CHELATING AGENTS IN WET CLEANING SYSTEMS

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ABSTRACT - An initial screening was made of selected chelating agents to identify those most promising for use in the removal of metal-bound soils during the wet cleaning process. Citrates proved to be the most practical and effective of the compounds tested. Three textiles were chosen for treatment with chelating agents: 1) a damask tablecloth stained green by copper in previous wash water, 2) a cotton plain-weave window hanging with cellulose degradation products that had not responded to conventional cleaning and with copper identified in the soiled areas, 3) a heavily soiled 18th century copper plate printed quilt (madder dye) with iron identified in the soiled areas.

1. INTRODUCTION

Chelating agents are compounds which can bind to metal ions at two or more sites, thereby creating ring complexes and changing the chemical behavior of the ion.

Chelating compounds have long been used in textile conservation and in the laundry industry. Phosphates are used to sequester metal ions in wet cleaning systems and thus act as water softeners as well as surfactant boosters. Oxalic acid is a well known chelating agent for iron and is used for local stain reduction as is sodium citrate.

Other conservation disciplines have also found chelating agents useful. Research in the laundry industry led Phenix and Burnstock (1992) to look more closely at chelating agents as part of cleaning systems for paintings. Carlyle and Townsend (1990) and Richard Wolbers (1990) have shown chelating agents to be effective in removing otherwise resistant soil from the surface of paintings.

The extensive surface area of textile fibers, attendant problems of accessibility and rinsability, as well as the sheer volume of the wash bath involved in the wet cleaning process pose problems that are quite different from those faced in the cleaning of painted surfaces. We wanted to look at some of the potentials and limitations for the use of chelating agents in these larger systems. This project was designed as an exploratory study only and was not expected to be an exhaustive study of chelating agents in cleaning systems.

There are many compounds which exhibit chelating behavior and these vary greatly in their specificity and binding strengths. There are chelating agents in biological systems capable of pulling a single ion species out of an ion mix, while a chelating agent such as EDTA (ethylenediaminetetraacetic acid) will strongly complex a wide variety of metals.

There are numerous factors which govern a chelating agent's preference for a given metal ion and the strength with which it will bind that ion (Bell 1977; Jones 1964). These factors include the size of the ring formed (five-membered rings tend to be more stable than others) and the number of rings formed by a single molecule (multiple rings are more stable than single rings). The size and charge of the ion come into play as do the orbitals available for bonding, as these factors influence the required geometry of the resulting complex. Other factors, such as pH (which may affect the number of binding sites available), accessibility of the ion (ions in solution will be complexed immediately, while ions in other complexes may require time to be “pried” loose), and competition by other ions and complexing
agents (particularly in the kind of mix presented in the bath of a heavily soiled textile) all affect the efficacy of a chelating compound. While this makes the action of chelating agents somewhat complicated and difficult to predict, it also promises potential for specificity and for manipulation of chelating agents, which is very attractive for conservation use.

2. PROCEDURES AND RESULTS

For the purposes of this study three objects in the Winterthur collection were identified with each having soils complicated by a metal component—either copper or iron.

The objects chosen included a nineteenth-century damask tablecloth, a loose-weave cotton window hanging, and a quilt made from eighteenth-century copperplate print fabric. All of these objects were slated for de-accessioning if the disfiguring soil could not be reduced. It was understood that treatment would be experimental.

Our search for effective chelating agents began with a review of the constants of formation recorded for various compounds complexing with copper or iron. The constant of formation is a measure of the strength of the complex, but as it is measured under ideal conditions and sometimes only by theoretical calculation, this number can only be considered an initial guide. The tables of constants gave us a preliminary list of compounds with affinity for copper or iron (Dean 1992). From these we eliminated compounds known to give colored complexes or to be toxic. Because of the large volume of solution required for wet cleaning, we also eliminated compounds whose cost would be prohibitive.

In order to screen these chelating compounds, we prepared test swatches by soaking swatches of muslin, some in copper and some in iron solutions. The swatches were washed in an Orvus bath, rinsed thoroughly and dried. X-ray fluorescence (XRF) analysis confirmed that substantial levels of the metals had been incorporated into the textiles.

Constants of formation suggested that citrate would be an effective chelating agent for copper. Further tests were conducted on copper-stained swatches in an attempt to determine an optimum chelating solution.

The citrate ion was introduced into the test solutions as the salt of citric acid both to facilitate solution and to provide a more appropriate pH. Copper-stained test swatches were soaked in 0.02 M solutions of ammonium citrate and of sodium citrate. The ammonium citrate performed extremely well—so much better than the sodium citrate in fact, that it was evident that the copper-complexing property of ammonium had a significant role. Stained swatches were soaked in a solution of ammonium bicarbonate to see if the ammonium ion alone could remove the stain, but this was not nearly as effective as the ammonium citrate. Screenings were then done of 0.02 M and 0.04 M concentrations of ammonium citrate over one, two, and three hour periods. A 0.04 M solution removed the stain from test swatches after one hour. It was found that more dilute solutions required longer times to achieve stain removal.

The first object treated was a nineteenth-century damask tablecloth with an overall cuprous green stain. It was one of three such tablecloths in the Winterthur collection.
Figure 1. a-c. XRF analysis of damask tablecloth showing copper content. Analysis was carried out on a sample.

Figure 1a. Before treatment.

Figure 1b. Proper left edge after treatment.

Figure 1c. Proper right edge after treatment (residual stain).
had been washed in the Winterthur lab in 1981 before our deionized water system was in place. The available water was well water which apparently had a high copper content or had leached copper from the building pipes, because all three cloths were similarly stained. The presence of copper was confirmed with XRF (figure 1a). Conventional wet cleaning had failed to remove the stain.

We decided to treat the tablecloth in a solution of triammonium citrate and to monitor color change to determine the length of time in the bath.

Because of the prohibitive cost of prepared triammonium citrate, the solution was made in the lab by combining citric acid and ammonium hydroxide. The solution was prepared as a concentrate before adding it to the bath. The large volume of the bath for the tablecloth (180 liters) and the limited in-house supply of citric acid dictated a 0.02 M concentration for this treatment. We realized that this would probably mean a longer treatment time than would be required with a 0.04 M solution, but the textile was strong and we felt a longer soak time posed no risk.

Because the tablecloth had been washed repeatedly in attempts to remove the stain, we knew it had no significant soiling other than the copper stain; therefore no surfactant was added to the bath. The initial pH of the bath was 7.1 and remained in the range of 7.1-7.2 throughout the treatment.

The tablecloth was soaked, with intermittent sponging, for 3 1/2 hours. At that time no further color change was taking place. The cloth was rinsed in a series of soaking and running water baths of deionized water, and was dried on the surface of the wash tank after aligning warp and weft threads.

The treatment produced a significant reduction in the stain. A slight gradient of white to pale green remained, running from one side of the cloth to the other. This may have been due to the drying process, because an edge of the cloth had to be folded on itself to accommodate the size of the wash tank. It was the folded edge which showed the greatest residual stain. We can only speculate whether a higher concentration of chelating agent would have completely removed the stain.

XRF showed that the copper content of the cloth was greatly reduced, although as expected, it was slightly higher in the area where some staining remained (figure 1-b and 1-c).

The second object treated in this study was a loose-weave cotton window hanging. The fabric of the hanging was embellished with cotton hand-embroidery and had been dated to the early 19th century. The construction, however, was modern and included modern twill tape and Velcro. The window hanging had hung for an extended time in front of a fluorescent light fixture and showed a degradation pattern typical of light-induced degradation, with dark orange-brown discoloration in exposed areas of the textile and almost no discoloration where the fabric was protected (figure 2). The very dark color and brittleness in the damaged areas indicated an extreme degree of degradation and suggested that something else was at work in this case.

XRF analysis showed that there was copper in the fabric, with a lesser concentration in the
healthy areas than in the damaged areas (figures 3-a and 3-b).

Since this hanging had been washed in the same water system that produced the green damask tablecloths, we did not doubt as to the source of the copper. The question was why it should be more concentrated in the degraded area.

The work of Judith Hofenk-de Graaf (1968) suggests that metal ions bind soil to fiber. We hypothesized that the converse may also be true. In this case the degradation products already present in the cotton may have bound copper ions which contributed to accelerated degradation upon re-exposure to light. We know from museum records that an attempt was made to wash the hanging in 1988, apparently with unsatisfactory results, as the conservators report adding increasing amounts of surfactant in an effort to move the discoloration.

The window hanging presented a more difficult problem than the tablecloth because it involved not only copper staining, but a combination of copper and degradation products, creating a less predictable combination for a wet cleaning bath. Furthermore, where the tablecloth had been a strong and stable textile, the window hanging was badly degraded and very fragile. Any wet cleaning procedure would present a high risk for this object, but as it was scheduled for de-accessioning in its current condition, the curator agreed with us that the treatment was worth trying.

The window hanging was first supported on a sheet of spun polyester in a shallow bath of
filtered water and sponged gently with a 0.5% solution of Orvus surfactant to remove as much loose soil and degradation product as possible. It was allowed to soak in this bath for forty minutes to allow some swelling of the fibers. It was then lightly rinsed in filtered water and allowed to drain on the polyester support.

We prepared a concentrated solution of triammonium citrate to charge the chelation bath to a final concentration of 0.04 M. The chelating bath was carried out in a large photo tray to provide a bath of small volume (60 liters) and to allow better control of the textile. Although considerable color leached into the bath, the window hanging was still quite dark. It was drained and fresh chelating solution added (0.04 M). Because it was known that time can be a factor in the efficacy of a chelating agent and because the fabric showed no further damage due to soaking, the hanging was allowed to soak overnight. After nineteen hours there was no apparent change in the color and the window hanging was moved once more to a fresh chelating solution, this time at 0.08 M, twice the starting concentration. After three hours in this bath with gentle, intermittent sponging, the hanging was removed and rinsed in a series of running and soaking rinses in deionized water.

Although XRF indicated that most of the copper had been removed (figure 3-c) discoloration was only slightly reduced. Deterioration had proceeded too far to allow full recovery. We like to think that if the copper had been removed early, degradation would never have reached the stage it did.

The final subject of investigation in this study was a quilt, the printed top of which dates to the eighteenth century (figure 4). The top
Figure 4. Before treatment, quilt made from eighteenth century copperplate print fabric showing area of severe soiling.

Figure 5. After treatment, quilt made from eighteenth century copperplate print fabric, soiling significantly reduced.
was a linen warp, cotton weft plain weave, copperplate printed in a design representing the apotheosis of Washington and Franklin, a design successfully marketed in the United States in the decades following the American Revolution. The top was rather crudely pieced together from three lengths of fabric and seven smaller rectangles. A pattern of light fading which follows the seam lines suggests that this fabric had been well used before it was made into a quilt. No dye analysis was done but documentary evidence of the widespread use of madder dye during this time period and the familiar hue of this pattern led us to accept that the dye was an alum mordanted madder.

The quilt included a single-layer lining of plain-weave linen and the backing was plain-weave cotton. It was remarkably strong but exceedingly soiled and darkened with cellulose degradation products. Light damage was evident along the proper left edge. Of special interest to us was a dual rectangle pattern of blackish soiling at the center. We don't know how this soil occurred. Evidently it accumulated while the quilt covered a bed, thus producing this distinct pattern.

XRF analysis showed the soiling to have an iron content much higher than that of the areas outside the blackened area (figure 6a and 6b). Our experience has shown such soiling can be very resistant to traditional wet cleaning methods.

Because the metal in question here is iron, not copper, we reviewed a variety of chelating compounds, this time for a preference for iron. Specificity is particularly important for dyed fabrics because the compound must complex with the soil-binding metal but leave the mordanting metal alone. EDTA, an extremely effective but rather indiscriminate chelating agent, has been known to lift the dyes off textiles.

Constants of formation suggested several likely candidates and we used iron-stained swatches of muslin to screen gluconate, salicylate, citrate and oxalate as well as the polyphosphates traditionally used in wet cleaning systems.

Whereas color change had proved an effective means of monitoring copper removal, none of the chelating agents screened here completely removed the iron stain. We used XRF to evaluate the relative effectiveness of the compounds. Citrate, while not removing all of the iron, proved once again to be the chelating agent of choice. (Oxalate was equally effective, but its toxicity precluded its being chosen over citrate.)

The ammonium ion does not complex iron as it does copper. Consequently ammonium citrate proved no more effective than sodium citrate for removing iron. We decided to use a trisodium citrate system to treat the quilt. Trisodium citrate is more readily available than ammonium citrate and doesn't have to be mixed. Its pH is slightly higher than that of ammonium citrate (an advantage in promoting chelation). Furthermore, it is not accompanied by the ammonia fumes of an ammonium citrate system.

Earlier in this century, Winterthur, like a number of other institutions, used historic textiles to construct accessories for the period rooms settings. Although we regard this practice with some dismay now, it did leave us with a resource we wouldn't otherwise have, in the form of a large collection of scraps of
historic textiles for testing. Thus we were able to test aged, madder-printed materials for fastness in a sodium citrate solution.

Neither blotter testing nor extended soaking in 0.08 M tri-sodium citrate solution produced any bleeding of dyes in the test swatches.

Blotter testing of the dye on the quilt with 0.08 M sodium citrate did, however, yield a slight transfer of color. We decided to go ahead with the washing and chelating procedure, knowing that the chelating would have to be carefully monitored and that extended soaking would not be possible.

The quilt was first washed in two successive baths with Orvus surfactant and rinsed in a series of soaking and running rinses. The black soiling was still very much in evidence after these baths.

For the chelating procedure the wash tank was tilted in order to reduce the volume of the bath and therefore the quantity of chelating agent required. A concentrate of trisodium citrate was added to bring the bath to a .04 M concentration and Orvus was added to 0.5% of total bath volume. The quilt was allowed to soak in this bath with intermittent gentle sponging.

We observed a faint coloring of the water after forty minutes, indicating some dye loss. The bath was drained after one hour and the quilt was rinsed with a running rinse followed by a soaking rinse and two additional running rinses in deionized water. The quilt was placed on a screen and covered with a cotton sheet to help guard against dye bleeding during drying.

Although there was a very slight loss of dye (evidenced by color in the chelating bath) there was no bleeding of dye into surrounding areas and the image remains crisp and clear. The soiling was effectively removed (figure 5) and XRF showed the iron to have been almost completely removed (figure 6c).

Figure 6a. Before treatment, central area of quilt with heavy, blackish soiling.

Figure 6b. Before treatment, edge of quilt where blackish soiling was not present.

Figure 6c. After treatment, central area of quilt (site of analysis in 6a.)

Figure 6, a-c. XRF analysis of copperplate print quilt showing iron content of soiled area. Analysis was carried out on a single layer of the quilt with a germanium target and 100 second exposure.
3. CONCLUSION

These are, of course, only initial studies and there are still many questions regarding the use of chelating agents. We cannot, for instance, demonstrate the rinsability of the citrates. Nor do we know the optimum concentrations, pH range, temperatures, or soaking times. But we hope that these beginning studies may promote interest in further investigations that will clarify optimum parameters for citrates and perhaps identify other compounds from the wide range of chelating agents that may serve the conservation of textiles.

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NOTES

1. For a 100 liter bath of 0.02 M triammonium citrate, 384 grams of citric acid is mixed with 384 ml of concentrated ammonium hydroxide (14.5 N) in several liters of deionized water. The pH of the concentrate is adjusted to seven with ammonium hydroxide. It should be noted that the mixing of these reagents is extremely exothermic and should be carried out gradually and under a fume hood.

2. pH was monitored by taking samples of the bath water at intervals and measuring pH with a Fisher Accumet pH meter, model #210, with gel-filled electrode.

REFERENCES


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