

## LEATHER

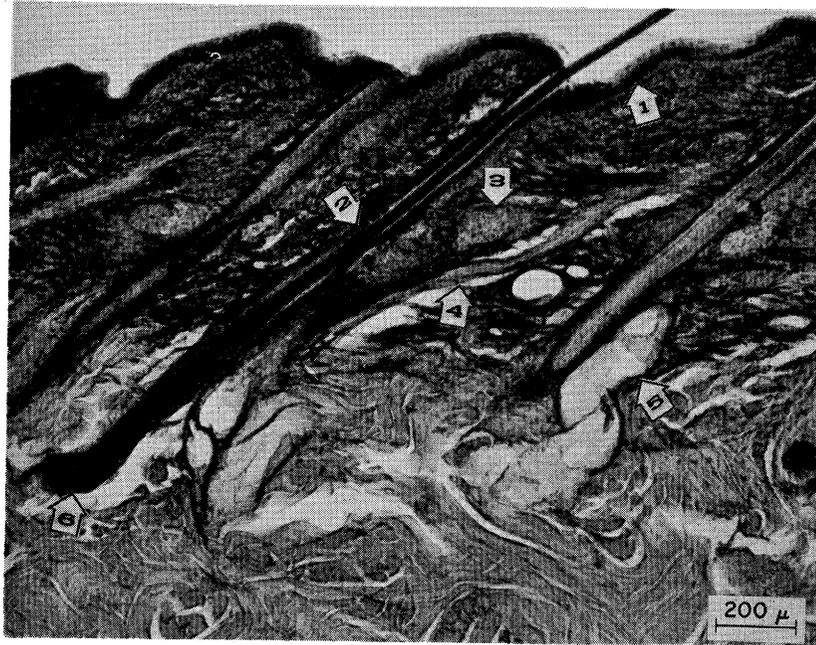
All leathers are made from animal hides or skins. Their unique properties depend upon the composition and structure of the hides or skins. The structure of skin is much more elaborate than that of any man-made material. There are variations in skin structure from one class of animal to another, from one breed of animal to another, from one individual animal to another, and even from one area to another within an animal's skin. This natural structure can be modified by chemical and mechanical processing. Its physical behavior can be modified by the incorporation of other ingredients as fillers or lubricants. Therefore, from the limited types of animal skins available commercially, it is possible to produce many types of leathers designed with specific properties and for specific uses. See also LEATHER-LIKE MATERIALS.

Since the structure of leather depends upon the structure of the hide or skin from which it is made, we should first examine the structure of skins. Hides and skins are the outer covering of animals. The distinction between a hide and a skin is chiefly in the thickness and size. Small animals tend to have thin skins, whereas larger animals tend to have thick hides. However, in commerce, a hide is a skin that weighs over 30 lb. There is no rigid scale connecting the weight of the animal with the thickness of its hide. Within a given species of animal, the thickness of the skin depends upon the degree of development of the animal and not necessarily upon its age. Intensive feeding (1) of meat animals to induce more rapid and efficient meat production causes the skin to thicken more rapidly than under standard feeding procedures. In this description, the term skin will be used to mean both skin and hide.

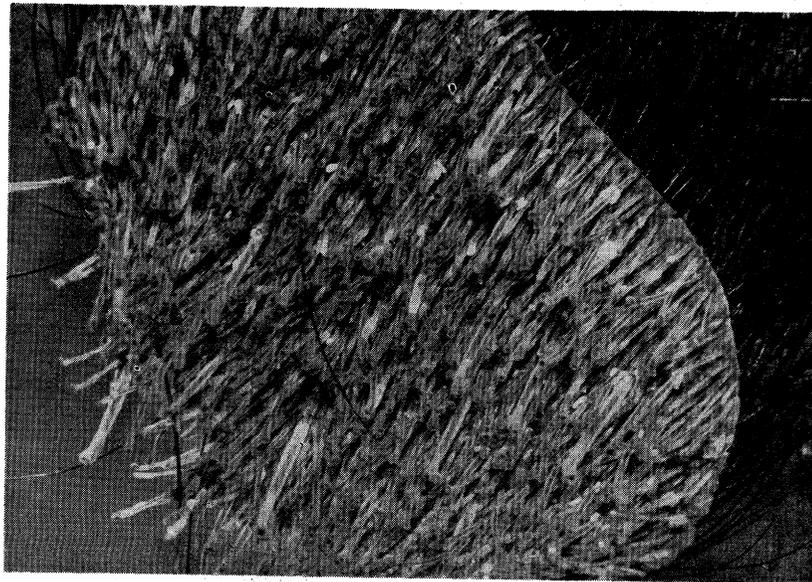
### Structure of Skin

**Epidermis.** In most animal skins, the structural organization consists of three easily demonstrable layers. The surface layer is a hard, horny material to protect the skin from abrasion. This layer, usually called the epidermis, is formed of cells which develop in the lower layers of the epidermis and gradually change (cornification) and dehydrate as they are pushed toward the surface by the newer cells being formed below them. It can be seen in Figure 1 that the epidermis not only covers the surface but also lines the hair follicles which penetrate into the underlying layer. The current methods of unhairing remove the epidermis as well as the hair. Figure 2 shows an enlarged view of the epidermis, with hair and glands attached, which was removed from a skin after soaking for five days in a 5% salt solution (2).

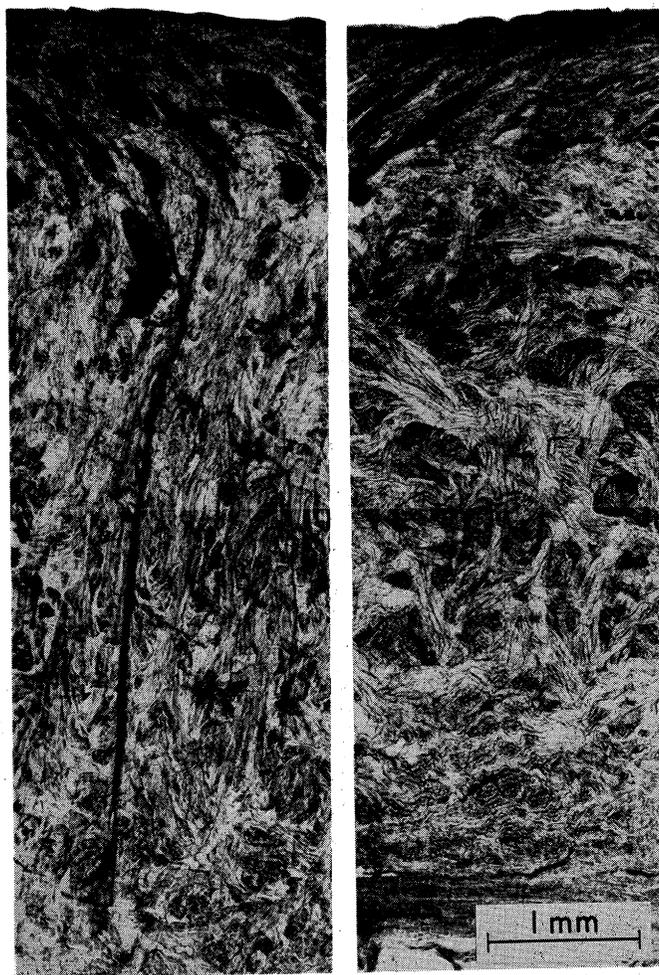
**Grain Layer.** The second layer, which is immediately below the epidermis, is the corium minor, or so-called grain layer, because its upper surface contains all of the characteristic markings which become the leather surface. It also contains all of the functional units of the skin: the growing root of the hair shaft; the sebaceous glands



**Fig. 1.** A cross section of skin showing: (1) epidermis, (2) hair follicle, (3) sebaceous gland, (4) erector pili muscle, (5) sweat gland, and (6) hair root. Courtesy of A. L. Everett.



**Fig. 2.** An enlarged view of epidermis, with hairs and glands attached (2). Courtesy *Journal of the American Leather Chemists' Association*.



**Fig. 3.** Vertical cross sections of cured hides: left, Hereford with vertical fibers; right, Angus with normal fibers. The dark vertical line in the left picture is a vertical blood vessel (22). Courtesy *The Leather Manufacturer*.

which provide oils to lubricate the hair shaft and coat the skin to prevent evaporation of moisture; the erector pili muscle whose contraction regulates the discharge from the sebaceous glands, erects the hair, and causes the appearance of "goose pimples" on human skin; the sweat glands which aid in controlling body temperature; and the blood vessels which nourish the skin and also aid in controlling the body temperature. These functional units, which can be seen in Figure 1, are set in a three-dimensional meshwork of elastic and collagenous fibers. These fibrous proteins are found in many organs, for they are the chief components of connective tissues; they are very prominent in the skin, bones, tendons, and ligaments (see also COLLAGEN). Finally, the space between the fibers and other structures is filled with a jellylike material called the ground substance, which is composed of mucopolysaccharides, mucoids, mucoproteins, and globular proteins from the blood. More detailed descriptions of the histological studies of skin structures are found in Ref. 3.

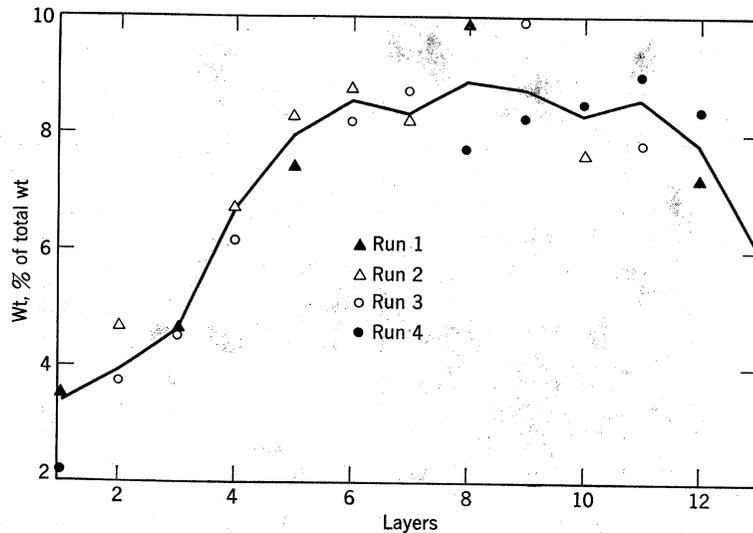


Fig. 4. Distribution of dry weight as a percent of total dry weight: median line and extreme points (5). Courtesy *Journal of the American Leather Chemists' Association*.

The grain area extends from the grain surface to slightly below the deepest hair follicles. The lower boundary cannot be defined exactly because there is a narrow region where the fine fiber bundles from the grain layer and the coarser fiber bundles from below are intermingled. The fiber bundles in the grain area are very fine and very numerous, and, in both a horizontal or vertical cross-sectional view, this layer appears to be quite dense. Measurements to be described later will show that this is an illusion. The grain layer reaches its full thickness quite rapidly with age, and it is almost fully developed in the calf. It increases greatly in area but only slightly in depth as the animal matures.

**Corium.** This is the third major division of the skin and is characterized by coarse bundles of collagen fibers. The transition from the fine fiber bundles of the grain layer to the coarse fiber bundles of the corium can be seen in Figure 3. The corium is composed almost entirely of large bundles of collagen fibers with a scattering of elastic fibers and increases in thickness with the development of the animal. It is about a sixteenth of an inch thick along the backbone in a calfskin and will become about a quarter of an inch thick at the back of a full-grown steer or cow. Although the grain layer has a comparatively even thickness (4) over the area of the skin, the corium varies greatly in thickness from one area of a hide to another. It is thickest around the neck, shoulders, the backbone, and sides of the animal, but is quite thin in the belly and flank areas.

**Void Space in Skins.** Stratigraphic studies of skin composition have shown that the components of skins (4,5) are not evenly distributed through the thickness of a skin. Sections cut parallel to the surface of a fresh skin have been analyzed for many of the components known to be present in skins and leather. When sections of equal thickness were cut and their dry weight determined, it was found that the concentration of dry matter in the grain layer was only about one-half the concentration found in the corium. This distribution is shown in Figure 4 (5). Layer 1 is at the grain surface, and layer 13 is at the flesh side of the skin. The transition between the grain

layer and the corium comes in the fourth layer. It is apparent that there is also a decrease in dry weight in the slices from the flesh side.

A remarkably similar curve was obtained for the nitrogen content. The nitrogen content is a measure of the proteins present, and the results show that there is only about one-half the amount of protein present per unit volume in the grain region that is present in the corium or central part of the hide. The flesh side also has less protein. About 88% of the nitrogen found in skins comes from the protein, collagen. A plot of the distribution of hydroxyproline (6), which is an amino acid found mainly in collagen and used to determine the content of collagen, follows a similar curve. The jellylike materials of high moisture content which fill the space between the fibers are removed by the pretanning processes. Therefore, these studies indicate that the grain layer of the resulting leather can be expected to have a more open structure than the leather from the corium or central part of the skin. Leather from the flesh region should also appear more open although to a lesser degree than leather from the grain.

Measurements of the contribution of the hair follicles and sebaceous glands (7) to the void spaces of leather show that the hair follicles account for only about 3% of the total volume of the grain layer, and the sebaceous glands account for only about 12% of the total volume in the limited region where they exist. Therefore, the void spaces produced by the removal of the hair follicles and sebaceous glands are only a small proportion of the total void space found in the grain layer. Measurements of the void spaces in degreased, vegetable-tanned leathers with a mercury-pressure porosimeter (8) showed that the grain split had the greatest volume of most sizes of pores, and the corium had the least volume of all sizes of pores. Thus, these studies also confirmed that there is more free space in leather from the grain and flesh layers than from the center of the skin.

The presence of free space in the grain and flesh sides of leather has an effect on many of the treatments which are given to skins and leathers. Almost any material introduced into leather will become concentrated in the grain and flesh areas. This has been shown to be true for the distribution of fat liquors (lubricants) (9,10), chromium-tanning materials (11), and silicon resins (12).

Another aspect of the free space in the grain and flesh layers is the reaction of the different regions of the skin to various reagents. Both acid and alkaline media will swell hides, but apparently most of this swelling occurs in the grain and flesh layers (4) where there is room for the swelling to occur. This is of particular importance in chromium tanning, which is considerably affected by the concentration of acid and salt. It has been claimed (13) that the degree of swelling of the skin at the moment of tanning is the governing factor in the distribution of chromium compounds within the leather. The greater the swelling of the fibers, the more deposition of chromium. When the tanning is carried out without restriction on the swelling of the fibers, the chromium content is always higher in the grain layer. When salt is used (14) in the chrome liquor to control swelling, the chromium content becomes uniform throughout the skin. It is believed (5) that the salt reduces the swelling of the collagen fibers in the grain to the degree of swelling exhibited by the corium fibers, which are restrained from swelling to their maximum degree by their compact environment.

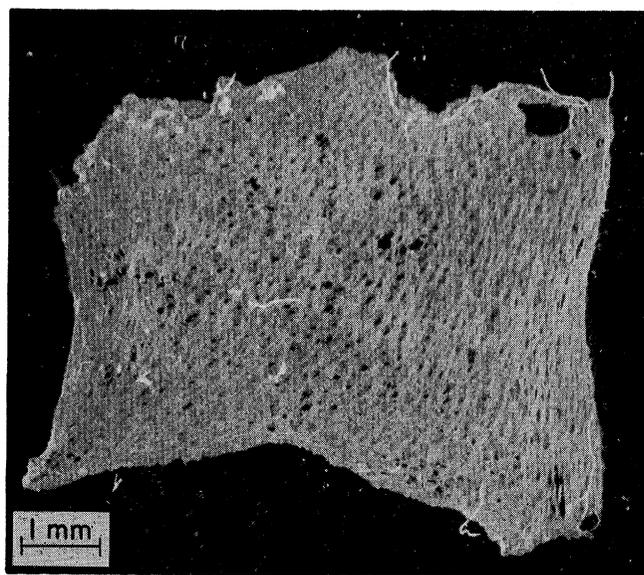
### **The Fibrous Structure**

Although the skins of some species of animals may not contain all of the functional units previously enumerated, all animal skins contain the meshwork of elastin fibers

and collagen fiber bundles. It is this meshwork which becomes the chief structural characteristic of leather. The pretanning treatment of skins removes almost completely the epidermis, hair, globular proteins, mucoproteins, mucopolysaccharides, mucoids, and fats. Therefore, about the only skin components remaining in leather are the collagen, elastin, and some of the natural fats. What then accounts for the various characteristics which can be developed in leathers? There are four main factors: the arrangement of the fibers in the skins; the modification of the fibers and their arrangement during processing; the effects of the tanning agent; and, finally, the effects of the lubricants, impregnants, and finishes used in the final processing of leather.

**Fibers in the Blood Vessels.** Some of the collagen and elastin fibers are found in the veins and arteries of skins. The arrangement of these is important because occasionally they cause pronounced veiny patterns which decrease the value of leather. It has been established that these vessels are arranged in three horizontal layers (15). Two of these are within the grain layer, and one runs through the lower levels of the corium. The blood vessels in the grain are small and seldom become prominent in leathers. The three levels of blood vessels are connected by vertical vessels, one of which can be seen in Figure 3. The veins and arteries in the horizontal layers of the corium are much larger than those in the grain layer. These large vessels sometimes collapse (16) and leave a large void space around them. If the surrounding fiber bundles are pushed into the voids by mechanical treatments, indentations appear on the surfaces of the leather. Some progress toward alleviating this defect has been made by zirconium retannage (16) or by resin impregnation (17).

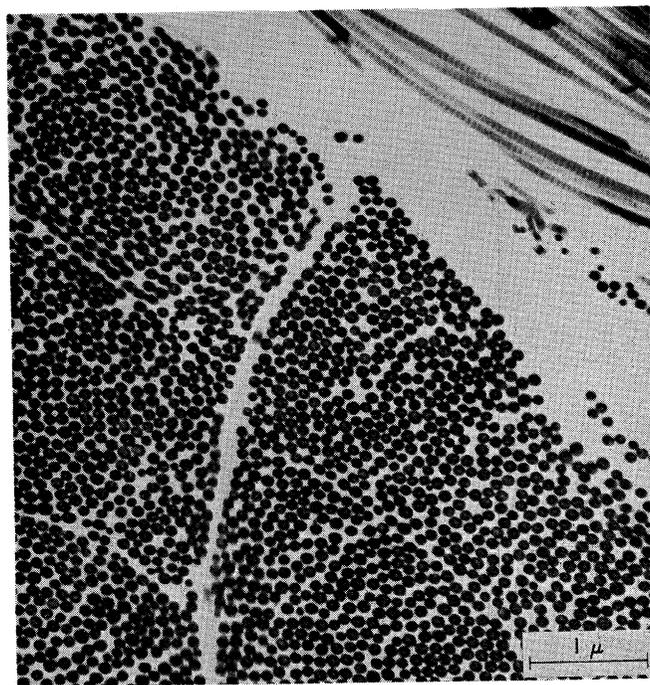
**Arrangement of Elastin Fibers.** The elastin fibers can be separated from the collagenous fibers by converting the latter to soluble gelatin (qv) and extracting it from the elastin residue. When this was done on a piece of skin, the elastin was ob-



**Fig. 5.** Elastin network from a horizontal section in the grain layer (19). Courtesy *Journal of the American Leather Chemists' Association*.

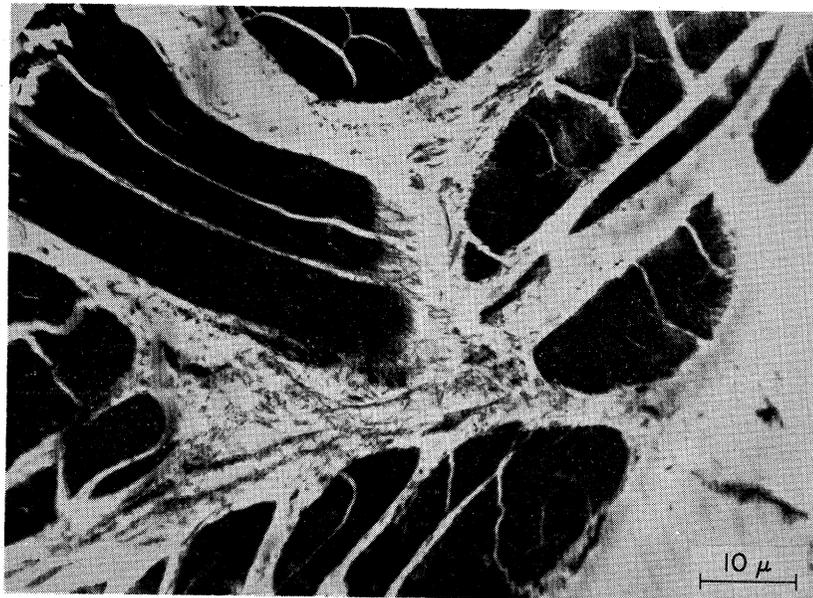
tained (18) as a dense sheet with some filmy material attached to its lower side. The dense section comes from the grain layer, and the filmier section comes from the corium and flesh side of the skin. Histological studies (3) have never detected more than a branching network of elastin fibers quite widely dispersed among the collagen fiber bundles and more prominent around the hair follicles. Stratigraphic studies of the elastin distribution (19) in the grain area of cattleskins by horizontal sectioning have shown that the elastic tissue is distributed throughout the grain layer. The distribution is not even but attains a maximum concentration about one-third of the thickness down from the grain surface. A microscopic view of the elastin network at this level (Fig. 5) shows that the elastin fibers in the grain are all connected into a three-dimensional network. The dense elastin membrane described above is the result of the network collapsing upon itself when the intervening collagen fibers were removed. The removal of this network by enzymatic procedures resulted (20) in leather that had a softer feel (temper), coarser ridges when the grain is cupped inward (break), and more pronounced (drawn) grain than the untreated leather. Because of the nature of the treatment, one is not certain that elastin was the only component removed. Therefore, the question of whether the elastin present in leather affects the properties has not been answered.

**Collagen Fiber Structure.** The chemical composition and molecular structure are discussed in the article on COLLAGEN. The smallest unit of collagen, the tropo-collagen molecule, has a diameter of 15 to 20 Å and a length of 2600 Å. These molecules aggregate linearly and laterally to form fibrils which are the smallest fibrillar forms of collagen. They can be "seen" only with the electron microscope. Figure 6 shows an

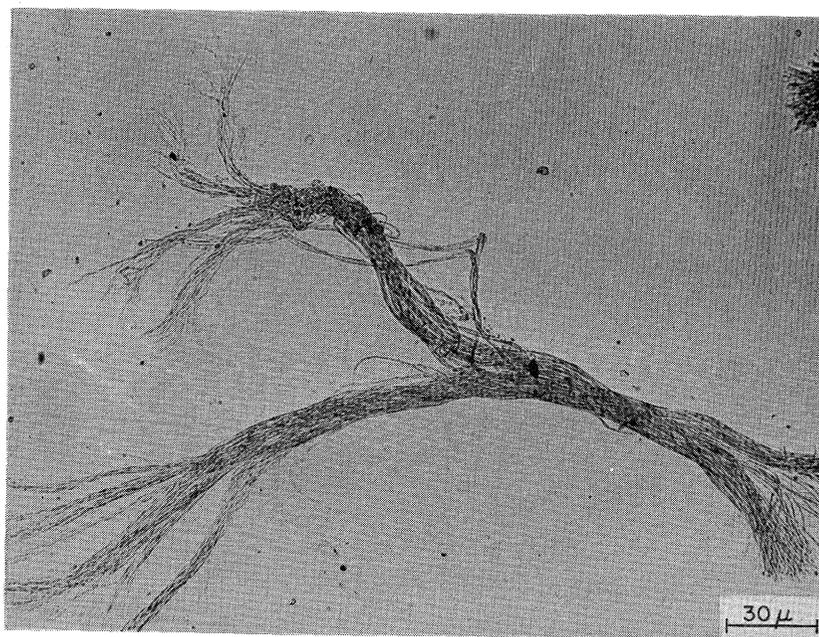


**Fig. 6.** Electron micrograph of skin section: longitudinal fibrils in upper right; two fiber bundles in cross section (22). Courtesy *The Leather Manufacturer*.

electron micrograph of a skin section showing longitudinal fibrils in the upper right and two fibril bundles composed of many fibrils in cross section. In tissues the fibrils are bound into bundles of various sizes depending upon the growth characteristics of the individual animal or tissue. Figure 7 shows a longitudinal fiber bundle in the upper



**Fig. 7.** Electron micrograph of skin section: longitudinal bundle in upper left, others in cross section (22). Courtesy *The Leather Manufacturer*.



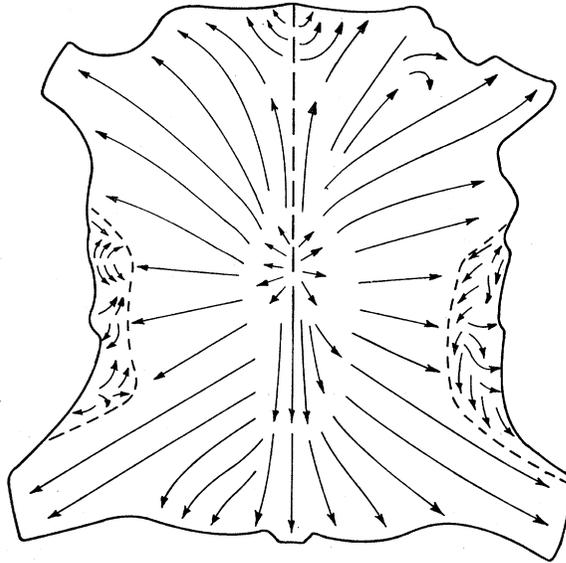
**Fig. 8.** Micrograph (by light microscopy) of a fiber bundle from the split surface of a skin. Courtesy A. L. Everett.

left and other fiber bundles in cross section. Each fiber bundle shows further subdivisions as though the larger bundles could be composed of smaller bundles. Figure 8 is another illustration of this and shows a fiber bundle obtained from a cut surface of a skin photographed with a light microscope. The left end of this bundle is subdivided into smaller and smaller bundles. The fibrils cannot be seen with the light microscope. Since no one has identified the natural end of a fibril or fiber bundle, it is impossible to say where the fibrils and fiber bundles begin and end. For example, in the right side of Figure 3, heavy fiber bundles in the center are so highly interwoven that one cannot follow a single fiber bundle very far. The fiber bundles also appear to subdivide with each smaller bundle going off in a different direction. Near the top and bottom of the corium the diagonal fibers of the center appear to become tied into a band of fiber bundles running more or less horizontally. A few fiber bundles of some length can be teased from the flesh surface; but, by going only slightly deeper into the hide, the fiber bundles are found to be tightly interwoven in all directions, and it is extremely difficult to obtain lengths of more than a few millimeters. This highly interwoven nature enables leather to be sewn close to the edge without danger of raveling.

The structure of the fiber bundles as well as their orientation within the skin can be altered to some extent by physical, chemical, and enzymatic processing. In general, these changes are brought about by relieving the confinement of the fiber bundles from their compact network and splitting the fiber bundles longitudinally into smaller bundles. This combined action is referred to in the tannery as "opening up" the structure. Most of the opening up occurs in the unhairing process where lime or, more usually, a lime-sulfide combination is used to free the hair from the hide. These alkaline solutions cause a swelling of the hide which pulls the fiber bundles out of their original positions, disrupts the binding agents which hold the fiber bundles together, and causes the bundles to separate longitudinally. In general, a straight lime solution produces a leather of low density and a high stretch because the fiber structure is opened more extensively owing to the longer time required to complete the unhairing. The lime-sulfide solution, which gives rapid unhairing, produces a more normal leather with a medium density and stretch. The degree of opening up controls the pliability or suppleness of the leather.

**Similarity of Fiber Structures in Skins.** The fiber structures of skins available commercially have many characteristics in common (21). They all have finer fibers in the grain layer. The fibers of the grain and corium interweave at the boundary line making this boundary difficult to define exactly. The fiber bundles on the flesh side tend to break up and become thinner, and the flesh side is limited by horizontally running fibers. They also show a comparable directional pattern similar to the directional pattern of the underlying muscle fibers, the longitudinal direction of the hair follicles (Fig. 9), and the direction of maximum tensions within the skin. The direction of these tensions can be displayed by punching holes with a cylindrical punch. The resulting holes are distorted by the unequal tensions within the skin and form ellipses whose major axes are in the directions of greatest tension. The fibrous structure also appears to follow this pattern, for, in different areas of the skin, the fiber bundles parallel to the surface have a predominant direction with the greater number of fibers running parallel to the directional lines.

**Species Differences in Fiber Structure in Skins.** Although many features are common to all skins, there are some very characteristic differences which dictate the use to which particular skins can be applied (21). Let us consider the main differences of the major commercially available skins.



**Fig. 9.** The direction of hair follicles in calfskin (21). Courtesy British Leather Manufacturers' Research Association.

Sheepskins are quite thin with a comparatively thick grain layer which comprises an appreciable part of the total thickness of the skin. The fiber bundles, which are quite loosely packed, are the thinnest of the domestic skins, and therefore the sheep and lambskins produce very soft and flexible leathers.

Goatskins are also thin skins, but the grain layer is a smaller part of the total thickness. The fiber bundles are bigger, more compactly woven, and require more plumping (swelling and opening up) than the fiber bundles of sheepskins. The fiber bundles of goatskins will also withstand a greater degree of plumping than most other skins without damage to the fiber structure. Goatskins have more strength and elasticity than sheepskins and are very suitable for making shoe upper leathers where strength, stretch, and flexibility are all required.

Calfskins are intermediate in thickness between goatskins and cattleskins. The fiber bundles are heavier than in goatskins but can be easily plumped. Therefore, calfskin leathers can be made quite firm or quite flexible, as the use demands.

Deerskins are very much like calfskins except that they have a thinner grain. Deerskin leathers are also very porous and exceptionally supple, making them attractive for gloves and garments.

Cattleskins are usually over a quarter of an inch thick across the shoulder and along the backbone. These areas also have the most compact and coarsest fiber structure.

When tanned in their full thickness, cattleskins are used mostly to make sole leather and industrial belting. In the belly area, the skins are much thinner, and the fiber weave is much more open. Therefore, more flexible leather can be made from the belly area than from the bend (backbone area). In current practice, most cattleskins are split parallel to the surface to produce two or three pieces a little thicker than

calfskins. Because the fiber bundles are larger, this split leather is firmer than the calfskin leathers.

Recent studies (22-24) have shown that there may be some important breed differences in the fibrous structure of the butt area of cattleskins. A defect known as pulpy or mushy texture was detected in leathers produced from some Hereford skins. Vertical sections cut through an affected area of a Hereford skin and the corresponding area of an Angus skin are shown in Figure 3. The Hereford skin on the left shows the typical vertical fiber pattern, while the Angus skin on the right shows the normal angle of weave for the butt area of most cattle. A decreased number of fibers in the horizontal direction of this area has also been demonstrated for the affected Hereford skin.

Horseskins are similar to cattleskins, except that in the butt area there is a region called the shell area where the grain is deeper and the fiber bundles are very small, quite regular and very compactly woven with a high angle of weave. This area yields leather, known as cordovan, which has exceptionally good wearing qualities.

Pigskin leather has a very characteristic appearance with a well-marked grain pattern and perforations which are due to the hair follicles extending through the full thickness of the skin. These perforations tend to make pigskin leathers more porous than other types of leathers. The grain layer is very hard and tough, which makes pigskin leathers very resistant to abrasion. Some of this characteristic is lost when the grain layer is softened by the scalding operation used to remove the hair. The fiber bundles of the corium are loosely woven, which makes these leathers quite flexible and decreases their resistance to tensile strains. The production of pigskin leathers has never been very great because of the difficulty involved in the removal of the skin from the carcass. Mechanical methods for flaying pigskins have been developed, and these are increasing the supply.

Also, snake, lizard, alligator, and other reptilian skins have special surface characteristics which produce interesting surface designs. The collagen structure is usually thin, but the surface structure may make these leathers more rigid than comparable thickness of goat or calfskins. They are used mostly for ornamentation.

With the few types of animal skins described, the tanner is able to make an extremely wide variety of leathers, each tailored to the demands of specific uses. Some of the means used to accomplish this are selection of specific skin areas, splitting the skin to obtain thinner stock and a different surface, and working the leather to increase softness and pliability.

**Area Variations in Skins.** Variations from area to area within a skin can be shown either by microscopic observations or by physical testing. A recent study (25) of the mechanical properties of sheepskins showed that the stress at constant extension varied with position in a pattern similar to that for calf and side leathers. The latter are leathers made from the sides of cattle hides which have been cut down the backbone. The pattern obtained included a bilateral symmetry such that physical and microscopic observations for an area on one side corresponded very closely with the same observations made on the other side. This phenomenon has led to the use of matched paired sides (26) for evaluation of treatments. One side is subjected to a standard treatment, and the matched side is subjected to an experimental treatment. Comparison of the physical properties of the two sides at corresponding areas will give a reliable evaluation of the effect of the experimental treatment. The similarity of patterns from one class of animal to another suggests that the main differences in physical characteristics from area to area are due to organized structural differences

within the skin. It has been shown (27) that the physical properties of collagen fiber bundles do not vary greatly from area to area in a single skin or from skin to skin in the same area. Therefore, the variations in physical properties of skins must be due to the interaction or organization of the fiber bundles in the various areas.

**The Effect of Splitting Upon Leather Properties.** Because the fiber bundles of the grain layer are thinner and the fiber structure is more open, the tensile properties of the grain are weaker (28,29) than those of the more compact central portions of the skin. If part of the grain is removed, the tensile strength of the remaining portion will be increased. Therefore, when making thin leathers it is quite common to buff off an appreciable portion of the grain with very fine sandpaper to obtain a higher tensile strength for the completed leathers. Another effect of splitting is the disruption of the three-dimensional fiber network. This causes a reduction of tensile properties, and the sum of the strength of the two split portions is less than the strength of the unsplit piece. Since the resistance of leather to stretch varies directly with the tensile strength, splitting will also cause a decrease in the resistance to stretching.

**Evidence for Directionally Orientated Structure.** Physical property measurements made in directions parallel and perpendicular to the backbone showed differences (29) which were interpreted to indicate an orientation of the fibrous network from area to area in skins. In general, the greatest strength is parallel to the backbone, and the elongations at break are greater at right angles to the backbone. It has also been shown (30) that the strength and stretch are inversely proportional and that the product of the two for a specimen cut parallel to the backbone equaled the product of the two for a sample cut perpendicular to the backbone. This indicates that most of the stretch measured for leather is due to distortion of the three-dimensional fiber network and not to the elongation of the fiber bundles. A practical result of this interrelationship is that the tensile strength of leather can be increased by removing the residual stretch, either by tanning under tension (31) or, more conveniently, as it is done with belting leather, by stretching the leather after tanning.

**Structural Changes Induced in Leather by Mechanical Action.** The collagen fiber structure which was opened up in the pretanning processes can also become coalesced during the tanning and drying processes. There are two ways that this can happen. The treatments used to dehair, plump, and open up the skin cause some of the fibrils to become slightly hydrolyzed or gelatinized, which gives them a greater tendency to adhere to each other. Also, the vegetable tanning materials which have a strong affinity for collagen can act as cementing agents and bind the fibrils together again. Thus, the effect of opening up of the structure is reversed, and the flexibility and softness of the leather are decreased. To some extent, this cohesion can be overcome by staking the leather. This process causes the leather to be stretched by bending it over a fairly sharp angle with the result that some of the weakly adhering fibrils are broken apart. The staking treatment is repeated until the right degree of suppleness or feel is obtained. Some of the cohesion can also be prevented by the incorporation of lubricants (fat liquors) before the drying process. These materials coat the fibers and reduce their cohesion to each other.

Laboratory investigations have shown that the stiffness values for sole leather depended upon previously mechanical conditioning (32) and that the porosity of heavy leather is increased (33) by flexing. When leather is stretched to some degree short of rupture and the stretching force is released, the leather does not return to its original length but remains partially extended. This phenomenon is called creep,

and the extent of creep is measured as percent set. For leather, the percent set decreases with increasing time of relaxation (34). The set is believed to be due to the reorientation of the individual fiber bundles within the three-dimensional fiber structure to relieve the strain developed in them. This ability to reorient under stress may be the basis for the remarkable resistance of leather to flexural fatigue. Because of the creep phenomenon, all of the stress-strain relationships of leather vary with time and with use (35); therefore, a single static test will not give a good indication of the useful properties of leather.

### **The Effects of Tanning on the Structure of Leather**

We have explained how the dehairing and bating processes used to prepare a skin for tannage can affect the structure and properties of leather. After bating, the skin is usually pickled for storage or to adjust the pH to the desired range for tanning. There are three main types of tannage in use today: mineral, vegetable, and aldehydic. The chief mineral tannage is with chromium salts, but alum and salts of zirconium are sometimes used for special purposes. Vegetable tannages use wood, bark, or leaf extracts containing either derivatives of the esters of phenolic carboxylic acids (hydrolyzable tannins) or derivatives of hydroxybenzophenones or polyhydroxyflavans (condensed tannins) (36). Until recently, the only aldehydic tanning agent of importance was formaldehyde, but lately glutaraldehyde has become commercially available and found (37) to be a good tanning agent. Some amino resins, such as water-soluble urea-formaldehyde resins and melamine-formaldehyde resins are also used in the production of leather. These are discussed in the article AMINO RESINS.

**Mineral Tannages** (38). The mineral tanning agents all come from the metals having a coordination number of six and are capable of forming complex ions with six neutral molecules or anions. The tanning action of chromium salts depends upon the pH, basicity, concentration of the tanning solution, and the nature and amount of the anions present. The fixation of chromium increases with increasing pH. It is common to start tanning with a low pH and gradually raise this to about 4.5 during the tannage. Although the chromium-tanning solutions may contain some large aggregates of the chromium complexes, they do not generally cause a filling of the pores of the leather. Chromium leathers contain only from 2 to 7% chromium oxide. In general, with increasing chromium content, the leathers progress from the softer, stretchier types used for gloves to the fuller, more solid leathers. Leathers with lower chromium content are stiffer, and increased amounts of oil or grease are required to obtain the maximum softness. One of the characteristic properties of chrome leathers is nonwettability.

**Vegetable Tannages** (39). The vegetable tanning extracts contain a wide range of particle sizes. It is not known whether these aggregates are in equilibrium. The size of the aggregates limits the rate of diffusion of the tanning materials. Therefore, vegetable tanning usually requires considerable time. Diffusion can also be limited by a case-hardening phenomenon if high concentrations of tannins are used initially. Thick sole leather in weak tanning liquors would require about twelve months. The tannage can be speeded by using more concentrated tanning solutions and by various methods of rocking, paddling, or drumming of the skins. Thick skins are usually tanned first with weak liquors to aid penetration. The concentration of tanning agent is gradually increased in a countercurrent flow system, then rather strong tanning solutions finish the tanning. Usually the last tanning steps are carried out at elevated

temperature (about 95 to 100°F) for five to seven days. The desired firmness is not obtained below 95°F. The total time for heavy leather is more than twenty days. Thinner skins are tanned more rapidly and usually in a drum. If heavy skins are drummed during vegetable tanning, the leather will be thicker, softer, and weaker than similar skins tanned in pits. This effect is not as pronounced in lightweight skins. The fullness of vegetable-tanned leather can be controlled to some extent by the pH and salt concentration. Low pH gives a firmer, redder leather, and increases in salts produces a softer, yellower leather. There is a minimum pH of about 3.0 below which the acid causes the fibrous structure to swell enough to prevent the penetration of the tanning materials. Above pH 5.0, some unevenness of color can be expected. The concentration of salts is usually 300 meq/liter, and much of this comes from the tanning extract itself. Vegetable tanning fills the leather much more than chromium tanning. The tannin content of most vegetable-tanned leathers is between 30 and 50% of the hide substance present.

**Aldehyde Tannage (40).** The only commercial tannages based on aldehydes use either formaldehyde or glutaraldehyde. They are quite rapid and are usually carried out in a drum. The ingredients for formaldehyde tannage, calculated on the weight of pickled hide used, are: 100% water, 4% Glauber's salt, and 6 to 12% formalin (37% formaldehyde). The starting pH is about 2, and the pH is raised gradually to about 6.8. The tannage is usually finished at an elevated temperature of about 95°F. Reactions at low pH do not give much plumpness to the leather but do give a greater area. Formaldehyde-tanned leathers are quite stretchable, and their primary use is in the manufacture of gloves. Glutaraldehyde-tanned leathers are made by a similar procedure and have similar properties, but in addition they possess greater fullness, mellowness, washability, and a resistance to deterioration by perspiration.

**Combination Tannages.** Many of the above tannages can be used in combination (41), usually by a process called retannage. Thus, chromium-tanned leather can be retanned with vegetable-tanning materials to produce a greater fullness and firmness. In most cases, the combination tannage emphasizes the desirable qualities of each separate tannage and minimizes the undesirable qualities.

### **Effects of Lubricants and Impregnants on Structure**

**Lubricants.** One of the important ingredients of leather is the fat liquor or lubricant which is added after tanning (42). This material, which is usually an oil or grease containing emulsifying agents and sulfonated oils, coats the fibers, enabling them to slide past each other. This enables leather to adjust more easily to relieve strains imposed upon it. This makes leather more flexible and also stronger because the fibers are able to align themselves to a greater extent in the direction of the stress. Addition of lubricants increases the strength only to a definite maximum, and additional lubricants produce no effect.

Lubricants can be distributed unevenly and, when in excess, tend to predominate in the grain and flesh sides of the leather where the greatest amount of pore space exists. When too much lubricant is used, the excess may eventually rise to the surface and cause a fogging deposit called spue. A limited amount of lubricant applied only to the surfaces of the leather will produce a tighter, firmer piece of leather.

**Impregnants.** Materials like rubber, polyisobutylene, silicone resins, acrylic plastics, and even excess vegetable tanning materials have been used to fill up the void spaces in the surfaces of leather. Each of these has some effect toward decreasing

the penetration of water or oils into leather and increasing the resistance to abrasion and wear. They generally make leather firmer, less elastic, and less flexible.

The incorporation of plastic compositions at specific locations (17,43,44) within a hide have been successful in making loose leather firmer and fuller. Thus, it is possible to alter the properties of leather in specific ways and places by introducing and condensing within localized areas organic compounds such as isocyanates, acrylic polymers, and amino resins.

### Bibliography

1. J. H. Bowes and A. S. Raistrick, *J. Soc. Leather Trades' Chemists* **50**, 181 (1966).
2. A. L. Everett and T. C. Cordon, *J. Am. Leather Chemists' Assoc.* **53**, 548-567 (1958).
3. W. T. Roddy, in F. O'Flaherty, W. T. Roddy, and R. M. Lollar, eds., *Chemistry and Technology of Leather*, American Chemical Society Monograph 134, Reinhold Publishing Corp., New York, 1956, Vol. 1, Chap. 2.
4. R. L. Stubbings and E. R. Theis, *J. Am. Leather Chemists' Assoc.* **45**, 138 (1950).
5. E. F. Mellon, S. J. Viola, A. H. Korn, and J. Naghski, *J. Am. Leather Chemists' Assoc.* **54**, 182 (1959).
6. E. F. Mellon, S. J. Viola, and J. Naghski, *J. Am. Leather Chemists' Assoc.* **55**, 622 (1960).
7. E. F. Mellon, M. C. Audsley, S. J. Viola, and J. Naghski, *J. Am. Leather Chemists' Assoc.* **58**, 514 (1963).
8. R. R. Stromberg and M. Swerdlow, *J. Am. Leather Chemists' Assoc.* **50**, 336 (1955).
9. H. B. Merrill, *J. Am. Leather Chemists' Assoc.* **27**, 201 (1932).
10. B. Roll, *J. Am. Leather Chemists' Assoc.* **47**, 40 (1952).
11. C. C. Kritzing and E. R. Theis, *J. Am. Leather Chemists' Assoc.* **43**, 379 (1948).
12. N. D. Cheronis, A. Kowitz, C. Chamales, R. Larson, E. Newbury, G. Tripp, F. MacArtor, P. Arvan, E. Gustus, P. Wildman, and M. Andler, *J. Am. Leather Chemists' Assoc.* **44**, 282 (1949).
13. K. H. Gustavson, *J. Am. Leather Chemists' Assoc.* **34**, 444 (1939).
14. E. R. Theis and C. L. Weidner, *J. Am. Leather Chemists' Assoc.* **33**, 581 (1938).
15. W. Montagna and R. A. Ellis, *The Biology of Hair Growth*, Academic Press, Inc., New York, (1958).
16. A. L. Everett, H. J. Willard, and J. Naghski, *J. Am. Leather Chemists' Assoc.* **61**, 112 (1966).
17. R. M. Reihsmann and E. K. Fugikawa, *J. Am. Leather Chemists' Assoc.* **61**, 468 (1966).
18. S. R. Hoover, S. J. Viola, A. H. Korn, and E. F. Mellon, *Science* **121**, 672 (1955).
19. E. F. Mellon and A. H. Korn, *J. Am. Leather Chemists' Assoc.* **51**, 469 (1956).
20. C. L. Ornes, W. T. Roddy, and E. F. Mellon, *J. Am. Leather Chemists' Assoc.*, **55**, 600 (1960).
21. G. O. Conabere, in *Progress in Leather Science 1920-1945*, British Leather Manufacturers' Research Association, London, 1948, Chap. 2; also *J. Intern. Soc. Leather Trades' Chemists* **28**, 3 (1944).
22. A. L. Everett and R. J. Carroll, *Leather Mfr.* **82** (8), 29 (1965).
23. A. L. Everett, H. J. Willard, and W. Windus, *J. Am. Leather Chemists' Assoc.* **62**, 25 (1967).
24. J. J. Tancous, R. Schmitt, and W. Windus, *J. Am. Leather Chemists' Assoc.* **62**, 4 (1967).
25. J. G. Poulter and A. G. Ward, *J. Soc. Leather Trades' Chemists* **50**, 130 (1966).
26. H. J. Hodus and R. Stubbings, *J. Am. Leather Chemists' Assoc.* **52**, 414 (1957).
27. J. Menkart, J. H. Dillon, K. Beurling, J. G. Fee, and E. F. Mellon, *J. Am. Leather Chemists' Assoc.* **57**, 318 (1962).
28. J. A. Wilson and E. J. Kern, *Ind. Eng. Chem.* **18**, 312 (1926).
29. J. R. Kanagy, W. H. Leser, E. B. Randall, T. J. Carter, and C. W. Mann, *J. Am. Leather Chemists' Assoc.* **47**, 329 (1952).
30. J. R. Kanagy, *J. Am. Leather Chemists' Assoc.* **50**, 112 (1955).
31. L. Seligsberger, C. W. Mann, and H. Clayton, *J. Am. Leather Chemists' Assoc.* **55**, 687 (1960).
32. L. P. Witnaer and W. E. Palm, *J. Am. Leather Chemists' Assoc.* **59**, 246 (1964).
33. W. T. Roddy and F. O'Flaherty, *J. Am. Leather Chemists' Assoc.* **42**, 190-195 (1947).
34. J. G. Butlin, *J. Soc. Leather Trades' Chemists* **47**, 3 (1963).
35. M. Maeser, in F. O'Flaherty, W. T. Roddy, and R. M. Lollar, eds., *Chemistry and Technology of Leather*, Vol. 4, Reinhold Publishing Corp., New York, 1965, Chap. 62.

36. R. Ghosh in Ref. 21, Chap. 11.
37. M. L. Fein, E. H. Harris, Jr., J. Naghski, and E. M. Filachione, *J. Am. Leather Chemists' Assoc.* **54**, 488 (1959).
38. E. B. Thorstensen, in F. O'Flaherty, W. T. Roddy, and R. M. Lollar, eds., *Chemistry and Technology of Leather*, Vol. 2, Reinhold Publishing Corp., New York, 1958, Chap. 22.
39. A. N. Kay in Ref. 38, Chap. 19.
40. E. F. Mellon in Ref. 38, Chap. 17.
41. G. A. Butz in Ref. 38, Chap. 29.
42. M. H. Battles in F. O'Flaherty, W. T. Roddy, and R. M. Lollar, eds., *Chemistry and Technology of Leather*, Vol. 3, Reinhold Publishing Corp., New York, 1962, Chap. 34.
43. P. R. Buechler, *Leather Mfr.* **73** (2), 19 (1961).
44. J. A. Lowell and P. R. Buechler, *J. Am. Leather Chemists' Assoc.* **60**, 519 (1965).

*Edward F. Mellon*  
Eastern Regional Research Laboratory  
U.S. Department of Agriculture