

Conservation Experience in Working with Chrome Tanned Leather

ABSTRACT

Leather is one of the earliest manmade products. Its use has been documented in archeological sites from early Middle Eastern civilizations. In the earliest years of tanning, many processes were developed such as vegetable, brain, and smoke tanning, and later, alum tawing—the only pre-industrial mineral process.¹ In the late nineteenth century, chrome and other mineral tannages and combinations of mineral and vegetable tans were perfected. This paper explains what chrome tanned leather is and how it is processed, why it is so stable, and gives some suggestions for alternative methods to traditional leather working.

INTRODUCTION

Leather is a strong, supple material that can be a pleasure to work, but due to acids that are created as most leathers age, it can deteriorate and cause the deterioration of adjacent materials such as paper, sometimes penetrating through several layers. Leather produced since the early nineteenth century tends to deteriorate at a faster rate than older leather, leading some to believe that either the tanning processes since the nineteenth century were faulty or the animals were inferior. Therefore, some have expressed the opinion that the use of leather in conservation should be eliminated.

Experience in working with chrome tanned leather shows us that it is difficult to manipulate using traditional methods. Chemistry, however, shows us that properly processed chrome tanned leather is stable. This stability is illustrated by the book, *Report of the Committee on Leather for Bookbinding*, in which many samples of leathers from various animal sources and tannages were placed in the inside covers of the book itself (Cobham and Wood 1905). The

This paper was presented as a poster at the AIC 30th Annual Meeting, June 6–11, 2001, Miami, Florida. Received for publication Fall 2002.

leather samples embedded in the covers were placed there in 1905—a naturally occurring aged leather sample. The chrome tanned leather is the only sample that has not discolored the paper adjacent to it.

An important question that needs to be answered is: why use leather in book conservation at all? Structurally sound treatments have been developed for board reattachment and spine repair. Paper and linen cloth can be toned and coated to match the color and surface qualities of the object. These treatments can be flexible, aesthetically pleasing, chemically stable, and relatively inexpensive. Why bother with such a problematic material as leather in general and chrome tanned leather specifically? This is perhaps not a treatment that should be applied to every leather repair, but because of the remarkable stability of chrome tanned leather, it should be viewed as viable option in book repair. As conservators, we look for stable, sympathetic materials for repairs. If using chrome tanned leather requires more work or different techniques, but will result in a long lasting treatment, it is worth consideration as a material used in conservation.

What was hoped for in experimenting with chrome tanned leather samples was to find methods that worked to the strengths of the material. Experiments on samples of chrome tanned leather that had various characteristics were performed in order to achieve the ultimate goal of completing a leather reback.

HISTORY OF CHROME AND CHROME TANNING

The discovery of the element chrome came in 1766, and it was used in the preparation of red, yellow, orange, violet, purple, maroon, and green pigments. It was given the name chromium, from the Greek word for color. Robert Warrington patented a process for the use of chrome in leather production in 1841. Several similar patents were granted in various European countries, although none was a commercial success until 1878. In that year, Christian Heinzerling patented a leather tanning process using alum

and zinc salts, chromic acid, potassium ferrocyanide, and barium chloride. Augustus Schultz, a salesman for a dyestuffs company, became aware of a problem in the manufacture of women's corsets. Because of cost, whalebone, the traditional material for making corset stays, was giving way to steel. The acids in the leather that cover the stays reacted with the steel and made ink. Chamois smells of fish, and the alum salts wash out of tawed leather with perspiration. How Schultz came to be interested in and able to create chrome tanned leather remains a mystery, but he took out a patent in 1884 for a two-bath chrome process that most consider the foundation of chrome tanning (Thompson 1997).

METHODS OF TANNING

Modern methods of tanning begin with the same process—pretanning. The goal of pretanning is to rid the skin of undesired elements and “opening up” the skin, leaving only the corium or middle layer of the skin. The process of opening up creates interstitial voids between clusters of collagen molecules that allow the tannins to work (Erickson 1998). The skins are cured through air drying or more commonly through salt, either dry or in a brine (OMRI 2000). The skins are dehaired in an alkaline bath, usually sodium sulfide (NaSH), washed, and degreased; then deliming takes place to neutralize the alkaline substances (OMRI 2000). Finally, the skin is bated using an enzyme preparation that rids the skin of the last of the undesirable elements. After these processes, what remains is mostly collagen—a tough, tightly coiled protein chain. From this step, the tanning processes differ, but after tanning, the finishing stages are often similar. Lubricants are added in a process called fatliquoring for the desired softness of the leather and surface coatings further alter the feel of the leather. Common surface coatings are nitrocellulose and vinyl polymers.

Vegetable Tanning

During the preparation of the skin, carboxylic acids on the proline and hydroxyproline side chains of the collagen molecules become deprotonated creating carboxylates. The resulting carboxylates bind with the phenol groups on any number of tannic acids. This process, tanning, creates a strong skin that is resistant to decay. Gallotannins are the most traditional tannins used and come primarily from oak and chestnut trees (Erickson 1998).

Alum Tawing

Alum tawing is not a true tanning process. The interstices between the collagen fibers are packed with microbe inhibiting salts such as aluminum sulfate (Erickson 1998).

Chrome Tanning

One of the benefits of chrome tanned leather is that it can be processed quickly. Sulfuric acid (H_2SO_4) is generally used. The acid creates carboxylates by deprotonating carboxylic acids on the side chains of the collagen. The trivalent chrome bonds with the resulting carboxylates on the collagen fibers (Erickson 1998). This bond is stronger than the bonds with the tannic acids and is the reason for the stability of the leather.

Chrome Retan and Combination Tans

A combination tan uses two or more tanning processes. A retan is a more specific term applied to leather that is completely or partially tanned by one process and followed by a second, usually different, process. A chrome retan is tanned by the chrome process first and followed by vegetable or synthetic tanning agents (Roberts and Etherington 1982).

The chrome forms strong bonds with carboxylates on the side chains of the collagen molecules. The result is a supple greenish-blue skin. In vegetable tanning, the large gallotannin molecules allow for movement in the interstices of the collagen fibers. There are no residual tannins in the chrome tanned skin (Erickson 1998). The chrome ions are much smaller than the gallotannin molecules and become tightly bound with collagen. This is the cause of both the desirable and undesirable qualities associated with chrome tanned leather: its chemical stability as well as its tough, spongy quality. It may prove possible, however, for the tanning processes to be altered to create more desirable qualities for conservation purposes.

EXPERIMENTS WITH SAMPLES

I experimented with two samples of calf and one of deerskin. Each of the calf samples had a different character and finish. Sample A was calfskin, dyed brown, and quite thick. It had a great deal of body and a shiny, hard surface coating. Sample B, also calf, was dyed green, was very soft, and had a light surface coating. Sample C was a very soft and pliable deerskin with no apparent surface coating and dyed a light creamy yellow. I tried different ways of thinning the samples overall, edge paring, and application of different adhesives. In addition, I tested stamping. The results varied, but with patience, I achieved the results I was looking for.

Paring and Thinning Overall

For thinning overall I used a spokeshave, a Scharf-fix machine, sandpaper (120-grit ruby sandpaper), and an orbital sander. For edge paring, I experimented using an English leather paring knife and a hand held rotary tool, such as a Dremel tool, fitted with an angled grinding attachment. The leather quickly dulled my knife. Frequent

stopping and occasionally taking the knife back to a sharpening stone was necessary.

Sample A worked well on the Scharf-fix machine and with a spokeshave. After thinning the leather overall, I pared the edges with a knife, which gave a feathered edge. Sample B also responded well to both the Scharf-fix and a spokeshave, as well as edge paring with a knife.

Sample C, the deerskin, did not respond well to either the Scharf-fix or to the spokeshave due to the sponginess of this particular leather. The Scharf-fix machine scored the leather and the spokeshave gouged it. In order to avoid gouging, tiny amounts of material had to be shaved with each stroke. Instead of the familiar curls of shaved leather, copious amounts of leather dust resulted. This method proved to be far too slow and tedious. Sanding the leather with a 120-grit ruby sandpaper was fairly quick and gave even results. An orbital sander was even quicker. After the skin was even overall, I pared the edges. Paring was difficult and it dulled the knife. I started with a very sharp knife, stropped the blade after every four to five cuts, and had to take it back to a stone several times. The action of cutting is not the same as in traditional leather working. A long cut was almost impossible. Short, biting cuts seemed to work the best. Because of the sponginess of the material, the cut resembled a tiny ragged cliff—the edge was feathered and there was a steep angle upwards resembling a shelf. This is not peculiar to chrome tanned leather, but means that the material must be pared in stages. The “shelf” that is created can be taken down in two to three passes of the knife. Because long cuts are difficult if not impossible, the process of shaving this down can be tedious. Another method is to use a hand held rotary tool with an angled grinding attachment to sand the edges to the desired thinness and then to pare the edge with a knife to feather the edge. This is an unorthodox method, but the result is an even slope from the body of the leather to the feathered edge. Overall, if power tools are used, the process is not much more difficult or time consuming than when working with traditional methods on vegetable tanned leather.

Adhesives

Because I ultimately decided to use the deerskin for the rebacks, I tested adhesives only on the deerskin and not the calf. To test adhesives, I used two different approaches. I first adhered chrome tanned leather to binder’s board. Secondly, I adhered chrome tanned leather underneath degraded vegetable tanned leather to simulate a leather repair. I used three different adhesives: precipitated wheat starch paste, PVA emulsion, and Lascaux 498.

For the first method, I applied adhesives to the samples and affixed them to binder’s board. All three adhesives worked well, but the wheat starch paste had to be thickly applied and therefore a long drying time was needed

before proceeding. A light coating of either PVA or Lascaux had the strongest adherence of chrome tanned leather to binder’s board.²

For the second method, I adhered chrome tanned leather to binder’s board underneath degraded vegetable tanned leather, mimicking an actual repair. I used five adhesives with water content varying from very high to anhydrous: precipitated wheat starch paste, PVA emulsion, Lascaux 498, a 50/50 solution of B72 dissolved in ethanol, and a 50/50 solution of PVAYAA dissolved in acetone.

The wheat starch paste predictably darkened the more degraded areas of the old leather. In addition, the water in the paste collapsed the space between the collagen fibers in the leather, creating a pocked look. Coating the underside of the degraded leather with Klucel G in ethanol can minimize this darkening. Polyvinyl acetate emulsion contains some water, but worked well in adhering the chrome tanned leather to the board and to the old leather. Slight darkening could be observed along the edges where degradation was the highest. Lascaux adhesive contains less water than PVA emulsion and worked as well as PVA. Less darkening was observed along the edges but occurred in one spot of higher degradation. B72 resin in ethanol worked well as an adhesive, and because it is anhydrous, left no darkened areas. The ethanol, however, penetrated from the back of the old leather to the surface causing noticeable tidelines. PVAYAA resin in acetone at first failed as an adhesive. The acetone penetrated the leather from back to front, drew the resin through the leather on to the surface, and caused staining. I allowed the acetone to volatilize under a fume hood until the resin was quite thick. The results were that the resin adhered the new leather to the board and the new leather to the old leather without staining or penetrating to the surface.

Wheat starch paste without the previous application of Klucel G in ethanol is unacceptable due to staining and pocking. The resins dissolved in solvents produced very smooth transitions between leathers and no darkening of the leather. There is, however, a lower open time for the resins. Ethanol can move degradation products leaving tidelines. Acetone is tricky—too much acetone can move the resin into the leather eventually causing the leather to become brittle, which is especially risky in the joints. The best results were achieved using wheat starch paste, PVA emulsion, or Lascaux. Although the synthetic adhesives are not water soluble, they are mechanically reversible, do not risk damaging the old leather, and are more flexible and reliable than pure resins. They are most useful where strength is a concern

Stamping

Gold stamping could be accomplished using a stamping machine. The best results were at a low temperature, 200° F.

USE OF CHROME TANNED LEATHER IN A TRADITIONAL REBACK

The book I chose for rebacking was covered in light brown calfskin that had been pressed to a smooth reflective surface. It was a tightback and the boards and most of the original spine piece had become detached.

The leather I chose for the reback was deerskin. The light yellow color allowed for dyeing the skin to achieve different effects. The major difficulties with the skin were that it was stretchy and spongy, causing difficulties in thinning and paring, and that it quickly dulls the knife.

The first step in the reback was the preparation of the new leather spine piece. First I thinned the leather using 120-grit sandpaper. I soon moved to an orbital sander for speed. I dyed the leather to match the color of the books. The two types of commercial dyes that I considered were from Asco and Leather Conservation. Asco dyes were easier to use, but contain organic solvents. Dyes from the Leather Conservation Center are water-based, a bit tricky, but less toxic. I used the water-based dyes and colored the leather to match the original and placed the damp leather under blotter paper with boards and weights to dry overnight. In the morning, the dyes had run to different areas of the leather, each with a corresponding tideline. After some fretting, I managed to restore a good color and then quickly dried the skin with a hair drier. This gave even results. Because I was trying to mimic calf leather, I crushed the skin with a very hot iron on a hard surface using a piece of waste paper between the iron and the skin. On one edge, I pared the leather with a paring knife in several passes to achieve a thin, feathered edge to sit under the old leather. On the other edges, I used a hand-held rotary tool to thin the edges and then pared with a knife to achieve a feathered edge.

I removed the spine covering and cleaned the spine using a poultice of methyl cellulose, then lined the spine with Japanese paper. I cut compensation strips on the boards and then lifted approximately one inch of leather on the boards. The leather separated easily due to adhesive failure. After I had prepared the volume for rebacking, I applied a thin layer of Lascaux to the underside of the lifted leather and the boards, inserted the new leather under the old leather of the boards, turned in the caps, nipped in a press, and boned to smooth. I coated the spine and the new spine covering with Lascaux and inserted the volume. I then applied SC 6000 wax to the new leather and buffed with a lint free cotton cloth. The results resembled the same sort of light brown, smooth, reflective calfskin as the original. I finished by applying the old spine covering to the new leather with Lascaux. Unfortunately, after applying the spine, I realized that I should have made the leather thinner as it is on the bulky side in the caps and along the joints. This can be avoided by more careful sanding and

measuring. Chrome tanned leather does not mold as easily as a vegetable tanned leather, so thinness is important. Other than the fact that the leather was too thick, the result was a satisfactory reback. The color and sheen of the new leather matched the old and the adhesive did not darken the old leather. The new leather was pared thinly enough to blend in unobtrusively under the old leather.

CONCLUSION

Chrome tanned leather can be used for the repair of leather volumes. It can be successfully thinned, pared, dyed, and safely adhered to both binder's board and to original materials. It provides another material from which a conservator can choose. It is sympathetic to the original material and, if processed correctly, is a chemically stable alternative to vegetable or combination tanned leather. It may prove that the processing of chrome tanned leather can be altered to suit the needs of conservation, which would require experimentation in tanning and finishing techniques. Perhaps a combination of older, less aggressive techniques of pretanning could be combined with chrome tanning to provide a skin with good working qualities and chemical stability. For now, available materials can be utilized by employing a combination of unorthodox methods and traditional leather working techniques.

NOTES

1. Alum tawing is not a true tannage since the alum salts used to preserve the skin can be washed away with water, leaving the hide subject to putrefaction.
2. The difficulty with wheat starch paste is water. Application to new leather works well. Degraded leather, to which the new leather will be adhered, reacts with water often giving unpleasant aesthetic results. Water can collapse the space between the collagen fibers giving the leather a pocked look, or it can "burn" the leather, darkening it by oxidizing the degradation products.

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Leather Conservation News 13.1.

ANN LINDSEY

Assistant Conservator

Francis Bacon/Arensberg Collection

The Huntington Library

San Marino, California

alindsey@huntington.org

