	7.24	7.24	7.40	7.29
Average pH reading of Spots 1-3:				**6.84**

3				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	**pH**			
Untreated	6.59	6.59	6.57	6.58
Spot 1	8.30	8.39	8.38	8.36
Spot 2	8.29	8.32	8.29	8.30
Spot 3	7.85	7.71	7.68	7.75
Average pH reading of Spots 1-3				**8.13**

Average pH reading across all sample set from all spots of treated fabric: 7.6

Sample set: L-S-10-2.5

1				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	**pH**			
Untreated	7.01	6.67	6.50	6.73
Spot 1	9.10	9.19	9.10	9.13
Spot 2	9.37	9.39	9.38	9.38
Spot 3	9.08	9.15	9.16	9.13
Average pH reading of Spots 1-3:				**9.21**

2				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	6.37	6.25	6.15	6.26
Spot 1	9.03	9.03	9.11	9.06
Spot 2	8.91	9.14	9.02	9.02
Spot 3	9.19	9.12	9.11	9.14
Average pH reading of Spots 1-3				**9.07**

3				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	6.79	6.52	6.50	6.60
Spot 1	8.81	8.50	9.06	8.79
Spot 2	8.85	8.91	9.05	8.94
Spot 3	9.00	9.06	9.06	9.04
Average pH reading of Spots 1-3				**8.92**

Average pH reading across all sample set from all spots of treated fabric: 9.06

Sample set: L-S-10-5-3

1				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	7.45	6.80	6.52	6.92
Spot 1	8.98	8.98	9.17	9.04
Spot 2	8.67	8.62	8.58	8.62
Spot 3	8.55	8.56	8.64	8.58
Average pH reading of Spots 1-3:				**8.75**

2				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	6.48	6.45	6.42	6.45
Spot 1	8.45	8.56	8.57	8.53
Spot 2	9.11	8.89	8.70	8.90
Spot 3	8.61	8.55	8.54	8.57
Average pH reading of Spots 1-3:				**8.66**

3				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	5.33	5.32	5.27	5.31
Spot 1	7.66	7.63	7.74	7.68
Spot 2	7.89	7.97	8.03	7.96
Spot 3	8.42	8.36	8.31	8.36
Average pH reading of Spots 1-3:				8.00

Average pH reading across all sample set from all spots of treated fabric: 8.59

Sample set: L-S-10-5-2

1				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	6.00	6.17	6.09	6.09
Spot 1	9.08	9.37	9.29	9.25
Spot 2	8.78	9.10	9.37	9.08
Spot 3	8.98	9.13	9.17	9.09
Average pH reading of Spots 1-3:				9.14

2				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	6.29	6.12	6.10	6.17
Spot 1	8.68	8.67	8.66	8.67
Spot 2	9.24	9.24	9.24	9.24
Spot 3	9.09	9.08	8.98	9.05
Average pH reading of Spots 1-3:				8.99

3				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	5.87	5.74	5.58	5.73
Spot 1	8.34	8.60	8.73	8.56
Spot 2	8.12	8.20	8.28	8.20
Spot 3	8.37	8.32	8.41	8.37
Average pH reading of Spots 1-3:				8.37

Average pH reading across all sample set from all spots of treated fabric: 8.83

pH Readings of MC/TSC on undyed cotton (3 fabric samples per set)

Refer to Chapter 5.3.3 for data analysis

Sample set: MC-7.5 (Control)

1				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.05	7.15	7.17	7.12
Spot 1	6.88	6.89	6.91	6.89
Spot 2	6.69	6.71	6.73	6.71
Spot 3	6.32	6.35	6.40	6.36
Average pH reading of Spots 1-3:				**6.65**

2				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.99	7.87	7.79	7.88
Spot 1	7.95	7.94	7.92	7.94
Spot 2	8.40	8.37	8.34	8.37
Spot 3	7.88	8.03	8.03	7.98
Average pH reading of Spots 1-3:				**8.10**

3				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.38	7.43	7.50	7.44
Spot 1	7.30	7.40	7.45	7.38
Spot 2	7.57	7.62	7.64	7.61
Spot 3	7.26	7.21	7.33	7.27
Average pH reading of Spots 1-3:				**7.42**

Average pH reading across all sample set 1 from all spots of treated fabric: 7.39

Sample set: MC-7.5-5-2

1				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	6.85	6.90	6.94	6.90
Spot 1	7.43	7.47	7.48	7.46
Spot 2	7.06	7.10	7.13	7.10
Spot 3	7.75	7.72	7.69	7.72
Average pH reading of Spots 1-3:				**7.43**

2				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.02	7.11	7.14	7.09
Spot 1	7.46	7.51	7.55	7.51
Spot 2	7.60	7.62	7.64	7.62
Spot 3	7.81	7.81	7.79	7.80
Average pH reading of Spots 1-3:				**7.64**

3				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.65	7.48	7.49	7.54
Spot 1	7.58	7.61	7.64	7.61
Spot 2	7.64	7.62	7.59	7.62
Spot 3	7.56	7.59	7.60	7.58
Average pH reading of Spots 1-3:				**7.60**

Average pH reading across all sample set from all spots of treated fabric: 7.56

Sample set: MC-7.5-5-3

1				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.12	7.10	7.08	7.10
Spot 1	7.31	7.34	7.34	7.33
Spot 2	7.28	7.29	7.29	7.29
Spot 3	7.26	7.21	7.18	7.22
Average pH reading of Spots 1-3:				**7.28**

2				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.45	7.38	7.41	7.41
Spot 1	7.34	7.40	7.44	7.39
Spot 2	7.29	7.29	7.30	7.29
Spot 3	7.49	7.53	7.57	7.53
Average pH reading of Spots 1-3:				**7.41**

3				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.23	7.22	7.21	7.22
Spot 1	7.58	7.46	7.58	7.54
Spot 2	7.57	7.57	7.57	7.57
Spot 3	7.39	7.33	7.34	7.35
Average pH reading of Spots 1-3:				**7.49**

Average pH reading across all sample set from all spots of treated fabric: 7.39

Sample set: MC-10-5-2

1				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	6.87	6.88	6.88	6.88
Spot 1	7.02	7.00	7.01	7.01
Spot 2	7.32	7.36	7.35	7.34
Spot 3	7.49	7.50	7.49	7.49
Average pH reading of Spots 1-3:				**7.28**

2				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	6.57	6.66	6.69	6.64
Spot 1	7.27	7.35	7.36	7.33
Spot 2	7.31	7.35	7.35	7.34
Spot 3	7.36	7.42	7.44	7.41
Average pH reading of Spots 1-3:				**7.36**

3				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	6.90	6.91	6.90	6.90
Spot 1	7.07	7.10	7.08	7.08
Spot 2	7.04	7.04	7.06	7.05
Spot 3	6.91	6.96	7.00	6.96
Average pH reading of Spots 1-3:				**7.03**

Average pH reading across all sample set from all spots of treated fabric: 7.22

pH Readings of final dyed silk samples

Refer to Chapter 6.5.3 for data analysis

Sample set: L-10-5

1				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.89	7.75	7.70	7.78
Spot 1	8.75	8.82	8.85	8.81
Spot 2	8.68	8.77	8.81	8.75
Spot 3	8.70	8.71	8.72	8.71
Average pH reading of Spots 1-3:				**8.76**

2				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.85	7.75	7.77	7.79
Spot 1	8.37	8.43	8.45	8.42
Spot 2	8.36	8.47	8.51	8.45
Spot 3	8.37	8.52	8.55	8.48
Average pH reading of Spots 1-3:				**8.45**

Average pH reading across all sample set from all spots of treated fabric: 8.61

Sample set: MC-7.5-5

1				
	15 sec	**30 sec**	**45 sec**	**Average pH reading of each area of fabric**
Area of fabric	**pH**			
Untreated	7.62	7.65	7.58	7.62
Spot 1	7.83	7.84	7.85	7.84
Spot 2	7.75	7.75	7.79	7.76
Spot 3	7.36	7.35	7.36	7.36
Average pH reading of Spots 1-3:				**7.65**

2				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	7.39	7.38	7.35	7.37
Spot 1	7.48	7.53	7.53	7.51
Spot 2	7.50	7.53	7.58	7.54
Spot 3	7.46	7.50	7.51	7.49
Average pH reading of Spots 1-3:				7.51

Average pH reading across all sample set from all spots of treated fabric: 7.58

L-10 (Control)				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	5.54	5.42	5.39	5.45
Spot 1	7.26	7.24	7.33	7.28
Spot 2	7.46	7.50	7.52	7.49
Spot 3	7.52	7.81	7.82	7.72
Average pH reading of Spots 1-3:				7.50

MC-7.5 (Control)				
	15 sec	30 sec	45 sec	Average pH reading of each area of fabric
Area of fabric	pH			
Untreated	5.90	5.76	5.88	5.85
Spot 1	6.05	6.04	6.04	6.04
Spot 2	5.95	5.92	5.92	5.93
Spot 3	5.85	5.85	5.85	5.85
Average pH reading of Spots 1-3:				5.94

APPENDIX B

Chromameter readings of final dyed silk samples

Refer to Chapter 6.5.4 for data analysis

Sample set: L-10-5

1			
Before treatment			
Spot	**L***	**a* (+)**	**b* (+)**
1	53.37	29.22	14.52
2	53.76	29.08	14.60
3	53.65	29.13	14.54
Average	53.59	29.14	14.55
After treatment			
1	54.72	27.31	13.88
2	55.46	26.98	13.96
3	55.07	27.10	13.93
Average	55.08	27.13	13.92
Difference between average untreated/treated	-1.49	2.01	0.63

2			
Before treatment			
Spot	**L***	**a* (+)**	**b* (+)**
1	53.34	29.05	14.42
2	53.86	28.84	14.44
3	53.65	28.84	14.39
Average	53.62	28.91	14.42
After treatment			
1	54.35	27.35	13.91
2	54.75	27.03	13.76
3	54.79	26.84	13.77
Average	54.63	27.07	13.81
Difference between average untreated/treated	-1.01	1.84	0.60

Sample set: MC-7.5-5

1			
Before treatment			
Spot	**L***	**a* (+)**	**b* (+)**
1	54.68	28.07	14.74
2	54.01	28.59	14.64
3	54.14	28.49	14.61
Average	54.28	28.38	14.66
After treatment			
1	55.39	26.69	14.70
2	55.02	26.72	14.79
3	54.88	26.88	14.69
Average	55.10	26.76	14.73
Difference between average untreated/treated	-0.82	1.62	-0.06

2			
Before treatment			
Spot	**L***	**a* (+)**	**b* (+)**
1	53.34	29.05	14.42
2	53.86	28.84	14.44
3	53.65	28.84	14.39
Average	53.62	28.91	14.42
After treatment			
1	54.21	27.24	15.28
2	53.65	27.61	15.40
3	53.75	27.86	15.17
Average	53.87	27.57	15.28
Difference between average untreated/treated	-0.25	1.34	-0.87

Sample set: L-10

L-10 (Control)			
Before treatment			
Spot	**L***	**a* (+)**	**b* (+)**
1	38.80	31.16	9.85
2	38.63	31.22	9.86
3	38.66	31.42	9.78
Average	38.70	31.27	9.83
After treatment			
1	38.75	31.04	9.25
2	38.58	31.26	9.27
3	38.63	31.32	9.25
Average	38.65	31.21	9.26
Difference between average untreated/treated	0.04	0.06	0.57

Sample set: MC-7.5

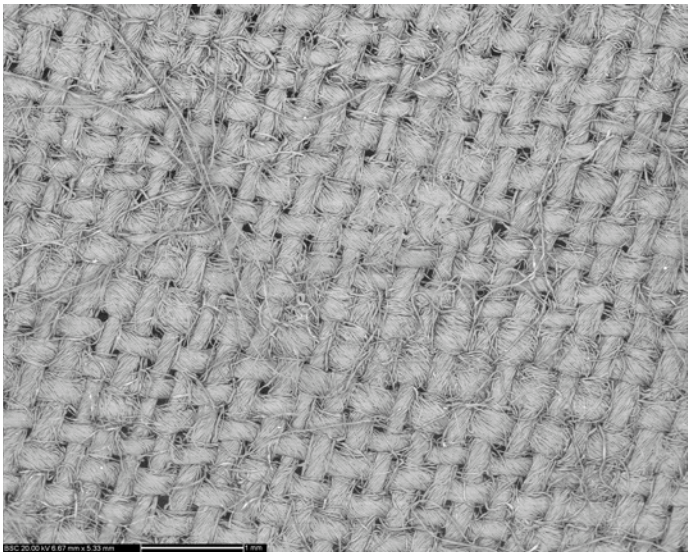
MC-7.5 (Control)			
Before treatment			
Spot	**L***	**a* (+)**	**b* (+)**
1	39.00	30.94	10.06
2	38.61	31.35	10.03
3	38.70	31.57	9.97
Average	38.77	31.29	10.02
After treatment			
1	37.70	29.44	8.81
2	36.91	29.78	8.80
3	36.87	29.79	8.76
Average	37.16	29.67	8.79
Difference between average untreated/treated	1.61	1.62	1.23

APPENDIX C

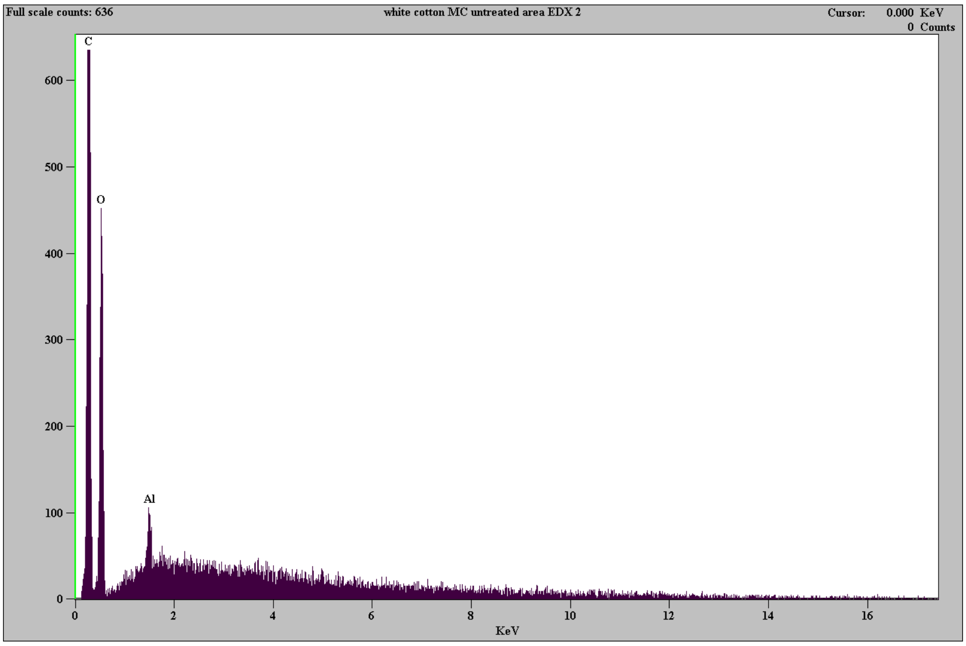
SEM-EDX Images

The following SEM BSC micrographs and graphs were also captured but were not included in the main body of the report.

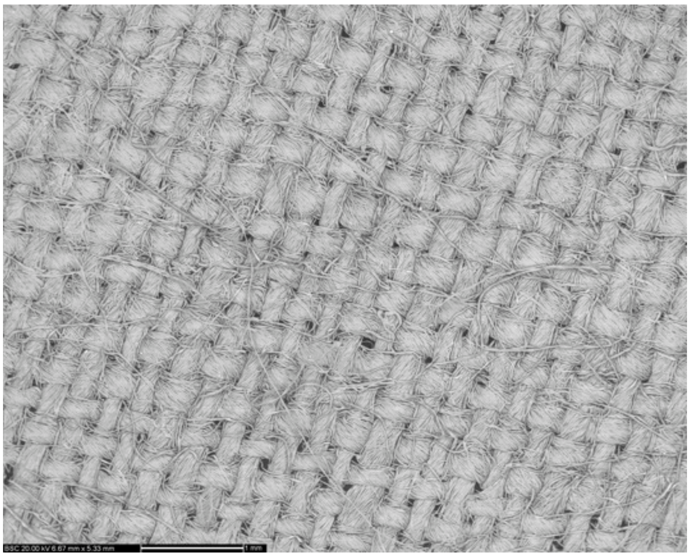
Sample MC-7.5-5-3: Methylcellulose/TSC on undyed cotton



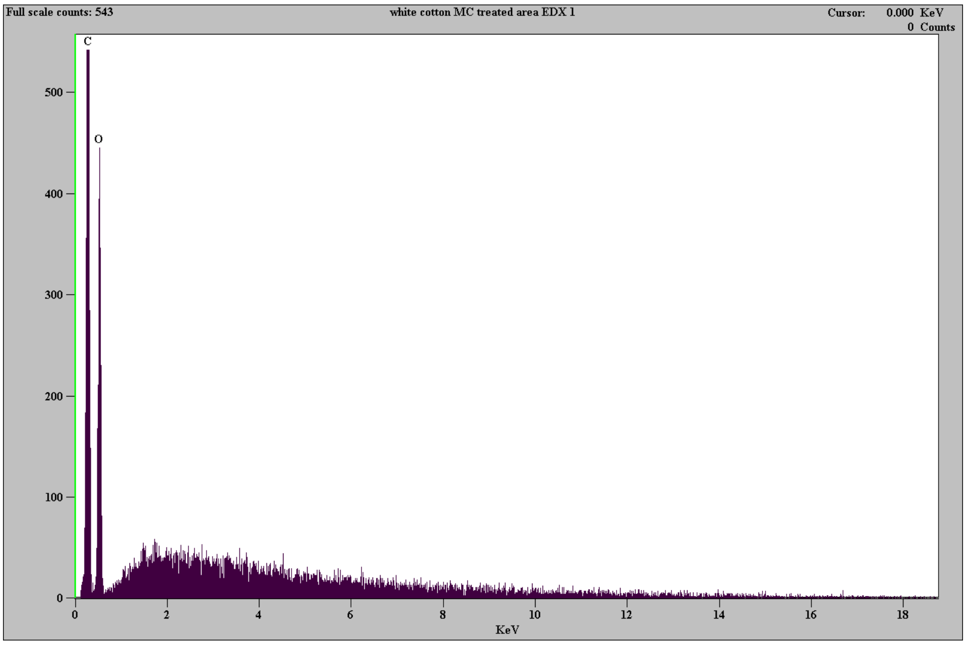
Untreated fabric x 18 magnification



EDX mapping of untreated fabric

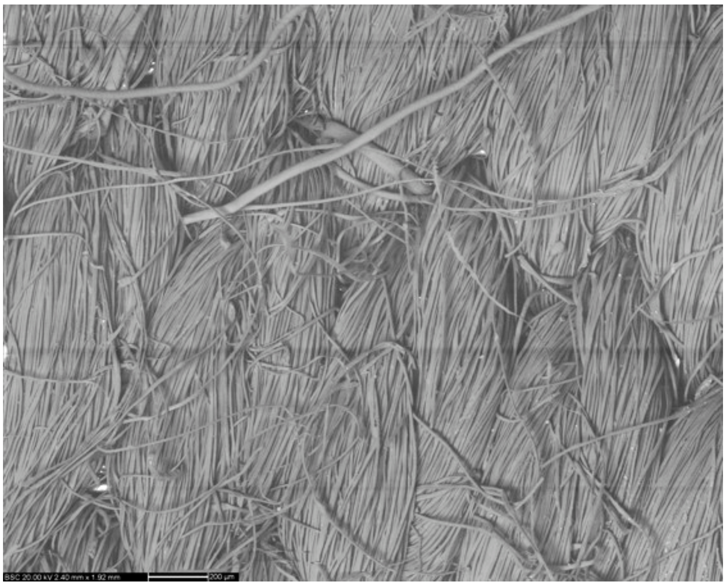


Treated fabric x 18 magnification



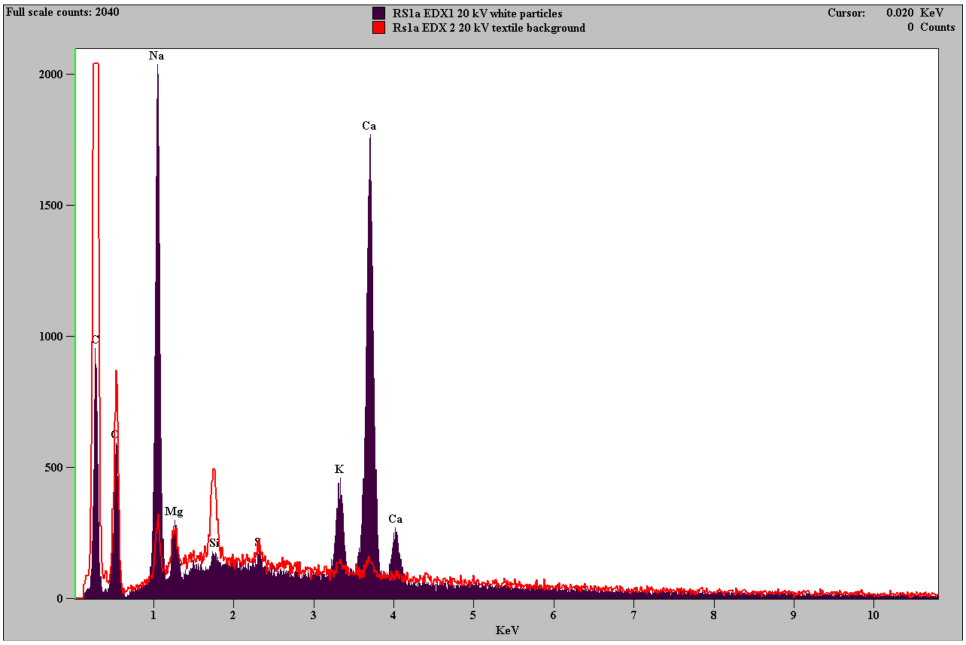
EDX mapping of treated fabric

Sample L-10-5: Laponite/TSC on dyed silk



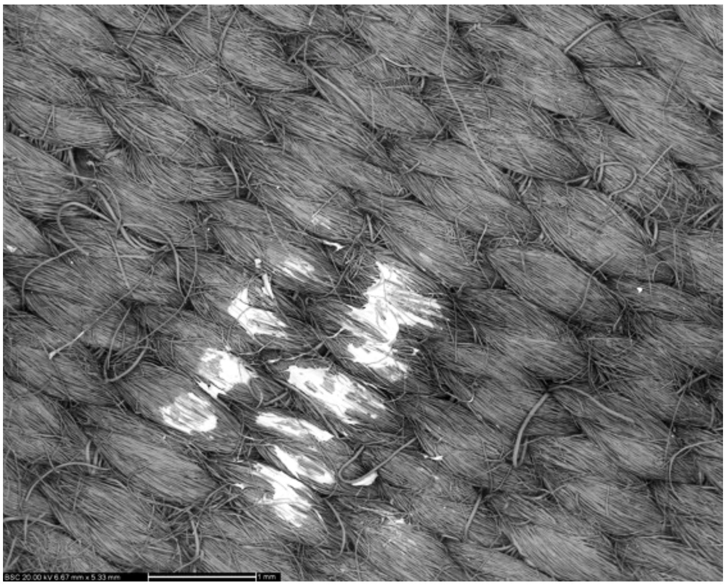
Treated fabric x 50 magnification

Treated fabric x 100 magnification

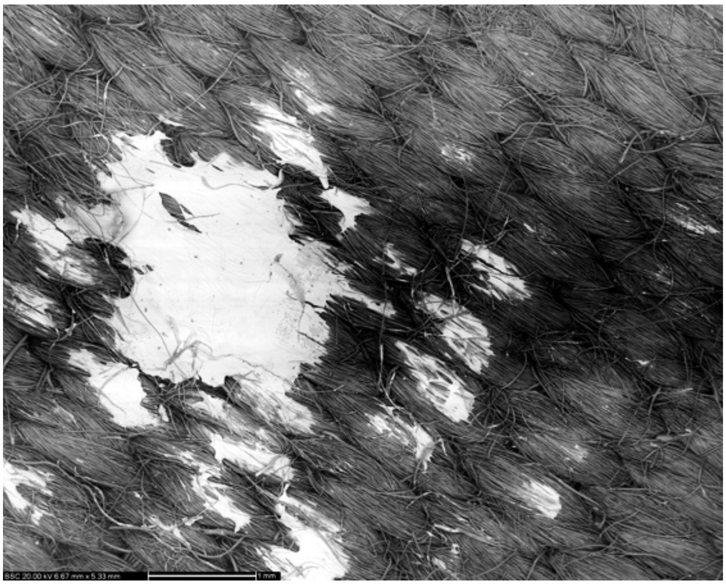


EDX comparison of white particles (purple line) found on treated fabric (red line)

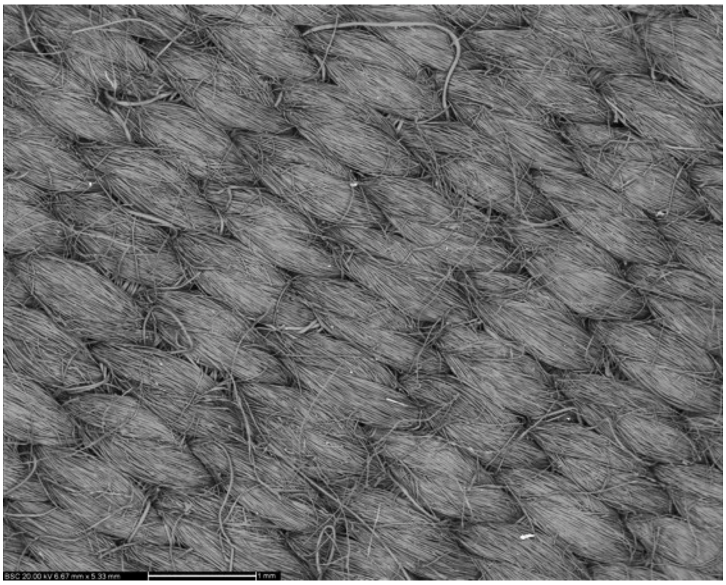
Sample MC-7.5-5: Methylcellulose/TSC on dyed silk



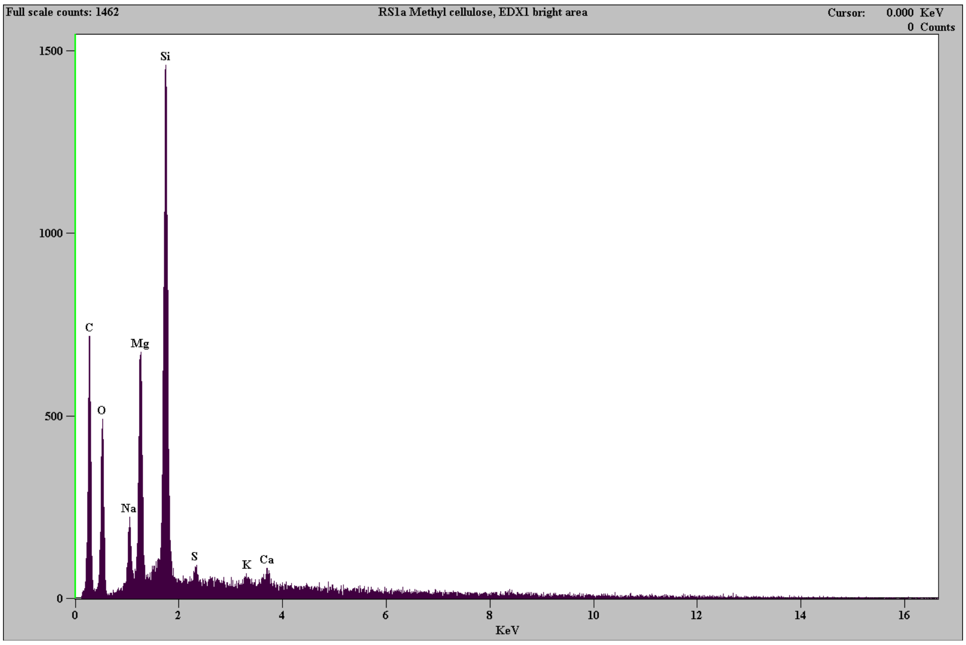
An untreated area of fabric depicting possible cross-contamination x 18 magnification



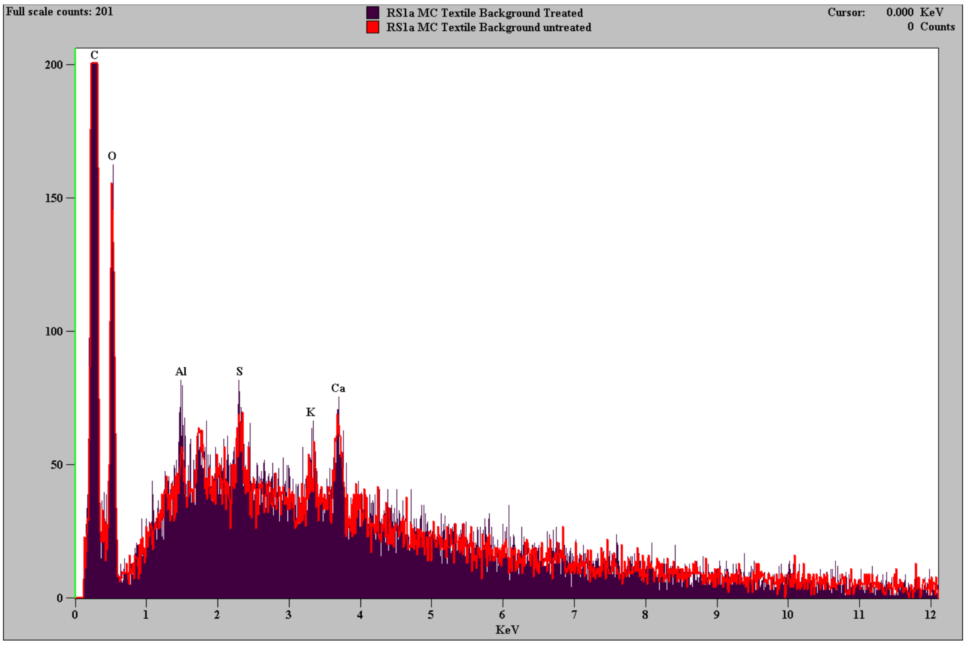
An untreated area of fabric depicting white deposits suggesting possible cross-contamination x 18 magnification



Treated fabric x 18 magnification



EDX mapping of white deposit



EDX comparison of untreated fabric (purple line) and treated fabric (red line)

APPENDIX D

Supplier List and costs

Material	**Approx. Quantity Used**	**Cost if known**	**Supplier**
Laponite RD	~150g	£24.65/kg	Conservation Resources UK Ltd Unit 2 Ashville Way, Cowley, Oxford, OX4 6TU
Methylcellulose	~100g	£49.95/kg	Preservation Equipment Ltd Vinces Road, Diss, Norfolk, IP22 4HQ
Tri-sodium citrate	<100g	£33.31/kg	Fisher Scientific UK Ltd Bishop Meadow Road, Loughborough, LE11 5RG
Copper (II) sulphate (anhydrous)	88.1g	£23.20/200g	Fisher Scientific UK Ltd
Copper (II) sulphate (pentahydrate)	249.7g	£19.36/500g	Fisher Scientific UK Ltd
Sodium hydroxide	4g	£19.66/500g	Fisher Scientific UK Ltd
Melinex® 125 micron 1524mm x 50m	~2m^2	Unknown	Preservation Equipment Ltd
Blotting paper 300gsm 750 x 680mm	~500mm^2	£39.85 for pack of 25 sheets	Preservation Equipment Ltd

APPENDIX E

Risk and COSHH assessment forms

RISK ASSESSMENT FORM

Please view the 'GUIDANCE NOTES ON COMPLETING RISK ASSESSMENT FORM' below.

RISK ASSESSMENT NO: ....

Brief outline of work/activity :	Investigating the use of chelating agents in gels to remove artificial copper staining from samples of fabric - mixing gels with chelating agent tri-ammonium citrate, applying mixture to fabric, staining fabric with copper solution

Location :	Textile conservation labs - Centre for Textile Conservation and Technical Art History

Significant hazards :	- Using hazardous substances - refer to relevant COSHH forms - Spillages of gels + chemicals - Breakage of glassware - risk of injury

Who might be exposed to the hazards :	Students, staff, potential visitors

Existing control measures :	PPE - gloves, goggles, lab coats, masks to be worn when required Fume cupboard + extraction used when required Broken glassware to be disposed of in glass bin Wipe up spillages if they occur with correct material - see COSHH forms if required Ensure chemicals are contained + stored adequately in containers to prevent spillages Washing hands, labelling containers, observing good lab practice at all times

Are risks adequately controlled : YES ☑ / NO ☐

	Additional controls :	**Action by :**
If NO, list additional controls and actions required :		

Completed by :	NIKKI CHARD *Name*	NChard *Signature*	10/5/12 *Date*

Supervisor :	ANITA QUYE *Name*	*Signature*	10/5/12 *Date*

Dates of Reviews:				

University of Glasgow

COSHH Assessment Form

School: Textile Conservation (History of Art)

File ref:

Title of Project: Staining ~~copp~~ fabric samples with copper

Date: 10/5/12

Room No. Chemistry lab

Building: Robertson Building

Persons involved: Student (Nikki Chard), staff (Anita Quye)

Description of procedure: Soaking silk + cotton fabric samples in Copper Sulphate solution, before rinsing in Sodium hydroxide solution

Substance used	Quantities used	Frequency of use	Hazards identified	Exposure route
Copper Sulphate ($CuSO_4$)	approx. 10 mols (10M)	1 day	Harmful if swallowed Irritating to eyes " " skin Toxic to aquatic organisms Long-term adverse effects to aquatic environment	Eyes, skin, ingestion, inhalation
($NaOH$) Sodium hydroxide	approx. 0·5M	1 day	Causes severe burns Corrosive	" " " "

Could a less hazardous substance (or form of the substance) be used instead ? yes / [✓ no]

Justify not using it:

What measures have you taken to control risk?

Engineering controls:
Both: use inadequate ventilation

PPE: Both: Goggles, gloves, lab coat,

Management measures: Both: vacuum or sweep up spillages + dispose in suitable container. Store in tightly closed container in dry, ventilated area. Wash hands after handling.

Checks on control measures:

Is health surveillance required? yes [✓ no]

Training requirements: None

Emergency procedures:
Eyes (both substances): Flush with plenty of water + seek medical ~~advice~~ aid immediately
Skin (both): flush with plenty of water + seek medical aid. Remove contaminated clothes.
Ingestion (both): do not induce vomiting + seek medical aid.
Inhalation (both:) Remove to fresh air + get medical aid.

Waste disposal:
NaOH: in accordance with local regulations
$CuSO_4$: " "

Name and position of assessor: NIKKI CHARD (Student)

Signature: NChard

Name of supervisor (student work only): ANITA QUYE

Signature: Anita Quye

Name of Head of School or nominee:

Signature: