Kirk-Othmer Encyclopedia of Chemical Technology.

LEATHER

Tanning and leather working are ancient skills dating from the earliest hunter/gatherer societies when the practical value of animal skins were adapted to human usage for clothing and foot protection allowing an existence outside of tropical climates. Because preservation of a hide is not practical during a hunt, it can be assumed that animals were either taken back to the camp without skinning or the skins were removed, then brought to the camp.

The temporary preservation of leather is an important practical problem. When an animal is killed and skinned, bacterial degradation starts immediately, but temporary preservation by drying or salting does not result in a usable leather. Treatment to prevent decay is not the same as tanning, which is a slow process and in modern leather production involves a series of chemically interdependent steps. Tanning not only preserves the hide or skin, but also makes the leather resistant to cracking from flexing. The desired properties of leather depend on use. From the same hide, leathers may be obtained for garments, shoes, or mechanical applications. There are, however, limitations to the possible use of a particular hide or skin. For example, sheep skin, and most other fur skins, has very little value for shoes. The heavy skin of alligator would not be satisfactory for gloves.

Tanning of hides by any of the primitive methods was a dirty job with little assurance of success. The tanner was a specialist generating little respect in the community. In some parts of the world, this ancient prejudice against tanners exists even as of this writing (ca 1994). The tanner in primitive societies was limited to making leather using the hides or skins available locally. Tanning materials were also limited to those in local supply. Techniques were dependent on the climate as well as availability of materials. The leather made was for local needs.

The Eskimos of Alaska have access to animals such as the seal or the polar bear. Seal skins make good furs that are essential for survival in the far northern climate. Because originally there were no tanning materials available, Eskimo tannage was done by scraping the skin to a minimum thickness and then exposing the skin to smoke. The smoke aids in the oxidation of some of the fats of the skin to aldehydes (qv) that help to preserve the skin. This system, which is satisfactory for tanning in frigid climates, would be of limited value in a tropical one.

In desert or tropical climates skin dries into a hard mass that does not soften even when soaked in water. By shaping a skin to a desired form and then drying, however, useful articles such as drum heads and shields can be made. Tanning for useful leather is not a simple skill.

In temperate climates extracts from some plants were found to be excellent preservatives for hides and skins. The hides, with or without hair, were placed in pits in the ground, then covered with alternating layers of bark or leaves and skins. Water was added and later, ie, days or months depending on the thickness of the hide, the hides could be removed, washed, and oiled. The resulting leather is flexible and lasts essentially forever. This procedure was used well into the seventeenth century as the most common method of tanning. In some isolated primitive societies, the method is used in the 1990s.

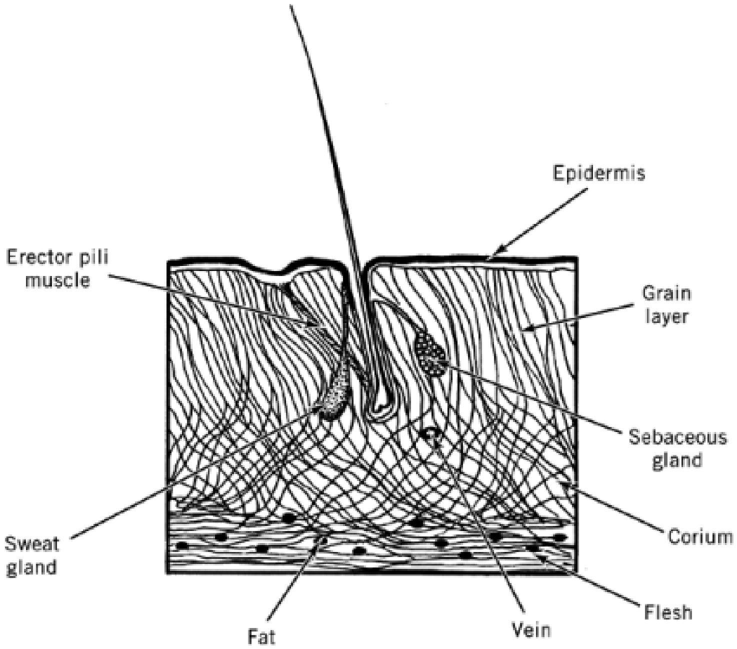


Fig. 1. Schematic of the cross section of a mammal's skin. The relative size and function of the parts depend on the species and breed of the animal. For goats, where the wool or hair is sparse because it is not needed for warmth, the skin is dense to provide protection; for sheep protected primarily by heavy wool, the skin contains more oil (sebaceous) glands to lubricate the wool; for cattle, both the hair and the heavy hide structure protect the animal (3).(Courtesy of Krieger Publishing Co.)

1. Hides and Skins

1.1. Structure

The structures of hides and skins are dependent on the needs of the animal and its environment. The functions of an animal's skin include protection from predators and infection, and maintenance of body temperature. The relative importance of these functions depends on the animal. Methods by which the skin accomplishes these functions is the same for most mammals.

Leather technologists have adopted the same histological techniques for the study of hide and skin structure as that used by the medical profession for the study of the structure and functions of human skin (1, 2).

In Figure 1, the lower edge of the drawing is the flesh side of the hide. The hide, as it is removed from an animal, has body fat and a thin membrane separating the hide from the fat and flesh of the body of the animal. The area near the inside of the hide is made up of the heaviest fibers of the hide. These fibers, intertwined in directions somewhat parallel to the surface of the skin, vary in size and shape and may be ~ 0.01 mm in diameter. The length of these fibers vary but may be several centimeters long. The fibers are the ultimate in nonwoven structure that give leather its remarkable strength and flexibility.

Above the heavy fibers there are glands and hair follicles. Mammals are warm blooded and the temperature of the body must be maintained within a very narrow range. The function of the sweat glands is to release moisture to the surface of the skin to cool the body by evaporative cooling. The sebaceous glands are oil glands that have two functions, ie, to slow the evaporative cooling for temperature control, and to lubricate the hair of the animal. The hair grows from the hair follicle as soft, low molecular weight proteins and changes into hard inert hair protein.

The fiber structure is very fine near the surface of the skin and this fine structure imparts a silky feel to the leather. The smaller the animal of a given species the finer the surface fibers. The value of the skin or hide is then dependent in part on this smoothness (2). Calfskin leathers are smoother and have a silkier feel than cattle hide leathers. Calfskin leather is used in the shoe uppers of high quality, expensive men's and women's shoes, and specialty items.

Sheep and fur animals are protected primarily by their wool or hair. The fiber structure of the skin is very fine and has less strength than calfskin or other nonfur mammals. The sheepskin has a high concentration of hair follicles and sebaceous glands. When tanned the fur skin has an open structure, is soft, and lacks strength relative to many other leathers.

Goats, the animal of choice in areas of harsh climates and limited food supply, are particularly suited to warm and sometimes arid climates. Although goats differ greatly through breeding and environmental adaptation, they have some common characteristics. The skin of the goat is thin and made of tight strong fibers. The hair is coarse and functions more for protection from predators than for warmth. The structure of the skin determines the suitability of the leather for a given purpose. Tanning methods to accentuate the desirable characteristics of each of the leathers is required.

1.2. Chemical Composition

From the point of view of leathermaking, hides consist of four broad classes of proteins: collagen, elastin, albumen, and keratin (3). The fats are triglycerides and mixed esters. The hides as received in a tannery contain water and a curing agent. Salt-cured cattle hides contain 40–50% water and 10–20% ordinary salt, NaCl. Surface dirt is usually about 2–5 wt %. Cattle hides have 5–15% fats depending on the breed and source. The balance of the hide is protein (1).

Leathermaking occurs in three broad steps: (*1*) removal of all materials that are not a part of the final product, (*2*) rendering the remaining hide substance biorefractive, ie, tanning, and (*3*) treating the stabilized tanned material to impart the characteristics desired in the final product. In all steps the solubility and reactivity of the components form the basis of the treatments employed.

The hide proteins differ in amino acid composition and physical structure. The principal amino acids (qv) of the hide proteins are listed in Table 1. Of particular importance is the difference in the water solubility of the proteins. All of the proteins are soluble in water when heated, and upon the addition of either strong acids or bases. Proteins (qv) are amphoteric, possessing both acid and base binding capacity.

Proteins have reactive carboxyl groups and amino groups on the polypeptide chain (4, 5). The more acid groups the greater the base-binding capacity of the protein. Conversely, the more basic groups the greater the acid-binding capacity; ie, the solubility characteristics of proteins can often be predicted from the acid–base amino acid composition.

Albumen has the largest number of acid and basic groups. It is the most soluble of the proteins present in a hide. The albumen is not a fibrous material, however, and therefore has no value in the leather. Keratin is the protein of the hair and the outermost surface of the hide. Unless the hair is desired for the final product it is removed by chemical and/or physical means. The elastin has little acid- or base-binding capacity and is the least soluble of the proteins present. The lack of reactivity of the elastin is a detriment for most leather manufacture. The presence of elastin in the leather greatly limits the softness of the leather.

Collagen, the principal protein of the hide, is the material that is made into leather. The reactivity of the collagen toward tanning agents and the dyeability, as well as the strength, flexibility, and durability of the collagen when tanned, are all important to making leather a material of choice for utility and fashion.

Table 1. Amino Acid Content of Proteins, %[a]

Amino acid	Collagen	Elastin	Keratin	Albumin
		Nonpolar		
glycine	20	22	5	2
alanine	8	15	3	6
valine	3	12	5	6
leucine	5	10	7	12
other	4	15	7	9
Total	*40*	*74*	*27*	*35*
		Acid		
aspartic acid	6	0.5	7	11
glutamic acid	10	2.5	15	17
Total	*16*	*3*	*22*	*28*
		Basic		
arginine	8	1	10	6
lysine	4	0.5	3	13
other	2	0.5	1	4
Total	*14*	*2*	*14*	*23*
		Others		
serine	2	1	8	4
cystine			14	
proline–hydroxyproline	25	15	6	5
other	3	5	9	5
Total	*30*	*21*	*37*	*14*

[a] Ref. 3.

1.3. Treatment

In each of the steps of leathermaking the chemistry of the system is designed to selectively react with the various proteins, particularly collagen (6). In the first step, the collagen is separated from the components that are not a part of the final product so that there is as little collagen degradation as possible. In the second step, tanning, collagen reacts with tanning materials to stabilize the protein to resist chemical, thermal, and biological degradation. The third and last step is to impart the desired mechanical and aesthetic properties to the product.

2. Leather Manufacture

The manufacture of leather follows the same general steps for a great variety of leathers (Fig. 2). The largest category of hides tanned is cattle hides. Of the cattle hides chrome tanning of unhaired hides is by far the dominant system used throughout the world. The tanning of other types of hides and skins requires variations in the systems used for cattle hides (3).

2.1. Curing

The temporary preservation of hides or skins is known as curing. Curing is not tanning in that the hides or skins are not stabilized to a biorefractive state (2). Cured hides immediately begin to decay if there is a change in conditions that removes the curing agent or permits bacterial action. The curing of hides or skins must meet several requirements: (*1*) the curing system must preserve the skin under the anticipated conditions of storage and transportation; (*2*) the curing agent must not damage the valuable leathermaking material; (*3*) the curing

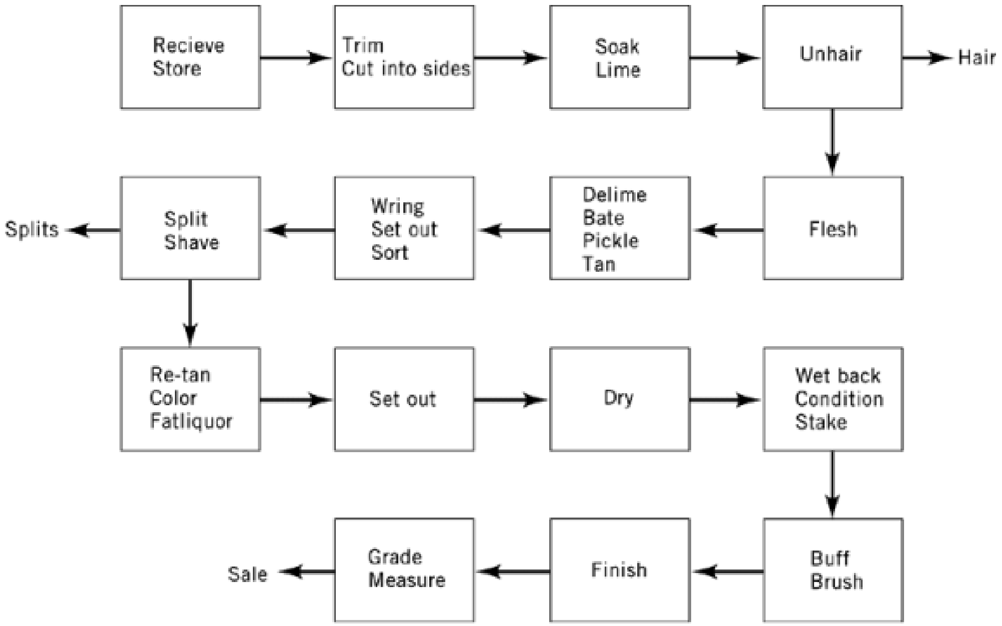


Fig. 2. Process flow diagram for the production of chrome-tanned cattle hide leather. Adapted from Ref. 3.

system must be reversible so that the hide or skin can be easily brought to a desired condition for tanning; (*4*) the curing system must be fast enough to be effective before the onset of biodegradation; and (*5*) the curing system must be economically practical.

2.1.1. Air Drying

Air drying, probably the oldest curing system, has the advantages of simplicity, speed, and low cost. The disadvantages are possible case hardening and excessive adhesion of the fibers. Drying (qv) involves the migration of water to the surface of the skin and subsequent evaporation. If the hide is thick and evaporation fast, a sealing of the surface of the hide may occur preventing continued migration of the water. As a result the water may be trapped in the hide and bacterial degradation can thus occur in the center of the hide.

When drying cattle hides in tropical arid climates, the hides are scraped clean of flesh, then stretched on racks, and dried slowly in the shade. An application of an insecticide may be used. This method is slow, labor intensive, and unreliable for heavy hides. The system is only used in rural tropical areas and is not applicable to modern commercial cattle hide production (3).

Drying has a place in modern technology primarily for the curing of furs and goatskins. Fur skins are thin and the fur side is protected by the thick mass of hair. The flesh side of the skin is scraped clean of adhering flesh and the skin is stretched on a form of flat board, flesh out. The skin is slowly dried with or without the addition of salt. The advantage of this system is quick curing with a minimum chance of bacterial damage. The fur skins are valuable and therefore the labor required is acceptable.

Drying methods vary according to the type and source of skins (1). The significant commercial sources of goatskins are in Africa, Asia, and South America. The methods of cure include air drying, salt drying, and salting depending on the local conditions.

2.1.2. Salt Curing

Salt curing is the generally accepted curing method for cattle and other large animal hides. Curing can be done using solid salt or brine. The solid salt method is the more general and is used worldwide.

In salt curing the hides are piled on a concrete floor and salt is applied to them. To effect the cure the salt must be in contact with both the flesh and hair side of the hide. Thus salt is spread between the hides, and the hides piled. The amount of salt needed is about 50–60% based on the weight of the hides, although this amount of salt may vary in specific cases. The hides remain in the curing pile for a minimum of about 20 days to effect the cure. At the end of the cure time the hides are removed, the excess salt brushed off, and the hides folded individually into bundles for shipping. If water and excessive heat is avoided, the hides are effectively preserved for commercial purposes, including international shipping.

In modern mechanized slaughter houses, particularly in North America, the commercial practice has shifted to brine curing. In conventional salt curing, the curing time of 20 or more days presents a problem of space as well as an investment in inventory. The modern practice is to chill the hides in cold water while washing off dirt and manure. The hides are trimmed to remove the parts such as ears and tails not suitable for leather, fleshed by machine, then placed in a saturated agitated brine bath. The brine cure takes from 24 to 48 hours depending on the type of hides and the equipment used. At the end of the cure time the hides are removed, wrung by machine, and bundled for shipping.

The sale of hides is on a weight basis. The value of a hide depends on the type of animal, the seasonal characteristics, the location of the slaughter, the type of cure, and the market conditions. Cost of the hides is about 50% of the sale price of the leather, so an accurate knowledge of the hides and the leathermaking potential of the hides is critical to commercial success. In the case of furs and exotic skin leather production, the value of the pelt is by far the most important factor (7).

2.1.3. Alternative Methods of Curing

The presence of salt in hides and skins has been a problem for tanners. Moreover, the quantity of salt, usually 10–20% by weight in cured hides, is an environmental problem. In the discharge of the water from the rewet and washing, the soluble solids are normally greater than $20,000$ mg/L. This amounted to $2000-4000$ mg/L in the combined waste stream of the tannery.

Several methods have received considerable research attention as alternatives to salt curing. These include use of sodium bisulfite as a disinfectant to allow preservation with or without decreased salt in a brine cure; use of disinfectants such as quatenary amines for temporary preservation in direct shipping to the tannery from the packing plant (see Disinfectants and antiseptics); preservation of hides by radiation sterilization (see Sterilization techniques); and substitution of materials such as potassium chloride for sodium chloride. These methods have found only limited commercial success.

2.2. Pre-Production Handling

Salt-cured cattle hides, when received at the tannery, are individually bundled to prevent excessive moisture loss. The bundles are tied with ropes that are later cut and removed; the hides may be sorted for different weight or quality classification at this point. It is best to have hides of similar size and thickness in a given production batch to assure an even reactivity of the processing chemicals and to avoid frequent adjustments in the machinery to compensate for size and thickness variations. In the modern large tannery, the size/quality classification is not necessary because the hides arrive in carload quantities under specifications as to size, type, and month of slaughter.

2.2.1. Soaking

The hides are weighed and counted into production batches. For pre-fleshed and trimmed cattle hides the batches are about 3–5 t when the processing is in drums. If the tannery has hide processors the batches may

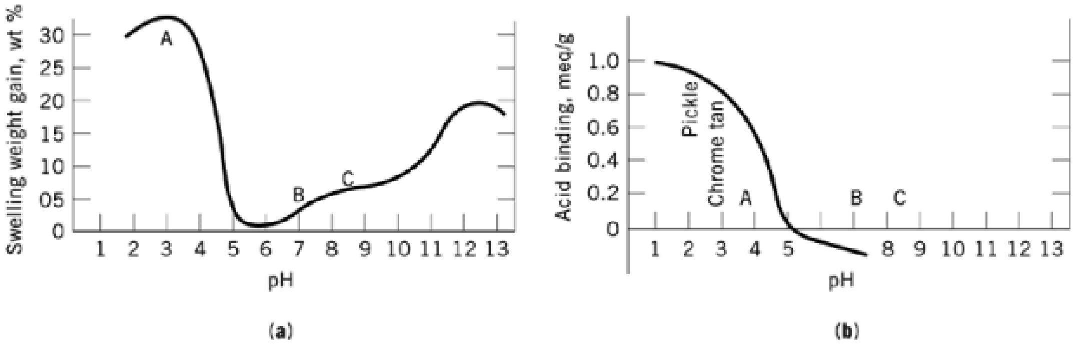


Fig. 3. The pH dependence, where A, B, and C represent regions corresponding to the pK_as of glutamic and aspartic acids, lysine, and argenine, respectively, of (**a**) protein swelling, and (**b**) protein acid-binding capacity. Adapted from Ref. 3.

be up to 10 t. Water is added to cover the hides and allow free movement of the load. The drum is turned intermittently during the normal 8 to 16-hour soaking period.

The quantity of water is two to three times the weight of the hides. The salt from the cure dissolves in the water and the reverse of the curing takes place. The water is drawn into the hides by osmotic forces. The concentration of the salt solution is about $3 - 5$ g/100 mL. At this concentration some of the soluble proteins disperse. The soak water removes the salt, some proteins, some loose fat, blood, dirt, and manure.

If the hides were not fleshed before curing, the soaked hides are usually fleshed and trimmed at this time. If the hides are not to be trimmed or fleshed, they are drained and washed to decrease the salt concentration, drained, and the drum refilled with cold water.

2.2.2. Unhairing

Unhairing can be done either by a hair save or a hair pulp system. The hair pulp system is preferred by most tanners for its speed and labor efficiency. In the hair pulp system the hides are treated with sodium sulfide (sulfhydrate) and lime (calcium hydroxide). The hair is quickly destroyed by the strong alkaline reducing conditions.

The differences in the amino acid chemistry of the hide collagen and the hair keratin are the basis of the lime–sulfide unhairing system. Hair contains the amino acid cystine. This sulfur-containing amino acid cross-links the polypeptide chains of mature hair proteins. In modern production of bovine leathers the quantity of sulfide, as Na_2S or NaSH, is normally 2–4% based on the weight of the hides. The lime is essentially an unlimited supply of alkali buffered to pH 12–12.5. The sulfide breaks the polypeptide S–S cross-links by reduction. Unhairing without sulfide may take several days or weeks. The keratin can be easily hydrolyzed once there is a breakdown in the hair fiber structure and the hair can be removed mechanically. The collagen hydrolysis is not affected by the presence of the sulfides (1–4, 7).

After about 4 to 12 hours the hides are drained, then floated with lime without additional sulfides. The drum or hide processor is run at slow speeds intermittently during the unhairing process. The continued action of the lime solution on the hides brings the pH to 12–13. At this pH the hides swell to about twice the original thickness. This swelling has a beneficial opening of the fibers to permit better tannage (Fig. 3**a**).

The mechanical and physical characteristics of the leather are also effected by the swelling (8). The charge on the protein is important for each step in leather production. When liming is completed, usually in about 12–20 hours, the hides are washed in running water. This washing removes the surface dirt, degraded hair lime, and sulfides. The unhairing and the wash water from the hair pulping system create the most serious environmental problems of the industry.

2.2.3. Trimming and Fleshing

The limed hides not fleshed before curing are usually trimmed and fleshed at this point in the production. The trimming is done by hand to remove any portions of the hide that could interfere with the subsequent machine processes, eg, the shanks, ears, and snout.

The fleshing is done on a multiroller machine that pulls the hide over a rotating blade, similar to a milling machine that cuts off the flesh from the inside of the hide. The machine includes a rubber roller that holds the hide near the rotating fleshing blades. Through the adjustment of the clearances or the thickness of the hides and the resilience of the rubber roller the flesh is effectively removed regardless of the differences in the thickness of the hide from back to belly and flanks.

The flesh and trimmings may be discarded as a waste in small tanneries. In the larger tanneries, the economies of size warrant the recovery of the fleshings for rendering or for glue or gelatin.

2.3. Splitting

In most modern large tanneries that make upholstery leather, and in some that make shoe uppers leather, the hides are split in the lime condition. In splitting the hides are cut to the desired thickness with a horizontal belt knife. The hides are fed into the machine grain up. The clearance between the grain and the blade is maintained by a series of narrow rollers supported by a rubber roller underneath the spacing rollers. The grain layer is then cut to the thickness desired to an accuracy of about 0.1 mm.

The grain layer is the most valuable part of the hide and serves as the outside of the shoe. Splitting allows the grain layer to spread to the maximum area yield and also allows an efficient use of the valuable tanning chemicals.

The split is of variable thickness, and some of the split is too thin for leather production. The thin parts are trimmed off and discarded for collagen recovery. The trimmed split is tanned separately.

2.4. Deliming and Bating

The limed hides have a pH around 12. Because chrome tanning is done at pH 2–4, the lime must be removed for pH adjustment. In addition, the undesirable materials in the hide, ie, both natural and the degradation products from the unhairing, must be removed (7, 9).

For deliming, ammonium salts and acids are used. The proportion of ammonium salts to acids and the type of acids employed is a matter of the tanner's choice. The acid neutralizes the lime, $Ca(OH)_2$, thereby adjusting the pH. The ammonium salts have two functions: to buffer the solution to a pH required for bating, and to form calcium ammonium complexes. The acidity and the complex formation solubilize the calcium and serve to bring the hide to the desired pH.

Bating is a part of the deliming step in cattle hide leather production. The hides contain some elastin proteins which are very inert to the action of acids and bases and react to tanning chemicals in a limited manner. If the elastin is not broken down sufficiently, the leather may be too firm and stiff for the desired use, and the grain may not be as smooth as desired. The bating materials are proteolytic enzymes having specific properties desired in the deliming. Commercial bating products are specialty dry chemicals supplied with enzyme carriers and sometimes ammonium salts. The bating enzymes and the pH adjustment disperse much of the degradation products from the unhairing. The resulting hides are clean and flacid.

2.5. Pickling

Bated hides or skins are at a near neutral pH and thus are immediately processed, because under these conditions the protein is subject to bacterial degradation. Pickling is the term used for acidification of the hides. For chrome tanning, the desired pH is about 2.0, thus the hides are placed in a solution of salt and acid

(2, 3, 7, 9). Proteins are amphoteric, and at neutral pH hides are flacid and have little acid or base bound. At pH ~ 2.0 the acid absorbed is about $95\ \text{meq}/100\ \text{g}$ of hide protein (see Fig. 3**b**). A high ionic strength is necessary to prevent osmotic swelling which would cause damage to the delicate hide fibers and destroy the leathermaking properties of the hide. Swelling can be avoided by raising the ionic strength of the solution by the addition of salt. In practical application, the salt, NaCl, is kept above 3–4%. An excess of salt is less objectionable than a deficiency. The acid is usually sulfuric, and about 1–2% of the hide weight is used, just enough to reach the acid-binding capacity of the hide protein.

Once pickled, the hides can be drained and stored indefinitely. The possibility of bacterial or mold damage is always present, but under proper pickling and storage the hides or skins can be traded on the world market. There is, however, little trade in pickled hides except for sheepskins where commerce in pickled skins offers commercial advantages. Salt curing of sheepskins is risky because the salt may penetrate slowly owing to the heavy wool. Sheepskins also contain a large quantity of fat that may inhibit the penetration of the salt.

The usual procedure in the manufacture of chrome-tanned leathers is the use of a continuous bate, pickle, and tan method. The hides or skins remain in the drum from the lime washing through the chrome tanning stages. The entire process usually takes about 22–24 hours. The bate, pickle, and tan can be done faster, but most tanners find that a one-day cycle fits well into production scheduling and results in a quality leather.

The degree of pickle, ie, the amount and type of acid used, depends on the type of hides or skins and the tannage to be used. The pickle is in preparation for tanning and the chemistry of the subsequent tannage determines the pickle method.

2.6. Chrome Tanning

Chrome tanning is the most widely used tanning system worldwide. Chrome tanning has the advantages of light color, speed of processing, low costs, and great stability of the resulting leather. Chrome-tanned leather is so stable that exposure to boiling water for short ($<2-3\ \text{min}$) periods of time usually shows no adverse effect (1–4, 6, 7, 9).

Tanning refers to a specific reaction of the tanning chemicals combining with the hide or skin to stabilize the protein and make it resistant to bacterial degradation. Tanned leather is so biorefractive that leathers even centuries old found under adverse natural storage conditions are often in almost usable condition. Prior to the 1900s essentially all leather was tanned by the vegetable tanning method.

Chrome tanning is done in a drum similar to that used for deliming. The salt solution from the pickle is present and the solution is at about pH 2.0. The chrome-tanning material is usually a basic chromium sulfate. The general formula for the most common commercial chrome-tanning product is $2\text{Cr(OH)SO}_4{\cdot}\text{Na}_2\text{SO}_4$. After the addition of the chrome-tanning salts, the pH of the solution rises to about 2.5. At this pH the chromium salt is taken up by the hide and the tannage begins.

Control of chromium penetration, essential to permit tannage of the center of the hide, is accomplished by pH adjustment. At a pH ≥ 3.0 the reactivity of the hide to the chromium complex is greatly increased. The pH is therefore raised gradually to the desired point by addition of a mild alkali, usually sodium bicarbonate. The chemistry of chrome tanning involves competing reactions that must be controlled for satisfactory results.

The chrome-tanned leather is removed from the drum and wrung to remove the absorbed tanning solution. The leather is then inspected for quality of the grain and other characteristics of importance for the leather being made. In large tanneries where very uniform hides are worked, the leather may be trimmed and split to the desired thickness. Hides split before tanning need no splitting at this point.

Following splitting the leather is further brought to the desired thickness by shaving. Shaving is done on a machine having a multibladed rotating cylinder. This machine is similar to the fleshing machine, but is much more precise in the accuracy of the thickness of the leather.

2.7. Retanning, Coloring, and Fatliquoring

Chrome-tanned leather is a light blue in color. The fibers are only stabilized against microbial action and do not have the feel of leather. If the leather were dried at this point only a stiff unattractive product would result. The characteristics of desired leather result from the retanning, coloring, and fatliquoring.

The application of vegetable tanning materials has an additive effect on the leather. The more vegetable tannins applied the more the leather becomes like vegetable-tanned leather. The color is changed, the fullness of feel increases, and the leather can be worked and embossed like vegetable leather.

In retanning, vegetable tannins may be used in conjunction with or may be entirely replaced by synthetic tanning agents called syntans. The syntans and other specialty chemicals allow the creation of leathers not possible using vegetable tannins alone.

Modern leather can be made in any color desired. The dyeing of the chrome-tanned leather is done normally as part of the retan, color, and fatliquoring steps where synthetic organic acid dyes are applied as needed. Both acid and basic dyes are used. Traditional examples are Acid Blue 2B [6408-78-2] and Bismarck Brown G [10114-58-6], respectively. The penetration of the dye is important. For suede leather or any leather subjected to rough wear the color should be deep into the leather to assure uniform color during use. For most shoe upper leather, or any leather that is finished with an opaque surface coating, the dye need be only surface coloring. The cost of the dyes and the final use of the leather are the determining factors in the choice of the dye system used.

Fatliquoring is the term applied to the oiling of leather. Heavy leathers, such as work boot leather or harness leather, may be lubricated by the application of oils and greases directly in a drum. The greases are melted and applied to the leather without additional water. This system is not used for light chrome-tanned leather; most leather is lubricated by the application of emulsified oils. The oils comprise sulfated or sulfonated animal or fish oils, synthetic oils, or specialty products developed for the industry that can penetrate the leather as desired and then be strongly adsorbed on the leather fibers. The temperature and pH of the system during fatliquoring is important.

2.8. Drying

The retanned leather is stretched to increase the area for the best yield and to produce a flat leather surface. The leather is then dried. There are several drying (qv) systems used which depend on the type and thickness of the leather. Thin garment leathers, made soft by retanning and fatliquoring, may be dried by hanging in a dry loft. Soft leathers can be reworked by mechanical means to the softness desired when dry. For shoe uppers the leather should be held in a stretched condition. Two or three types of drying are commonly in use in the industry: toggle drying, paste drying, and vacuum drying. In toggle drying the leather is held in an extended condition with clamps on the edge of the leather stretched on a screen. The screens are placed in a temperature and humidity controlled dryer until the leather is dry.

In paste drying the leather is spread on glass or porcelain plates and held in place with a low strength water-soluble paste. The plates are on a conveyor and the drying is done in a drying tunnel. The dryer usually has several temperature- and humidity-controlled zones to control the rate of drying and to prevent overdrying.

Vacuum drying is done by spreading the leather grain on a smooth, heated, stainless steel surface. A cover is placed over the drying surface and the drying chamber evacuated. The advantage of vacuum drying is the speed at which each piece is dried using low temperatures. The vacuum drying system is beneficial for the production of some types of quality shoe leather. The equipment is expensive, however, and is only found in modern, well-financed tanneries.

2.9. Staking

Dried leather is somewhat stiff because of the slight adhesion of the fibers to one another. Staking is a mild flexing of the leather to bring it to the desired final softness. The ultimate softness of the leather is controlled by the retannage and fatliquoring and cannot be built into the leather by mechanical flexing. The methods of flexing include hand staking in cottage industry tanneries or machine staking by any of a number of commercial machines. Modern tanneries use a staking machine employing a number of vertically opposing oscillating rounded rods. The leather is fed through the machine between soft rubber belts. The machine can be adjusted for clearance and the desired degree of softness.

2.10. Buffing

Most leather is buffed before finishing. The buffing step consists of a light sandpapering of the grain. If the grain surface of the leather is free of blemishes it may be good enough for full grain where the full beauty of the natural hide surface is visible. Full-grain leathers are preferred and therefore are more expensive.

Buffing may be only to remove surface blemishes such as insect bites or minor healed scratches, or the buffing may be to make a suede surface. Newbuck is a light suedeing of the grain of cattle hide leather. Sheepskin suede is usually buffed on the flesh side of the skin. Splits may be buffed to make buck shoe leather or heavy garment leather, often called ranch hide. The variations depend on the desires of the customer.

2.11. Finishing

The finishing of leather is parallel in some ways to the finishing of wood (qv). In both cases the application of the finish results in a protective and/or decorative coat. The finishing of leather has changed greatly because of the development of resin systems in the coating industry (see Coatings). Leather finishes must minimally be abrasion resistant and flexible, and must adhere to the leather. Formation of a tough water-resistant film is also desirable.

Leather finishes penetrate to a greater or lesser extent and have a profound effect on the grain or wrinkle characteristics of the leather. Penetration of the resin into the leather tightens the grain but may produce a surface stiffness and a tendency toward grain cracking upon flexing. The development of leather finish resins and the application of these finishes is done by specialty houses.

The application of the finishes can be by brush, roll coater, spray gun, or by flow coater. In small tanneries hand finishing without machinery is common. In larger tanneries the most common method is by spraying. The spray-finishing machines are usually multistage and have temperature-controlled drying stages in line. The spray guns may be actuated by photoelectric cells to spray onto the leather and not an empty conveyer belt. Roll coaters and flow coaters are not as common as spray lines but have great value in the production of some specialty leathers (see Coating processes).

The finishing usually requires several coats. The first coats are water-based latex finishes containing pigments or dyes. The final coats are liquids for protection and sheen as desired. Two or three pigment coats and one or two top coats are normal. For expensive aniline-type leathers the grain surface is visible through the finish; the color arises from the dye in the leather. For pigment-finished products the surface is colored with the pigment in the finish, which is similar to painting. Top dressing adds protection and the desired surface reflectance.

As a part of the finishing, the leather is almost always pressed with a warm press. The press plate may be an embossing plate to give a decorative surface, thus the grain may be made to simulate an exotic animal such as alligator or ostrich; even the familiar football grain can be made. Many poor-grade hides may be embossed. Heavy embossing covers hide defects and also upgrades the hide to novelty leather.

Hot pressing with a smooth plate has an advantage in smoothing the grain, and the heat can be used to cure the resin of the finish. The hot pressing is anticipated in the design of the finish system and in the choice of the resins by the finish manufacturer.

2.12. Grading, Measuring, and Shipping

Prior to shipment each hide, side, or skin is inspected and sorted. The grading is done on the basis of hide defects, shape of the skin, manufacturing defects, or any other factors of importance to the specifications of the sale.

The leather in the grade to be shipped is measured for area. In a cottage industry the area may be measured by placing a wire grid over the hide and estimating the area by counting the squares. In modern tanneries an electronic measuring machine is used. In the electronic system the leather passes under a bank of lights where measurement is carried out by photoelectric cells. The area of the leather is calculated and the area stamped on the back of each piece of leather. The degree of sophistication of the measurement and correlation with materials used and other manufacturing costs depend on the computer system of the company.

3. Chemistry of Tanning

3.1. Chrome Tanning

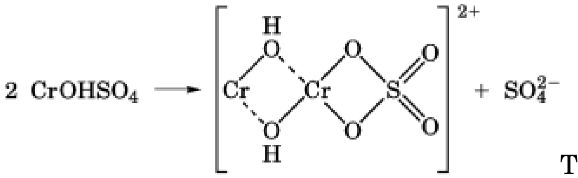
The original chrome tanning was a two-bath process. The unhaired hides, delimed and bated, were treated with a solution of sodium bichromate [10588-01-9]. The amount of bichromate used was about 3–5% based on the weight of the hides. The bichromate was absorbed or adsorbed into the hide, the solution drained, and the hides refloated. Sodium bisulfite was added and two important reactions resulted in the formation of a basic chromium and colloidal sulfur in the hide. This gave a chrome tannage and also helped to fill the hide with the solid sulfur. This crude system, which continued in the industry in some types of leather for over 50 years, is obsolete.

Modern chrome-tanning methods are well controlled and employ an extensive knowledge of the chemistry of the system. The most common chromium-tanning material used is basic chromium sulfate [12336-95-7], $Cr(OH)SO_4$, made by the reduction of sodium bichromate with sulfur dioxide or by sulfuric acid and a sugar.

$$Na_2Cr_2O_7 + 3\ SO_2 + H_2O \longrightarrow 2\ CrOHSO_4 + Na_2SO_4$$

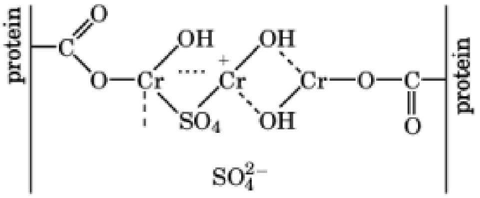
Chromium sulfate is described as being 33% basic and in solution gives a pH of ca 2.5.

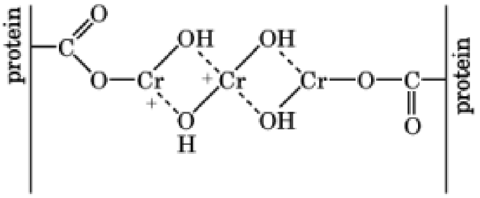
Ionization of the basic chromium salt results in the formation of complex ions such as



The basic complex structure penetrates the hide at $pH < 3.0$. There is a fixation of the chromium to the hide protein primarily by reaction of the chromium and the carboxyl groups of the hide.

After penetration of the hide by the chromium the pH is raised to about 3.5–4.0. At this higher pH a change occurs in the chromium complexes as the basicity of the chromium increases and binding to the protein becomes possible. Chromium binds firmly to the protein forming a cross-link species, and as the pH increases the hydrogen is removed from the complex forming a stable structure.





The chromium can be stabilized in a limited way to prevent surface fixation by addition of formate ions. The formate displaces the sulfate from the complex and masks the hydroxyl ions from forming the larger higher basicity complexes. This stabilization can then be reversed in the neutralization to a pH of about 4.0 and tannage becomes complete. This simple formate addition has decreased the time of chrome tanning by about 50% and has greatly increased the consistent quality of the leather produced.

3.2. Vegetable Tanning

Vegetable tanning materials became a significant commodity in international trade from the 1700s through the early 1900s. The demand for vegetable tanning has decreased but remains a principal factor in the production of heavy leathers. Vegetable tannins have the general structure of polyphenolic compounds. There are two general classes of vegetable tannins: the hydrolyzable and the condensed. The hydrolyzable tannins are derivatives of pyrogallol [87-66-1] (1,2,3-trihydroxybenzene). The condensed tannins are derivatives of catechol [120-80-9], also known as pyrocatechol, *ortho*-dihydroxy-benzene, and 1,2-benzenediol (r1,r2,r4,r7,r10).

Any vegetable tanning extract used commercially is a complex mixture of related substances. The individual tanning properties of the extracts have been extensively studied and are well known in the industry.

The mechanism of the tannage is accepted to be largely one of replacement of the bound water molecules by the phenolic groups of the tannin and subsequent formation of hydrogen bonds with the peptide bonds of the protein. The effect of this bonding is to make the leather almost completely biorefractive.

The size of the vegetable tanning molecules and the colloidal nature of the system result in the fixation in the hide of filling materials. The filling action is essentially an impregnation of the hide to form a dense firm leather. These properties are greatly desired in sole and mechanical leathers.

Vegetable tanning does not significantly cross-link the protein chain. Thus this leather can be mechanically shaped and easily embossed or tooled to a desired shape. Vegetable-tanned leather is the leather of choice for handicraft work. Shoe soles made of vegetable-tanned leather break in to the wearer's foot shape and become comfortable even though the sole may be thick and heavy. The use of vegetable extracts in the retanning of chrome leather adds these vegetable leather characteristics.

The vegetable-tanning materials are sold on a tannin analysis. The materials are dissolved to a specified solution strength, then portions are filtered (10). From the weight of the total solids, and that of the dissolved solids, the solids content and the soluble substances are calculated on a percentage basis. The tannins are measured by tanning a chrome-tanned hide powder, prepared as specified, then the solution is filtered and dried. The tannins are determined by difference to yield percent solids, insolubles, nontans, and tannin. This system can be used on both liquid and dried products.

Vegetable-tanning materials in commercial quantities come from many different countries. Quebracho is a principal tanning material from South America. Wattle or Mimosa is supplied from several African sources. India and other Asian countries supply a variety of materials including Myrabolans, Gall Nuts, and Tara Pods (3).

The vegetable-tanning materials are commercially extracted using hot water. The extraction is normally done in countercurrent extractors that permit the final removal of the extracts with fresh water. The dilute extracts are then evaporated to the desired concentration in multiple effect evaporators. Some extracts may be further dried by spray drying or any other means that proves effective without overheating the extract. Extract preparation depends on the type of extract, the size of the operation, and the desired concentration of the final product.

The tanning rates and the distribution of the tannins in the leather is dependent on the characteristics of the tanning material and the colloidal conditions in the solution and inside the hide (1, 2, 7). The tanning materials, extracted at high temperature, are applied at ambient or slightly raised temperatures, usually $<40^\circ\mathrm{C}$. Penetration is controlled by pH and temperature conditions. The lower the pH the more the weak-acid, negatively charged, colloidal particles coagulate and combine with the hide. In conventional vegetable tannages the pH was historically controlled by the choice of the extracts and the degree of fermentation of the tanning materials. The advent of accurate pH measurements has shortened the time of tannages.

The speed of the tannage is important. At the end of the nineteenth century tanning times of several months were normal for vegetable tanning; modern production using chemical controls and drum tannages has cut the time in process to a few days. Pre-tanning the hide by chrome tanning stabilizes the hide to eliminate the effects of swelling, and frees much of the bound water. The hides, pre-tanned with chrome, can be drum tanned using vegetable-tanning materials to make leather that was formerly tanned only by vegetable tanning. The leathers more commonly made with this system are upholstery, bag, case, and strap leathers. Many of the sole leathers are still made using only vegetable tanning. In these leathers the filling of the leather to make a firm yet moldable material is the governing factor.

4. Dyeing of Leather

Leather dyeing for any desired color can be done using the dyes developed for the textile industry (see Dyes and dye intermediates; Textiles). The penetration of the dye depends on the pH of the leather and the tannage. For leathers that are given a heavy finish, such as patent leather, only a surface dye is desired. The cost of the dyes is an important factor so if only surface dyeing is desired, placement of the dye is significant. For suede leathers or leathers that may be subject to scratching during use, a penetrating dye is desired (2, 3, 6).

Chrome-tanned leather has chromium bonded to the leather fibers. This chromium can act as a mordant for acid dyes resulting in fast colors and intense shading at the surface of the leather.

The dyeing of shearlings or wool sheepskins illustrates some of the technology. Shearlings, often made for the production of garments, have a sueded outside and a wool fur inside. The leather is tanned by chrome tanning leaving the wool on. After drying in the crust condition the wool is clipped with a precision machine to the desired wool length. Dyeing of the leather can be accomplished without any significant coloring of the wool. Because the skin has been tanned by chrome tanning, dyes are used that require mordanting and the chromium of the sueded leather aids in the development of the desired shade. The wool is thus unaffected.

5. Environmental Aspects

The processing of hides and skins into leather results in a large quantity of waste materials (9). The hide in the salt-cured condition contains salt in a crystalline form, water as salt solution, and as hide liquid components, flesh, blood, manure, and surface dirt from the animal.

Pollution control technology is a concern for the world tanning industry. Environmental considerations have been a primary factor in the expansion of the leather industry in developing countries. Whereas cottage industries continue to operate without significant pollution control, regulations are being enforced gradually in these countries.

The processing wastes come from the hides and processing chemicals. The hide wastes are the largest problem. For each metric ton of hides received at the tannery the following wastes are generated:

Organic waste	Quantity, kg/t of hides
fleshings	50–200
salt	100–200
surface dirt	10–20
manure	5–20
hair	5–20
oil and grease	30–50

Chemical waste	Quantity, kg/t of hides
salt	50–100
sulfides, as Na_2S	20–40
chromium(III)	10–20
suspended solids	50–100
biochemical oxygen demand	30–60

Additionally, the pH of the wastes can be from 2.0–12.5, depending on the place in the process, and the water usage is from $30 - 100\ m^3/t$ of hides. There are pollution control requirements covering tannery wastes in all developed countries and almost all Third World ones as well. The cost of pollution control is very high and may require a capital investment of from 10 to 50% of the total value of the plant and production equipment. As a result many tanners, particularly in the developed countries, have stopped the operations of unhairing and tanning, limiting operations to the retanning and finishing of hides tanned elsewhere.

The environmental problems associated with the leather industry have spurred the development of some process changes to affect more efficient fixation of chemicals and the replacement of some toxic substances used in processing (Fig. 4). Pollution control within the industry has been largely concentrated in the areas of waste treatment techniques. Separate treatment of concentrated waste streams has been most successful and cost effective. These treatments include air oxidation of sulfide wastes from the unhairing process, high exhaustion processing of the trivalent chromium which is then recycled or precipitated, primary waste treatment for high suspended solids, coprecipitation and secondary waste treatment to lower the biological oxygen demand (BOD), and use of the solid wastes for fertilizers or other animal by-products. Moreover, a shift away from highly volatile solvents in the finish drying process to a low solvent system has been effected.

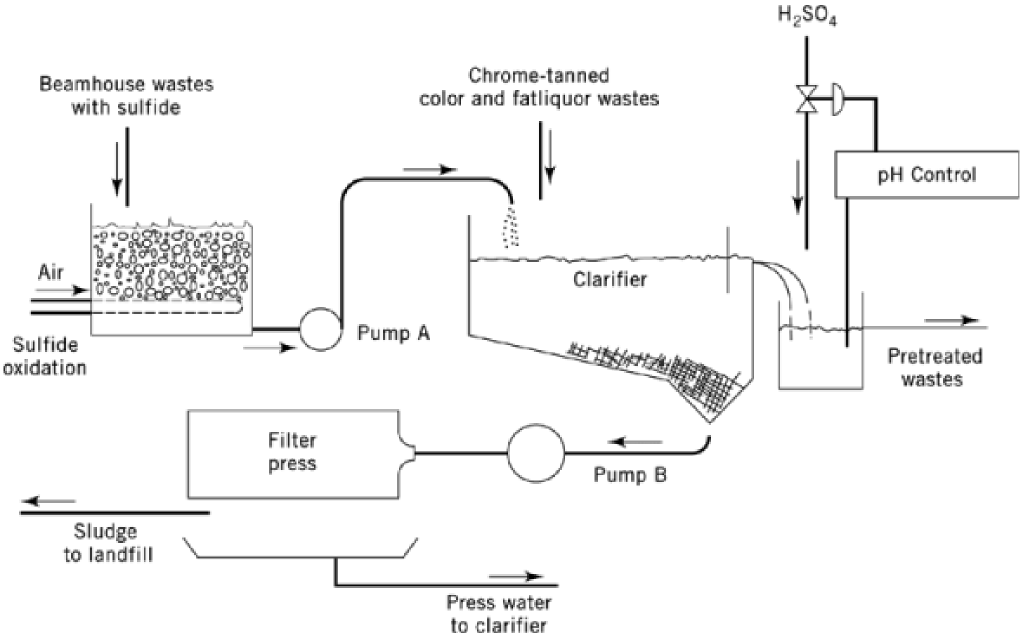


Fig. 4. Schematic of a leather tanning facility fitted with a wastewater treatment plant. Treatment of the combined wastes using sulfide oxidation and waste effluent pH adjustment greatly decreases the suspended solids and BOD loading (3). Courtesy of Krieger Publishing Co.

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