Albertina Cogram
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DUST, SWEAT AND TEARS:

RECENT ADVANCES IN CLEANING TECHNIQUES

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UKIC
UNITED KINGDOM INSTITUTE FOR CONSERVATION OF HISTORIC AND ARTISTIC WORKS

TEXTILE section

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FOREWORD

The Spring Forum and the 12th Annual General Meeting of the UKIC Textile Section, 2003, was held at the Royal College of Art in Kensington, London on the 7th April.

The Forum was titled 'Dust, Sweat and Tears: Recent advances in cleaning techniques'. The cleaning of historic textiles is always a delicate matter, and is an area of textile conservation that is continually in the process of development and improvement. The Forum showed that a great deal of research is being undertaken, resulting in increasingly sophisticated methods of application.

We heard very little about conventional 'washing' during the presentations on the day of the Forum, rather, we were treated to outlines of methods that had been adapted to deal with highly complex cleaning issues. These included the removal of adhesives and their stains, the removal of rust and dye-bleeding stains, and a considerable amount of information on the chemical aspects of the subject matter.

With a subject such as cleaning, it seemed impossible to publish the information without including photographs to illustrate the problems and achievements. It is therefore, with pride and pleasure, that the Textile Section has decided to invest in reproducing several colour images in this publication.

Many thanks to Albertina Cogram and Helen Bacchus for organising the Forum, and to Marion Kite for acting as chair, to all the speakers for their contributions, and to all the Textile Section Committee members who contributed towards the smooth running of the day.

Lisa Dawson and May Berkouwer.

DEVELOPING A PRACTICAL METHOD FOR THE REMOVAL OF PREVIOUS ADHESIVE TREATMENTS FROM LARGE SCALE TEXTILES

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1. Introduction

During the 1950's and 60's a range of adhesives became available, which were quickly adopted by restorers and conservators, and often used in conjunction with more traditional adhesives. The use of these adhesives presented a quick and cost effective solution to the repair of large-scale textiles in particular.

These adhesive treatments are now beginning to fail; partly due to their inherent chemical nature and partly because they were often used in circumstances and with materials for which they were not designed. In order to carry out the further support treatment required by the objects, these adhesive treatments often need to be reversed. Adhesive removal can be seen as a specialised form of cleaning, removing unwanted material.

This paper describes work carried out at the National Trust's Textile Conservation Studio over the last ten years, which has resulted in the development of a practical technique to enable the use of large volumes of organic solvents to remove previous adhesive treatments from large-scale textiles.

To date our experience has been solely working on tapestries, but future Studio projects will include bed hangings from the National Trust's collection.

2. Case Histories

The three case histories to be discussed are:

1. a 17th century Mortlake tapestry from the National Trust property, Blickling Hall in Norfolk;
2. a 17th century Mortlake tapestry from Chastworth House in Derbyshire; and
3. a late 17th century Flemish tapestry from the National Trust property, Ham House, in Surrey.

2.1 Mortlake Tapestry from Blickling Hall

The first large-scale adhesive removal treatment was carried out by the Studio in 1992, on one of a set of Mortlake tapestries, depicting the History of Abraham, that hang in Blickling Hall. The conservation of this set is an ongoing Studio project.

The Abraham set was extensively repaired in the 1950's, and this tapestry is one of three on which the adhesives shellac and latex were used. In 1992 the condition of the tapestry was such that further conservation was required. Before any further treatment could be carried out it was necessary to remove this adhesive, as over time, it had become discoloured, hard and stiff, making the necessary further stitched support treatment impossible.

The 1950's treatment had involved cutting out the weak areas of silk and replacing them with patches of cotton treated with adhesive, these areas were then backed with a second larger adhesive coated patch. Most of the patches could be removed by simply peeling them off, however, the adhesive remained impregnated in the tapestry.

Fig 1 *Reverse of tapestry showing extent of adhesive tapestries.*

Tests showed that a 50:50 solution of Industrial Methylated Spirit and softened water was effective in removing the shellac. In many areas the latex had been applied over the top of the shellac. An initial hope was that by removing the shellac the latex layer might also be removed. In order to soften and release the shellac it was necessary to prolong the contact with the solvent over a couple of days.

After treatment with the IMS:water solution, the shellac was softened and removed to some extent, however, the latex had only softened. There were also concerns about ring marks forming around the treated areas. It was therefore decided to wet clean the tapestry.

The washing process involved prolonged soaks and mechanical action in a wash solution.[1] The wash bath was discoloured yellow with the released adhesive. However, the conservators were disappointed with the results of this treatment, because although it had been largely successful in removing the shellac it had not removed the large areas of latex. The effect of the treatment had been to swell and soften the latex, leaving it more apparent and tacky but still firmly bonded to the tapestry.

Further investigations and an article by Mary Ballard of the Smithsonian Institution outlined a two-stage treatment (Ballard 1987). The latex would be best removed by a pre-treatment with a 10% ammonium acetate solution to break down the cross-linked bonds, followed by 1,1,1 tricholoroethane to remove the latex.

The tapestry was given a 6-hour soak in a 10% ammonium acetate solution in deionised water and then rinsed with deionised water. On drying, a colour change was noticed in the red and yellow dyes. This had not been evident during the ammonium acetate treatment. To counter-act this, the tapestry was immersed in a bath of 1% acetic acid solution, which successfully reversed the colour change.

Before starting the treatment with trichloroethane in the open environment of the Studio, advice was sought from an independent Health and Safety Consultant. Following this advice a mobile fume extraction unit was hired. The conservators wore respirators fitted with the appropriate organic vapour filters, goggles, gloves and lab coats throughout.

Working from the reverse of the tapestry, trichloroethane was applied to the areas of latex adhesive. The solvent was applied to the adhesive using soaked cotton wool pads to soften and release the latex, allowing it to be mechanically removed using a spatula and blunt tweezers.

Any residual adhesive was then removed by placing a polypropylene tray under the tapestry and pouring the solvent directly through the tapestry. Once the localised adhesive removal was completed the tapestry was viewed from the front. There were several areas where ring marks caused by the solvent could be seen. These were removed by feathering out the edges with further solvent -soaked cotton wool swabs. This treatment was very effective in removing the latex.

In total the time taken to devise and carry out the adhesive removal treatment was 172 hours.

Following this treatment, the condition of the tapestry was greatly improved, being supple enough to allow a full stitched conservation treatment.

Although this treatment was successful, the conservators had been left with some concerns, mainly:

- the amount of handling necessary;
- the time that the tapestry had spent immersed in water and organic solvents; and
- the effect, although reversible, on the pH sensitive dyes.

In many ways, the Studio had tackled one of the hardest adhesive removal projects first. The experiences with this tapestry, the knowledge that there was a larger adhesive treated tapestry yet to come and being asked to work on further adhesive treated tapestries and textiles led to a re-evaluation of the technique and equipment to be used.[2]

2. 2 Mortlake Tapestry from Chatsworth

In 1993 the Studio was commissioned to undertake the treatment of a 17th century Mortlake tapestry from Chatsworth in Derbyshire. The tapestry was in a weak condition and the previous adhesive treatment had left the tapestry hard and brittle, so that further stitched support was not possible. The brief was to remove the adhesive treatment and wet clean the tapestry so that a stitched support could be given.

As the adhesive was failing some of the patches could be simply peeled off. Again the adhesive remained impregnated in the tapestry.

The adhesive was analysed by Ciba Geigy and found to be a resin, probably shellac. Tests were then carried out on these adhesive coated patches, to determine which solvents would be most effective in removing the remaining patches and the adhesive residues from the tapestry. It was found that the patches could be released using a pad of cotton wool soaked with IMS.

After removal of all the patches, the tapestry was left very weak. In order to protect it during the subsequent treatments, a layer of nylon net was sewn over the entire front of the tapestry.

Tests indicated that the most effective method for removing the adhesive residue was flushing through with a 50:50 mixture of IMS and acetone, followed by wet cleaning.[3]

Various methods of carrying out the treatment were researched, following which the Studio commissioned the building of a mobile vacuum suction table.

The table has a flat stainless steel top that has set within it a removable grid, 20cm square. The textile is placed over the table and the solvent is poured through the textile and collected in the sump below. Using this apparatus, small sections of the tapestry can be treated using measured volumes of solvent (Fig 2 and Fig 3).

The netted tapestry was mounted onto a frame. The tapestry was marked out into 20cm wide strips, to correspond with the width of the suction plate on the table. A mobile fume extraction system was also set up above the tapestry and table.

Following some experimentation, it was found that the best way of treating the tapestry was to work from the front, drawing the adhesive away. A hole, the same size as the suction plate, was cut in a sheet of Melinex and placed over the area of tapestry to be treated. 200 – 300ml of the 50:50 IMS/acetone mixture was poured through this marked out area of tapestry and covered with a layer of clean cotton sheeting and a further layer of Melinex to reduce evaporation of the solvents. It was left to 'work' for 5 minutes, after which the top Melinex and fabric were removed, the vacuum suction switched on and a further 200 – 300ml of solvent mixture poured through the tapestry to flush out the adhesive. The suction was left on for a further 5 minutes to remove the majority of the solvent.

After the treatment of one area of the tapestry, the table was moved along to the next section. This process was repeated until all of the tapestry had been systematically treated. Areas where the adhesive was particularly thick were retreated. This process was extremely effective.

As with the previous treatment, precautions were taken to comply with Health and Safety legislation. The conservators wore protective respirators, goggles, gloves and lab coats. The levels of the organic solvent vapours in the Studio were measured using a Dräger pump and tubes; they were found to be well below the Occupational Exposure limits for ethanol, methanol and acetone. A specialised company disposed of the large volumes of used solvents.

As IMS and acetone are both flammable, only limited quantities could be kept in the Studio. Therefore, the bulk of the solvents was kept in an outbuilding.

After wet cleaning, the condition of the tapestry was greatly improved, being clean and flexible so that a full stitched conservation treatment could be carried out.

Fig 2 *Set up for use of solvents to remove adhesive on the Ham House tapestry.*

Fig 3 *Taking air samples using a Drager Tube system while work in progress on the Ham House tapestry.*

2.3 Flemish Tapestry from Ham House

In February 2000, the Studio undertook the conservation of a late 17th century Flemish tapestry from the National Trust property, Ham House, in Surrey, from a set of four depicting scenes from the life of King Pyrrhus.

It is a large piece, approximately 3m high and over 5m wide, with a high silk weft content. In the 1960's this tapestry was given a full support of an adhesive coated Terylene net on the reverse. Unlike the other case histories so far discussed, the previous adhesive treatment was documented and published in Studies in Conservation, Pow (1970). The treatment was carried out by the Victoria and Albert Museum when they owned the contents of Ham House.

The 1970 article discussed the rationale behind the choice of treatment. The 'King Pyrrhus' tapestry was thought to be a good candidate for an adhesive treatment because of its size, poor condition and secondary importance in the collection, and because, to quote, 'time could not have been spared to repair it by more traditional means' (Pow 1970).

This decision was taken despite the concern that due to the size and weight of the tapestry, there was a risk of differential movement between the net and textile. Further concerns about the adhesion to the weft-faced weave are also discussed in the article.

The V&A treatment had used four coats of a polyvinyl acetate (PVA) mixture of 87.5% Vinamul 6515 and 12.5% Mowolith DM5 on a terylene net. The adhesive coated net was heat set onto the reverse of the tapestry using domestic and spatula irons in large patches or strips; it was not lined.

The tapestry was monitored and at some point additional stitch lines were put in, but by 1995 all the stitch lines were broken and the adhered net support was failing. The tapestry was stiff to the touch and there were ripples and uneven tensions in the tapestry due to the net. The silk sky was in a particularly poor condition, with open slits and broken weft, and the net was beginning to peel away. It was therefore decided to reverse the previous treatment in favour of a full stitched support and the tapestry came to the Studio in 2000.

After initial documentation and surface cleaning, any net that was lifting was carefully removed with a spatula and tweezers.

Tests indicated that IMS was the most successful solvent for the removal of the adhesive.

Prior to starting work, a risk assessment was written and the relevant personal protective equipment worn, as already outlined in the other case histories. The same portable extraction equipment and fume hood were also used (see Fig 2).

The tapestry was laid face down on tabletops in the laboratory and rolled to locate the areas of remaining net for their removal. Laboratory paper brushed with IMS was laid over the netted areas, covered with a layer of Melinex™ and left for a few minutes. Both the Melinex™ and the laboratory paper were removed and the net came away easily from the tapestry. There was loss of weft, although it was impossible to tell if this damage was caused while the tapestry was hanging or at the point of net removal.

Long, loose warp ends on the reverse had all been thickly coated with adhesive. A layer of blotting paper and Melinex™ was placed under the warp ends to isolate them from the tapestry, and cotton wool soaked in IMS was laid over the warp ends. This was covered in a further layer of Melinex™ and left for one and a half hours. The top layer of Melinex™ was removed and the impregnated cotton wool was rubbed gently over the warp ends to remove even more of the adhesive. This proved very successful, although traces of the adhesive remained on the warps.

Despite the complete removal of the net and the treatment of the loose warp ends, as had been anticipated, adhesive residue remained across the whole of the tapestry.

This phase of the treatment took 30 hours to complete.

Once the terylene net had been removed, a fine net was stitched over the tapestry's weakest areas to protect it during the next phase of treatment.

The whole tapestry was flushed with IMS by means of the mobile suction table and mobile fume extraction system to remove the residual adhesive, using the same procedure as carried out on the Chatsworth piece. Modifications to the contact time and the volumes of solvent used were made. Approximately 200ml of IMS were used in a 20 x 25cm area and it took 15-20 minutes to work. The process was repeated until the entire surface area of the tapestry had been treated.

To monitor the levels of Organic Solvent in the working environment, spot readings were taken using a Drager Tube sampling system. The Ethanol and Methanol components of IMS were tested for separately (see Fig 3).

The Long Term Exposure Limit (LTEL) for Ethanol is 1000 parts per million (PPM), and the Long Term Exposure Limit for Methanol is 1000 parts per million. The Occupational Exposure Limit for IMS (8hr time weighted average) is 100ppm.

All the readings in the room were extremely low, and well within the Occupational Exposure Limits (OEL). Readings from the suction table extraction outlet were also taken. These too were low. All work was completed an hour before the end of the working day, to allow the extraction system to remove any remaining solvent vapour in the room. To meet health and safety regulations, the Studio purchased a purpose built, free standing, external metal chemical store for the storage of large amounts of solvent.

The IMS flushing was deemed successful in removing nearly all the adhesive and no ring marking had occurred. A total of 59 litres of IMS was used and it took 226 hours to carry out. This time included setting up, collection and disposal of IMS from the chemical store, the emptying of the suction table, taking spot vapour readings and the additional netting of weak areas prior to wet cleaning, Following the adhesive removal, the tapestry was wet cleaned at the Studio and given a full stitched conservation support.

The case histories so far outlined in this paper have illustrated the successful development of a method for overall solvent cleaning of three large tapestries. However, modifications of the method are inevitable as new equipment and research is made available.

3. Future Projects

Two of the Studio's forthcoming adhesive removal projects will build on the techniques and experience previously described.

One of the Studio's biggest challenges is likely to be the treatment of the Venetian Ambassador's Bed hangings from Knole in Kent. The hangings are of a blue/green Genoa velvet and are part of a suite made for James II in 1688.

The hangings have been extensively treated in the past with gutta-percha, a form of natural latex found in certain trees, but they have been rendered extremely brittle and have become discoloured as the adhesive has aged and failed.

Research by the former Head of Conservation at the National Trust, Dr Nigel Seeley, suggests that dichloromethane will be the most effective solvent for the removal of aged latex. Initial investigations into this solvent have highlighted the following points:

Dichloromethane is a toxic substance and is classified as a category 3 carcinogen. The Occupational Exposure Level for dichloromethane is 100 parts per million over an 8hr time weighted average; this compares to trichloroethane (as used in the first Blickling Mortlake tapestry) which has an OEL of 350 ppm. It is therefore significantly more hazardous than any solvents the Studio has used to date.

Should this solvent be used, it will be necessary to protect the conservators working on the project by reducing to as low as possible, the levels of dichloromethane and to ensure exposure levels are well within the OEL. The National Trust's Textile Conservation Studio moved in August 2002 to a new premises with a purpose built laboratory containing a more powerful extraction system with adjustable extraction arms. In conjunction with the suction table, this should reduce the levels of dichloromethane in the working environment.

One of the main dangers with dichloromethane is that it has very poor warning qualities. It is intended to use a hand held instrument that gives a continuous measurement of organic solvent vapour, rather than the spot readings obtained from the Drager tubes already discussed, in order to alert the operator immediately of any danger. The appropriate personal protective equipment requires assessment, if the levels of dichloromethane in the working environment can be controlled by the extraction systems to half the OEL, then operators can wear the same type of half faced masks shown with the appropriate filters. The next stage is to do a mock up of the situation, carry out a risk assessment and devise a working method.

Work has already begun on the Studio's second forthcoming adhesive removal project, another tapestry from the Blickling Mortlake set. It is a larger piece than the previous one measuring 3.5m high x just over 4m wide and it has been extensively treated with shellac and latex and has large cut out areas.

After removal of the lining, the full extent of the adhered patches became evident. To date, the failed shellac adhesive patches on the reverse have been peeled away where possible and the adhesive coated cut infills dropped out. Adhesive still remains on the tapestry.

It is planned to explore the possibility of reducing the number of treatments required to remove the shellac and latex. An early test with dichloromethane suggests that the solvent could remove both adhesives in a single treatment. As already outlined, the use of this solvent cannot be undertaken without thorough consideration of the health and safety issues. It is hoped that these two projects will be published in due course.

Acknowledgements
The authors would like to acknowledge and thank the many other conservators involved with the projects discussed in this paper. They are:
Ksynia Marko, Melanie Leach, Claire Golbourn, Mary Everard, Sally Price and Lynn Maclean.

Endnotes

1. Washing solution- 0.1% Synperonic N detergent and 0.05% sodium carboxymethylcellulose (SCMC) anti-redeposition agent in softened water.
2. This treatment has been previously published, (Leach 1997).
3. Washing solution- 0.1% Synperonic N detergent and 0.05% sodium carboxymethylcellulose (SCMC) anti-redeposition agent in softened water.

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Timar-Balázsy A. and Eastop D. 1998 *Chemical Principles of Textile Conservation*. London: Butterworth-Heineman.

Suppliers Information

Adhesive analysis
Ciba Geigy Plastics
Duxford
Cambridge CB2 4QA

Solvents, organic vapour
Masks, goggles, nitrile gloves
Hays Chemical Distribution Ltd
Station Road
Attleborough
Norfolk NR17 2AT

Dräger pump and Tubes, also a
Continuous Monitoring system
Drager Safety UK Ltd
Ullswater Close
Kitty Brewster Estate
Blyth
Nothumberland NE24 4RG

Fume extraction systems
Manufactured by Nederman Ltd
Supplied by CLE Designs Ltd
69 – 71 Haydons Road
Wimbledon
London SW19 1HQ

Similar mobile suction tables
CLE Designs Ltd

MONITORING DUST IN HISTORIC HOUSES

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In recent years, there has been an increasing amount of interest in the problem of dust deposition in museums. This has mainly been generated by large building projects, for instance at the V&A, the British Museum and the Museum of Scotland. These surveys have mostly been carried out using the "loss of gloss" method developed by Stuart Adams, a very simple technique that measures the decrease in reflectance of ordinary glass microscope slides after exposure to a dusty environment.

Dust, or the accumulation of dust, can cause damage to museum objects, and is a particular problem in historic houses and palaces where objects have to be on open display. This is especially the case for objects made of materials that are susceptible to corrosion, such as metals. But removal of dust can also cause damage, particularly on historic materials that have become more fragile with time such as textiles (especially silk), leather, paper, lacquers and varnishes.

Housekeeping, which includes the removal of dust, is labour intensive and time consuming, so understanding where dust comes from and how it accumulates could be useful in devising ways of minimising the deposition of dust and thus extending the intervals between cleaning.

A novel dust monitoring technique has been developed at Historic Royal Palaces, and was described at the meeting. Although some dust monitoring had been carried out in the past, it was deemed important to have our own 'In-house' method for which staff would have a sense of ownership. The main aim is to investigate ways to minimise dust deposition on beds and other vulnerable textiles, and extend intervals between vacuum cleaning to minimise the gradual removal of original silk fibres.

The results of dust monitoring undertaken by the University of East Anglia, at four historic properties owned by English Heritage, Historic Royal Palaces, and the National Trust as reported in the Times and more recently published in The Conservator, were summarised.

A full paper detailing this work is already published:

Howell D. 2003 Monitoring dust in historic houses. In: *Conservation Science 2002: papers from the conference, Edinburgh, 22-24 May 2002.* (ed. Joyce H. Townsend, Katherine Eremin and Annemie Adriaens) pp. 8-10. London: Archetype.

ADAPTING TECHNIQUES: CLEANING A COVENANTING BANNER

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1. Introduction

The conservation treatment of the Avendale banner is both varied and complex. The focus of this paper is on the cleaning aspects of the treatment. This includes the reversal of previous adhesive treatments using humidification and the adaptation of an enzyme poultice treatment, currently used in paper conservation. The enzyme treatment was also used to remove adhesive residue, and was followed by an adapted non-immersion wet cleaning method.

The Avendale banner is of great historic importance and a rare survivor from the Covenanting movement in Scotland. It was carried by members of the Covenanting army who came from Avendale, in the south-west of Scotland, when they fought against the Royalist forces at the battles of Drumclog and Bothwell Brig in 1679. The Avendale banner has been in the collection of the Museum of Scotland since 1898. It will be exhibited in the Museum as part of the display that tells the story of the Reformation in the Church and the Scottish Covenanting wars.[1]

2. The Avendale Banner

2.1 Description

The Avendale banner has been in the Collections since 1898, and was displayed at various times in a glazed wooden frame with a panelled wooden backboard. Evidence suggests that it had undergone various treatments in the past. The banner has been in storage since 1996.

The banner measures 1750mm high by 2120mm wide. It is constructed from three widths[2] of fine, plain-weave cream coloured silk fabric, over-stitched together along two horizontal seams. The banner is stitched to a pole sleeve made up of four pieces of cotton with a nap, overstitched together edge to edge and then folded lengthways. There are cotton ties, two each at the upper and lower edges, stitched at the join of the pole sleeve and the banner. A cream silk ribbon is stitched over the outer edges of the banner with small running stitches along both edges. All stitching is worked by hand.

The banner is decorated on one side with painted motifs in shades of red, green and black.[3] The tracing lines for the motifs and the inscription are still evident as black lines. The motifs are:

- A book, possibly a Bible with signatures;
- A Covenanting inscription 'AVENDAILL FOR REFORMATION IN CHURCH AND STATE ACCORDING TO THE WORD OF GOD AND OUR COVENANTS';
- A thistle.

(See Fig 1).

2.2 Condition

The banner was removed from the frame in order to assess its condition. The banner was found to be backed onto a single layer of fine plain-weave cotton fabric (this will be referred to as the support fabric). The support fabric was adhered with starch around the outer edges to the fabric-covered backboard, and secured in place with a row of tacks through all layers including the banner. The fabric covering the board was a plain-weave bast fibre in four strips nailed on all sides around the edges of the board, rather than a continuous layer. Consequently the majority of the banner and the support fabric had been resting on bare wood for at least fifty years. The wooden board was badly light damaged, suggesting that there may have been considerable damage to the object too.

The banner was generally in poor condition. There was overall particulate soiling, and a number of stains from previous adhesive treatments, and as a result of damp. The silk was structurally weak and there were numerous splits and losses. Loss of silk was predominantly in the upper right quarter and around the book. Much of the flower of the thistle and lower section of the leaves was also missing. There was a central 'cross' where the silk was weak and split, indicating that the banner had been folded in the past. The red paint in this area has shifted in places, suggesting that the banner has been subjected to damp in the past. This is particularly evident from the 'A' of 'Avendaill', which has a mirror image across the 'fold' of the fabric (supporting the theory that the banner was folded) and from red diagonal streaks of paint caused by abrasion when damp.

Stitched and adhered previous repair treatments had contributed significantly to the poor condition of the banner. Observation of the repairs led to the conclusion that they had been carried out at different times and that treatment had been on-going as the condition of the banner deteriorated.

The first previous repair is thought to have included the stitching of the banner to the all-over support fabric and the addition of coloured fabric repairs and the ribbon around the outer edge.

Fig 1 *All over view of the banner before treatment.*

Fig 2 *Detail next to the book before treatment, showing adhesive repairs and in-fill paint.*

Fig 3 *Detail next to the book after enzyme treatment and wet cleaning.*

Fig 4 *Elizabeth-Anne (left) removing in-fill paint, Lynn separating the silk from the support after humidification.*

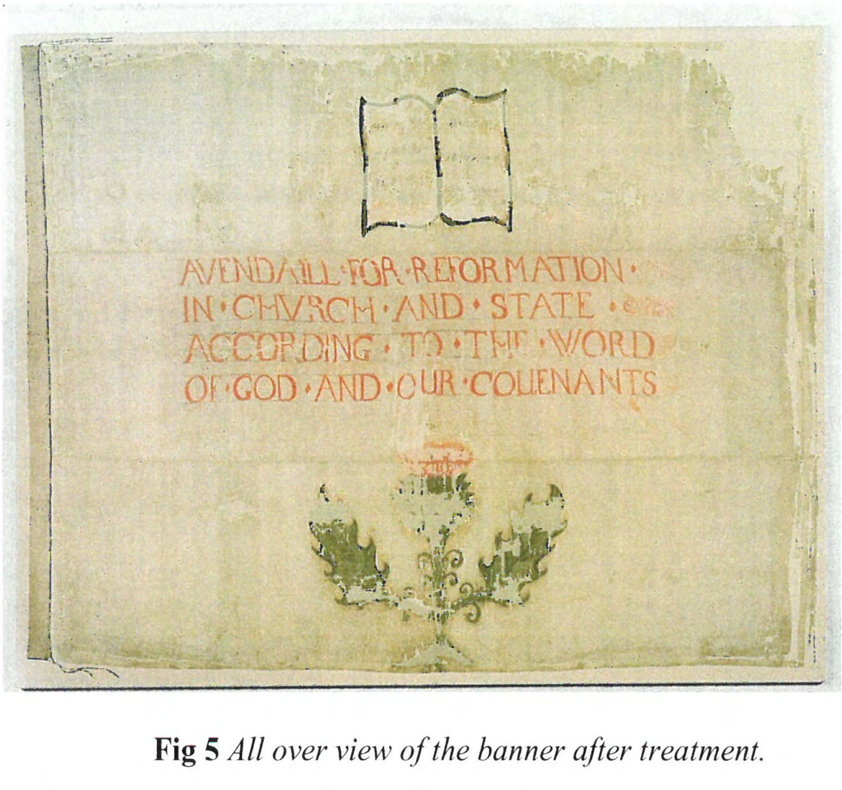

Fig 5 *All over view of the banner after treatment.*

Photographs ©Trustees of the National Museums of Scotland

The second major previous repair was the use of adhesives to adhere the outer edges of the banner and many of the internal damaged areas to the support fabric. The placement of these adhesive repairs, particularly along the upper edge, has led to the conclusion that the banner had started to tear away from the support and that 'first aid' was required.

The adhered silk was extremely fragile, crisp, friable and discoloured. More than one type of adhesive was present. A pale semi-transparent white coloured adhesive contained starch;[4] a brown coloured, streaky adhesive with some thick shiny spots (Fig 2) contained protein,[5] probably an animal glue. Mixtures of starch and protein were also found. There are few references to this adhesive mixture in textile conservation literature. It is however, a mix commonly encountered in paper conservation. Animal glue was added to starch paste to give it more slip and make it easier to apply.

Patches of a Glassine-like[6] paper repair were found behind some areas of loss, between the silk and the support fabric, adhered with a third adhesive. This was evident as a small, clear, shiny hard spot on one of the letters and is thought to be synthetic. It was found to be insoluble in water but soluble in acetone. It was likely to be a quick repair carried out some time after the starch/animal glue repairs.

A number of areas of loss in the top third of the banner had been in-filled with a beige-coloured paint (Fig 2). The paint was mostly confined to the support fabric, but had been applied clumsily, going over the edge of the silk.

3. Treatment

The banner was released from the fabric-covered board using a Gore-Tex humidification poultice[7] to soften the starch adhesive. The layers were separated using a spatula.

Before removing the banner from the support a number of issues had to be addressed:

- Removal of paint in-fills;
- Decisions on the removal or not of old repairs;
- Removal of the stitching attaching the banner to the support;
- Release of areas of banner adhered to the support;
- Removal of glassine paper repairs.

For the purpose of this paper only the final two points will be discussed.

3.1 Release of areas adhered to the support

The starch and animal glue repairs appear to have been applied quickly, as large brush strokes are clearly identifiable (Fig 2). It seems probable that the adhesive mixture was also prepared in a hurry and that the mix was inconsistent, which would account for the varying proportions of starch to glue in different areas of the banner.

The brown spots of animal glue with starch adhesive were readily removed with swabs moistened with filtered water[8], indicating that the mixture was predominantly animal glue. This success encouraged experimentation with removal of larger areas with water, applied with a combination of a small paintbrush and swabs. The residue was soaked up with blotting paper placed under the silk, and by blotting it off from the top.

The very fragmentary upper edge of the banner appeared to be adhered with an adhesive that was mainly composed of starch. Contact humidification, initially with a Gore-Tex poultice and then with damp pieces of blotting paper placed directly on the object, was used to soften the adhesive so that a spatula could be inserted between the layers to separate them (Fig 4). This technique was successful in places but some sections were stuck so firmly that they were impossible to separate. Attempts to do so caused the fragile silk to break up.

There were two options for these areas:

- To cut away most of the released support fabric, leaving the strongly adhered patches in place. This would be unsatisfactory due to the different weights of the fine silk and heavier support fabric, and would also make the proposed adhesive treatment difficult. It would therefore be used as a last resort.
- To investigate the use of the enzyme Amylase to break down the starch adhesive, enabling release of the silk.

3.2 Enzyme Research

Previous published treatments on textiles have generally involved immersing the textile in an enzyme bath (Bott 1990; Shibayama and Eastop 1996; Uden 1997). Factors that prohibited this type of treatment for the Avendale banner included its large size, maintenance of optimum conditions for the enzyme, and the water solubility of the original paint.[9] The extreme fragility of the banner also made total immersion undesirable. In addition, it would have been difficult to keep track of the numerous fragments as they were released from the support.

The alternative was to apply the enzyme locally in a gel. Enzyme gels have been used in paper conservation since the late 1970's (Hatton 1977). In paper conservation a new pre-fabricated enzyme gel poultice for the treatment of starch based adhesives has been developed. The product 'Albertina-Kompresse' is the result of a collaborative project principally between the conservation departments of the Staatliche Akademie der Bildenden *Kűnste, Stuttgart and the Graphic Collection Albertina, Vienna. It was* developed in response to a problem similar to that of the Avendale banner. The aim of their project was to find a way of quickly and safely dismounting prints pasted into bound albums with a modified starch paste known as 'Alaunkleister' without affecting the integrity of the albums. 'Alaunkleister' is composed mainly of starch paste with some animal glue and the addition of aluminium sulphate as a preservative. This adhesive had become hard and brittle over time and it did not respond to humidification treatment designed to swell the paste allowing separation of the layers.

The first stage of the development of the enzyme gel was presented at ICOM-CC in 1996 (Blüher et al. 1996). The enzyme used was a very pure form of alpha-amylase as artificial

ageing tests had shown that there was a greater risk of paper discolouration from crude products than purer forms of the enzyme. The gel chosen was methylcellulose.
In order to prevent it contaminating the object an interleaving layer of tissue paper was required between the object and the gel, which did not allow the methylcellulose to pass through.

However, this paper and the viscosity of the gel hindered the progress of the enzyme to the surface to be treated. This problem was greatly reduced by the addition of small amounts of additives:

- The surfactant Triton X-100 acts as a wetting agent to reduce the viscosity of the gel, making it easier for the enzyme to penetrate the interleaf paper;
- Water-soluble proteins in the form of gelatine act with the surfactant to preferentially bond with the interleaf paper, easing the passage of the enzyme through the paper to the object and the adhesive layer.

The influence of the additives means that the amount of enzyme required for the treatment is very low. Samples were tested for the presence of any enzyme residues. Only very small amounts were detected and these were reduced to almost negligible amounts if the surface was cleaned with moist swabs after treatment. The system relies upon the natural acidity of the object to provide the necessary environment for the enzyme to function so the gel is not buffered. The process can be successfully carried out at room temperature.

The enzyme gel was effective but difficult to produce and it had a limited shelf life. The project evolved into the development of a longer lasting 'Ready-For-Use Poultice', making routine application feasible.[10] The research was published in Restaurator (Schwarz et al. 1999). The product 'Albertina-Kompresse' is commercially produced and is available from the German firm Walter Klug & Co.

3.3 Method

The Conservation Department of the National Archives of Scotland has used the 'Albertina-Kompresse' for over a year with good results and was able to supply a test sample to try on the banner.[11] The poultice is supplied in a pack with three components:

- Thin interleaf paper;
- Non-woven polypropylene 'fleece' material, which has been impregnated with the enzyme gel then dried for storage;
- Thick blotting paper.

Water is necessary for enzymes to function as catalysts; therefore, the poultice only works when the enzyme has been re-activated with water. The three components of the poultice are cut to the required size and each is separately wetted out using either a brush or a spray. As the interleaf paper is in direct contact with the object it can be blotted to reduce its moisture content. When wetting out the fleece it is important to make sure that the enzyme gel is not 'washed' out.

The interleaf paper is placed directly on the object with the enzyme fleece on top, followed by the blotting paper. The poultice is covered with Melinex, and light weights are placed on top (Fig 6).[12] The poultice can be checked after 15 minutes to see if it has worked; if not, it can be left on for longer, or a fresh poultice applied. The treatment of the banner was very successful. Adhered areas that had not responded to humidification were detached with ease, generally within 15 minutes.

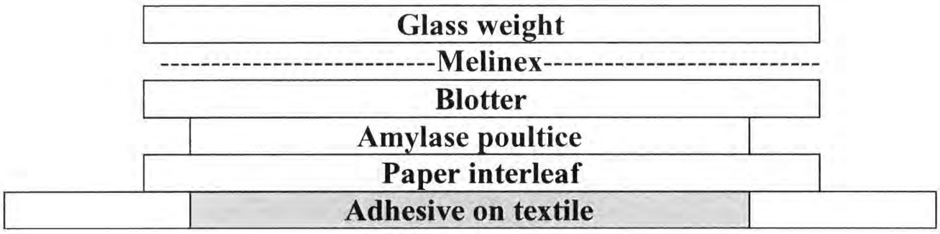

Fig 6 *The sequence of layers in the Albertina-Kompresse. (After Klug and Co.)*

The minimum amount of water required for the poultice to work has been quantified (about 0.08ml per 2cm^2 treatment area) but judging the quantity of water to use and applying it evenly is a matter of practise and experience. During treatment we found that spraying the water was the best method when a 'drier' poultice was required as it was easier to control the amount of water being applied. When the 'drier' poultice was used it was possible to treat the silk and separate it from the support without leaving any watermarks behind.

When a 'wetter' poultice was used we found that the starch liquefied more readily and was soaked up into the poultice and deposited on the uppermost side of the interleaf paper. This also meant that the object became wet with the starch solution. In the case of the banner, where the adhesive to be removed was soaked into the silk making it stiff and vulnerable to damage, this was an advantage as it made the starch easier to rinse out. However, this 'wetter' poultice would not be recommended for objects, which could not be wet cleaned.

Following separation of the layers, the silk was rinsed locally several times with filtered water to remove the adhesive deposits. Ringing was controlled though the use of blotting paper.

The enzyme treatment was used to release the remainder of the banner adhered to the support with the starch and animal glue mix. Using the 'wetter' poultice, the amounts of adhesive residues in the silk were reduced, resulting in a marked improvement in the flexibility of the silk.

3.4 Residues

During development of the 'Albertina-Kompresse' extensive tests were carried out to see if any enzyme and detergent residues were left behind after treatment. The residues found were very small and range from 6.1 μg (micrograms) per 3cm^2 of enzyme without cleaning, to 5.6 μg when the sample was cleaned with a damp swab after treatment. When the sample was washed in demineralised water the residual amount of enzyme fell below the detection limit of the analytical procedure to less than 0.2 µg. Detergent residues followed the same pattern, although the residues were proportionally larger as the gel contains more detergent than enzyme. Residues ranged between 29.7µg per 3 cm^2 to 2.7µg per 3 cm^2. More residue was present in the paper in direct contact with the poultice. It has been recommended that, where possible, the poultice is applied to the reverse side of the object so that the support material is in direct contact with the poultice and the contamination of the object is reduced.[13]

3.5 Removal of glassine paper repairs

During the enzyme treatment some areas did not respond to the poultice, due to the presence of the third adhesive. A brush dipped in acetone was slid gently between the banner and the support, releasing them from each other. However, the glassine paper patches, also adhered with the third adhesive, were difficult to detach from the extremely fragile silk. The patch at the top left of the banner was partially removed but another large patch of paper was left in place rather than risk damage during treatment.

3.6 Wet cleaning

Given that the banner had responded so well to localised wetting during the enzyme treatment, wet cleaning of the entire banner now seemed feasible. Benefits of cleaning would include:

- Removal of any remaining enzyme residues;
- Reduction in staining and water marks;
- Removal of impurities and degradation products from prolonged proximity with both the cellulose- based support fabric and the wooden mount board;
- Relaxing of creases.

It was felt to be important to undertake the cleaning with the object face up in order to closely monitor its condition, in particular the painted areas, while wet. However, this meant that the banner still could not be completely released from the support along the horizontal seams.[14] Melinex strips were slipped between the silk and the support fabric where possible, to prevent soil transfer from the support fabric and to enable the silk to be smoothed out after cleaning.

Wet cleaning was carried out in small sections that measured approximately 1/12th of the overall banner size. Cleaning started at the edge next to the pole sleeve as the silk was attached here, and continued towards the opposite edge. The pole sleeve and unreleased seamed areas were covered with several layers of blotting paper held in place with glass weights during the treatment. Filtered water was carefully applied to the silk with a brush and the areas then blotted off with paper. This method was chosen in preference to spraying as it afforded greater control. The blotting paper soaked up a large amount of yellow/brown soiling from the silk. The blotting layers over the seams turned very brown and had to be changed frequently. The process was repeated several times in each area, keeping a careful eye on the condition of the silk.

It was possible to wet out the silk with the painted lettering more than first anticipated; the red paint was stable but the red ribbon repair was very fugitive. The small pieces of ribbon were kept dry with blotting paper. A warm air dryer was used where accidental wetting of the ribbon occurred. The green paint of the thistle was also fugitive, so wet cleaning of this area was not attempted. The spread of water around the thistle was controlled with Melinex and blotters.

After cleaning, the silk was wet out enough to 'float' on the Melinex and the creases eased out and the weave re-aligned where possible. This was often difficult because of the two seams that were still attached to the backing fabric. Once the silk was dry any ringing marks were removed by dampening with a brush and blotting off. The amount of ringing was quite small because the wet/dry interface was covered with blotting paper during drying, soaking up most of the soiling. The cleaning process was carried out on the whole banner over a period of several days.

Once wet cleaning was completed, the banner was covered with Melinex and a layer of Polyfelt for cushioning, and clamped between two boards for turning. The last of the stitches holding the support fabric in place were cut enabling the support fabric to be removed, revealing the reverse of the banner.

4. Conclusions

The 'Albertina-Kompresse' worked extremely effectively on this banner. It was easy to prepare and control, and the reaction time was fast. There was no need to maintain specific temperatures and conditions, and local use was very important as the banner could not be immersed.

The adapted wet cleaning process was undertaken because the localised cleaning during adhesive removal had been successful. Ringing was very minimal, and removed by chasing with a damp brush and blotting paper. The silk regained lustre, flexibility and was improved in colour. Staining was reduced and the flushing out of acid products was an advantage. There was a dramatic difference to the condition of the banner following these processes in comparison to the stiff, friable soiled banner before treatment.

The enzyme treatment and wet cleaning was a slow and painstaking process. It took approximately 250 hours to release the banner completely from the support. Without the enzyme poultice treatment, it is difficult to imagine how the very fragile and crisp areas of the banner could have been treated.

The fragile and fragmentary nature of the banner precluded the use of a stitched support treatment alone. The improved condition of the banner made it possible to proceed with an all-over adhesive support treatment prior to encasing and mounting for display.[15] (Fig 5)

Acknowledgements

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Endnotes

1. Covenanters were originally the supporters of the National Covenant of 1638, and later the more extreme Solemn League and Covenant of 1643. These were manifestos drawn up to consolidate opposition to innovations in Protestant worship proposed by Charles I. By the 1670 - 1680's the Covenanters represented the radical Presbyterian wing of the Scottish Church, and fought an increasingly bitter and bloody war against the Royalist force of Charles II and James VII.
2. Selvedge width 580mm.
3. Paint cross-section analysis was carried out by Dr Joyce Townsend, Senior Conservation Scientist, Tate Gallery
4. Iodine test carried out with a 0.01n solution of Iodine Potassium Iodide (0.13 g of Iodide and 2.6g Potassium Iodide in 5ml water, diluted in 100mls water)
5. Two drops of 2% solution of copper sulphate in distilled water were applied to the sample, followed after a few minutes by 1 drop of 5% solution of sodium hydroxide in distilled water. A violet-pink colour indicated the presence of a protein.
6. A glossy transparent paper made from very clean chemical wood pulps, heavily super-calendered.
7. A membrane of Gore-Tex (vapour permeable material) laminated to a non-woven 100% polyester support fabric.
8. Ordinary water, (Scottish water is soft), filtered through a Cuno Activated Carbon Filtration System for dirt particles and colloidal contaminants.
9. The in-fill paint was also water-soluble but could have been removed before treatment. There was also concern about the amount of soiling and degradation products, which could be released into the bath from the support fabric.
10. If stored properly the supplier, Klug &Co, states that the poultice can be kept for at least 12 months.
11. Dr G. Banik was contacted but he had not heard of the poultice being used on textiles before.
12. It is recommended that 150 – 200g weights are required for a 10cm2 area; this is equivalent to a 5mm thick glass weight. As the silk was very fragile we were concerned about using such a heavy weight and chose to use between 2 and 3 layers of 1mm thick glass microscope slides instead, equivalent to approximately 55-85g.

13. Dr Anita Quye, NMS, is currently investigating testing textiles for enzyme residues as there may be a difference from paper, particularly with non-cellulosic textiles.
14. Some stitching had to be left in place until the object was turned over: for example it was difficult to distinguish between the original seam stitching and the stitching over the seam attaching it to the support fabric The banner was considered too fragile at this stage to turn over and back again if not absolutely necessary.
15. The banner will be stitched to a fabric-covered board for display in a frame.

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Materials and suppliers

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87509 Immenstadt
Germany
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http://www.klug-conservation.com

Gore-Tex and Polyfelt
Preservation Equipment
Shelfanger
Diss
Norfolk IP22 2DG

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.

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1. Introduction

The following paper is an investigation into the efficiency and effects of three chelating agents, namely tri-sodium citrate, tri-ammonium citrate and di-sodium EDTA (ethylenediaminetetreaacetic acid), on the removal of copper and iron staining from cellulosic textiles. The investigation was undertaken as part of the MA Textile Conservation course at the Textile Conservation Centre, University of Southampton.

A chelating agent has the ability to bind a metal ion, sequestering it from its environment and rendering it inactive. The word 'chelating' comes from the Greek word for claw (χηλη=chele) because the chelating agent molecule can be seen holding onto the metal ion like a claw.

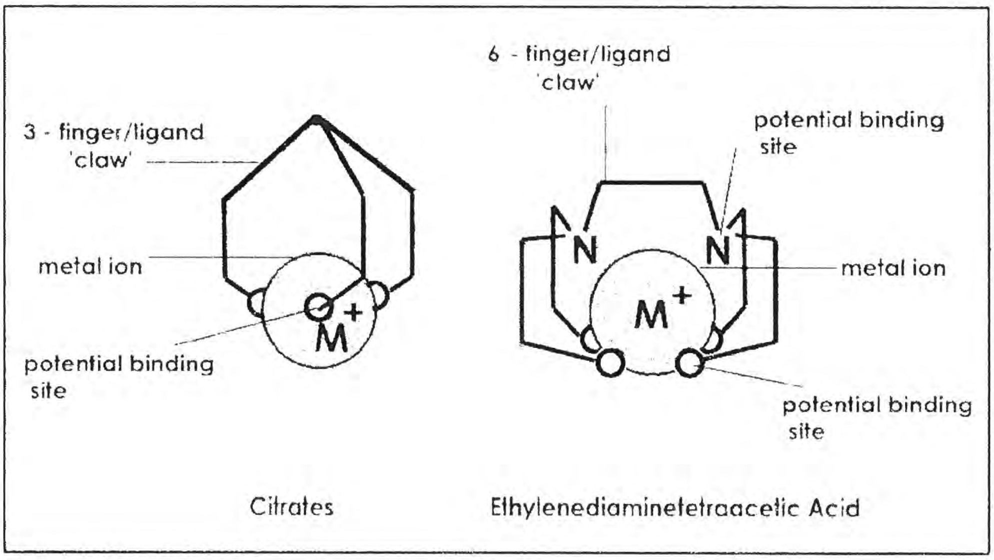

Fig 1 *Diagram to show the claw-like structure of a chelating agent holding a metal ion.*

Chelating agents are encountered in conservation. They are used to treat archaeological and corroded metal objects (Cronyn 1990). Painting conservators found chelating agents a useful tool for cleaning painted surfaces (Phenix and Burnstock 1992). They have a key role in the removal of iron stains from paper (Burgess 1991) and residual metal ions from photographs (Gent and Rees 1994). Textile conservators have relied on chelating agents for the removal of metal staining from textiles (Adler and Eaton 1995) and as buffers to enhance the performance of aqueous cleaning systems (Tímár-Balázsy and Eastop 1998).

The aim of the investigation reported here was to identify and evaluate both the efficiency and effects of certain chelating agents used for the removal of copper and iron staining from textiles. The objectives were:

- to identify which chelating agents are mainly used in conservation in general and in textile conservation in particular;
- to identify the current usage of chelating agents in textile conservation;
- to design, undertake and evaluate experiments which would enable an assessment of the efficiency and effects of the tested reagents;
- to test the applicability and reproducibility of the experiment results by transferring them to object treatment;
- to provide recommendations for the use of chelating agents in textile conservation.

2. Chelating agents

The terms chelating agents, chelates, sequestering agents and complex builders have all been commonly used to describe these reagents.

Chelating agents are multi-dentate ligands, which form coordinate bonds with metal ions to form a complex. If the complex is water soluble, the chelate is also a sequestering agent or sequestrant. The metal ion is solubilised but rendered inactive (sequestered) within the system. Chelating agents are usually quite large molecules which can wrap themselves around the metal ion, with the donor groups co-ordinating to specific sites on the cation (Phenix and Burnstock 1992:28).

Chelating agents can be either inorganic or organic. They can form complexes with metals in both aqueous and non-aqueous environments (Burgess 1991:36).

Stability constants are a means of expressing the thermodynamic stability of the complex species, and derive from the equilibrium reactions involved. This can be described by the equation:

$$\boxed{M \qquad + \qquad L \qquad \leftrightarrow \qquad ML}$$

metal ion + chelating agent ↔ soluble complex ion

The position of the equilibrium is determined by the equation:

$\boxed{\text{Stability constant } K = [ML] / [M][L]}$ where [ ]= concentration.

The greater the value of K, the greater the equilibrium favours the formation of a stable complex. The stability constant is a measure of the affinity of the chelate to the metal ion (Phenix and Burnstock 1992:29). The greater the K for a specific metal ion, the greater the affinity of the chelating agent for that ion.

2.1 Tri-sodium and tri-ammonium citrates

Tri-sodium and tri-ammonium citrates are soluble salts of citric acid (Fig 2). Citric acid contains three potential binding sites. As citric acid is a weak carboxylic acid, citrates have a very good buffering action. The carboxylic group (-COOH) serves as the buffer.

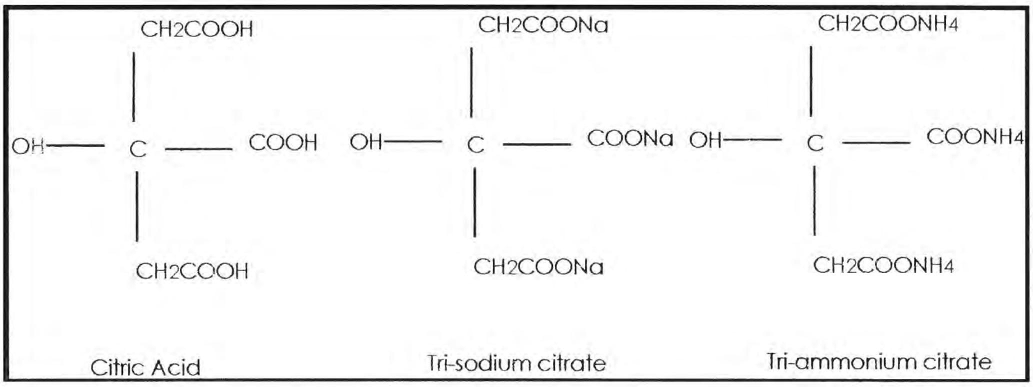

Fig 2 *Molecular structures of citric acid and the two citrates.*

2.2 Di-sodium EDTA

Di-sodium EDTA is a soluble salt of ethylenediaminetetraacetic acid (Fig 3). It has been available commercially since the mid-1930s. It was originally marketed by a German firm under the name 'Trilon B' (Burgess 1991:38). EDTA contains six potential binding sites.

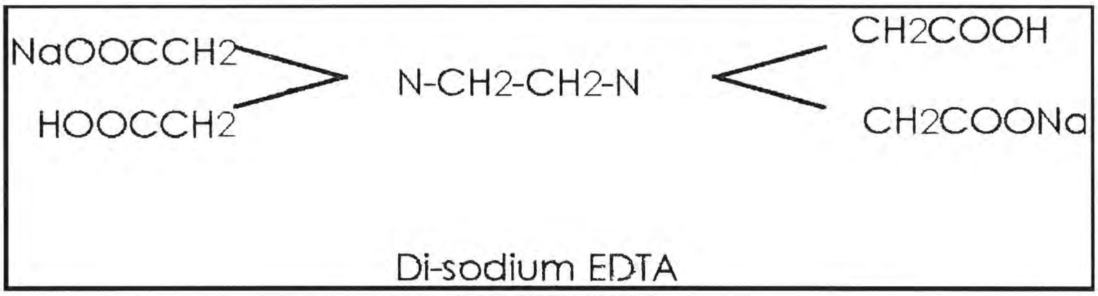

Fig 3 *Molecular structure of di-sodium EDTA.*

EDTA has been linked to certain environmental concerns (Hofenk de Graaff 1982:94). EDTA is a synthetic substance produced from crude oil. It is difficult to break down by biodegradation and can form a hazard to drinking water. In addition, its production requires large amounts of energy and long processing chains (ECOVER® 1995). Nevertheless, EDTA has been, and still is, widely used in both the cosmetic and personal hygiene industries.

3. The experiments

3.1 Aims and Objectives

In order to design the experiments and decide on the methods of evaluation, it was of key importance to define the questions to be answered through the experiments. These questions were:

- which is/are the most effective reagent/s in removing copper and/or iron corrosion products from textiles;
- which is/are the most effective concentration/s;
- which is the most effective pH for each reagent tested; which reagent/s, at which pH has/have the least damaging effects on textiles.

3.2 Variables

3.2.1 Temperature

The temperature of the wash solution is another very important factor for the performance of the chelating agents. However, time constraints only allowed for a certain number of variables. Therefore, it was decided not to include the temperature in the variables and use room temperature (approx. 21°C) throughout the experiments, as is the custom practice for the wet cleaning of historic textiles.

3.2.2 Types of Staining

Copper and iron were chosen to be the type of staining for three reasons.

1. They could easily be found on historic textiles as a result of washing with water coming from copper pipes; storage in iron containers; securing with iron nails; presence of copper or iron metal threads, fastenings, etc.
2. In the articles discussed in the literature review, whenever soiling could be analysed (e.g. Burgess 1991; Adler and Eaton 1995), these were the types of metals more commonly found.
3. Both of these metals produced very distinctively coloured corrosion products (greenish blue for copper and orange brown for iron), which meant that stain removal could be detected both subjectively (by eye), and quantitatively (with the use of a chromameter).

3.2.3 Method of Staining

The samples were stained as follows. They were immersed in the metal solution and then treated with sodium hydroxide, allowing the metal ions to react to form metal hydroxides. The samples were then rinsed to remove loosely bound material. Due to time constraints it was decided to use a single fabric type, namely undyed, bleached, cotton fabric. Each sample was cut to 120 x 120 mm.

3.2.4 Chelating Agents, pH and Time Duration

The literature review identified the three chelating agents most commonly used by conservators as being: tri-sodium citrate, tri-ammonium citrate and di-sodium EDTA. The three chelating agents were tested at three different concentrations (0.01M, 0.05M and 0.25M), and at three different pH values (6, 7 and 8). A mixture of a non-ionic (Synperonic A5), and an anionic surfactant (sodium dodecyl sulphate, SDS), was used. Each sample was immersed separately in the wash solution for 15 minutes. Mechanical action was achieved by means of an ultrasonic bath to ensure each sample received the same amount and intensity of mechanical action. Aqueous cleaning was followed by four rinses, three with softened and the last with de-ionised water.

3.3 Artificial Ageing

In order to determine any deleterious effects the chelating agents may have on textiles, a set of unstained samples was tested under the conditions shown to be most effective from the copper and iron experiments above. The treated samples were then artificially aged in an ageing oven for 1, 2 and 4 weeks. A combination of heat (70-75C) and moisture (RH 55-60%) was used in order to accelerate the ageing of the cellulose.

3.4 Methods of Evaluation

Four different methods of evaluation were used.

1. Measuring the weight of the samples before and after staining, and after treatment, as the staining proved to substantially increase the weight of the sample.
2. Taking chromameter readings before and after treatment gave clear results as both corrosion products had very distinct colours. A Minolta CR-210 chromameter was used to measure Y x y values of the sample colour at light D65.
3. Drawing the speciation plots of the metal ions and the ligands to determine the percentage of metal bound to the ligand. These were drawn with the IUPAC Stability Constants Database 3.09, Academic Software 1997.
4. Measuring the tensile strength of the aged samples with an Instron 4301.

3.5 Experimental Protocol

The experimental procedure was broken down to nine different sets of experiments.

1. Copper/Iron: Staining method.
2. Copper/Iron: Test duration (This experiment showed that chelating agents are not efficient for the sequestration of iron staining. Iron stained samples needed an additional reagent. Sodium dithionite was found to be the reducing agent most appropriate from the literature review.).
3. Copper: Efficiency of the chelating agents.
4. Copper: Artificial ageing.
5. Iron: Efficiency of sodium dithionite.
6. Iron: Catalytic effect of sodium dithionite
7. Iron: Efficiency of the chelating agents
8. Iron: Catalytic effect of Fe(II).
9. Iron: Artificial ageing.

5. The results

5.1 Copper

Tri-ammonium citrate proved to be the most effective of the three reagents tested. The more the pH moves away from neutrality, the more effective the chelating agents become. pH 6 was the most effective, and afforded the fastest rate of stain removal of all the pH values tested. pH 8 came second, and pH 7 third. Concentration and time are interdependent. Either one of these parameters can be increased to improve the performance of the chelating agents. The chelating agents appeared to have no deleterious effects on the cellulosic textiles tested.

5.2 Iron

Tri-ammonium citrate proved to be the most effective of the three reagents tested. Tri-sodium citrate came a close second, but di-sodium EDTA proved much less effective. The more acidic the pH, the more effective sodium dithionite is. Concentration and time are interdependent. Either one of these parameters can be increased to improve the performance of the chelating agents. There appears to be a catalytic effect of both sodium dithionite and Fe(II), but the reaction is very slow. The chelating agents tested and sodium dithionite appeared to have no deleterious effects on the cellulosic textiles tested.

6. Case studies

The results from the experiments were applied to two objects from the TCC Reference Collection, a study and research collection.

6.1 Object stained with copper corrosion products

The first object was a woollen apron decorated with copper, silver coated metal strips and sequins, parts of which were covered with copper corrosion products.

One area of the object was treated with a solution of 0.05M tri-ammonium citrate, 0.1%v/v Synperonic A5 and 0.1% w/v SDS at pH 6 (the solution was buffered with citric acid) for 15 mins. The copper corrosion products had not migrated onto the textile fibres but were still firmly attached to the metal elements.

The object was laid on its reverse side on silicon release paper. A piece of cotton was inserted underneath the area to be treated and another piece of cotton, soaked in the wash solution, was placed on top. This was covered with polythene and weighted with glass plates to prevent the solution from evaporating. Every 5 mins the cotton wool was lifted and the metal elements were gently rubbed with a cotton-wool swab immersed in the wash solution. As time progressed an increasing amount of copper corrosion products was detected on both the upper and lower cotton-wool layers, and on the swabs. Treatment was discontinued after 60 mins because one of the dyes started to bleed. The treated area was rinsed with softened water applied with a pipette, blotted with cotton fabric and blow-dried with a cold air dryer.

The solution identified from the experiments as the most effective for the removal of copper staining proved to be successful on the object.

6.2 Object stained with iron corrosion products

The second object was an English sampler, dated 1810. The sampler was trimmed with a 10 mm wide cotton tape, attached around the edges with stitching, and was used to secure the object onto a wooden (?) support with iron nails. A substantial amount of rust is present around the edges of the nail holes.

A section of the cotton tape attached to the lower side of the sampler was removed. It was cut into four pieces. One piece was immersed in the wash solution; the second was treated with cotton-wool pads, soaked in the wash solution; the third was treated with the same method at a different pH; and the fourth was left untreated for evaluation.

The first piece was immersed in a wash solution of 0.05M tri-ammonium citrate, 0.15M sodium dithionite, 0.1% v/v Synperonic A5 and 0.1% w/v SDS, at pH 6 for 15 mins. Every 5 mins mechanical action was introduced by means of sponging. After the first 5 mins no staining could be detected by visual observation.

The stained areas of the second piece were sandwiched between two pieces of cotton-wool, soaked in the wash solution, covered with polythene, and left for 15 mins. After 5 mins a significant amount of staining had been removed and after 10 mins no staining remained. No mechanical action was necessary. After 15 mins all the staining had been removed and no halos or stains were created.

The third piece was treated in the same way, but the solution was buffered at pH 7. Results were similar to those above, except that the staining was totally removed after 15 mins rather than 10 mins.

The pieces treated by the immersion method appeared cleaner and lighter than the piece treated with the cotton pads method. Although the method was altered for the second and third pieces, no longer time was necessary as in the copper case. There are two most likely explanations. There was a smaller amount of staining present, and the staining had migrated onto the textile fibres rather than bound onto any metal element. Lowering the pH increased the treatment rate but not the amount of staining removed.

7. Recommendations for the use of chelating agents in textile conservation

7.1 Choice of a chelating agent

According to the results of the experiments and the literature review, the following reagents are recommended: Tri-ammonium citrate is highly recommended as it had the best performance of all three chelating agents and gave no indication of any deleterious effects on the cotton textile samples. Moreover, there are no environmental concerns for this reagent. Tri-sodium citrate is also recommended as an alternative to tri-ammonium citrate as it showed a good performance, it gave no indication of any deleterious effects on the cotton textile samples and it has a lower cost than tri-ammonium citrate.
Di-sodium EDTA is linked with certain environmental concerns and as it did not perform better than the citrates, it is not recommended for use in textile conservation.

Tri-ammonium citrate proved to be the fastest and most efficient in removing both copper and iron staining. Tri-sodium citrate and di-sodium EDTA had a similar performance in the removal of copper staining; tri-sodium citrate proved to be more effective than di-sodium EDTA in the removal of iron staining. Sodium dithionite (a reducing agent) in combination with a chelating agent proved to be necessary for the successful removal of iron staining.

7.2 Preparation of tri-ammonium citrate

Tri-ammonium citrate is available ready-made, however, it could also be prepared from other reagents. There are two methods proposed here for preparing tri-ammonium citrate in a conservation laboratory.

7.2.1 Method 1

1 mol of citric acid has three carboxylic groups (-COOH). To neutralise these one would need to add 3mols of ammonium hydroxide. Thus, the ratio of citric acid to ammonium hydroxide would be 1:3 represented by the equation:

$$\underset{\text{ammonium hydroxide}}{3NH_4OH} + \underset{\text{citric acid}}{C_6H_8O_7} \longrightarrow \underset{\text{tri-ammonium citrate}}{(NH_4)_3C_6H_5O_7} + \underset{\text{water}}{3H_2O}$$

Citric acid comes in a crystalline form, whereas ammonium hydroxide comes in a liquid form, known also as ammonia solution.

Example: Making up 1l (one litre) of 0.05M tri-ammonium citrate.
1mol of citric acid is needed for 3mols of ammonium hydroxide.
1mol citric acid = 1 x MW of citric acid = 1 x 210.14g = 214.10g
3mols ammonium hydroxide = 3 x MW ammonium hydroxide = 3 x 17.03g = 51.09g ≈ 225ml
The ammonia supplied by BDH is 0.91 at 25% concentration. This means that there would be 91g ammonia in 100ml, or 910g in 1000ml, if the concentration were 100%. The ammonia concentration is 25% ≡ 25g in 100g so ammonia in 1000ml = 910 x 25/100 = 227.5g ammonia. So 227.5g ammonia in 1000ml
51.09g ammonia in x ml → x = 51.09/227.5x1000 = 225ml
Mixing these amounts and topping up with water to 1l (one litre) gives 1M solution of tri-ammonium citrate. In order to get a 0.05M solution of tri-ammonium citrate weigh:
0.05 x 214.10 = 10.705g citric acid, and 0.05 x 51.09 = 2.55g ammonium hydroxide, and then top it up with water to 1l (one litre) total volume.

Note: Use of ammonia requires strict control and COSHH assessment must be carried out before preparing the solutions.

7.2.2 Method 2

Weigh the quantity of citric acid necessary for the final volume of wash solution and add water (less than the final volume). Add ammonium hydroxide until the pH becomes neutral. Then top up the solution with water to the desired volume.

Example: Making up 1l (one litre) of 0.05M tri-ammonium citrate.
Weigh out 10.705g citric acid (metal containers should be avoided).
Add 800ml water.
Start adding ammonium hydroxide until the pH becomes neutral (test with a pH electrode meter or with pH indicator paper strips).
Top up with water to 1l (one litre) total volume.

7.3 Concentration / Time / pH

Concentration, time and pH are interdependent. Four main observations were made:

1. The higher the concentration of the chelating agent, the faster the reaction, and the shorter the treatment time.
2. Slightly acidic pH (not lower than 6) significantly increases the rate of the reaction.
3. Tri-ammonium citrate proved to be equally fast and efficient at both slightly acidic (not lower than 6) and alkaline (not higher than 8) pH values.
4. Both the citrates and EDTA were less effective at neutral pH.

Any one of the three variables could be increased or reduced to achieve a desired result. For example, if an object were robust enough to withstand prolonged soaking, then a longer duration rather than a higher concentration could be chosen. Similarly, a higher concentration of a chelating agent and sodium dithionite could be used when the object to be treated cannot withstand a prolonged treatment duration.

The pH of the solution can also be adjusted in order to allow greater variation in the duration of the treatment. A neutral pH could be used for an object that would not be adversely affected by a longer treatment. The pH could be buffered to a more acidic value (not lower than 6), in a case where a shorter treatment was considered to be more appropriate. The ammonia present in tri-ammonium citrate appears to enhance the chelating action of the ligand at alkaline pH values, hence tri-ammonium citrate would be the appropriate chelating agent to use when washing at higher pH values.

7.4 Method of Application

The case studies revealed a significant versatility as far as the method of application is concerned. Total immersion would be the most appropriate method where an object suffered from overall staining. Local application could be chosen in cases where the staining was restricted to a confined area and/or the nature of the object would not allow for total immersion in the wash solution. Depending on the nature of the staining and the method of application, mechanical action could be introduced by means of an ultrasonic bath, sponging and gentle brushing/rubbing.

7.5 Testing / Precautions

Thorough testing should precede stain removal, as is the case with all interventive conservation treatments. Both the chelating and reducing agents could affect several components found on textile objects, such as dyes, especially mordant dyes, finishes and weighting agents. Dye materials should be tested for dye-bleeding and for colour change.

In general, stains are likely to have a higher concentration of metal ions than a mordant. In the case of weighting, the amounts of metal used are high but it is less likely to have the same type of metal as the staining (i.e. copper or iron). An exception to this is certain blue and black textiles, which were usually weighted with iron; therefore, iron stains on iron-weighted cloth is a possibility. In theory, one could quantify the amount of metal present on the stain and on the mordant/finish/weighting by X-Ray microanalysis, taking samples from the stained and an unstained but similar area. To the author's knowledge, such testing has not been reported.

Sodium dithionite should be used in either a fume hood or alternatively in a room adequately ventilated.

Care should be taken not to use metal beakers, tools (such as tweezers and stirrers) or wash baths, since there is always the possibility that the chelating agents might react with that metal. Glass and/or plastic are preferred.

8. Conclusion

The experiments undertaken were successful in identifying the most efficient chelating agent for the removal of copper and iron staining.

Tensile strength testing of the unsoiled aged samples indicated that there are no deleterious effects of either the chelating agents or sodium dithionite on cellulosic fabrics. However, it should be noted that there were certain indefinite results. When carrying out tensile strength tests, the fabric chosen for the experiments should be tested with an Instron machine in advance to ensure it gives consistent results.

Research and experimentation could be expanded to include the investigation of other naturally occurring chelating agents, the identification of reducing agents other than sodium dithionite, and experimentation on the removal of other metal ions. It could also encompass a more thorough investigation on whether there are any residues of chelating agents left on objects and the effects these may have on the textile fibres in the long-term.

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Timar-Balázsy A and Eastop D. 1998. *Chemical Principles of Textile Conservation.* Oxford: Butterworth-Heinemann, pp. 252-257.

Suppliers

Tri-sodium citrate, tri-ammonium citrate, di-sodium EDTA, sodium dodecyl sulphate, iron(II) sulphate 7-hydrate, sodium hydroxide pellets.
BDH Merck Ltd
Laboratory Supplies
Poole, BH15 1TD

Citric acid, copper(II) sulphate 5-hydrate.
Fisher Chemicals
Fisher Scientific UK, Ltd
Bishop Meadow Road
Loughborough
Leicester LE11 5RG

Sodium dithionite
Hogg Chemical
Laboratory Supplies Ltd
Sloane street
Birmingham B1 3BW

Synperonic A5
ICI PLC Surfactants
Eversiaan 45
B-3078 Everberg
Belgium

EXPERIMENTS IN RUST REMOVAL ON A PAINTED INDIAN CHINTZ

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1. Introduction

The project on which this paper is based was prompted by the existence of an important collection of Indian chintzes at the Victoria and Albert Museum which had become rust marked. In these objects, the problem is compounded by the presence of iron (and other metal) mordants in some of the dyed areas, which would be adversely affected by any attempt to remove the very disfiguring rust marks. Immersion of an object in a rust removing solution was therefore impossible, so a spot method was sought. The work was done at the V&A as my final year project on the V&A/RCA conservation course.

There are two reasons why rust removal is desirable. The iron acts as a catalyst for the degradation of cellulose to oxycellulose, which reduces the strength of the fibre considerably and can go on to destroy it completely. The strong visual impact of the rust gives the second reason. Even a low concentration of rust gives a strong yellow colouration, while higher concentrations give dark brown areas. From a conservation point of view the first reason is more pertinent, while the second one is relevant in terms of museum display.

A major problem with rust removal is the stability of the compound. Only mineral acids or strong reducing agents have any effect on it and these may be deleterious to the already weakened fibres. Yet, if the rust is not removed, more damage may ensue. The series of experiments described below are an attempt to reconcile these antagonisms and find a method to remove the rust while leaving the fibre and the dyes as little damaged as possible.

2. Experiments on sample fabric

2.1 Production of rust stained fabric for preliminary experiments.

Rust stains on fabric are usually produced by contact with iron under damp conditions. It would have been possible to produce experimental stains in this way, but it was decided to use fabric evenly (more or less) coloured by rust. Although this fabric did not replicate the normal conditions of a rust stain such as one-sidedness, unevenness and a definite boundary, it allowed several important parameters of the treatment to be assessed. It was necessary to limit the area of application, which was achieved by the use of a gel, so any spread of the active agents beyond the gel boundary had to be monitored. Rust can be mobilised and redeposited if the treatment does not stabilise it and this too had to be investigated. As it was possible that only part of a stain might be treated using this method the site of action of the gels needed to be fully evaluated before a museum object was tested.

2.2 Method of application of the gels/poultices

The experimental gels containing the active agents were routinely applied to the fabric samples in two different ways: (i) a Melinex overlay with a shape cut out was placed on the fabric and the gel applied over it; and (ii) a pencil was used to draw a shape on the sample and the gel was applied within the shape using a small paintbrush. A depth of between 0.5 and 1 cm of gel was used. As fabrics take up moisture very readily by capillary action, it was important to assess whether the active agents would be caught up in this and move beyond the gel boundaries. In addition, some of the treatments were carried out with an isolating layer such as Bondina or paper between the textile and the gel to see if the active agents would work efficiently under these conditions. Work was also done on wet and dry samples to see if this had any effect on the mobility of the active agents.

2.3 Preliminary experiments to select the best gel/poultice material

2.3.1 Introduction

It was decided to test a number of different gels and poultices, and active agents (Table 1). Gels and poultices have different properties which is why both were tested. A gel is a colloidal solution which has set to a jelly. Gels contain very large particles in a dispersion medium such as water. They tend to keep these particles closely associated by electrostatic forces. A poultice on the other hand is an inert carrier used to keep another substance or property (such as a liquid or heat or cold) in close contact with a substrate. Thus a gel should hold the active agents in suspension and restrict the area of activity better than a poultice.

It was impractical to attempt all combinations of gels/poultices and active agents as this would have led to an unmanageable number of samples. Instead, all the gels/poultices were first tried with sodium dithionite and a chelating agent. The best performing gel and poultice were subsequently tested with the whole range of active agents. Poultices were tested as well as gels, although it was expected that gels would be more suitable for the purpose of confining the active agents to the area of application of the carrier. However, many of the rust removing agents tested were acid and likely to have a detrimental effect on gel structure, while poultices are not colloidal and so would not be affected in the same way. Poultices could be more appropriate than gels if an acid was chosen to remove the rust.

Table 1

Gels	Poultices
Klucel G	Bentonite
Carbapol	Sepiolite
Laponite	Airolite Cok polar
Agar agar	
Gelozone	
Gelatine	

2.3.2 The choice of reagents for testing the gels/poultices

The mixture of sodium dithionite with a chelating agent was chosen as all of the other agents tested are acid and many gels are not recommended for use in acid conditions. For this reason, acids would not be very useful in assessing the relative merits of the gels. However, none of the gels were ruled out, as the treatment time was to be short in comparison to the length of time stability was required by the manufacturers.

Sodium dithionite is a strong reducing agent which converts the insoluble ferric ions of rust to ferrous ions which are soluble. These ferrous ions are then chelated by the *tri*ammonium citrate, so that they cannot revert to the ferric state and precipitate again. Both *di*sodium EDTA and *tri*ammonium citrate were used as chelating agents in the first series of tests. *Tri*ammonium citrate was mixed directly with the gel in its solid form, but *di*sodium EDTA is an acid and had to be dissolved and the solution adjusted to a neutral pH using sodium hydroxide before use. The pH was kept at this level as an alkaline pH (above 8) favours the formation of ferric salts which are insoluble and cannot therefore be chelated. EDTA was used at a concentration of 0.1M which seems to be fairly standard in conservation (Phenix and Burnstock 1992; Heuman 1992). Similarly, *tri*ammonium citrate was used at 5 - 10% (weight/weight or weight/volume depending on which measurement was used in the recipe), as previous publications suggest this to be a reasonable working strength (Heuman 1992; Carlyle *et al.* 1990). The literature gives various concentrations for the use of sodium dithionite and at this stage the amount was not standardised (Häkäri 1992; Horne 1990). The results of these tests have been summarised in Table 2.

Table 2. *Different gels and poultices tested.*

Gel or poultice type	Incubation time	Active agent(s)	Observations
Carbapol (gel)	5 - 35 minutes	*Tri*ammonium citrate, sodium dithionite	Rust removal fairly efficacious. Active agent leached out from gel to give a 'halo'. Bondina overlay reduces rust removal considerably. Carbapol sticky and rather difficult to remove using a spotting method.

Gel or poultice type	**Incubation time**	**Active agent(s)**	**Observations**
Klucel G (gel)	5 minutes	EDTA, sodium dithionite	The sodium dithionite started to destroy the gel structure of the Klucel G immediately. The rust was removed efficiently but the area of activity was not limited by the gel.
Laponite (gel)	5 - 60 minutes	*Tri*ammonium citrate, sodium dithionite	Rust removal generally good - some lack of penetration to the back of the fabric. Minimal leaching of the active agents beyond the gel boundaries. Laponite peeled fairly easily from the fabric and the small fragments left were easily rinsed away.
Laponite (gel)	60 minutes	EDTA, sodium dithionite	Good rust removal. Halo apparent round the area where the gel was applied. Probably due to slightly thinner gel.
Sepiolite (poultice)	10 minutes	EDTA, sodium dithionite	Good rust removal. Active agents spread slightly beyond gel boundaries and also slight halo effect.
Bentonite (poultice)	60 minutes	EDTA, sodium dithionite	Bentonite turned green (from pale brown). Rust removal from textile poor. This is not unexpected as Bentonite contains a proportion of iron compounds.

2.3.3 Conclusions

It was found that the best results had been achieved with Laponite, which was quite effective in limiting the area of activity to the area of gel application. It was easier to remove from the sample than Carbapol, which was the next best choice. Laponite, like Carbapol is not recommended for use below pH 6.0[1], and as all the other rust removing agents to be tested were acids or in acid solution, it was decided to use both a gel, Laponite, and a poultice, Sepiolite, for testing them. Other gelling agents were also tested for their suitability for use with acids.

2.4 Laponite and Sepiolite with a range of rust removers

2.4.1 Introduction

Further investigations concentrated on the use of Laponite and Sepiolite with oxalic acid, titanium trichloride, hydrofluoric acid, orthophosphoric acid and citric acid. The acids chosen are all commonly available rust removers which are widely used in industry. Most, if not all of them, have been used at some time in conservation for the removal of rust (Cruikshank and Morgan 1992; Häkäri 1992; Horne 1990). All the reagents are hazardous and appropriate safety measures were taken during the preparation of the gels and poultices, the treatment of the sample and the subsequent disposal of any waste.
The results obtained are summarised in Table 3.

Table 3. *Different Rust removing Agents tested using Sepiolite (poultice) and Laponite (gel).*

Active agent(s)	**Sepiolite**	**Laponite**
Oxalic acid.	Pale brown mark left where poultice applied. Rust totally removed in a 'halo' round the edge, then a more intense rust coloured 'halo'.	Some rust removed. Slight dark 'halo'. On using a higher concentration of oxalic acid (solid added to give a 10% final concentration) gel structure of Laponite began to break down and agent was not controlled.
Titanium trichloride	Good rust removal but agent not controlled by poultice. Slight dark rim round area of rust removal.	Good deal of rust removed. Some leaching of active agent from the area where the gel applied. 'Halo' of darker stain round the area from which rust was removed. Titanium deposited on the textile.
Hydrofluoric acid.	Very little rust removal.	No rust removed.
Orthophosphoric acid	Good rust removal but agent not controlled by the poultice	Some rust removed. Laponite very sticky and obviously broken down by the acid. Some evidence of 'halo' round gel due to active agent not being controlled properly by gel.
Citric acid and *di*odium citrate	not tested	Very poor. No gel retention of active agent and very little rust removed. Formation of ring mark.
Sodium dithionite and EDTA	Good rust removal. Lighter 'halo' round area where poultice applied	Good rust removal. Little 'halo' but defined edge to area where gel applied and rust removed.
Sodium dithionite and *tri*ammonium citrate	not tested	Good rust removal. Slight 'halo' plus defined edge to area where gel applied and rust removed

2.4.2. Conclusions

When all these tests had been completed and evaluated, the best treatment was felt to be sodium dithionite and *tri*ammonium citrate in a Laponite gel. The area of activity was largely confined to the area of gel application, it was quick and the gel was fairly easy to rinse from the textile. Further experiments were performed to refine the method. Controls using the reagents separately showed that both were necessary for optimal action. Sodium dithionite alone removed some rust but not as much as when the chelating agent was present. *Tri*ammonium citrate had no noticeable visual effect on the rust (Fig 1). A maximum time limit of twenty minutes treatment was set, which did not include rinsing time.

2.5. The use of other gelling agents with acids only

The gelling agents, agar agar, gelatine and Gelozone[a] were tested with Titanium trichloride and orthophosphoric acid, but no combination gave satisfactory results.

2.6. Experiments to find the optimal amounts of reagents

Two sets of experiments were undertaken. The first set took a standard amount of *tri*ammonium citrate with varying amounts of sodium dithionite[2] while the second varied the amount of the chelating agent relative to the reducing agent.[3] All experiments were performed on wet and dry samples to see if the presence of water round the fibres affected the spread of the active agents. There was no increased removal of iron when the chelating agent concentration was increased relative to the amount of reducing agent. This implies that the chelator was already in excess at a 5% (wt/vol gel) concentration so that increasing the amount could not enhance the effect (Heuman 1992). The best results were obtained with a 5% concentration of each of the reagents (Fig 2). There was no discernable difference between the treatments on the wet and dry fabric. Removal was always better on the side on which the samples were treated. This was not felt to be a problem as 'real life' rust stains are also one sided (Fig 3).

2.7. The effects of the treatment on dyes

As it was intended to use this treatment on dyed textiles, some modern dyed cloth was treated to see how the dyes might be affected. Indigo and madder were chosen as the dyes to test as they are commonly used on Indian chintzes and were likely to be affected by the treatment. Indigo dyeing relies on a reduction process and can be carried out very successfully by using sodium dithionite, so it would be solubilised by the treatment, though not necessarily removed from the textile. Certain shades of madder are achieved by use of an iron mordant, so madder too was likely to be affected by this treatment. Two madder dyed samples were used, one with alum mordant, the other with alum and iron. The sodium dithionite and *tri*ammonium citrate removed some indigo but only where the gel was applied. With the madder samples some lightening of the colour was observed, particularly with the iron mordanted sample, where the treated area became pink rather than purple.

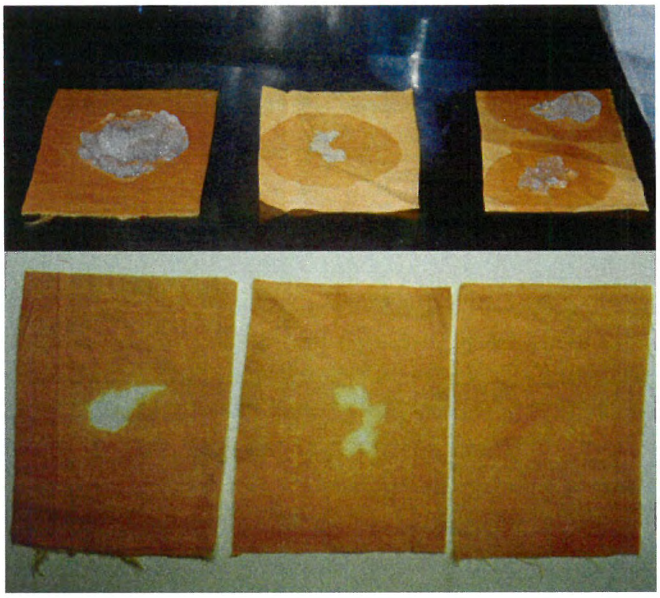


Fig 1 *Experimental samples treated with 4% sodium dithionite and 10% triammonium citrate*

Top: *undergoing treatment*
Bottom: *after treatment*
Samples from left to right treated in the following way:
Left: *gel applied over Melinex cutout*
Middle: *gel applied freehand using a sable brush*
Right: *gel alone (top) and gel with triammonium citrate only*

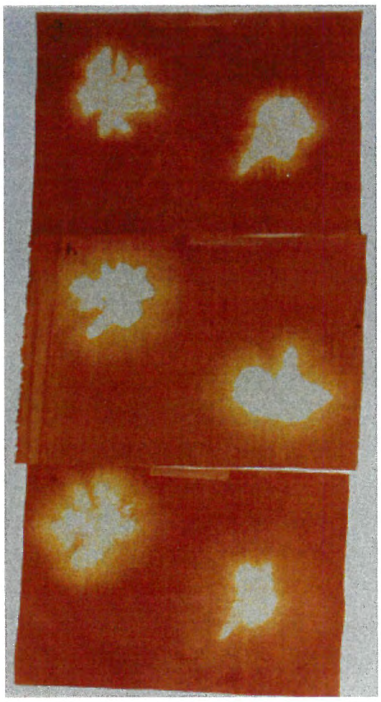
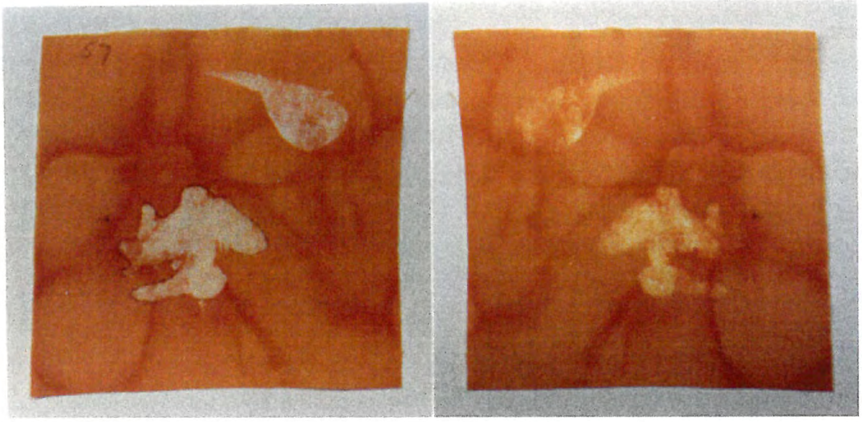


Fig 2 *Experimental samples after treatment with sodium dithionite and triammonium citrate*

Top: *5% sodium dithionite,*
2.5% triammonium citrate
Middle: *5% sodium dithionite,*
5% triammonium citrate
Bottom: *5% sodium dithionite,*
10% triammonium citrate



a b

Fig 3 *Experimental sample treated with 5% sodium dithionite in Laponite showing the one-sidedness of the rust removal when using a gel*
a. top surface *b. underside*

2.8 Discussion

From these extensive tests it was decided that the most appropriate treatment to try on the experimental object, was that of a Laponite gel with sodium dithionite and *tri*ammonium citrate in equal proportions.

A number of factors influenced this decision. Laponite is less sticky than Carbapol and seems to control the active agents slightly better. It is also easier to remove which is an important consideration when dealing with very fragile areas of a textile (Chapman 1986). Often the whole lump of gel could be removed at once by judicious use of a spatula, so that no scraping was required. Any small fragments left could be removed during the rinsing process by use of a fine paintbrush. *Tri*ammonium citrate was preferred to *di*sodium EDTA as its pH is in the neutral range rather than the acid. Sodium dithionite is also neutral (Hodges 1986), so providing a suitable environment for the treatment of fragile textiles. Any object with rust stains is liable to be very fragile in and around the stained area as iron affects fibre strength very rapidly (Bell and Gibson 1957). None of the acids tested were compatible with gel use, even though they are efficient rust removers in solution.

The rust removal is better on the surface where the gel is applied. The samples were made so that the rust was evenly distributed throughout the fibres but this is not true of accidental staining, where the stain is worst on the surface nearest to the rust producer Therefore, stains should always be treated from the top surface for maximum rust removal. This may mean two separate treatments, as a real object may have both surfaces stained in the same small area. A Melinex overlay was the quickest and most efficient way of applying the gel.

The reaction with sodium dithionite was quick and easy to control. A maximum treatment time of twenty minutes was felt to be acceptable. Although the combination of these three reagents is novel, all of them have been used in conservation, some for many years, with no hidden problems. The treatment is felt therefore, to be a safe and efficient way to remove rust stains without causing damage to objects.

XRF studies were carried out on various samples from the experimental series and on small detached fragments from the object, which confirmed the visual evaluations of rust removal. A Scanning Electron Microscope was also used to examine the surface appearance of selected samples and object fragments. Full details of these studies can be found in the original project report (Potter 1994).

3. Treatment of the *patka*

3.1 Introduction

The *patka*[4] (IS 88 1950) chosen for treatment came from the Baker collection (Fig 4). This sash is part of a collection of one hundred and sixty six textiles given by G. P. Baker to the Victoria and Albert Museum in 1950. The collection had been buried in a tin box by the owner to protect it from bombing raids in the Second World War. The textiles emerged unscathed by the Luftwaffe but some of them were badly damaged by mould and rust during their incarceration. Unfortunately most of the damage has occurred in the painted areas at the ends of the *patka*, where there are large holes with much rust and mould damage. The *patka* was also very creased, crumpled and generally dirty.

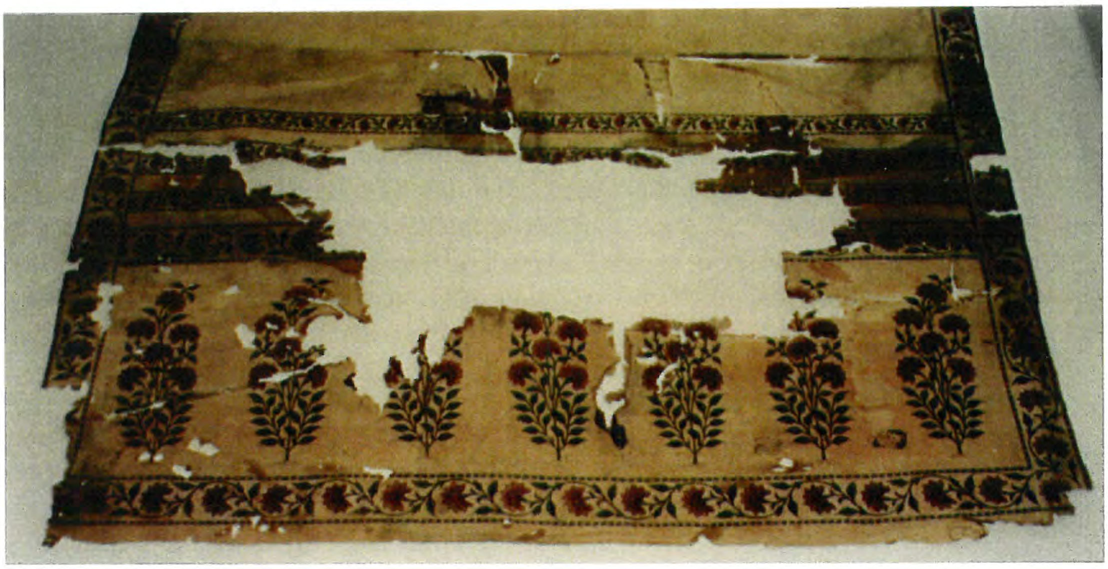


Fig 4 *Detail of one end of the Patka (after treatment) showing the extent of the damage. Most of the rust stains are on the top surface but there is a long line of staining on the back of the textile at the top right of the picture.*

3.2 Treatment

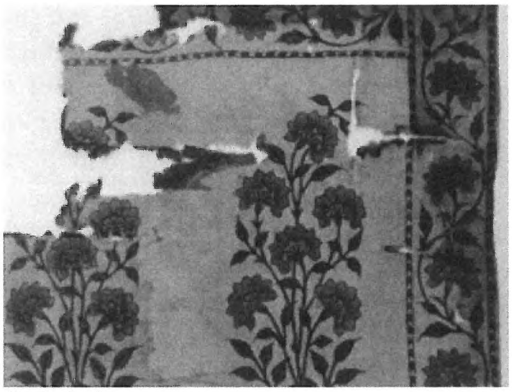
After testing it for dye fastness, the *patka* was washed. This enabled the rust removal trials to be accurately assessed against the true background colour of the textile. Had the textile been treated while still dirty, there was a danger of the treatment causing 'tide marks' of degraded cellulose and soil which might not be completely removed in subsequent washing. As the chosen treatment sodium dithionite is a bleach as well as a rust remover, it is important to control its action so that the treatment does not result in disfiguring pale patches in place of the rust.

Rust staining had occurred on both sides of the *patka* and the stains could be related to the way it had been folded for storage in the tin box. Thus the holes on the patterned ends of the *patka* and the associated stains correspond, though the damage was much worse on the end which must have been nearest to the side of the box. The most badly damaged end had most staining on the right side of the fabric, the other on the wrong side where they had been folded together. The object was examined under a hand held UV lamp to ascertain which of the stains were truly rust and which were foxing. This was a useful confirmation of the visual assessment of the rust stains, which are yellow/orange/brown as opposed to foxing (mould damage) which is mid brown in colour. Foxing is not reckoned to have the same deleterious effect as iron and does not respond in the same way to treatment (Carter 1984). Microscopic examination showed encrusted rust stains on the worst affected end. This end was therefore chosen as the site for rust removal trials.

The first area chosen for rust treatment was very heavily stained with much particulate matter adhering to the fibres. As much as possible of this particulate matter was removed by gentle mechanical action under magnification, followed by vacuum extraction of the loosened particles. As the staining was so heavy, a 7.5% concentration of each of the active agents was used in a 12.5% Laponite gel. The gel was applied three times over a twenty minute period. All mixing and application of the gel was performed in the fume cupboard as sodium dithionite is a respiratory irritant. In the preliminary experiments using custom made rusty cloth, the best method of applying the gel was found to be using a Melinex overlay to screen off all but the area to be treated. The overlay protected the rest of the object from accidental splashes and allowed the gel to be applied quickly and evenly. A thick layer of gel was used to exclude oxygen as far as possible from the area under treatment. Sodium dithionite works by reducing the iron to a soluble form, allowing the chelating agent to react with it to form a stable compound which cannot be re-oxidised. Any oxygen present would work against this process, either by combining with the solubilised iron or with the sodium dithionite, therefore hindering rust removal. After about five minutes, the first application of gel was removed by easing it up gently with a spatula. Yellow staining of the Laponite and small fragments of metal were seen. The gel was reapplied twice in this manner (Fig 5).

After the final treatment there was only some black staining (probably mould) left and some particulate matter. Preliminary rinsing was carried out in the fume cupboard using deionised water and a soft brush with blotting paper under the object. It was then removed to the spotting table for more thorough rinsing. The particulate matter, which looked like small flakes of metal, was flicked off the surface using the brush, as were small fragments of Laponite. When rinsing was complete the damp area was blotted and left to dry.

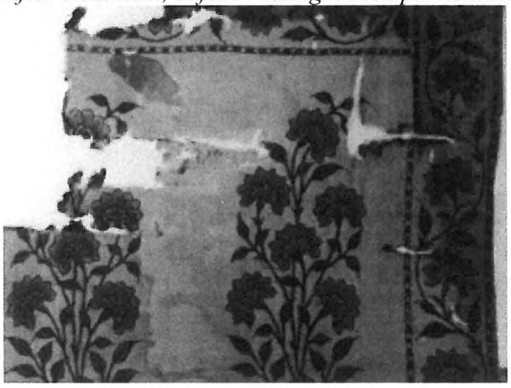
Fig 5 *Stages in the first treatment to remove rust staining.*



Stain before treatment.

Under treatment with Laponite containing 7.5% sodium dithionite and tri ammonium citrate.

After treatment, before rinsing. Much particulate matter is still present.



After rinsing and drying.

Three areas were chosen for the second treatment (Fig 6). The largest of these involved some of the painted flowers while one of the others was not rust but a brown stain which may have had a fungal origin. Such brown stains on paper are known as foxing and are thought to be due to amino acids and cello-oligosaccharides (Arai 1990). As sodium dithionite has a bleaching action as well as a reducing one it was felt that it may have a beneficial action on the stain. This type of stain is difficult to remove and has a habit of recurring after a period of months so any effect may be temporary (Carter 1984). The third area was heavily rust stained. Lower concentrations of the active agents were chosen for this treatment as the main rust stain was not as heavily encrusted as the first areas treated. The areas included parts which were dyed, so the treatment time was limited to ten minutes with one change of gel.

Finally, two further areas were treated (Fig 7). Again, one of these involved a painted area of the *patka*, associated with black fungal staining. The other rust patch extended into the dyed area but only the part of the stain in the undyed textile was treated. 5% concentrations of sodium dithionite and *tri*ammonium citrate were used in a 10% Laponite gel. The treatment time was 15 minutes.

3.3 Results

The results of the treatment on the rust stains have been very encouraging. The first area treated showed some bleaching relative to the background which was due to the higher concentration of sodium dithionite used. The brown foxed area treated was lightened but the difference was by no means as startling as that seen in the rust treatment. The decision to treat some of the printed areas was taken after much discussion with a member of the curatorial staff, when it was decided that this was permissible with a test object. The yellow dye was affected but this was already very pale. The effect on the madder and indigo was minimal. It is not known whether the disappearance of the yellow is due to the treatment or to the action of the rust itself, as the staining obscures much of the colour. The removal of the rust improved the appearance of the treated area considerably, even though the yellow was gone.

The practice of applying the gel several times is an advantage, especially in the dyed areas, as treatment can be terminated as soon as there is no evidence of rust. Manipulation of the gel when removing it from the textile has to be very gentle as the fibres have been weakened by the rust and the gel tends to stick to them. Where an area is heavily incrusted the remaining fibres will be very frail and thin and it seems as though a lot of bulk is removed.

Fig 6 *The second treatment.*
Three separate areas (marked on the top picture) were treated. The bottom picture shows them after treatment.

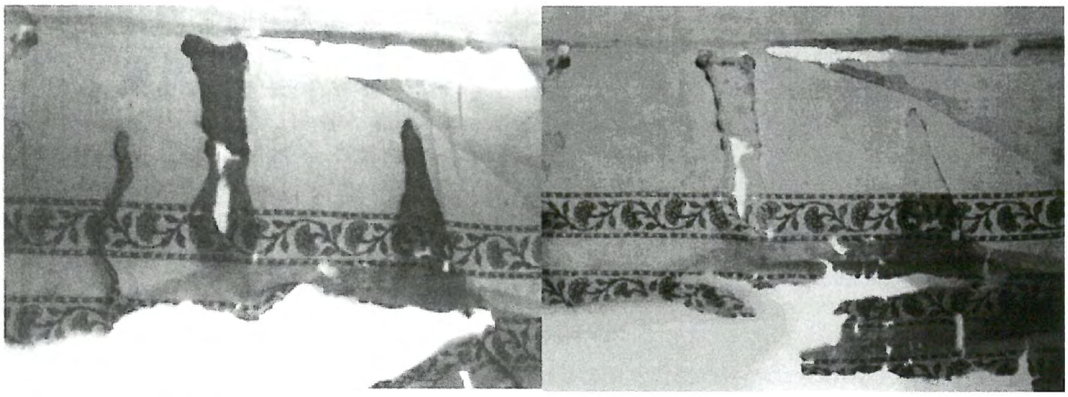


Fig 7 *The third area treated.*
The rust stain to the right has only been treated in the undyed portion, while the left hand one was treated fully.

4. Conclusions

The method developed for removing rust stains by the use of sodium dithionite and *tri*ammonium citrate in a Laponite gel was found to be satisfactory. The neutral pH of the active agents, combined with the inert nature of the Laponite should make it a relatively safe treatment for textiles. Sodium dithionite only remains active for approximately twelve hours in solution, so there is unlikely to be any residual activity to damage fibres, even if there was any left after rinsing. Any Laponite residue should not cause any further damage to the object though every effort should be made to remove it totally. It dries to a film, rather like starch, and has a stiffening effect, though its presence can only be detected by the use of a microscope.

A 10% Laponite gel with 5% wt./wt. of each of the active agents was found to give the best results. Higher concentrations seem to cause more bleaching of the fabric. Mould stains, whether foxing or black mould, cannot be removed in the same way. Any lightening of the stain is liable to be a temporary phenomenon (Carter 1984). The use of a Melinex overlay with holes cut out in the position of the stains, was found to be the most efficient way of applying the gel. It is necessary to be accurate in the cutting of the holes and their subsequent positioning to ensure that all the stained area is treated and no bleached edges are formed. The Melinex protects the rest of the object from accidental splashes.

The use of a gel enabled an area to be treated evenly and controllably. It is probably best suited to the treatment of relatively small areas, but as any rust stained object is liable to be fragile, great care should be taken over handling.

The greatest problem, which has both ethical and practical aspects to consider, is the treatment of rust stains which extend into a painted area. Not only are the fibres weakened by such a stain, but the painting and colours are obscured by it. The main area of weakness is at the junction of the stained and unstained zones (Bell and Gibson 1957). This phenomenon is well known to any textile conservator who has worked on Indian chintzes with heavily mordanted brown areas. Motifs tend to drop out and if still present, the junction usually shows more signs of weakness than the rest of the motif. Any rust stained object will have these lines of weakness which will still be present after the rust is removed. If however, only half the stain is removed because it goes into a dyed area, then a new line of weakness could form over time, leading to the eventual loss of the coloured area. The visual impact of the stain will still be considerable even if it is confined to the patterned areas of the object, while a slight loss of colour in one particular place may be more acceptable. Each individual object for treatment would have to be assessed with these considerations in mind. In some cases, where there are large areas of green or dark backgrounds, treatment will probably be considered unsuitable and the stain left in situ. In others, which depend for their effect on delicate patterns on a pale background, treatment may be considered the best option. The treatment has not been assessed on an object with metal embroidery. As sodium dithionite contains sulphur atoms, there is a danger that silver in particular could be adversely affected, so any treatment of such an object should be carefully considered and monitored closely.

Rust stains are often associated, as here, with mould damage, including foxing, which cannot be successfully removed, so some damage will still be obvious.

All the stains were treated from the 'right' side; the side on which the rust had formed. Gel treatment is a one-sided process as shown by the test samples. There is a more effective action on the side of the fabric to which the gel is applied. In the test samples, the rust was evenly distributed so that edge effects and gel treatment could be properly evaluated, but naturally produced rust stains are usually formed by contact with an iron object and are one-sided. The most efficient action is obtained by treating them from the side on which they were formed. This may mean that both sides of a multiple stained textile have to be treated, as folding it for storage may have exposed both surfaces to the iron.

These experiments have produced a satisfactory method of removing rust stains from some Indian chintzes. The difference in appearance of the treated areas is quite striking, with very little unwanted bleaching and a reduction of the iron content to background levels, showing that the iron has been removed and not just reduced to a colourless form which could reoxidise later. The gel formula is controllable, easy to make up and handle, and washes away well. This promising technique should help substantially with the problem of rust removal.

Acknowledgements
I would like to thank Lynda Hillyer and Alan Cummings who supervised this project and also the staff in the textile section at the Victoria and Albert Museum and those at Imperial College London for their support during it.

Endnotes

1. Personal communication, Laporte scientists.
2. 5% *tri*ammonium citrate with 2.5, 5 and 10% sodium dithionite.
3. 5% sodium dithionite with 2.5, 5 and 10% *tri*ammonium citrate
4. *Patkas* are a feature of Mughal dress. They are wound round the body several times as they are about three metres or more long, then tied tightly around the waist of the *jama*, effectively displaying the finely decorated ends. They were often given as a traditional ceremonial gift and were highly treasured as such. This accounts for the fine craftsmanship often seen in these pieces. They often have inventory marks or *toshkhana* seals which are not normally applied to garments, being reserved for the durbar hangings, tent hangings, carpets and the like. This *patka* displays three such marks, all of which are situated on the most badly damaged end of the textile.

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Materials and Suppliers

Sodium dithionite (syn sodium hydrosulphite), triammonium citrate, ferrous, sulphate, oxalic acid, titanium trichloride, hydrofluoric acid, orthophosphoric acid, citric acid, agar-agar, gelatine.

Merk Ltd
Hunter Boulevard
Magna Park
Lutterworth
Leics LE17 4XN

Laponite (Laporte Ltd)
Conservation Resources
Units 1, 2 & 4
Pony Road
Horspath Industrial Estate
Cowley
Oxon OX4 2RD

Gelozone
Supermarkets

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REMOVAL OF DYE BLEEDING ON EMBROIDERED COSTUME ITEMS THROUGH WET CLEANING ON A VACUUM SUCTION TABLE

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1. Introduction

The subject of this study is a group of traditional embroidered costume items from Setesdal in Norway. The items all contained early synthetic red dyes, which exhibited dye bleeding. The aim of this research was to identify dye types and to discover whether they could be categorised by their degree of wet fastness. It was hoped that this information would then be used to propose treatments that would prevent or control dye bleeding during cleaning, or reduce the existing dye bleeding in the selected objects.

This investigation was carried out for a dissertation, which formed part of an MA in Textile Conservation at the Textile Conservation Centre in 2001.

2. The objects

A group of objects from the Setesdal Museum and a private collection in Norway was surveyed. They included bonnets and cheek-cloths, part of the costume tradition for swaddling children in the Setesdal Valley in Southern Norway (Fig 1).

The textiles used for swaddling were either partially woven or embroidered with red wool yarn. The majority of bonnets and cheek-cloths were embroidered, predominantly with red wool in running stitches on a cotton tabby substrate. The embroidery is accentuated with contrasting colours. This technique mimics a brocade weave and is known as *Smøyg*.

The earliest recorded use of these bonnets found by the author was in a water colour dated 1848[1]. After the Second World War the bonnets ceased to be widely used. The bonnets surveyed fall between these dates. This limited time of production for the bonnets and the embroidery yarn, supported the author's assumption that some of the embroidery yarn could have been dyed with synthetic dyestuffs.

The main criteria used to select objects for treatment were their condition, the degree of bleeding and diversity in types of red yarn used. One flat and one three-dimensional object were selected, a cheek-cloth and a bonnet respectively.

The bonnet[2] was in poor condition and was badly discoloured from bleeding on the cotton tabby side panels. More severe bleeding had caused streaks of colour, which coincided with crease lines on the cotton tabby (Fig 2 and Fig 3).

The cheek-cloth[3] was in fair condition and dye bleeding was minimal. These traces of dye bleeding were visible on the reverse edge near the mid section, in one corner and on the mid section close to the embroidery (Fig 4).

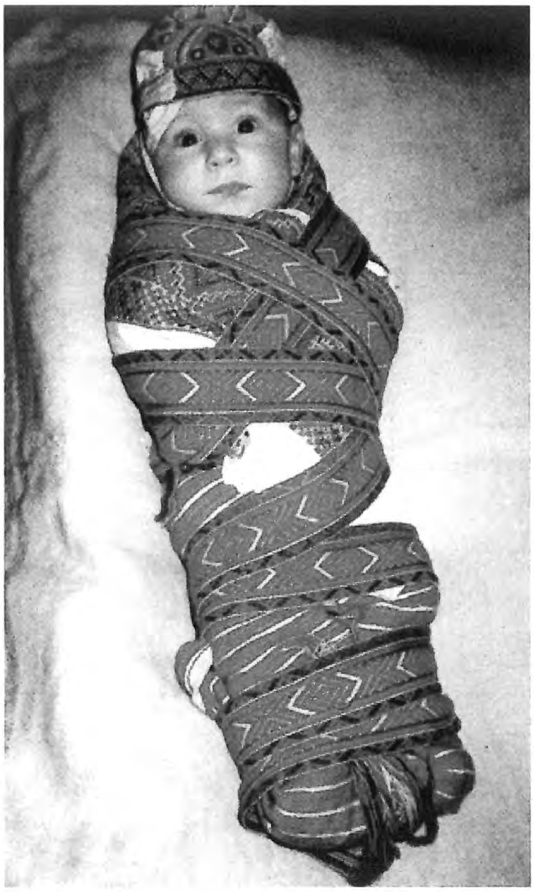

Fig 1 *Traditional swaddling of an infant in Setesdal, Southern Norway.*

Fig 2 *Bonnet before treatment, right side.*

Fig 3 *Bonnet before treatment, left side.*

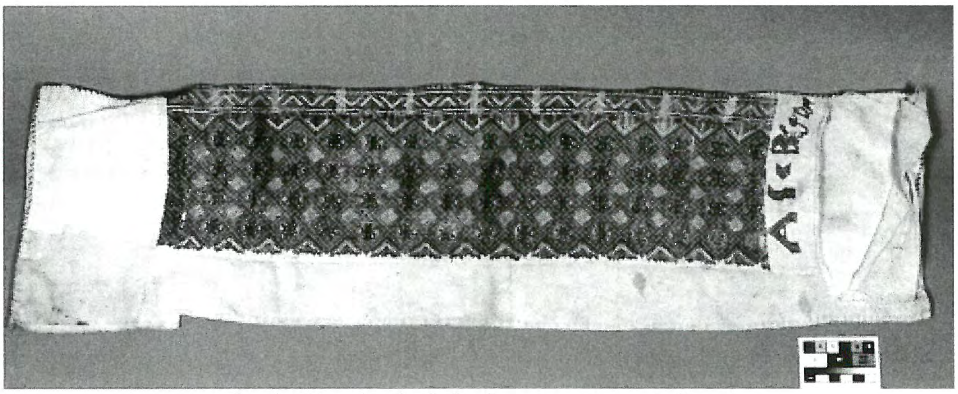

Fig 4 *Cheek-cloth before treatment, front.*

3. Dye analysis

A review of the periodical *Dyes in History and Archaeology* was undertaken and a questionnaire sent to conservators regarding their experience of dye identification and dye bleeding. The common dye identification methods were found to be wet chemical analysis or instrumental analytical techniques, or a combination of the two.

The analytical methods described by Dr. Helmut Schweppe in *Practical Information for the Identification of Early Synthetic Dyes and Practical Hints on Dyeing with Early Synthetic Dyes* (1983) were used to analyse the objects for this investigation. His methods are widely used and seemed suitable before using more sophisticated and more costly analytical methods.

Dr. Schweppe's test called *Extraction test to identify the bleeding of dyes*[4] was chosen for this investigation. In this test method the dye group is identified by whichever known solvent extracts the greatest stain from a sample, as shown in Table 1. A sample of approximately 1 cm long is boiled in 5ml of softened water in a test tube, for 1 minute. The procedure is repeated in the following solvents: ethanol, glacial acetic acid and finally ammonia. The solvent that shows most evidence of staining indicates the probable dye class[5].

Table *Extraction tests to identify the bleeding of dyes*[6]

Dye class	Expected staining
Acid dyes	Some in water, more heavily in ammonia
Direct dyes	Some in water, more heavily in ammonia
Basic dyes	Stain ethanol, extracts heavily in glacial acetic acid
Metal complex dyes (incl. chrome dev. and mordant dyes)	Do not bleed in these tests, might lightly stain the ammonia extract
Vat dyes (indigo)	Appreciable bleeding in this test only with glacial acidic acid

4. Testing treatment methods using sacrificial objects

Prior to carrying out treatment on the Norwegian objects various methods were tried out on a vacuum suction table, using sacrificial objects to discover which technique would be the most suitable. It was believed that the use of a vacuum suction table was the best way to keep fugitive dyes and cleaning materials localised during the treatments. This is consistent with Scharff's (1999) argument that,

"...the subject of chemically setting dyes still requires much research, considering the sensitivity of the fibres to chemicals, alternative methods should be considered, such as using a washing method that may minimize the bleeding of dyes e.g. the use of a suction table".

The three-dimensional object used for testing was a replica of an original Norwegian bonnet[7]. It was important that the replica duplicated the pleated effect on the original as it was thought this would be a challenging area to clean. To achieve dyebleeding Lanaset[8] dyestuff from Ciba was used in a 10% depth of shade to dye the embroidery yarn. The embroidered replica was then soaked in an ammonia solution[9], in a 20% concentration (Fig 5).

A two-dimensional object was selected from the TCC reference collection[10], a sampler severely discoloured by migration of blue dye.

General tests of the equipment and cleaning method were undertaken using a vacuum suction table. The objects were washed using deionised water with Synperonic N[11,12] and Sodium carboxymethylcellulose (SCMC).[13,14] Then solvent cleaning tests were carried out using Acetone and IMS.

The tests did not reduce the bleeding on the replica bonnet to any real extent. The dye removed from the sampler was mainly solubelised dye migrating from the embroidery yarn. Dye was removed most successfully with the detergent solution by wet cleaning and solvent cleaning with acetone. These tests enabled possible difficulties to be predicted before treating the Norwegian objects.

The results of the analytical tests suggested that acid dye was present in the bonnet samples. In 1998 Tímár-Balázsy and Eastop wrote that "staining" from acid dyes can best be removed with several solutions: dilute ammonium hydroxide, methanol, anionic detergent and the mildly alkaline solution of sodium dithionite (Table 2).

For the initial use of the method it was decided not to use solvent cleaning and bleaching. The use of a detergent was preferred as wet cleaning involves less Health and Safety considerations, is likely to cause less damage to the object and is a cheaper and more obtainable treatment method.

Table 2 *Solvents and solutions which may be appropriate for the removal of dyes*[15]

Stain	**Solution**
Acid dyes	Dilute ammonium hydroxide, methanol, anionic detergent solution, mildly alkaline solution of sodium dithionite
Basic dyes	Methanol, ethanol, dilute acetic acid, detergent solution with slightly acid pH (not less than pH 6), mildly alkaline solution of sodium dithionite
Direct cotton dyes	Anionic detergent solution with slightly alkaline pH, mildly alkaline solution of sodium dithionite

Fig 5 *Replica bonnet, prior to testing.*

Fig 6 *Bonnet during cleaning.*

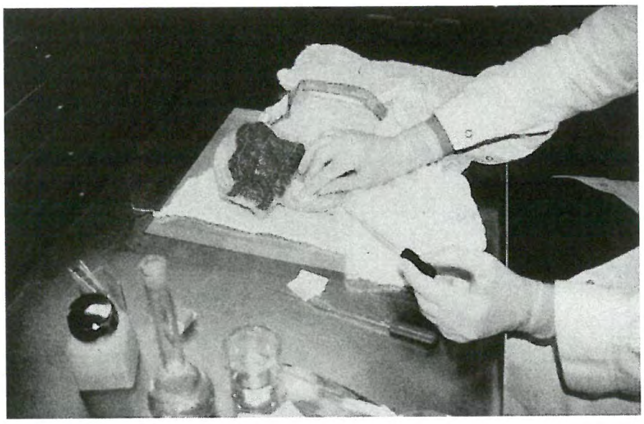

Fig 7 *Detail, cleaning of bonnet.*

Fig 8 *Bonnet after treatment, left side.*

Fig 9 *After treatment, detail left side.*

Fig 10 *After treatment, detail right side.*

5. Treatment of historic objects

The bonnet and cheek-cloth were wet cleaned on a vacuum suction table[16] using a combination of a non-ionic and an anionic detergent. Synperonic N and SCMC, in the same solution as during testing, was used in combination with the anionic detergent sodium dodecyl sulphate[17].

Wash tests were carried out on samples of all coloured yarns from the two Norwegian objects using deionised water, acid/alkaline solution and detergent solution. None of the dyes bled in any of the tests.

Before cleaning pH readings were between 5.7-5.9.

Before treatment chromameter readings[18] were taken from the two objects in areas with soiling, in areas with varying degrees of dye bleeding and on the embroidery. The chromameter readings before and after treatment were taken so that the effect of cleaning could be assessed by a method other than visual examination.

The bonnet was cleaned first. This treatment was expected to be more challenging than that of the flat object due to its construction, but as the bonnet was more discoloured by dye bleeding the opportunity to remove bleeding counterbalanced any perceived challenges.

The object was wet cleaned from the edges of the stained section towards the embroidered area in order to push back the migrated dye towards the embroidery. A small area of the stained section was wetted out with deionised water and at the same time blotted with blotting paper. In this way dye and moisture could be transferred onto a muslin cloth, laid between the object and the suction table. The muslin cloth had to be frequently replaced. This process was repeated with the detergent solution. Three or four rinses with deionised water were flushed through the wetted area to remove dye and any detergent residues. During the rinses it was particularly important to use blotting paper, as so much moisture was introduced at one time. The object was left under suction on the vacuum table for approximately two minutes after the last rinse to minimise any risk of dye bleeding during drying. The object was monitored throughout the drying period to ensure no solubilised dye migrated, as the construction of the bonnet meant that drying occurred at an uneven rate (Fig 6 and Fig 7).

The same method was used for cleaning the cheek-cloth.

pH readings after treatment in both objects were pH 5.5 –5.6.[19]

6. Results and evaluation of cleaning

Dye bleeding was reduced on the stained section of the bonnet, but a slight pink discolouration was still visible.

Soiling on the cheek-cloth was reduced in the area cleaned, but only minor change in the degree of dye bleeding could be observed. The majority of dye and dirt removed was released during the rinse phase.
The aim of the treatment, to reduce dye bleeding, was achieved with the use of a detergent solution (Fig 8 and 9).

The visual change on the bonnet after cleaning was confirmed by a series of chromameter readings. There was a clear change in brightness and hue, especially on the tabby front corner and on the side, indicating that the areas were cleaner and that dye residues had been removed[20]. Readings taken on the wool embroidery indicate that there had been some loss of dye from the embroidery yarn during cleaning. Readings taken from the cheek-cloth also showed increased brightness although the hue had not noticeably changed. This indicates some soiling has been removed although there had been little success in removing the dye bleeding on this object.

It was found that the bonnet was easier to clean than the cheek-cloth, as the tabby side panels of the bonnet were only one thin layer of fabric and more accessible than the areas of bleeding on the cheek-cloth, which had two layers of cotton tabby. Because of the layered construction of the cheek-cloth, cleaning could only be carried out successfully in one corner. Dye bleeding in the pleated areas was successfully reduced, but this necessitated a lot of handling in order to manoeuvre the fabric into position. Cleaning of a three-dimensional object using a vacuum suction table requires more handling in order to create sufficient access to achieve suction in different sections of the object.

The cleaning method and equipment chosen proved to be highly suitable for removal of dye bleeding through wet cleaning. The vacuum suction table ensured a controlled wet cleaning process, as the moisture introduced was kept within the area being treated. The cleaning method worked well for a three-dimensional object, but the efficiency of the method would depend on the accessibility of the area to be cleaned.

7. Conclusion

The identification of dye groups made it easier to decide on a treatment with the aim of reducing and preventing further dye bleeding. Schweppe's extraction test proved to be quick, easy and required only basic equipment.

As none of the dyes bled in the wash tests and there was no more bleeding during treatment, it can be assumed that the bleeding on the objects was caused by excess dye released during domestic washing. The fugitive character of some of the red dyes used on these objects might therefore have been a result of the dyeing process rather than a problem with wash fastness of the dye.

The project was my initial test of this wet cleaning method. It is hoped that the treatment method described in this article can be tested further in future projects.

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Endnotes

1. Noss, Aa. 1981, p. 104.
2. TCC 2643.3.
3. TCC 2643.6.
4. Destructive test.
5. Description of this test is extracted from Schweppe 1983, p 1. Tests were also carried out for smaller samples by reducing the volume of the solution accordingly.
6. Content of table is a summary of Schweppe 1983, p 1.
7. Replica made by the author.
8. 1:2 metal complex and reactive dye.
9. Ammonia (NH3) was chosen as dyes are known to be more fugitive in alkaline conditions.
10. The TCC Karen Finch Reference Collection consists of textiles used for study and research purposes, which is available for students and staff of the University of Southampton.
11. Non-ionic surfactant.
12. At the time of this investigation Synperonic N was still the most commonly used detergent at TCC.
13. Dirt redeposition inhibitor.
14. 2mls/ litre and 5g/ litre.
15. Information in the table is taken from Tímár-Balázsy and Eastop (1998) Chemical Principles of Textile Conservation, pp. 239-240. Permission was kindly given to reproduce part of the relevant table from the publication.
16. Vacuum suction table made by Mercury Associates.
17. 0.01 % concentration.
18. Chromameter readings taken using Minolta Chroma Meter CR-210.
19. Although pH readings showed a more acidic pH after treatment the change was seen as minor and was not believed to contribute to a more rapid deterioration of the object. On the contrary a lower pH would be beneficial for prevention of further dyebleeding as dyes are less fugitive in acidic conditions.
20. According to the readings the areas have both become brighter and has less value for hue. The readings on TCC 2643.3 Bonnet taken from area with severe dye bleeding on left side panel indicated most improvement. Readings before treatment were respectively, L 65.86, a + 16.44 and b + 16.57 and after treatment, L 77.04, a + 5.21 and b + 12.48.

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Poster

THE IDENTIFICATION AND REMOVAL OF AGED DEODORANTS, ANTIPERSPIRANTS AND PERSPIRATION STAINS ON WHITE COTTON

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INTRODUCTION

Human beings have been trying for centuries to overcome the negative effects, mainly odor and wetness, associated with perspiration. From Cleopatra's use of perfume in 69-30 B.C. Egypt, to today's use of Botox, people have tried many methods to deal with perspiration (Lester 1940; Draelos 2000). The introduction of deodorants at the end of the nineteenth century and antiperspirants at the beginning of the twentieth century, offered different solutions to consumers.

Consumer use of deodorants and antiperspirants in the U. S. was slow at first, but by the end of the twentieth century, sales exceeded a billion dollars annually, with antiperspirants responsible for 82 percent of the market (Calogero 1992, 63). A build-up on the fabric from excessive amounts of deodorant or antiperspirant, or transference through sweating, can retard the removal during washing, especially in a cold water and low alkalinity bath. Most deodorants or antiperspirants utilize aluminum salts in their formulae. These salts can combine with soap or detergent to form a water-insoluble component that remains on the fabric (LABS 1985). These substances tend to leave fabrics stiff, discolored, and brittle, especially those fabrics made of cellulose fibers.

Many studies have shown the harmful effects that perspiration, deodorants, and antiperspirants have had on dyes (Goldchien 1963 and El-Zoghbi et al. 1986). Even more have discussed their effects on fabrics (Bien 1945; El-Zoghbi et al. 1986; Goldchien 1963; Olmsted 1974; Chong et al. 1994 and Bhat 1990). Various patents granted in the early twentieth century were concerned with the protection of fabrics from damage by deodorants and antiperspirants (Plechner 1957, 719). Yet, little material related to the removal of these potentially harmful substances has been found. A need for adequate sources for the removal of these substances is noted.

DEODORANTS

- Considered cosmetics by regulatory agencies in the U. S. (Harry 1982, 124).
- Decreases offensive underarm odours caused by bacteria present in the underarm.
- Common Ingredients: antimicrobials, enzyme inhibitors, antioxidants, odour absorbers, and fragrances.
- First Deodorant: specialist from Philadelphia created a product in 1880 to help eliminate body odour in terminal cancer patients (Laden 1988; *Mum Online* 2000).
- In 1888 Bristol-Myers marketed the product as Mum deodorant; on the U. S. market until 1998 (Bristol-Myers Squibb Consumer Affairs 2001).
- Reduces the tensile strength of fabrics (El-Zoghbi et al 1986).
- Build-up on fabric can cause a white-coloured fabric to turn yellow, while dark-coloured items develop a whitish tint or become darker.
- Affects cellulose fibres (Lyle 1983).

ANTIPERSPIRANTS

- Reduces underarm wetness.
- Considered drugs by U.S. FDA since they affect the body's sweating function (Harry 1982, 124).
- Common active ingredients: aluminium salts and other polyvalent metallic ions.
- First Antiperspirant: Everdry – 1903.
- Reduces tensile strength of fabrics (Goldchien 1963 and El-Zoghbi et al. 1986).
- Build-up on fabric can cause a white-coloured fabric to turn yellow, while dark-coloured items develop a whitish tint or become darker.
- Further degradation to the fabric can occur through prolonged exposure to high temperatures, such as ironing (Plechner 1957).
- Affect linen, cotton, and rayon but, are harmless to silk, wool, and acetate (Bien 1945), although a report by Lyle (1983) suggests that aluminium chloride, an active ingredient in antiperspirants, affects silk.

PERSPIRATION

- Approximately 2,380,000 sweat glands are distributed over the bodies' surface.
- Perspiration or sweat can contain many components, but these components together make up only about 0.3 to 0.8 % of the total amount, the rest being water.
- When perspiration is first produced it is alkaline ~ pH 8.
- Once perspiration is secreted and touches the skin, it becomes acidic, pH ~ 4.5.
- Once perspiration dries, it again turns alkaline, pH ~ 8.
- The loss of tensile strength due to contact with perspiration depends on such factors as the pH, the length of time of contact, the amount of moisture, and the pH of the cleaning product used by launderers (Barail 1947).
- A recent study on cotton (Bhat et al. 1990) showed that the loss in tensile strength from perspiration was due to swelling of the fibers and subsequent splitting and peeling off

of the fibrillar layers. After prolonged contact with perspiration, the fibrillar layers are completely removed, and deep corrugations develop along the fiber axis.

- Dried perspiration can cause white crystalline salt rings to occur on the surface of the fabric creating a hard and brittle area.
- Dried perspiration can cause yellowing of a fabric, especially cellulose fabrics, as described in studies by Bhat et al. (1990), and Chong et al. (1994).

REMOVAL

Underarm stains in pre-twentieth century garments are most likely to be perspiration only, however, with the increasing availability of deodorants and antiperspirants in the twentieth century, garments could have stains from both perspiration and the agents that control it. This is especially true with garments worn after 1960, as the new aerosol delivery system helped to increase the market for deodorants and antiperspirants.

Two studies were devised to identify and remove aged deodorant, antiperspirant, and perspiration on cotton fabrics. The first study focused on the stains of deodorants and antiperspirants on cotton garments. With little information regarding the removal of these stains found in the literature review, the ability of a number of solvents to remove deodorant and antiperspirant stains were evaluated.

The second study focused only on perspiration stains found on cotton garments. The literature review provided numerous methods for the removal of perspiration stains in home laundry publications, plus methods for dry cleaners and textile conservators. This study focused on evaluating these published methods to determine how well they removed perspiration stains.

ANTIPERSPIRANT AND DEODORANT TESTS AND RESULTS

The first study used a collection of stained men's 100 % cotton undershirts. These undershirts were severely stained after repeated use and home laundering with a liquid detergent. Mitchum Antiperspirant and Deodorant Unscented Roll-on, Original Formula, had been used throughout the wearing of these undershirts. The stains were located in the underarm areas and had turned the white fabric a light red-orange hue. The fabric was stiff and had a greasy hand in the areas of the stains.

Investigating deodorant and antiperspirant formulations was the first step in determining how to remove them from cotton fabric. The review of literature revealed many formulae for deodorants and antiperspirants; common ingredients include aluminium chloride, aluminium zirconium tetrachlorohydrex GLY, glycerine, propylene glycol, and triclosan. Chemical references identified solvents for the ingredients of each formula (Merck Index, 1985). Glacial acetic acid, perchloroethylene, diethyl ether, toluene, mineral spirits were selected to test for their ability to remove deposits.

PROCEDURE

- Fabric Preparation
    - Cut 2 cm squares from underarm areaTreatment Conditions
    - 10 ml baths
    - Room Temperature
    - Treatment Times
        - 30 minutes
        - 1 hour
    - Blot and Air DryEvaluation
    - Hand-held Spectrophotometer
    - Color change (•E)
    - CIE L*a*b* system

The test showed that perchloroethylene and diethyl ether were the most successful solvents in removing the deodorant and antiperspirant stains, but the staining and residue were not completely removed. Further ways to dissolve deposits were explored.

Using the theory that "like dissolves like," a given solvent is most likely to dissolve stains or components that have the same polarity. The fractional solubility parameters of a solvent or stain component can be plotted on a simple planar Teas graph based on the 1968 work of Jean P. Teas (Barton 1983). The Teas Time Program by Walter Henry (1989) was used to identify solvent mixtures with fractional parameters matching the parameters of perchloroethylene and diethyl ether. Many of the solvent blends generated with this computer program are not generally available. Two solvent mixtures generated with the computer program were chosen to be evaluated. These were 47.9 % mineral spirits/ 52.1 % glacial acetic acid, and 60 % toluene/ 40 % glacial acetic acid.

The same application procedure as before was used. Readings with the hand-held spectrophotometer were taken before and after testing The parameters for perchloroethylene, diethyl ether, toluene, mineral spirits, acetic acid and water were plotted on the same Teas graph for comparison.

The 47.9 % mineral spirits/ 52.1 % glacial acetic acid mixture reduced the stain less than perchloroethylene or diethyl ether. The 60 % toluene/ 40 % glacial acetic acid mixture completely removed the deodorant and antiperspirant stain, leaving the fabric white and with a soft, flexible hand.

The results from the first experiments showed that no pure solvent was effective in completely removing the deodorant and antiperspirant residue and staining. Of the solvents tried, perchloroethylene and diethyl ether worked well in reducing the deodorant and antiperspirant residue and staining, but did not completely remove these substances from the fabric. 60 % toluene / 40 % glacial acetic acid worked exceptionally well in removing the deodorant and antiperspirant residue and staining.

PERSPIRATION TEST AND RESULTS

Initially, dried perspiration is invisible, though once aged, it becomes alkaline and yellows a fabric. This is especially noticeable on white fabrics (Eckert 1997). The longer the decomposed perspiration has contact with a fabric, the higher degree of damage, and greater colour change and loss in strength. With the negative effects of perspiration on fabrics, especially those made of cellulose fibres, the identification and removal can be important.

Methods for perspiration removal in published literature are for home launderers, dry cleaners, and textile conservators. Often the prescriptions were similar. A method from each category was tried on perspiration-stained cotton blouses from the University of Rhode Island Historic Textile and Costume Collection. The women's white garments dated from 1900 to 1910. The location and appearance of the stains on the three plain-weave cotton blouses were evaluated. The stains on the blouses were located in the underarm area and had yellowed the fabric.

CHOSEN METHODS

- Home Consumer: rub detergent and water on stained area and rinse (Removing Stains 1991).
- Dry cleaners: use an available dry cleaning solvent (Elledge 1923).
- Textile Conservation: 0.5 % acetic acid in acetone solution (Balázsy and Eastop 1998).

Three methods for removing aged perspiration stains were evaluated. The results from this experiment showed that the 0.5 % glacial acetic acid in acetone, the suggested method from literature published for textile conservators, worked the best in removing the aged perspiration stains. Visually, the yellowing in the underarm area of the blouse tested was completely gone when treated with this solvent mixture and then wet cleaned. The other two blouses treated by other methods only slightly improved in appearance.

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