

# Leather Manufacture

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Leather, a relatively soft and flexible product, is the skin of an animal treated to render it resistant to spoilage. Leather making is one of the oldest and most highly developed arts known to man. Skins or hides from the larger animals are most often by-products of the meat industry. Herds of different animals such as cattle, sheep, and pigs are raised primarily for food and at a designated time in their growth are slaughtered. The pelts are removed and preserved for use as the raw materials of the tanning or leather making industry.

The hide or skin is about 6 to 10% of the total animal weight and is divided into three main layers: (1) a tough outer layer of epithelial tissue called the epidermis, containing keratin or hair; (2) a much thicker layer of connective tissue called the dermis, or true skin; and (3) the flesh or subcutaneous layer. Figure 1 is a photomicrograph of a vertical cross section of cowhide showing the structural elements in it.

The epidermis and the flesh layers are removed in processing leaving the dermis, the collagen-rich portion, to be converted into leather. The dermis is made up of two distinct layers, the grain or papillary, and corium or reticular. It is a network of interweaving fibrous proteins predominantly collagen, but with small amounts of reticulin and elastin. Interspersed among the protein structures is a ground substance composed of mucopolysaccharides, albumins, cellular elements, and water.

Figure 2 is an enlargement of the grain layer area showing the components in it. Each hair follicle is accompanied by a sebaceous gland, a sweat gland, and an erector pili muscle. Finely dispersed fibers of elastic tissue are shown running parallel to the grain surface, and larger interweaving collagen fiber bundles are apparent in the lower grain and upper corium.

## Preservation of Rawhides and Skins

The preservation (1) of hides and skins is called curing. This process retards bacterial action and putrefaction and must be done properly and immediately after slaughter to assure top quality material for the tanning industry. The usual and most satisfactory method in use today is salt curing, either by application of sodium chloride to a washed hide using 1 lb of salt for 1 lb of hide, or by soaking it in a saturated salt or brine solution. Salt or brine cured hides can be kept without deterioration up to six months. In some countries, hides and skins are sun-dried in a procedure that must be carefully controlled so that the hide is not destroyed by bacterial attack.

This feature presents relevant applications of chemistry to everyday life. The information presented might be used directly in class, posted on bulletin boards, or otherwise used to stimulate student involvement in activities related to chemistry. Contributions should be sent to the feature editor.

## Consecutive Steps in Normal Hide Processing

Wet Operations	Dry Operations
Trimming and Sorting	Drying
Soaking	Conditioning
Fleshing	Staking
Unhairing and Liming	Buffing
Bating and Delimiting	Finishing
Pickling	Plating
Tanning	Measuring
Wringing	Grading
Splitting and Shaving	
Retanning, Coloring	
Fatliquoring	
Setting Out	

Tanners buy salt or brine cured hides from meat packing houses. In the tannery, hides are stored in hide cellars, where they are inspected, trimmed, and sorted into packs as soon as they are received. *Trimming* is the removal of portions of hides not suitable for leather making. *Sorting* is the selection of hides according to weight and size and their distribution into packs ready for use.

## Wet Operations for Leather Used in Shoe Uppers

Hides and skins are tanned to preserve the hide proteins. They are made imputrescible and suitable for use by removing impurities and reacting their protein fiber components with chemicals.

In modern practice most leathers are produced by chrome-tanning and chrome- and vegetable-retanning. All the common materials used for tanning in the United States are imported: chestnut extract from Europe, wattle extract from South Africa, quebracho extract from South America, and chromium from Turkey and Rhodesia. There are no domestic tanning materials commercially available since the destruction of large stands of chestnut trees by blight.

Hides and skins are processed differently because the end use for each is different. The time of processing and amounts of chemicals are varied. The table shows consecutive steps in both wet and dry operations used in a tannery (2). The operations listed are common to all tannery practice. Some are preparatory in that they put the hide in the proper condition for subsequent steps in the process. Other steps cause major changes in the properties or appearance of the hides. All operations have a relationship to each other, and the interdependence of one operation on another can cause production problems. Strict control must be exercised over the process at all times.

The procedure for making cattle hide into leather used in

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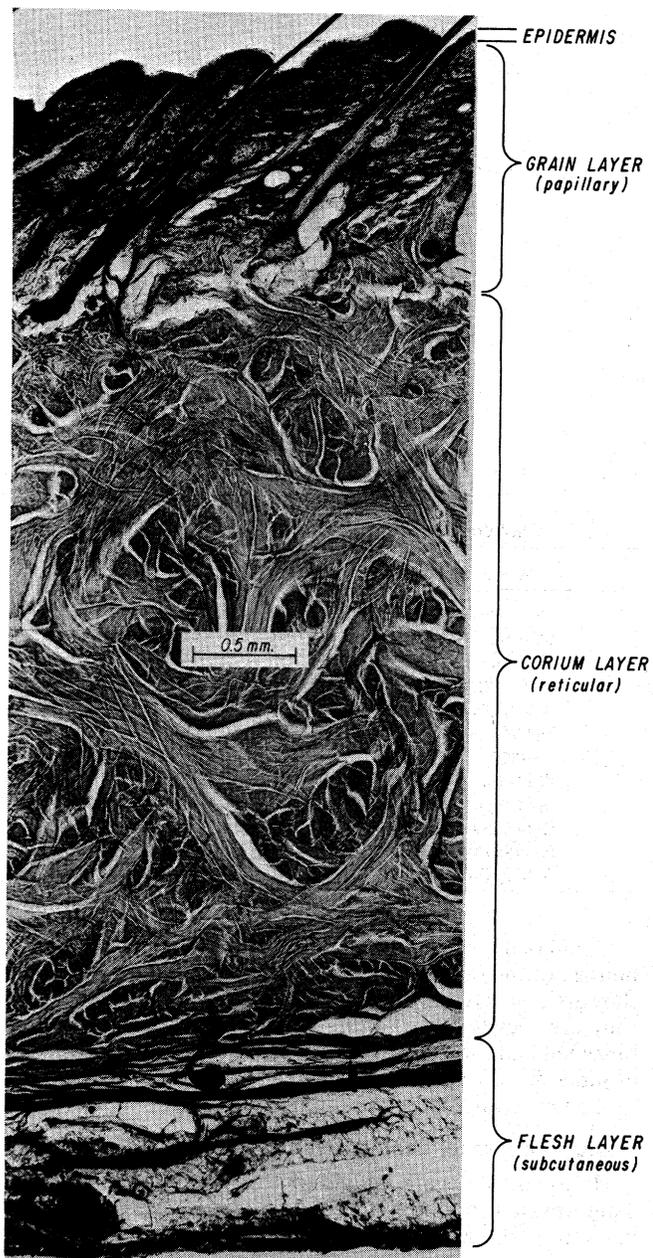


Figure 1. Vertical cross section of cattlehide: (a) epidermis, (b) grain layer, (c) corium, (d) flesh layer.

shoe uppers will be described. The hides are sent from the hide cellar to the beamhouse where the wet pretanning procedures are carried out. From the hide cellar, the hides are put into a water soak.

**Soaking and Fleshing.** The salted hides are cut down the backbone into sides, soaked to rehydrate them (salt reduces water content), washed in drums or hide processors to remove salt and solubilized proteins, and fleshed on a fleshing machine to remove subcutaneous tissue such as fat and muscle.

**Unhairing and Liming.** The hides are now ready for unhairing with a lime and sodium sulfide solution, which removes the epidermis and hair. It also removes mucoproteins and opens up the collagen fiber structure, making it receptive to tanning materials. Amounts of all chemicals and water used are based on the salted hide weight. Unhairing can be done in one or two steps. The two-step method is the use of: (1) a lime and sodium sulfide solution to destroy or burn off the hair chemically at the grain surface, and (2) a reliming bath to further remove additional epidermal debris and to pump the

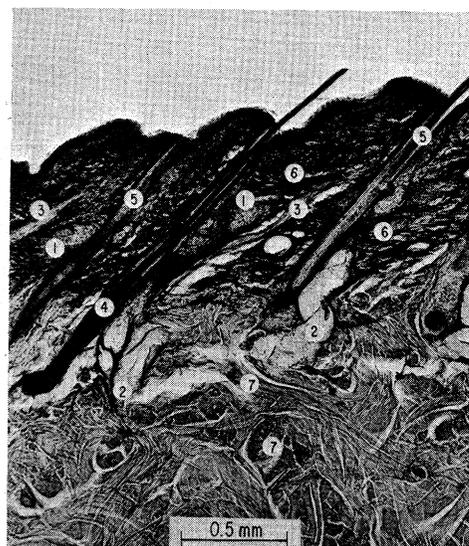


Figure 2. Vertical cross section of grain layer of cattlehide (1) sebaceous glands, (2) sweat glands, (3) erector pili muscle, (4) actively growing hair, (5) resting or club hair, (6) elastic tissue, (7) collagen fibers.

### Glossary

**Beamhouse** is an old name originally applied to the building where skilled artisans scraped away all hair and epidermis over an oval wooden beam.

**Brine** is a saturated solution of salt and water used for preserving hides and skins.

**Buffing** is the smoothing of the grain surface of leather by mechanical sanding to remove apparent defects. Grain surface treated this way is called corrected grain.

**Calfskin** is skin from a young bovine, male or female.

**Cattlehide** is a general term for hides from a bovine of any breed or sex but essentially mature; includes bullhides, steerhides, and cowhides.

**Coloring or dyeing** is a process for imparting color to leather.

**Curing** is the treatment of hides and skins to retard bacterial action and putrefaction.

**Fatliquoring** is a process done with an emulsion of oils to lubricate the fibers and to add flexibility to the leather.

**Finishing** is making completely tanned leather more attractive, serviceable, and durable, by applying tough colorative and/or decorative coatings.

**Finishing materials** are film-forming polymeric substances such as polyacrylates, butadiene polymers, nitrocellulose, polyurethanes, and selected pigment for coloring. Polyurethanes are used to produce surface coatings on patent leather that will withstand severe wearing conditions and have high gloss.

**Flesh split** is the inner or under layer of hide or skin separated from the whole by the splitting machine.

**Grain split** is the outer layer of hide or skin containing the grain and upper corium.

**Setting out** is a multipurpose operation which smooths and stretches the leather while compressing and squeezing out excess moisture.

**Shrinkage temperature** is a measurement of the effects of chemicals and tanning materials used in the process of changing rawhide to leather. Tanning materials increase the resistance of rawhide to heat. This may differ for each type of tannage.

**Suede** is a type of leather produced by running the surface of leather on a carborundum or emery wheel to separate the fibers in order to give leather a nap. The grain side may be suede finished but the process is most often applied to the flesh surface.

**Staking** is the flexing of leather, to soften it, by mechanical stresses which separate the fibers which are sticking together.

**Trimming** is the removal of portions of hides or skins which are not suitable for making into leather.

hides. This can be done in one operation over a longer period of time by combining lesser amounts of sodium sulfide with lime. The pH of the lime/sodium sulfide and reliming baths is about 12.5. Unhairing and reliming can require from 12 to 20 hr depending on the established processes. Enzymes are also used for unhairing, but enzyme-unhaired hides require special processing.

**Bating and Deliming.** After washing and draining, while the hide is still in the drum or hide processor, the limed stock is delimed and bated with a solution containing ammonium sulfate or other acidic salts and a pancreatic enzyme mixture. The temperature is carefully controlled at 85°F for 1 hr during which time the drum is moved intermittently (15 min on and 15 min off). The pH is reduced to 8.5.

The bating mixture removes additional debris from the hair roots as well as denatured products remaining from the unhairing procedure. The bated hide is so changed from the plumped condition of the limed state that the imprint of the thumb can be made in the bated stock.

**Pickling.** This process designed to adjust the pH of the hide, is carried out by immersing hides in water containing 6–9% sodium chloride based on the limed hide weight and enough sulfuric acid to give a liquor pH of about 1.5. The degree of acidity is varied by the tanner depending on the type of leather that is in production.

**Tanning, Dyeing, and Fatliquoring.** Tanning is the stabilization of hide proteins. The pickled hides are put into a chrome-tanning solution containing 5% salt and 4, 6, or 8% of 33% basic chromium sulfate. The chromium salts penetrate into the collagen fibrils. There is no reaction at the low pH. When the penetration is complete, the pH is raised to about 3.6–4.0 by the addition of sodium bicarbonate over a period of several hours. Two to six hours are required for the cross-linking of chromium sulfate complexes with the carboxyl groups on the collagen protein (3, 4). The tanned hides are removed from the drum and piled overnight. Tanning continues during this time. This type of leather should have a shrink temperature of 100°C maintained for 3 to 5 min in boiling water (1). Shrink temperature is used as the measure of increased hydrothermal stability of collagen caused by the reactions of selected tanning materials with it. The tanned hides are washed, wrung out, split into grain and flesh splits, and shaved to desired thickness. The machinery used to carry out the essential steps in production of quality leather is accurate within  $\frac{1}{100}$  of an inch in splitting and shaving operations. The hides are returned to the drum for retanning with more chromium salts or vegetable extracts, dyeing with color dyes, and fatliquoring with oils or emulsions. They are now ready for setting out, which is a multipurpose operation to smooth the hides and remove excess moisture. Immediately after setting out, the retanned hides are dried.

### Dry Operations

**Drying.** The removal of all but equilibrium moisture from the tanned stock is carried out under controlled conditions of temperature and humidity. The fibers tend to stick together during the initial drying. To break up cohesion between fibers, the leathers are conditioned by rewetting with controlled amounts of moisture so that a uniform moisture content (30–40%) is obtained. The leathers are staked, made pliable by mechanical stresses, redried, and buffed to minimize any surface imperfections prior to finishing.

**Finishing and Grading.** Finishing is making completely tanned leather more attractive and of greater commercial value by various operations and finishing processes. The finishing procedure is the application of film-forming materials such as polyacrylates, vinyl and butadiene polymers, nitrocellulose, or polyurethanes (and pigments for color) to the grain surface to enhance the beauty of the finished product and to provide resistance to scuffing or other surface damage. The amount and kind of finish applied depends on the nature and quality of the hides or skins. Finishing is followed by

plating, which is an application of pressure to smooth the surface of the coating materials and to fix them firmly into the grain. Finishing and plating are carried out in conjunction with each other. These two processes make leather more attractive, more serviceable, and of greater commercial value. The leather is graded for quality and measured for yield. After approximately 4 to 6 weeks of various treatments, previously described, the raw material has been made into leather and is ready for the marketplace.

### Properties of Leather

Leather has unique physical properties which can be translated into important consumer values. The unusual random fiber orientation of leather provides flexibility, stretch, and comfort in shoes or garments. Leather has a natural insulating property. It can breathe, absorb, and transmit moisture, and has an unusually high tear strength as well as an appealing esthetic quality.

Tanners are striving to build into leather improved properties, such as scuff and abrasion resistance in footwear, washability and dry-cleanability in garment leather. This is accomplished by incorporating polymers into finishing materials or into the hide itself in the tannage.

The demand for leather products exceeds the worldwide supply. Eighty-five percent of all leather made in the United States is used in shoe manufacture as upper, lining, insole, and sole material. The rest is made into handbag, upholstery, case, garment, and mechanical leathers.

Some other leather products of interest are suede and grain leather coats and jackets made from sheepskins, as well as shearlings made from sheepskins tanned with the wool on. These are made into jackets, hats, gloves, and novelties. Shearlings are also tanned with glutaraldehyde to stabilize them to repeated washings and dryings and are made into medical bedpads (5) for preventing sores on bedridden or chair-confined individuals. The wool side is placed beneath the patient, allowing air to circulate throughout the wool fibers to keep the surface area of the skin dry.

Calfskin makes the finest leather, but fewer calves are available for slaughter each year. Horsehide is desirable for jackets, but it is also in short supply. Pigskin is becoming a very important item in the marketplace today because of an impending shortage of cattlehide. Whole pigskins, rather than pieces, are being made available to the tanner because of improved skin removal in the slaughterhouse and unhairing methods in the tannery.

### Problems of the Industry

Hides, like all natural products, are troubled by animal diseases, parasitic infections, and biological (6) and man-made defects (7) such as hot branding. Healed scratches usually are considered a sign of a natural product rather than a blemish. Defects caused by parasitic infestations such as demodectic mange, warble fly (grubs), scabies, and ticks, as well as by hot branding, cause tremendous losses to the tanning industry, despite available preventive methods.

The industry uses vast amounts of energy to produce leather. Tanning creates pollution problems, particularly in the disposal of sodium chloride and chromium wastes; also in the accumulation of unusable hide pieces, some of which are now being utilized in the manufacture of pet treats and sausage casings. Gelatin is a recognized food staple made from collagen.

Today's tanners are anxious to comply with the Environmental Protection Agency laws and are striving to produce leather in accordance with the regulations. They are experimenting with and searching for more effective technology, with less pollution and greater utilization of the raw materials.

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