Bookbinding and the Conservation of Books
A Dictionary of Descriptive Terminology

AP-42 Section 9.15
Reference 6
Report Sect.
Reference

leather

See illustration

The outer covering from an animal (usually a mammal) tanned, or otherwise dressed and prepared in such a manner as to render it usable and resistant to putrefaction, even when wet. Leather is a unique and flexible sheet material that is somewhat analogous to textiles, and may in fact be considered to be the first and only natural fabric.

The unique characteristics of leather are due largely to its structure, which is an interwoven, three-dimensional network of fibers inherent in the natural raw materials--hides and skins. This raw material is principally a fibrous protein called collagen and is composed of one continuous network of fibers.

In the raw skin, at least four distinct structures can be distinguished: 1) the thin outermost layer termed the EPIDERMIS ; 2) the grain layer or dermal surface; 3) the juncture between the grain layer and the dermis or corium; and 4) the major portion of the skin (the DERMIS or corium), which is the part converted into leather. In addition, there is the flesh layer, or hypodermis, which is the structure adjacent to the body tissues.

Before tannage, the approximate composition of a freshly flayed hide is:

Water	64 %
Protein	33 %
Fats	2 %
Mineral salts	0.5%
Other substances (pigments, etc.)	0.5%

The 33% which is protein consists of:

1) Structural proteins, or	
Elastin (yellow fiber woven in the collagen fiber)	0.3%
Collagen (which tans to give leather)	29 %
Keratin (protein of the hair and epidermis)	2 %
2) Non-structural proteins, or	
Albumens or globulins (soluble, non-fibrous proteins)	1 %
Mucins or mucoids (mucous materials associated with fibers)	.7%

While all mammalian skin is made up of these constituents, the figure for keratin will vary widely, depending on the amount of hair present; the figure for fat will also vary. The division between albumen and mucins is debatable.

Beginning with the outer surface of a skin, there are: 1) the hairs, embedded in the skin, each in a sheath of epidermis known as the hair follicle and each with a hair root at its end, fed by a tiny blood vessel. Chemically the hairs consist of the protein keratin, and penetrate deeply into the papillary layer of the dermis. See: HAIR .

Most animals have hair of two types, primary and secondary. The positions which these hairs occupy relative to each other as they enter the surface of the skin, together with their different thicknesses, determine the characteristic marking or grain of the dermal surface, i.e., the grain pattern of the leather, which is exposed upon removal of the hair and other epidermal structures; 2) the epidermis, which is a protective, hard-wearing layer of keratinous cells. Those on the outside are dead and, upon drying and shrinking, fall off the skin. On the underside, adjacent to the skin proper, they consist of soft, jellylike living cells, which have little resistance and are readily attacked and degraded by bacterial action or enzymes, as occurs with stale skins or in enzyme unhairing. They are usually disintegrated by alkalis, especially sodium sulfide or hydrosulfide. See: LIMING ;UNHAIRING ; 3) the sudoriferous (sweat) glands, which are also lined with epidermal tissue and discharge sweat from the skin through the pores in the grain surface. and the sebaceous glands, which are located at the side of the hair follicles and discharge into them an oily, waxy substance, which protects the hair. (The gland is operated by a muscle, called the erector pili, which also causes the hair to stand upright); 4) the skin proper or dermis (corium), consisting of a network of collagen fibers, very intimately woven and joined together. In the grain layer these fibers become thin and tightly woven and are so interlaced that there are no loose ends on the surface beneath the epidermis. Thus, when the epidermis is removed, a smooth layer is revealed (sometimes known as theHYALINE LAYER), which gives the characteristic grain surface of the leather. Toward the center of the dermis the fibers are coarser and stronger, and the predominant angle at which they are woven indicates the properties of the resultant leather. If the fibers are more upright and tightly woven, the leather will be firm and hard, with little stretch, while if they are more horizontal and loosely woven, the leather will be softer and stretchier. The dermis is also the strongest part of the skin; and 5) the flesh of the dermis, i.e., that layer next to the body wall of the animal, where the fibers have a more horizontal angle of weave, and fatty (adipose) tissue may also be present.

In the living skin, the collagen fibers and cells are embedded in a watery jelly of proteinlike substance, called the GROUND SUBSTANCE .

The living collagen fibers are formed from this substance, which ranges in constitution from the blood sugars to substances which are almost collagen. The latter fibers have been called "interfibrillary" proteins, also known as nonstructural proteins, or pro-collagens. These are essential for the growth of the skin and also render the fiber structure nonporous. When the skin is dried (as in some forms of curing), they dry to a hard, gluelike substance, which cements all of the corium fibers together and makes the skin hard and horny. In producing a leather which is to be soft or supple, it is essential that these inter-fibrillary proteins te removed.

The corium fibers are composed of ropelike bundles of smaller fibrils, which in turn consist of bundles of sub-microscopic micelles. These in turn are made up of very long, threadlike molecules of collagen twisted together. All together, this gives a very tough, strong, flexible, three-dimensional structure, forming a network on which many of the qualities of leather depend. It is this structure which makes leather unique for, as of today, it has not been possible to produce it artificially. It is also unquestionably the basis for the remarkably high tensile strength of leather.

The skin also contains small arteries and veins which convey blood to the living tissues, as well as the nerve structures necessary for the sense of touch.

While all mammalian skins are structured along this basic pattern, they vary tremendously in size, e.g., from the hide of an elephant or ox to the skin of a rabbit or mouse, and they also vary considerably in shape and thickness. In addition, some animals have but little hair or wool and a thick epidermal layer--e.g., the pig--while others, such as the sheep, have a heavy fleece with curly wool and curly hair follicles but a relatively thin epidermis. The state of development of the animal is also important. A calf, for example, has finer structured hair than a full grown cow, consequently, leather made from the skin of a calf is relatively smooth and very fine-grained, while that of a cow is rougher and has a very pronounced grain pattern.

The skins of certain animals (at certain times of their lives) also contain considerable quantities of fat in globular cells, which lie approximately in the center of the dermis. Notable examples are the pig and sheep. Sheepskin may actually contain fat of this type, that is, in the interior of the skin and not merely on the flesh layer, amounting to 25% of the weight of the skin. Such excessive growth of fat cells disrupts and weakens the dermal fiber structure to such an extent that some sheepskins can be split into two layers along the line where the fat is located.

In general, the younger the animal at time of slaughter the thinner and smaller the skin, the smoother and finer the grain structure, and the less likelihood of damage due to disease, scratches, insects, etc. See:LEATHER DEFECTS . The more natural the animal's feeding and living conditions, the better the quality of the resultant leather; overfeeding, for example, produces greasier, weaker skins, while starvation results in thin, weak, misshapen skins showing skeleton markings The skin of the female is usually finer grained than that of the male, and has a looser fiber structure, especially in the flanks, giving a somewhat softer, stretchier leather. The less hair or wool there is on the animal the tougher and stronger the resultant leather, especially in the grain layer. Heavily wooled Merino sheep, for example, are inferior in this respect to goats and pigs.

Leather occupies a unique position among the covering materials used by bookbinders. Its structure gives it a very desirable softness and strength, while its chemical nature gives it the property of adhering well to paper, hoard, linen, etc. Its outstanding characteristics include its durability (when properly prepared and cared for), suppleness, porosity, beauty, temper and feel, in addition to its strength and softness. In terms of permanence, when properly tanned, stored, and maintained (See: LEATHER DRESSINGS), it is probably the most permanent covering material known at this time.

The manufacture of leather predates recorded history. There is evidence that some leather samples found in Northern Germany may have been produced perhaps 12,000 years ago. Leather artifacts believed to date from the Neolithic and European Bronze Ages have been discovered, and it is an established fact that the Egyptians knew the art of vegetable tanning, as well as alum tawing, as long ago as 2000 B.C., and that tanning practices there were well established by 1600 B.C.

Leather has been used for covering books since at least as early as the 3rd century A.D. (See: COPTIC BINDINGS), and its use in craft bookbinding continues to this day. Although virtually every conceivable type of skin has been used, calf, deer, goat, pig, and sheepskin, as well as horsehide (RUSSIA LEATHER) have been used most often, at least in Europe and the United States. Pigskin, as well as goatskin and deerskin, were often alum-tawed; however, vegetable tannage was and is the predominant method of preparation. Goatskin has been used to cover books in Europe for more than a thousand years and has been used extensively in Europe since the 16th century. See: VEGETABLE TANNING ; VEGETABLE TANNINS . See also: ALLIGATOR LEATHER ;AMERICAN RUSSIA ; BABY CALF ; BUCKSKIN ; BUFFALO ; CABRETTA LEATHER ; CALFSKIN ; CHAMOIS ; CHEVRETTE ;

CHEVROTAIN ; CORDOBAN LEATHER : CORDOVAN LEATHER ; COWHIDE ; DEERSKIN ; DOESKIN ;GOATSKIN ; HAIR SHEEP ; HOGSKIN ; KANGAROO SKIN ; LAMBSKIN ; MOROCCO ;

PARCHMENT ; PIGSKIN ; SEALSKIN ; SHEEPSKIN : VELLUM ; WALRUS HIDE .

(26 , 83 , 207 , 236 , 248 , 282 , 291 , 29 , 306 , 343 , 351 , 352 , 353 , 362 , 363)

Matt T Roberts &
Don Etherington

liming

One of the beamhouse operations employed in leather manufacture. Its purpose is to degrade, and thereby loosen, the epidermal structure of hide or skin, including the hair, epidermis, sweat glands, etc., so that they may be removed. Methods of liming vary both in the chemicals used and in procedures. Unhairing and liming can be carried out simultaneously by immersing the skins in the lime and water mixture, often with the addition of other chemicals known as sharpeners, e.g., sodium sulfide.

Lime, which is calcium oxide (CaO), reacts violently with water to form hydrated lime (calcium hydroxide ($Ca(OH)2$)), which can be used with safety in liming and unhairing because it will not damage the collagen fibers of the skin, assuming it is properly used. This is because calcium hydroxide is not very soluble in water, and, in fact, a saturated lime solution contains only approximately 1/8 part lime per 100 parts water. Even this limited solubility, however, is sufficient to produce a solution with a pH in the range of 12.4 or 12.5, and, under such very alkaline conditions, some of the young keratin protein decomposes to produce sulfur compounds in the lime liquor. These compounds, in conjunction with the lime, accentuate the further breakdown of keratin. The lime therefore promotes unhairing, and the more keratin breakdown impurities it contains, the more rapidly it unhairs. Liming, however, must be carried out with extreme care, as the alkali also modifies and will eventually degradate the collagen fibers of the skin. Skins limed for an overly prolonged time produce thin, loose, and weak leather.

Liming also causes the hide or skin to swell. In order to promote gradual and uniform swelling, so as to avoid distortion or buckling of the stock, the skins are left in the lime solution for 1 to 2 days, following which a sharpener is usually added to promote the process. The addition of sodium hydrosulfide ($NaSH$), sodium cyanide ($NaCN$), sodium hydroxide ($NaOH$), sodium carbonate ($Na2(CO)3$), dimethylamines, etc., quickens the process in two ways: 1) by attacking the keratin, resulting in faster loosening of the hair; and 2) by increasing the alkalinity, and, therefore, the rate of swelling. If too much sharpener is added too quickly, however, rapid unhairing results, accompanied by excessive swelling of the surfaces of the skin, while the interior remains unswollen. This results in buckling, which makes subsequent unhairing, fleshing (if not done before liming), or splitting difficult. It may also result in permanent distortion and weakness of the grain, and, in addition, any naturally occurring wrinkles or "growth marks" may become accentuated. After liming, the skins are then ready forUNHAIRING . (248 , 298 , 363)

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chrome tanning

A method of tannage stemming back to the discovery, in 1858, that leather could be produced by treating skins with basic chromium sulfate (Cr(OH)SO4). The two basic methods employed today are the one bath and two bath methods, the former being most often used. The most widely used chemical in chrome tanning is sodium dichromate (sodium bichromate) (Na2Cr7O7.H2O), from which chromium sulfate is produced.

As in vegetable tanned leather, the degree of control exercised in the tanning process has great influence on the nature of the leather produced. If, for example, the final pH of a chrome-tanned leather is too low, the leather will be flat, hard, and wet, and may show grease spots on the surface; if it is too high, the leather will probably be plump, loose, dry, and may have a drawn grain or be too soft in the BLUE SORT . It is, therefore, imperative in chrome tanning to obtain the optimum pH, i.e., 3.4 to 3.5 in the one bath method, or 3.2 to 3.4 in the combination single and double bath method, and to maintain it.

The two bath method has almost been completely superseded by the one bath tannage, except in certain cases where the older two bath process is thought to give a particularly uniform tannage and a deposit of colloidal sulfur in the leather.

The major characteristics of chrome-tanned leather are its blue-green color and absence of filling power, i.e., an empty tannage. Chrome-tanned leather tends to be softer and stretchier than vegetable-tanned leather, and is very stable in water. Unlike vegetable-tanned or alum-tawed skins, chrome-tanned leather can withstand boiling water and has a shrinkage temperature higher at times than 100 deg. C.; however. it does not resist perspiration or organic acids well and is difficult to emboss. In addition, it does not take gold tooling well and is difficult to fabricate in such operations as turning-in, etc. It is, on the other hand, a very durable leather. (101 , 164 , 248 , 306 , 363)

This page last changed: May 15, 1996

soaking

1. The process of treating raw hides and skins with water. The restoration of moisture lost during curing and storage, as well as the removal of extraneous matter are of prime importance in converting raw stock into leather. The restoration of moisture is essential because: 1) the stock may otherwise be physically damaged by the action of washing under agitation, and flexing during green or lime fleshing; 2) sufficient moisture within the stock is necessary for solution and elimination of salts and globular proteins contained within the fibrous hide structure: and 3) the replenished water serves as a diluent as well as a vehicle for penetration into the fibrous structure of the astringent chemicals employed to effect hair loosening, plumping. and required alkaline action. Removal of extraneous organic and inorganic matter, except epidermis and flesh, by soak-washing is essential because: 1) solid matter in excessive amounts can result in both stock and machine damage during fleshing a nd unhairing; 2) manure and urine are ideal foods for bacterial growth during soaking. (Such matter, along with certain salts in the soaks, can result in discoloration and stains on the stock that cannot subsequently be removed): 3) the cementing effect of globular proteins upon dried tanned fibers reduces fiber mobility necessary for softness and good handle in the final leather; 4) curing salts transferred to the lime liquors affect the alkaline plumping action, reduce the rate of unhairing, and cause a contraction of the grain surface of the stock; and 5) the presence of extraneous matter presents a false and variable hide substance weight in determining the amounts of materials required for liming.

Because of many variable conditions. the time and temperature of soaking varies considerably according to the kind of stock being treated. Generally, few soaking aids are used in soaking cured and brined stock unless a considerable number of a given lot have been stored under exceptionally dry and warm conditions. In such cases. either sodium sulfide (63%) or sodium hydroxide may be used to the extent of 1.0 to 0.S pound respectively per 100 gallons of water. These chemicals are frequently employed in the soaking of dry stock. Excessive amounts will cause a high grain in the leather.

2. The process of wetting the grain side of a leather with water and the flesh side with paste to improve the pliability of the leather preparatory to covering. (161 , 248 , 291 , 298 , 306 , 363)

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unhairing

The beamhouse process in leather manufacture of removing the hair (or wool) and other epidermal structures from hides and skins, following liming (or any other preliminary unhairing process), but before tannage. Unhairing is generally considered to be the second of the three major beamhouse operations, the others being LIMING and BATING . The term "unhairing" is perhaps limiting in scope, because not only does the liming-unhairing process loosen the hair and other epidermal structures, it also cleans, loosens, and expands the dermal fiber network and alters the swelling characteristics of the skin.

Unhairing may be accomplished by: 1) treatment with lime (calcium hydroxide), caustic soda (sodium hydroxide), barium hydroxide, sodium carbonate, or ammonium hydroxide, etc.; 2) treatment with lime, as in treatment 1, sharpened by the addition of sodium sulfide, sodium bisulfide, antimony sulfides, or other appropriate chemicals; 3) treatment with lime, as in treatment 1, sharpened by the addition of amines, such as methylamine, or degradation products themselves from the skins being processed; 4) treatment with aqueous buffer systems containing inorganic salts, e.g., ammonium sulfate, sodium chloride plus enzymes with proteolytic and/or carbohydrase activity, usually derived from molds, bacteria, fermenting plant materials or animal tissues; 5) treatment with aqueous solutions of inorganic salts, such as potassium perchlorate, potassium thiocyanate, sodium chloride or sodium silicofluoride; 6) treatment with hot water, i.e., scalding; 7) treatment with strong aqueous solutions of sodium hydr oxide, sodium sulfide, etc., i.e., pulping; 8) action of bacteria, or SWEATING (1) ; 9) treatment with ammonia; and 10) alternating cycles of freezing and thawing in water. The last two methods are not in commercial use; scalding is used only for certain skins, such as peccary and pigskin; and treatment with strong aqueous solutions of strong alkalis, e.g., sodium hydroxide, is useful only when the tanner has no market for the hair. Treatment by sweating is virtually obsolete.

Conventional unhairing involves loosening the hair by means of one of the lime solutions given above, followed by mechanical unhairing by machine. The unhairing machine is similar to the fleshing machine, except that the blades of the cylinder are smooth instead of sharpened, and the machine runs at a slower speed so that the spiral blades scrape or rub the hair off without damage to the grain surface of the hide or skin. The hair is generally gathered, washed, dried, baled, and weighed for shipment. (248 , 291 , 306 , 363)

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deliming

The process of neutralizing the alkali, e.g., calcium hydroxide, used in liming and unhairing hides and skins. Deliming, which usually takes place in conjunction with BATING , is accomplished by running the hides or skins in a drum or paddle to which has been added water and a proprietary compound consisting of a mixture of an ammonium salt (preferably ammonium sulfate) and proteolytic enzymes at a water temperature of 80 to 90 deg. F. For more efficient control, and to produce a particularly fine grain in the leather, the ammonium sulfate (or boric acid), in the amount necessary to neutralize the lime, is added before the addition of the bating enzymes. (291 , 363)

This page last changed: May 15, 1996

bating

A process which is usually defined as "reducing" or "removing." The basic purposes of DELIMING and bating are to remove calcium hydroxide (or other alkali) from the skin, to lower pH, and, of great importance, to treat the skin substance with proteolytic enzymes so as to obtain desired grain appearance in the finished leather. Bating also serves to impart softness, stretch, and flexibility to the leather, while at the same time providing the basis for a clean, smooth grain by loosening scud consisting of hair roots, pigment materials and grease. It also eliminates all traces of the firm, plumped, and swollen state of the skin induced by the alkaline unhairing liquors by bringing the skin into a soft, fallen condition. Today bating is employed mainly in tanning light leathers, such as those used in bookbinding, where drape, flexibility, and softness of handle are of primary importance.

The origin of bating is somewhat obscure but probably dates back to the time when LIMING was not a common practice. It may have been originated by a tanner who noticed that skins badly soiled with dung often produced a softer, stretchier, silkier leather.

As recently as the early years of the present century, the process of bating consisted of immersing the delimed skins in water at a temperature of 35-40 deg. C., and then adding a liquid paste of pigeon or hen dung. The skins were run in this liquor until they acquired a particularly soft, flaccid and silky handle. The finished leather was found to have a very smooth, clean flat, flexible grain and was very soft and stretchy. Considerable variations in time, temperature and quantities were used for various types of leather. The effect of bating was produced by enzymes, which, under appropriate conditions of temperature and pH, are capable of dissolving and digesting some of the protein constituents of the skin. In a properly controlled process they are given only sufficient time for further removal of undesirable interfibrillary proteins, or to modify or weaken those fiber structures which, by binding the collagen fibers tightly together, would cause the grain to be wrinkled and the resultant leather to have no stretch.

Today bating is accomplished by the the use of enzymes extracted from animal tissue, e.g., the pancreas of swine or sheep, or from microorganisms such as molds and bacteria, called respectively pancreatic and bacterial bates. (248 , 275 , 291 , 306 , 363)

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fatliquoring

The process of introducing oil into a skin following tannage but before the leather is dried. In fatliquoring, which is usually applied to light leathers, the oil is introduced into the leather in such a manner that the individual fibers of the skin are uniformly coated. The actual percentage of oil on the weight of the leather is relatively small, being about 3 to 10%.

The principal function of fatliquoring is to influence the degree of fiber cohesion which takes place before drying. If there were no cohesion whatsoever, the skin would separate into its constituent fibrils, leaving no leather structure. On the other hand, if all the fibrils and fibers cohered, the skin would then take the form of a hard and horny material having no value as leather. Somewhere between these two extremes there is an ideal degree of cohesion for any given purpose for which the leather is to be used.

The fatliquoring process probably acts to control the differential shrinkage of grain versus corium (dermis) of the leather during drying, thus playing an important role in controlling the degree of tightness ofBREAK of the leather. In addition, it also influences the handle, drape, flexibility, durability, stretch, and water resistance of leather, and also adds greatly to its strength. These are factors of primary importance in leather used for covering books.

Fatliquoring is usually carried out in a drum at the highest temperature practical for the type of leather, or about 45 deg. C. for vegetable tanned leather and 60 to 65 deg. C. for full chrome tanned leather. The skins are run in a drum for 30 to 40 minutes. After drumming, the leathers are usually struck out on the flesh side, carefully set out to smooth the grain, nailed or toggled out flat to dry, or paste dried.

To allow a small amount of oil to be spread uniformly over the very large surface area of the leather fibers, it is necessary first to dilute the oil. Although this could be done by means of a solvent, e.g., benzine, it is more economical, safer, and more convenient to emulsify the oil. In an EMULSION with water, the oil is dispersed in microscopically small droplets. It is important that the drops of oil in the water remain as an emulsion until they penetrate the leather, and not separate out as large drops or as a layer of oil, which could not penetrate the leather fiber and result in merely a greasy surface layer.

The properties of the finished leather can be varied by controlling the degree to which the emulsion penetrates before it "breaks," depositing the oil on the fibers. Relatively shallow penetration, which leaves the inner layers of the leather with comparatively little oil, gives a leather that has a tight break and is soft and resilient. On the other hand, if the oil is allowed to penetrate uniformly through the leather, the result will be a leather that is soft and stretchy, with any natural grain looseness accentuated.

The liquors incorporated into the leather are called fatliquors, of which there are several types. One of the earliest was the soap fatliquor, consisting of neatsfoot oil and common soap. When a vegetable-tanned leather is drummed in such a fatliquor, the slight acidity of the tannage neutralized the soap, causing fine drops of oil to be deposited on the fibers. The greater the acidity of the leather, the more rapidly this occurs, so that the oil may be deposited before it has penetrated sufficiently. Consequently, soap fatliquors are described as having poor emulsion stability, and are generally used where a fairly heavy surface fatliquoring is required. It is possible, however, to modify many types of oils chemically so that they become miscible with water without the use of emulsifying agents.

Sulfated oils are used frequently because they give good, fine-oil dispersions and are less sensitive to acid than soap fatliquors. This results in deeper penetration of the oils into the leather before they are deposited. Sulfated oils are prepared by treating fish, animal, or vegetable oils with sulfuric acid at a temperature of 10 to 20 deg. C. The resultant product is washed with a strong brine solution to remove excess acid. The salt is necessary to prevent the sulfated oil from emulsifying with the water. Soda ash is then added to form the sodium salt of the sulfated oil and to neutralize the last traces of the acid. The more the oil is sulfated, which is to say, the more sulfuric acid that has been fixed, the greater will be its stability to acid and the more thorough its penetration into the leather. Conversely, the more acid the leather, the less the penetration. However, increasing the amount of sulfation or water miscibility, decreases the "oiliness" of the oil and therefore its lubricating powers.

Sulfonated oils are prepared by a similar process, usually at a higher temperature; the fatliquor contains the sulfonic group which gives greater stability and emulsions which penetrate deeper into the leather under acid conditions.

Still another method of obtaining emulsifying properties is to sulfite the oil. In this process, the oil is mixed well with a strong solution of sodium bisulfite ($NaHSO_3$), while the mixture is thoroughly aerated by means of compressed air. Sulfited oils behave in a manner similar to sulfated oils, but are usually said to be more acid stable and to afford deeper lubrication.

In addition to the emulsifying element of the fatliquor, a raw oil, such as mineral, castor, neatsfoot, cod or coconut oil is frequently included in the formulation. See also: CURRYING ; STUFFING (2) . (248 , 275 , 291 , 306 , 361 , 363)

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This page last changed: May 15, 1996

Sulfated oils are used frequently because they give good, fine-oil dispersions and are less sensitive to acid than soap

vegetable tanning

The process of converting the protein (collagen and its related proteins) of a raw hide or skin into LEATHER by means of vegetable materials. Vegetable tanning produces a relatively dense leather, one that is firm and solid and yields a high weight of leather per unit of raw stock. It also produces a leather that is pale brown in color, and which tends to darken upon exposure to natural light. Depending upon the finishing treatment employed, the tanning material washes out of the leather very slowly.

Vegetable tannages are used to produce bookbinding leather not only because of tradition, but because they produce leathers having a soft drape and handle (in addition to their firmness), which retain applied grain patterns particularly well. Unless specifically treated, however, vegetable tanned leathers have but little water resistance.

The classical method of vegetable tanning, especially where flatness of the leather (and particularly of the grain surface) is of great importance, as with bookbinding leather, is pit tannage-usually accomplished by means of suspension in a rocker vat. Traditionally the skins are limed and unhaired, and delimed to a pH of 4.0 to 5.0, bated (and sometimes drenched with bran or acetic acid). The stock is then suspended as smoothly and flatly as possible in rocker vats containing used or new tanning liquor of a relatively low BARKOMETER reading. The strength of the tan liquor is gradually increased (the stock being transferred into pits containing progressively stronger liquor) until the tanning has just penetrated through the entire thickness of the skin, i.e., it has struck through. Splitting, if required and if not done previously, finishing, etc., are then carried out after drying.

The traditional method of vegetable tanning was slow and expensive and, furthermore, did not always give the characteristics desired in the leather. Not only was there sometimes too much firmness to the leather, but frequently the color of the leather was not as pale or as uniform as it can be made by the use of more modern methods of tanning.

The use of stronger liquors, mechanical action, pH control, and control of the contents of acids and salts have enabled the tanner to produce satisfactory leather in a much shorter time, and efforts are constantly being made to reduce the time of tannage even further. Increased mechanical action, such as drumming, accelerates the speed of tannin penetration but also results in pebbling of the grain, unless some form of pre-tannage is employed. Some tanners in both Europe and the United States employ such systems, in which a comparatively short rocker pit tannage is used to assure sufficient tannage to protect at least the outer quarter or third of the stock, with the stock then being drummed with strong liquors so as to rapidly tan the interior of the corium. There are many variations of this method, ranging from stock struck through in the rocker pits, and then being tumbled in liquors of 100 deg. Bk. or more for as long as 48 hours, to stock only partially penetrated and then being hung on sticks in slowly rotating rotors, being drawn through a comparatively small volume of tanning liquor of gradually increasing strength.

Leather to be used for bookbinding should be tanned to give a pale, uniform, biscuit shade-one which can be readily dyed and finished in a variety of colors. The tannins in the leather should be well fixed and not easily removed by wetting the leather, otherwise they may cause stains when the leather is paste-washed or otherwise moistened.

Light leathers, e.g., goatskins, calfskins, etc., in the finished state, are usually sold on the basis of area (price per square foot); therefore, there is not the temptation to fix an unduly high proportion of tan on the fibers, as is sometimes done in the case of leathers sold by weight. Overly prolonged vegetable tannage is to be avoided as it may cause difficulties in dyeing and finishing. See also: BATING ; DRENCHING ; FATLIQUORING ;LIMING ; SOAKING (1) ; SPLITTING (1) ; UNHAIRING . Cf: CHROME TANNING .

(248 , 291 , 306 , 351 , 363)

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This page last changed: May 15, 1996

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vegetable tannins

A group of complex hydrocarbon substances common throughout most of the vegetable kingdom, and having the capability, to a greater or lesser degree. of converting hide and skin, i.e., protein, into leather. Tannins are complex organic materials, and frequently have very large molecules and high molecular weights, on the order of 2,000 or greater, although it is still not certain whether they might better be considered macro-molecular substances. i.e., those with very large molecules and high molecular weights which break down into smaller fragments. Tannins were at one time classed with the glucosides because of the sugar groups that most of them contain but they are now more often regarded as constituting a class by themselves, as some, e.g., the hemlock tannins, do not have the sugar group in the molecule. In addition to carbon. hydrogen, and oxygen, some nitrogen, phosphorus, as well as traces of inorganic ions, may be present.

Vegetable tannins for the most part are uncrystallizable colloidal substances with pronounced astringent properties. They have the ability to precipitate gelatin from solution and to form insoluble compounds with gelatin-yielding tissues. which is the property which enables them to convert raw hide and skin into leather, consolidating the dermal network of the hide into firmer and drier structures of improved thermal stability, durability, and water resistance.

Because they are extremely complex substances, vegetable tannins are difficult to classify; however, they are usually considered to consist of polyphenolic systems of two types: the hydrolized tannins (the pyrogallol class), the main constituents of which are esters of glucose with acids such as chebulic, ellagic. gallic and m-digallic; and the condensed (catechol) tannins. which are based on leuco-anthocyanidins and like substances joined together in a manner not clearly understood. The pyrogallol tannins may be hydrolyzed by acids or enzymes and include the gallotannins (from plant galls) and the ellagitannins. which produceBLOOM (1) on leather, and which are characteristic of divi divi, myrabolans, sumac, tara, valonea, and other well-known tannins. The condensed tannins are not hydrolyzable and are characteristic of hemlock, mangrove, quebracho, wattle, and the like. The condensed tannins are more astringent, i.e., they tan more rapidly, than the pyrogallols have larger molecules and are less well buffered. They yield less sediment. or lose less upon standing, but the leather they produce often tends to turn a reddish color upon exposure to natural light. They also yield phlobaphenes or REDS .

The terms "condensed" and "pyrogallol," as such do not mean that the tannins contain these substances but simply indicate that dihydric and trihydric phenols are produced respectively when the materials are heated (dry distillation). Quite often the "tannin" derived from a plant material. e.g., oak bark. has characteristics of both groups and consequently is generally considered to be a mixture or compound of the two principal types.

The two classes of tannin also display different reactions towards acqueous solution of iron salts. The condensed tannins produce green-black colors while the pyrogallol class gives blue-blacks (a reaction important in the manufacture of some inks). Furthermore, they differ in their tanning properties. Pyrogallol tannins, for example, being less astringent than the condensed class, tan more slowly and produce leather of less solidity. In addition, when extracted from the plant they generally contain smaller molecules of tannin. and, being better buffered. i.e., containing weak organic acids and their salts, they resist changes in pH value when acid or alkali is added.

For a complete and even reaction with the skin or hide to take place during tannage, it is necessary to use the tanning material in the form of a liquor, i.e., an aqueous infusion of the plant material. Modern tanneries use extracts that are concentrates of acqueous liquors. the latter usually being concentrated under reduced pressure to provide highly viscous or even solid products. Other materials extracted are known as non-tannins (abbreviated non-tans) and may include: hydrolysis products of the tannins, starches, gums, hemicelluloses, poly-saccharides, hexoses, pentoses, uronic acid. organic acids (lactic and acetic), together with their salts, inorganic salts, proteins and zymoproteins (enzymes), if the temperature is not too high, as well as coloring matters such as brasilin, fisetin, and quercetin.

Vegetable tanning liquors are extremely complicated in their chemical composition, and the tannin/ non-tannin ratio, the color, and the particular substances involved have a considerable (and far from completely understood) bearing on their tanning properties and, therefore, on the quality of the leather produced.

Although tannins occur throughout the greater part of the vegetable kingdom, they are more prevalent among the Angiosperms, or higher plants, especially in certain Dicotyledon families, than they are among the lower types, such as fungi, algae, etc. The Gymnosperms also have classes in which tanning is well developed, e.g., the pines, spruces and hemlocks.

The Dicotyledons include many families in which tannin occurs quite freely, among which the most noteworthy are the Leguminosae, e.g., the black wattle; the Anacardiaceae, e.g., quebracho and sumac; the Combretaceae, e.g., myrabolans; Rhisophoraceae, e.g., mangroves; Myrtaceae, e.g., eucalyptus; and Polygonaceae, e.g., canaigre.

Tannin may occur in almost any part of a plant, including roots, stems or trunk, hark, leaves, fruit, and even hairs. It may occur either in isolated individual cells, in groups or chains of cells (the more common occurrence), or in special cavities or sacs. It may also be present in latex vessels and lactiferous tissue accompanied by other substances.

In the living plant, tannin is present chiefly in solution in the vacuoles. As the cell ages and loses its protoplasmic contents, the tannin usually becomes absorbed in the cell wall; in dead plant tissue tannin often accumulates in considerable quantities. Tannins often occur in green or immature fruits, the quantity decreasing as the fruit ripens. and they may also occur in seeds. often becoming more abundant following germination. Tannin is also quite prevalent in tissues as a result of pathological conditions, such as plant galls. Certain of these galls constitute the richest sources of tannin in plants, e.g., Chinese galls, which have a tannin content ranging from 50 to 80%.

The use of vegetable tannins in the manufacture of leather probably predates recorded history, and there is creditable evidence that they were in use in Egypt as far back as 5000 B.C.

The ancient Greeks and Romans were well versed in the art of vegetable tanning and evidence indicates that vegetable tannins were used in China many thousands of years ago. (175 , 248 , 291 , 306 , 363)
