Imputrescible Corium:
The Production and Structure of
pre-1900 Bookbinding Leather

INF 392E:
Technology and Structure of Records Materials

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Introduction

Mankind began to produce leather very early in our history. The base material, animal hide, was available as a byproduct of the killing and eating of animals, and the further use of those hides for clothing and shelter was demanded by the necessary economy of early man’s existence. Decay and bacterial action begin shortly after the death of an animal and an unmodified animal skin must be chemically and structurally modified for any long-term use. The manufacturing of leather involves a series of steps intended to halt the natural deterioration of the material and to improve on its handling properties (Lanning pt. 1). Leather workers have employed a variety of methods to modify hides to these ends, but the method of principal importance for pre-1900 bookbinding is vegetable tanning. Other methods, including mineral processes such as alum tawing and chrome tanning and oil processes such as brain tanning and chamoising were not commonly used on early bookbinding leathers (Mills and White 86). In this paper, I will discuss the physical and chemical structure of pre-20th century bookbinding leather, with the aim of understanding leather deterioration and forming a basis for evaluating possible conservation treatments.

Animal Skin

Animal skin consists of living cells and the byproducts of their activities. It has three well-defined layers – the epidermis, dermis, and hypodermis. The epidermis, or surface layer, of the skin largely consists of hard, dead cells, and the hypodermis, or flesh layer, of the skin is made up of muscle and fat. Both of these layers are removed in leather-making, leaving the dense, fibrous dermis. The dermis also contains three layers – the corium, grain, and junction. The lowest level, the corium, forms the bulk of the dermis and has large, strong collagen bundles. Under the epidermis layer and closer to the surface of the skin is the grain layer. The fibers here are smaller and very densely packed. The junction layer lies between these two dermis layers. In sheepskin, which has a tendency to delaminate, this layer is fatty and very weak (Lanning pt. 2).

Chemically, the derma consists of fat cells, water, proteins, carbohydrates, and minerals, the exact proportions varying between individuals and species. The protein in the derma largely
consists of collagen, and most of the carbohydrate matter is glycogen. Collagen is the principle structural protein found in the bone, hide, and muscle of animals. As a protein, it is made up of long sequences of amino acids and, similar to the keratin protein found in hair, it is fibrous – the polypeptides are oriented parallel to each other in long chains. Collagen fibers consist of three long chains tightly bound together in an α-helix (Mills and White 86).

When discussing bookbinding leather, the terms grain side and flesh side are used to refer to the upper and lower sides of the skin. The grain side is smoother and patterned with hair follicles. The flesh side is rougher and (except with pig skin) has no visible pores. The grain of a leather refers to the pattern of follicles on the grain side (Reed 23). A major factor in the appearance of the skin is the source animal – generally goat, calf, sheep, or occasionally pig. For a grown animal the material is referred to as a hide (of a goat, cow, or sheep), while for a young animal the material is called a skin (of a kid, calf, or lamb) (Waterer 5).

Leather from sheep comes in two varieties, that from hair sheep and that from wool sheep, the former being better for leather production. Although there is much variation in quality by breed, the skin of wool sheep has a much looser fiber network and more glandular structures than hair sheep skin. Due to the density of wool growth on the skin of the sheep, the grain layer of the derma (where the hair is attached) is thick and poorly integrated into the rest of the skin (Haines 68). In addition, the large quantities of fat created as part of wool growth are removed during tanning, leaving empty spaces in the leather. As the leather ages the space left by these fatty deposits can lead to separation of the dermal layers. This peeling effect and the spongey texture of the material are two significant clues to a particular skin’s origin. Overall, the lack of strength and evenness in sheepskin makes for a cheaper and less durable leather (Reed 41-43).

Closely related to sheep, goats have significantly different skin characteristics. Since they do not grow wool, their skin has a much more firm structure when tanned. The grain layer is compact and can withstand more intensive processing and finishing than sheepskin. This results in a very soft, strong, and attractive leather. Because of the close relation between sheep and goats, their skins can be difficult to distinguish visually. They both exhibit thick hair follicles interspersed with smaller holes, and particularly with the hair sheep and the more coarse-woolled sheep, the surfaces may be impossible to categorize definitively. Frequently, the best indication of species is the better strength, firmness, and aging properties of goatskin (Reed 43-44).
Calfskin has a very smooth grain and a very even texture. The hair follicles are small and regularly spaced out, although as the cow gets older the hair becomes thicker (Reed 40-41). Pigskin can be distinguished by the stiffness of the material and the large hair follicles, or pore holes, which occur in widely spaced groups of three penetrating the entire depth of the derma.

As an animal ages, its skin gets thicker but more uneven in texture. Animals also tend to deposit more fat in their skin as they age, and when that fat is removed during tanning pockets of empty space remain. Defects in the skin surface are also found more often in older animals as they have had more exposure to biting insects, incidental scars, and disease (Reed 36). When thick leather is pared, or thinned, for use in bookbinding, bulk is removed from the corium, leaving the weaker grain layer. If this is overdone, the resulting leather has almost no strength left (Haines 70).

Understanding and identifying leather from historical artifacts can be complicated by several factors. The first, of course, is deterioration – a leather item may have changed significantly from its original nature simply through aging. The animals too were different, generally being smaller and having less fat in their skins. One hesitates to make too strong of a comparison between the skin of a carefully bred modern feedlot calf and the skin of its well-exercised, grass- and scrub-fed ancestor. The surface appearance of leather can also be deceptive - certain grain patterns are frequently imitated on leather and non-leather materials. In particular, the hard grained goatskin pattern is often stamped onto cheaper calf or sheepskin (Reed 25).

**Tanning**

Once the skin is removed from the animal it will begin to decay. The aim of tanning the leather is to permanently halt that process by removing most of the fat and mineral parts of the skin while retaining and strengthening the remaining connective tissues (Mills and White 86). If, as in most cases, the tanning process cannot be immediately begun, the skin must be temporarily preserved. This *curing* can be done in a variety of ways, but generally involves salting and drying (Waterer 5). Processing a skin into leather takes many steps, each of which affects the physical and chemical properties of the finished material. The actual tanning does not happen until the skin has been prepared by soaking, dehauling, fleshing, scudding, deliming, and bating.
The first step, *soaking*, removes the water-soluble minerals and salts, washes off dirt, blood, and dung, and rehydrates the dried skins. Next, the leather is prepared for removal of the hair, or *dehairing*. This step begins by loosening the hair for removal and opening up the fiber network of the skin for further processing. Before the mid-19th century, this was accomplished either by controlled rotting (*sweating*) or by soaking the skin in a suspension of lime. After the 1850s, the addition of sodium sulfide in an aqueous solution significantly speeded up this process. Most of these dehairing processes raising the alkalinity of the leather, though this is most pronounced in modern leather manufacture (Haines 71). Lime and sodium sulphide plump up the fibers and begin to dissolve the keratin of the hair and epidermis while leaving the collagen in the derma intact. Once the keratin is loosened, the hair and epidermis are mechanically removed with a blunt knife (Reed 48-53). Modern leather production adds strong alkalis to the bath to actually dissolve the hair root and epidermis (Lanning pt. 2).

The next step is directed at the flesh side of the skin. *Fleshing* cleans and levels the lower side of the skin, smoothing out natural irregularities in thickness and removing unwanted hypodermal tissue. A process known as *scudding* cleans any remaining hair and dirt from the grain side with a blunt knife. At this point, thick skins can be split laterally into two skins – a flesh side layer and a grain side layer. The very thin grain side is called a skiver and is frequently employed in bookbinding for making labels (Reed 53-55). As noted earlier, the fiber bundles in the grain layer are weaker and less interwoven than the fibers of the corium. Thinning or splitting a skin quickly decreases its strength, so such skivers are of little structural use in book bindings.

Leather is naturally stable at a fairly low pH, so if a skin’s alkalinity has been raised to permit dehairing, it must subsequently be lowered. Pre-Industrial Revolution processes achieved this through the use of weak acids. These acids were not sufficiently powerful to displace all the calcium for the skin and left a beneficial buffer of calcium salts to counter the effects of atmospheric pollution. The modern processes of *deliming* use more powerful acids and the calcium salt buffer is lost (Haines 71-72). The final pre-tanning step is to *bate* the skins. Although similar effects were obtained with earlier tanning methods, bating as a separate process was introduced in the early 19th century. Bating originally involved soaking the skins in a warm solution of water and dung; this vile mixture was understandably replaced in the 20th century with enzymes and certain bacteria and molds. These enzymes remove some of the muscle fibers.
to allow the skin to move more freely. The chemical effects of bating are not clearly understood, but the process results in a skin that is noticeably softer, more even in texture, and more pliable. The pH of the skin is further reduced, and the fibers of the leather settle down from their earlier plumped state (Reed 54-56).

These preliminary steps are intended to remove all of the undesirable elements of the skin. They do not, however, address the principle problems of leather preservation – the propensity of the skin to putrefy when wet and to harden when dried. Several methods exist of treating skins to render them imputrescible and supple; the main categories are vegetable, mineral, and oil processes. Extensively used in bookbinding for centuries, vegetable tanning relies on the properties of a group of complex substances known as tannins derived from plant matter. Mineral processes like alum tawing and oil processes such as brain tanning and chamoising are also historically significant, though used infrequently in bookbinding. The development of chrome tanning (a mineral processes) in the mid-19th century expanded the available options. More recently, the chemical industry has developed synthetic tans, or syntans, to mimic the effects of vegetable tanning (McLean pt. 3). Because of its central place in the history of western bookbinding, it is worthwhile to discuss the process of vegetable tanning in more detail.

Water exists in the structure of the fiber bundles in two ways. Most of it is present in the spaces around the fiber bundles, but some of the water is closely bound to the collagen molecules. These water molecules prevent the collagen chains from becoming hydrogen bonded to each other and consequently inhibiting the flexibility of the leather. When the skin is sufficiently dried out this water is lost, and the chains begin to link together. Any hydrogen bonds can be broken when the skin is rewetted, but the chains can also cross-link and form bonds that are much more permanent. One of the aims of tanning is to inhibit that cohesion when the skin is dry so that it remains supple through repeated wetting and drying. When a raw skin is wetted, the fibers are subject to hydrolysis. This chemical reaction breaks the protein chains between the amino acids, creating shorter and weaker chains and gradually dissolving the protein. Another aim of tanning a skin is to lessen or eliminate the effects of hydrolysis (McLean pt. 3).

As mentioned above, vegetable tanning relies on a class of substances called tannins. Tannins can be derived from a wide variety of plant materials and achieve their effect by
displacing the hydrogen bonded water on the collagen molecule and consolidating the fiber network of the dermis. By taking up most of the available hydrogen bonding sites, they prevent the collagen chains from becoming hydrogen bonded or crosslinked to each other (McLean pt. 3). The result is a material that is much more stable through temperature changes, is water resistant, and is much more durable than the raw animal skin (Reed 73).

Tannins are generally of two types, the catechols, or condensed tannins, and the pyrogallols, or hydrolysable tannins. Catechol tannins, such as Mimosa and Quebracho, tend to bind very strongly and quickly to the fibers and are relatively inexpensive. They are favored by manufacturers for these reasons but tend to age poorly – changing color and releasing acids which break down the fiber structure of the leather. Pyrogallols, like Sumac and Myrabolans, are slower acting, penetrate more thoroughly into the leather, and are resistant to oxidization. Additional non-tanning materials in these extracts have the beneficial effect of buffering any future acid activity (Mclean pt. 4). It should be remembered that most tannins are also dyes, and that the choice of tannin liquor would be influenced by the choice of desired color (Reed 80).

Historically, tanning was a very time-consuming process where the skins were moved gradually through ever stronger tannin baths. This allowed the liquor to penetrate fully before becoming entirely fixed to the fibers. Modern leather production has speeded up the tanning process considerably through the use of mechanical agitators (McLean pt. 4) and the use of very concentrated tannin baths (Fredericks 29). When considering leather from pre-industrial periods, it should be understood that several of the pre-tanning and tanning steps above could be and frequently were combined into a single step (Reed 81-82).

**Coloring and Finishing**

Leather is frequently modified after tanning to make it easier to work and to achieve a desired appearance. The processes called dressing can modify the original result of tanning to make the material softer, more water resistant, or easier to work, and finishing affects the appearance of the leather and can involve staining, dying, embossing, or stamping the surface (Waterer 8-9). Adding fatliquors and currying the leather are methods of dressing it by reintroducing fatty materials to change the leather’s handling properties as well as improving its water resistance (Reed 47). As the outward appearance of a bookbinding is very important to the
consumer, the various means of finishing are frequently employed. Dying and staining affect the color of the leather, and embossing and stamping affect the grain texture. The distinction between dying and staining is one of method – dying requires immersion in a bath, while staining is simply application onto the surface. Earlier, expensively produced processing methods were later reproduced with finishing methods that mimicked their effects. For example, Morocco leather was originally tanned with sumac and boarded while wet to produce a distinctive “hard grain”. The term Morocco is now applied both to any goat skin leather and to the skins of other animals embossed with the pattern of Morocco, a practice which has the delightful euphemism of “assisted Morocco”. The habit of boarding leather, or folding the leather in half to the grain side and rubbing with one’s hands or a board over the fold, both creates a desirable hatched pattern in the leather and makes the leather easier to work with (Waterer 48).

**Aging of Leather**

In Douglas Cockerell’s 1929 book, *Some Notes on Bookbinding*, he states, “Leather of good quality is without a doubt the best material for covering books.” He mentions its flexibility, durability, and ability to be molded to shape as its most desirable qualities and cites the existence of many original 15th century leather bindings as proof of its permanence. Despite this endorsement, he has a long list of criticisms of modern leather manufacture and binding practices. Chief among these are the unsuitable methods of dressing leather and the 19th century practice of paring leather to an extreme thinness for cosmetic effect. He discusses the fact that around the turn of the 20th century, book owners began to notice that many of their most recent bindings were deteriorating in the space of just a few years. A commission was formed to investigate this phenomenon, and the results were damning. Many of the changes in leather manufacture instituted in the mid-19th century were actively causing the material to disintegrate. The replacement of sumac and oak tannins (both pyrogallols) with the more swiftly acting catechols had a deleterious effect on the material, and the excessive thinning of leather by binders to produce hard right edges and clean folds stripped away the strongest inner parts of the leather thickness (Cockerell 43-50, appendix II).
The deterioration of leather that Cockerell refers to is called “red rot”. It is a breakdown in the fibrous structure of leather that results from the action of acids; as it progresses, the leather becomes loose and powdery. A number of factors contributed to the dramatic rise in the incidence of this type of deterioration. The Industrial Revolution began in the mid-19th century, and one of its effects was the production of the atmospheric pollutant sulfur dioxide, a potent source of acid. The new synthetic dyes and mechanical means of shaving skins required the use of other powerful acids, such as sulfuric acid, in the tanning processes (Barlee pt. 7). At this time, tanners also began to replace pyrogallol tannins with catechols because of their swift action and lower cost. Unfortunately, catechols have no non-tan buffers to resist these acids (Waterer 13). One of the reasons that goatskin was considered to be the highest quality of bookbinding leather is that the original method of processing with Sumac tannins created a leather which was not subject to “red rot” (Waterer 20).

In response to this problem, several research programs began to examine the various methods of tanning leather. The PIRA (Printing Industry Research Association) test was created by R. Faraday Innes of the British Leather Manufacturers’ Research Association to test for leather deterioration in the presence of sulfur dioxide. It is a form of an accelerated aging test and is best used to pre-test leather before it is incorporated into a binding. Because the test is destructive, it is not very useful for testing valuable records material (Waterer Appendix II). In 1935 a natural aging experiment was set up to test the predictions that the PIRA test made about the permanence of various types and tannages of leather. After several decades, the results were somewhat problematic. While the test was able to predict permanence to a certain degree, it had a failure rate of about one third – unacceptably imprecise for conservators and those interested in the long term survival of leather artifacts (Haines 76).

**Recent Developments**

In her discussion of a 1997 conference held at the University of Texas at Austin, Maria Fredericks identifies five factors responsible for most leather deterioration over time: relative humidity and temperature and their effects on the moisture content of skins, chemical deterioration, biological attack, mechanical damage from improper handling, and inappropriate conservation treatment. This list can be useful in understanding the various methods of
degradation to which leather is subject. Relative humidity (RH) readings above 75% can lead to hydrolysis and mold development, and readings below 25% can desiccate the skins, causing shrinkage and embrittlement. High temperatures contribute to the drying of skins and can turn skin oils rancid, and low temperatures can solidify those same oils. Wide variations in the ambient temperature and RH can cause deformation of the material through repeated swelling and shrinkage and can cause the tannins to migrate to the surface of the leather. Chemical deterioration, either through oxidation or acid hydrolysis, weakens leather by breaking down the collagen fibers. Biological deterioration is caused by insects and by mold, and mechanical damage arises from the structure of the leather object and how it is used (Fredericks 30 and CCI 1). The last factor Fredericks lists, inappropriate conservation treatment, can lead to any of the first four deterioration factors.

In an attempt to more systematically study the deterioration of leather, the European Economic Commission funded the Science and Technology for Environmental Protection (STEP) Leather Project in 1991. The STEP Leather Project was a three-year research program designed to investigate the effects of environmental factors, particularly atmospheric pollutants, on vegetable tanned leathers, to establish standards for artificial aging of leather samples, and to develop tests for evaluating the stability of new leathers (Fredericks 31).

The examination of environmental effects indicated that the deterioration of leather fibers is due to two processes, oxidization of the collagen and tannin structures and hydrolysis of the peptide bonds within the collagen. Oxidation occurs because of oxidative pollutants and light and heat exposure. It can occur within the polypeptide chains, between the three chains in the helix, or between the helices in the fibers. The hydrolysis reaction is catalyzed by acidic pollution. Both reactions are accelerated by tannins, with catechol tannins being of significantly worse effect. The STEP project researchers observed that in polluted environments, hydrolysis was the dominant reaction because many of the pollutants suppress oxidative reactions. In relatively clean environments, oxidation can become the dominant reaction. Both of these reactions cause irreversible deterioration in the leather fiber network, and as the reactions proceed, conservation treatment becomes less effective (Larsen 1994 11, 77, 82).

One of the most important goals of the STEP Leather Project was to avoid the mistakes of the 19th and 20th centuries and to ensure that the leather we make today will not deteriorate with such speed. Rather than await the verdict of time, it was important to find accurate
predictors of permanence. Many factors were investigated, including presence of sulfates, presence of alkaline and acidic amino acids, physical condition of the leather fibers, initial pH, and shrinkage temperature of the leather. The last two proved to be the best predictors of stability over time and of current fiber durability. The shrinkage temperature (T) of a leather sample can be determined by gradually raising the temperature of the sample and observing when the fibers contract (Fredericks 31). In untreated skin, the chemical bonds between the collagen molecules are stable at temperatures below about 65° C (149° F). Above that temperature, the bonds are destabilized and the skin can shrink. Tanning the skin increases that shrinkage temperature, allowing the skin to retain its shape at higher temperatures (Haines 71). Fredericks notes that a “good-quality new vegetable-tanned leather will shrink at 75°-85° C [167°-185° F], and show a pH of 3.5-4.5” (31). As the leather deteriorates, this T value will decrease, and poorly tanned skins tend to have lower initial T values. One of the main recommendations of the STEP Leather Project was that this test be implemented both to predict the stability of new leather and to gauge the current level of degradation of artifacts (Larsen 1995 151-159).

One of the more recent developments in leather conservation is the move away from trying to aggressively combat the inherent acidity of leather. Instead of attempting to buffer or reduce the acid already present in the material with potassium lactate or other chemical interventions, the tendency of late has been to address the environmental factors which lead to additional, excess acidity and degradation and to ensure that the leather we produce and use today is stable in the long term (Fredericks 32).
Works Cited


