

LADDER AND SPIRO POLYMERS. See Index Volume.

LEATHER

Prehistoric humans learned to make leather by preserving hides and skins with juices extracted from plants. From that time on, leather has provided footwear, garments, shelter, and other articles affording protection, comfort, durability, and aesthetic properties available from no other natural product. Despite many attempts, no synthetic material has been produced to date to match all the properties of leather. The demand for leather exceeds the supply and the principal function of substitutes is to fill those needs for which the supply of leather is inadequate.

The unique physical properties of leather make it ideally suited for the manufacture of a variety of products, most notably footwear. Large variations can be found in the physical properties of leather made from different species of animal hides or skins (1). Similarly, variations in processing of a type of hide can also produce very different properties for specific end uses. Even when leather is manufactured for a single use, eg, shoe uppers, a variation in properties is desirable to allow for differences between casual, military, work, or dress shoes. Values for various physical properties of cattlehide shoe upper leather are shown in Table 1. Heat resistance and shrinkage depend on moisture content; leather without any moisture decomposes at 160–165°C (10).

The most important property of leather is its unmatched ability to provide comfort in footwear, partly because of its unique ability to conform to the shape of the foot. Feet varying widely in shapes and sizes are able to fit comfortably into standard shoes because leather gives at points of pressure. The physical properties of leather that provide a balance between plastic and elastic flow are responsible for this property. Plastic flow imparts the necessary flexibility to provide foot comfort. Elastic flow allows the maintenance of shape by ensuring proper recovery during flexing action.

The other unique property of leather is its ability to dissipate moisture produced by perspiration (9,11–15). The mechanism of the transmission of water vapor through leather is a function of the material rather than a linear diffusion process (16–17). Water is sorbed by polar groups in the protein molecules and conducted by an activated diffusion process along the fibers, even against air pressure. Transmission of water vapor through leather is affected by filling the

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Table 1. Physical Properties of Shoe Upper Leather

Property	Range	Representative value	References
tensile strength, MPa ^a	15.26–37.48	27.6	2–4
elongation at break, %	29.5–73.0	40	2–4
stitch tear strength, N/cm ^b	1280–2275	1751	2,3–6
tongue tear strength, N/cm ^b	226–961	525	2,4
thickness, mm	1.5–2.4	1.8	3,5
bursting strength, kN/cm ^b	1.10–24.5	17.5	2,3,5
grain cracking, N/cm ^b	525–1489	1051	2,3,5
wet shrinkage temperature ^c , °C	96–120	100	5,7
apparent density, g/cm ³	0.6–0.9	0.75	1,3
real density, g/cm ³	1.4–1.6	1.5	1,3
flexibility (Flexometer)			
bending length, cm	6–9	7	3
flexural rigidity, mg/cm	10,000–50,000	20,000	3
bending modulus, MPa ^a	19.7–68.9	34.5	3
compression modulus, MPa ^a		0.345	3
cold resistance ^d , K		92 ^e	8
Temper of chrome side leather (butt)			
flexibility factor, g		400	9
recovery, %		57	9
resilience, %		21	9

^a To convert MPa to psi, multiply by 145.

^b To convert N/cm to lbf/ft, divide by 14.6.

^c Chrome-tanned leather values.

^d Ordinarily limited by finish-crack or lubricant hardening properties.

^e Workable without cracking in the absence of finish or fat liquor.

interstices of the leather with grease or other materials. Filling often causes a change in air permeability of as much as ca 200 to 1 while causing a change in water-vapor permeability of only ca 2 to 1. No leather substitute has this combination of properties.

Raw Materials

Most hides and skins used as raw material for leather manufacture are by-products of the meat industry. The supply of raw material bears no relationship to the demand for leather and leather goods. Although the supply of hides and skins worldwide has been increasing, their availability on the world market has decreased. Many countries do not permit the free export of hides and skins, preferring to encourage the export of higher value leather and leather goods. In the United States the demand for red meat has declined over the past decade and with it the supply of cattlehides. Decreasing raw material supplies and increasing growth of the consumer-goods industries, demanding more leather for footwear, gloves, luggage, handbags, small personal leather goods, upholstery, and garments, have combined to make cattlehides a valuable commodity.

Chemical Composition. Fresh cattlehides, like most biological materials, contain 65–70% water, 30–35% dry substance, and <1% ash. The dry substance is largely made up of the fibrous proteins collagen, keratin, elastin, and reticulin.

Collagen (qv) is ubiquitous in the animal kingdom, with a unique amino

acid composition and physical properties. Collagen is responsible for the strength and toughness of the raw hide and of the leather made from it. It is the principal component of connective tissue: changes in collagen structure have been postulated to be related to the aging process. A great deal of research has been carried out regarding the structure and function of collagen, and a number of reviews have been published (18–26). Leathermaking could be described as a series of collagen-purification steps followed by tanning.

Keratin (qv) is the sole protein component of hair and the second most common protein in the hide. Depending on the age of the animal and season of the year, keratin may constitute 6–10% of the total protein. One of the first steps in the manufacture of most leather is removal of hair (keratin) from the hide.

Smaller amounts of other proteins are also present in the hide. Myosin, a muscle protein, is found in the *erector pili* muscle in the grain layer. Elastin is the primary protein, other than collagen, present in the grain layer. Another class of proteins, the proteoglycans, are found in the corium in small amounts. Recent research indicates that, although small in amount, these proteoglycans and associated smaller molecules such as dermatan sulfate and hyaluronic acid may have a great deal of influence on the tanning process (27). The grain layer also contains a small amount of carbohydrates in the form of polysaccharides associated with glycoproteins and proteoglycans.

Lipids are present in the grain layer to the extent of about 9% based on dry weight. The corium layer may contain from 1 to 11% lipids. Diet and age seem to correlate with the presence of fat cells in the corium.

Microstructure. The skin forms a tough, protective, thermal blanket on the living animal and provides the raw material for leather. Microscopic examination reveals the physical structure that is responsible for the skin's unique properties (Fig. 1). In general, mammalian skins are composed of a dense, interwoven, fibrous mat in the center (dermis, including grain and corium); a thin, cellular outer layer (epidermis) with protruding hairs; and a loose, fatty, inner (subcutaneous) layer attached to underlying muscles. The looseness of the inner layer facilitates mechanical removal (flaying) of the skin in the slaughterhouse. An excellent review of skin structure and defects of skin found on cattle and pigs is given in Ref. 28.

The dermis of most animals commonly used as raw material for leather is composed of two layers with distinctly different structures. The upper portion, which includes the entire length of the hair follicles in most species, is called the grain layer by tanners. The pigskin is an exception to this because its hair follicles extend through the entire thickness of the dermis. The dermis serves protective, sensory, and excretory functions in the living animal as well as a control of the skin temperature by increasing or decreasing evaporative cooling at the surface. At the junction of epidermis and dermis, there is a coarse basement membrane that, after separation of the epidermis, becomes the grain surface (enamel) of leather. The grain layer also contains a network of small blood vessels and cap-

Fig. 1. Cross section of cowhide showing subdivision into four principal layers. The dermis, which includes the grain and corium layers, becomes the fibrous substance of leather.



Epidermis

Grain layer
(papillary)

Corium layer
(reticular)

Flesh layer
(subcutaneous)

0.5mm

illaries. Interwoven among these cellular components is a three-dimensional mat of thin collagen fibers that becomes the leather substance. Interspersed among these fibers, especially in the upper half of the layer, are thinner, elastic, tissue fibers that are arranged mostly parallel to the surface. When the cellular structures have been decomposed by chemical processing, the resultant fibrous mat has many voids and a reduced density. Defects in the grain, whether natural or synthetic, have a detrimental effect on leather quality (29).

The corium is a much simpler structure than the grain layer and is composed mostly of thick bundles of collagen fibers. These bundles are interwoven in a random, three-dimensional pattern, but the angle of weave in a vertical direction tends to vary with animal species and especially with location on the body. The excellent strength and stretch properties of leather depend largely on corium fibers and their prevailing orientation. In certain cattle breeds, defects in the fiber orientation can lead to a condition known as vertical fiber defect. Leather made from hides with this genetic defect has a lower physical strength than leather from normal hides (30,31). There also are some scattered blood vessels and elastic tissue fibers in the corium layer and variable fat deposits in animals that were fed intensively. In fresh skin, the dermal structures are embedded in a semifluid gel or ground substance. Chemical processing opens fine spaces between fibers but otherwise does not alter the gross physical structure of the corium as it does the grain layer.

At the molecular level, collagen is synthesized in the dermis by elongated cells called fibroblasts. The collagen molecules aggregate into fibrils and then into fibers. Fibrils are extremely small and can only be visualized with the aid of an electron microscope. Figure 2 (32) shows a thin section of cowhide at high



Fig. 2. Electron micrograph (ca $\times 17,000$) of hide cross section showing, at upper right, longitudinal collagen fibrils with typical striations and elsewhere a cross section of fibrils comprising two small fibers (32).

magnification. Fibrils, with their characteristic cross striations, can be seen in one corner; other fibrils are seen in cross-section as they are organized into two small fibers. Although mammalian skins are generally similar, the variations in hair density and surface texture of the skin are responsible for the characteristic appearance of leather made from different animals. These differences add to the aesthetic appeal and variety of leather (33–35).

Manufacture and Processing

Conversion of a raw hide into leather takes place in three distinct phases. Historically, the first phase takes place in the beam house, where the hair is removed and the hide prepared for tanning. The beam house is so named because this part of the process was carried out by hand with the skin draped over a wooden beam. Tanning, the second phase, was originally done outdoors in pits containing vegetable tannin extracts. This area was called the tan yard. Today leather is tanned in large drums or mixers, containing hundreds of hides, with chromium as the primary tanning agent. Only a small percentage is tanned with vegetable tannins. Finishing, the last phase, was developed much later to protect the grain surface of the hide and enhance its appearance. Although methods have changed greatly, areas called the beam house and tan yard still exist in modern tanneries. Additional technical information about the leather manufacturing process can be found in the several general references that describe modern tanning practices in detail (1,36–40).

Hides can be processed into leather immediately on removal from the animal, although this is not generally done. Once a hide or skin is removed from an animal, deterioration begins immediately. Efforts to preserve the hide and prevent this deterioration from affecting the leather must be started within a few hours after slaughter. The hide is usually cured in brine or salt, which provides a satisfactory preservation from the time it is taken from the animal until the tanner is ready to begin processing it into leather. Salt curing has several disadvantages that are related to effluent pollution and the corrosive nature of concentrated salt solutions. As a result, a wide variety of alternative preservation methods have been investigated (41–48); however, none has been adopted commercially on a large scale.

Salt-cured hides, as received by the tanner, contain as much as 14% of their weight as salt. A fresh hide contains ca 64% water; after brine curing it contains ca 45% water and 41% protein, only two-thirds of which is leather-making collagen. The tanner first removes the salt and rehydrates the fibers by soaking the hide. A detergent usually is added to speed hydration. The soaking procedure also removes water-soluble proteins and washes the hide free of manure and dirt.

The soaking stage is followed immediately by the hair removal process. Hair is entirely made up of the protein keratin. This protein contains a large number of sulfur-containing amino acids, mainly cystine. The cross-links of cystine disulfide stabilize the protein molecules, resulting in a stable hair fiber. Hair is removed by a saturated solution of calcium hydroxide (lime) alone or in combination with a sharpening agent such as sodium sulfhydrylate. The lime removes the hair by dissolving the substance in the hair follicle that holds the hair in the

hide. This treatment, referred to as a hair-save process, leaves the hair fiber intact. To loosen hair in cattlehides using only lime requires from 5 to 7 days.

More commonly, a mixture of lime and sodium sulfide is employed. At high pH sulfide ions rapidly rupture the disulfide linkages between keratin molecules, causing the hair fibers to disintegrate. This procedure, referred to as a hair-burn process, takes 4–6 h. Almost all side-leather and upholstery-leather tanners use the hair-burn process. The hair-save process is used primarily in vegetable tanneries. The effluent from the sulfide process must be treated before discharge into a public wastewater treatment facility to prevent the release of dangerous quantities of hydrogen sulfide. As a result, several alternative processes have been studied, including enzyme unhairing (49–53), to reduce or eliminate sulfide unhairing (54–61). In most tanneries, the relatively brief unhairing step is followed by a longer (4–16-h) liming step. The spent unhairing liquors containing the dissolved hair are drained from the hides and a fresh saturated lime solution is added. The action of lime loosens the hair and opens the collagen fiber structure. Collagen swells in 8–48 h if the pH is on the acidic or basic side of the isoelectric point. This swelling leads to subsequent fiber separation and allows rapid penetration of tanning chemicals. Additional proteins are also removed in the liming stage, and some hydrolysis of amide side chains of the collagen to acid groups takes place. This aids the tanning reaction because the acid groups are the primary binding sites for chromium tanning agents.

The liming step is followed by delimiting and bating. The hide is washed to remove soluble lime and hair particles. At this point the stock has a pH of 12.5. The most widely used delimiting salt is ammonium sulfate. It lowers the pH to 8–9, the optimum range for enzyme action. The bate is often a preparation of pancreatic enzymes that are usually absorbed on sawdust. The most effective enzymes are proteases, which break down miscellaneous proteins. Bating is usually short, ie, ca 1–4 h. Ammonium sulfate has the disadvantage of increasing the amount of ammonia nitrogen in the tannery effluent. In many areas of the United States, direct discharge of ammonia is strictly regulated. Other delimiting salts have been proposed to solve this problem (62,63).

Immediately after bating, the hides are pickled with sulfuric acid to lower the pH to 1–2. Sodium chloride is added at the same time to prevent acid swelling. Complete pickling requires at least 2 h. The addition of a strong acid to aqueous solutions generates heat, and care must be taken to prevent denaturation of the collagen. Once the hide is in the acid condition, it is ready for tanning.

Chrome Tanning. The primary function of a tanning agent is to stabilize the collagen fibers so that they are no longer biodegradable. At the turn of the century almost all leather was tanned with vegetable extracts. In contrast, 95% of all the leather manufactured in the United States today is chrome-tanned (64,65). At a pH of 2.8, the chromium sulfate is soluble and does not react with hide proteins. After the tanning solution has been allowed to fully penetrate the hide, the pH is raised slowly with sodium bicarbonate. At pH 3.4–3.6, the chrome has reacted with the collagen, producing a fully tanned hide. At this point, the hide is said to be “in the blue.” Although specific procedures are followed in the beam house for a particular type of finished leather, the blue stage allows many options for the following phases of leather manufacture.

The tanned hides are run through a wringer to reduce the moisture level

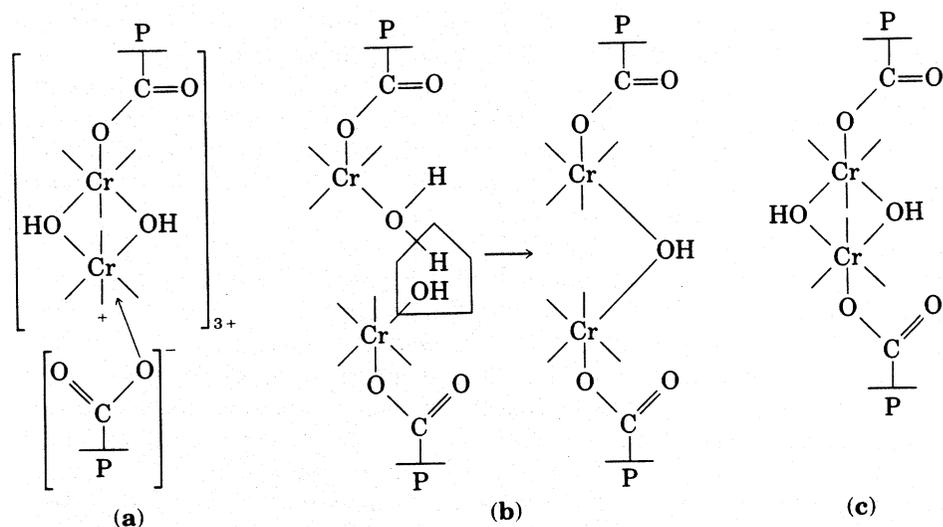


Fig. 3. Cross-link formation from chromium complexes (P = protein). (a) Complexing; (b) olation; (c) oxalation.

hydronium ions are released and highly stable oxalate bridges are formed (Fig. 3c).

Similar coordination complexes are involved in other mineral tannages. These complexes can be reversed or modified by acids, salts, strong bases, and chelating agents. Chromium complexes, although more difficult to form, have the advantage over other complexing cations of reacting much more slowly in these ligand replacement reactions. Thus chrome-tanned leather is more stable and serviceable in use. Trivalent chromium is also unique in its resistance to oxidation.

Vegetable Tanning. Vegetable tanning has decreased in importance in the United States. Sole leather, by far the main use for vegetable-tanned leather, has been replaced by synthetics in all but the most expensive shoes. Leathers made with a full vegetable tannage are also used for machinery belting, saddles, upholstery, lining, and luggage (72,73). Vegetable tanning produces a fullness and resilience characteristic of only this type of tannage. It has excellent molding characteristics allowing, for example, in sole leather, adaptation to the shape of the foot. Vegetable-tanned leathers have good strength and dimensional stability and are still used in power-transmission belts. Because of their hydrophilicity, vegetable-tanned shoe linings absorb perspiration efficiently.

Vegetable tannins are water-soluble materials extracted from different parts of certain plants, including the wood, bark, leaves, fruits, pods, and roots. Some sources contain up to 20% tannin. The extraction process yields a mixture of tannins and nontannins: the higher the tannin content, the more valuable the extract. The tannin content is analyzed by an empirical method involving the reaction of the extract with a specially prepared hide powder under specified conditions. In general, the hide is prepared for vegetable tannage in the same way as for chrome tannage. Hair is removed by lime, but in a much slower process requiring as many as five days. The hides are first exposed to saturated solutions of lime for one day and then moved into pits containing small amounts of sodium

sulfide. Initial exposure of the keratin to the alkali in the absence of sulfide ions produces a reaction known as immunization. The cystinyl disulfide linkages in the keratin are converted to thiol groups (lanthionyl), providing a much more stable cross-link (74). The resulting hair is much more resistant to chemical attack than the nonimmunized fiber. After five days, the epidermis and hair have been loosened from the follicles and can be readily scraped mechanically from the hide. This lengthy liming and dehairing step is necessary to open the hide fibers for penetration by the vegetable tannins.

The hides are then mechanically fleshed and returned to vats where they are chemically delimed with ammonium sulfate and bated with pancreatic enzymes. After adjusting the hide pH to about 5, they are tied to frames and slowly lowered into vats containing a weak tannin solution and gently agitated. Over a period of three weeks the frames are moved through a series of vegetable tannin solutions of increasing strengths. In this way slow, complete penetration of the hide is accomplished without surface accumulation of tannins (case hardening). The tanning liquors normally contain phenolic syntans (synthetic tannins) for color control and naphthalene syntans for sludge dispersion.

A more rapid, minimum-effluent, vegetable-tanning system is known as the Liritan process (75). The limed and bated hides are treated for 24 h in a pit containing 5% sodium hexametaphosphate (Calgon) solution and sufficient sulfuric acid for a pH of 2.8. This part of the process has become known as the Calgon pickle. The solution is reused daily, being regenerated with additional Calgon and sulfuric acid, and is discarded only once a year. The treatment presumably prepares the hides for a more rapid vegetable-tanning process. The recommended tanning agent is wattle (mimosa), requiring only 11 days to complete. Again, the tannin liquors are recirculated and reused. Leathers that have been prepared by the Liritan process are finished in the same way as those prepared by conventional processes. First introduced in 1960, the Liritan process has spread throughout the world and is used by the major U.S. vegetable-leather tanners.

Functionally, vegetable tannins are polyphenolic compounds. They are divided into hydrolyzable and condensed tannins. The former are pyrogallol derivatives that dissolve when boiled in dilute mineral acids. Chestnut and myrobalan are typical examples. The latter are catechol derivatives that undergo condensation reactions when heated with mineral acids, thereby producing precipitates. Hemlock and wattle are in this category.

Most likely no cross-linking of the protein, other than by the formation of hydrogen bonds, takes place as a result of vegetable tanning (76). The large amounts of tannin used produce a coating on the fibers and fill the voids of the leather. In some cases, as much as 50% by weight of tannin is incorporated into the hide.

Other Tanning Agents. Chrome and vegetable tannages have considerably greater commercial importance than those considered below. Most of these tannages provide a pretreatment or posttreatment for chrome or vegetable processes and are employed to confer specific properties to the final leather product, depending on its ultimate use, ranging from soft garment to firm boot leather. They are only rarely used alone.

Minerals. The principal mineral tannage other than chromium is zirconium tannage (77,78), used to produce white leather. Aluminum tannage requires

a very low initial pH and large quantities of neutral salt to repress both swelling and rapid flocculation of aluminum salts as the pH is raised. This type of tannage results in leathers that tend to dry out and become hard and horny unless large amounts of salt are used; even then, the leather tends to be flat and papery to the touch. Aluminum tannage is best used in combination with other tannages such as vegetable tannins. Such combination tannages are being used more, as solid wastes from chrome-tanning become increasingly regulated (79–84).

Syntans. Syntans are used extensively in combination tannages, usually following chrome tannage. They provide control of leather fullness, area yield, color, and electrical charge. The last affects dyeing and fat-liquoring operations. In an attempt to improve the efficiency of chrome utilization, an organic pretan has been introduced to be followed by chrome (85–88). In addition, several organic tannages have been proposed as alternatives to chrome tanning (89,90).

Oil Tannage. Oil tanning produces leathers with unique characteristics (91). Oil-tanned chamois leather is very soft and stretchy and readily absorbs water, which can be squeezed out so the chamois can be used over and over again. It also absorbs grease, making it an ideal material for cleaning glass windows and spectacles. The softness and suppleness imparted by oil tannage make it ideal for tanning furs.

Aldehyde Tannage. Only two aldehydes have commercial use as tanning agents, formaldehyde and glutaraldehyde. They are always used in conjunction with some other tanning agent, usually chromium, except for the tanning of light-colored glove leathers (36). The functional group in proteins that reacts with aldehydes to form cross-links is the primary amino group of protein side chains of lysinyl residues. Details concerning the reactions that take place between the aldehydes and the protein amino groups are not known. Formaldehyde forms cross-links that are ruptured easily by simple hydrolysis, whereas glutaraldehyde forms stable cross-links resistant even to strong acid. Thus there is a considerable difference in the stabilities of the two tannages. Furthermore, formaldehyde tannage yields a white leather, whereas glutaraldehyde tannage produces a light-tan leather. When these aldehydes are used with other tanning agents, the final color depends on the additional tanning agent. The combination of formaldehyde and aluminum produces a white leather.

Glutaraldehyde is most frequently used for additional tannage of chrome-tanned leather; highly stable cross-links are formed in the protein (92). Although numerous investigations of the nature of these cross-links have been made, they remain obscure. The stability of this tannage to hydrolytic conditions has led to its use in the production of leathers with improved resistance to hot soap solutions, perspiration, and alkalis. For example, leather for gloves, garments, work shoes, and nurses' shoes is frequently made by tanning chrome-tanned leather with glutaraldehyde.

Posttreatment. It is easier to control the final properties of leather at this stage of processing, where color, retanning, and fat-liquoring (CRF) occur, than at any other. Leather can be prepared with physical properties ranging from soft and supple for high fashion clothing to firm and stiff for use in the manufacture of men's work shoes and boots. Through the use of different retanning materials, dyes, and fat liquors, a wide variety of leathers is available to meet the demands of the market.

The binding of CRF components, which are generally anionic, to leather is due to their interaction with the cationic sites on the chrome-tanned leather. The sequence of application of the dyes, retanning agents, and fat liquors is important. As each is added, the cationic character of the leather is reduced, thus modifying the affinity of the leather for the next chemical added.

The acidic chrome-tanned, split, and shaved stock is transferred to a drum where it is neutralized to the desired pH. Freshly chrome-tanned leather is highly cationic because its pH is well below the isoelectric point of the collagen. When the stock is neutralized, the surface charge on the protein is reduced. Subsequent CRF steps may be carried out in rapid succession in the same drum.

Retanning materials are used primarily to fill voids within the stock and produce a firm, full piece of leather. Otherwise, the final product may feel more like paper than leather. Retannage also affects the surface charge. The natural vegetable tannins and polyphenolic syntans are anionic in character. With heavy vegetable tanning, the leather composite becomes anionic and may require basic dyes. Vegetable retanning agents increase fullness and temper, and the ability to be tooled. Mimosa, quebracho, and chestnut tannins are the preferred vegetable tannins today. Synthetic retanning agents based on phenol-sulfuric acid complexes have tanning properties of their own. A variety of these agents are commercially available for improving lightfastness and for producing a wide variety of softness and fullness in leather. Resin retannages, based on urea, melamine, or dicyanamide formaldehyde condensates, are cationic in nature, resulting in limited penetration of dyes and strong surface shades.

Fat-liquoring is the application of oil-in-water emulsions to the leather. Its principal function is to reduce the amount of fiber cohesion during the drying process. Lubrication of the leather is an important but secondary effect. Fat-liquoring usually follows dyeing but some tanneries apply them simultaneously rather than in rapid succession (1,36,37). The oil emulsions are usually drummed in at elevated temperatures. The oils are animal or vegetable in origin and of relatively low iodine number; cod and other marine oils are sometimes included in minor amounts. Fat-liquoring emulsions may be anionic, nonionic, or cationic. Anionic fat liquors are prepared from mixtures of sulfated or sulfonated oils with raw oils. Cationic fat-liquors contain alkylated long-chain amines blended with raw oils. The surface-active character of most fat liquors helps level the dyeing of the leather.

Dyeing. The dyeing of leather is an art unto itself. Color is a complicated phenomenon, and coloring leather is particularly complicated because leather is not a uniform substrate.

The most important characteristic of a leather dye is its leveling power. The surface of leather often contains some areas that absorb dye more readily than others. Dyes that accentuate this difference are unsuitable for leather. The most useful dyes minimize this effect, and are referred to as leveling dyes. These dyes tend to be those able to penetrate leather rapidly. Strongly emulsifying fat liquors can be used as auxiliary agents to improve leveling. Anionic auxiliaries improve the ability of the dye to adhere uniformly to the leather surface but tend to reduce the shade. Most dyestuffs are anionic and thus the previous treatment of the leather with retanning agents and fat liquor weakens the attachment of the dye to the leather. This is one reason for the simultaneous addition of fat liquor

and dye. Dyestuffs are generally more soluble at higher pH and this property is used to obtain penetration of the dye beyond the surface. The dye is then fixed to the leather by reducing the pH. Different dye shades are obtained by offering different concentrations of the dye, from 0.5% to 3% based on the weight of the leather.

Drying. After all of the wet operations have been completed, the leather is dried. This involves removal of excess water and completes the reactions of hide with the tanning agents, fat liquors, and dyes (36,93,94). The water is first removed from the surface and then from within the leather fibers by controlled diffusion. If dried too rapidly, the surface becomes dehydrated and hard, preventing interior moisture from escaping. This is called case-hardening. The surface cannot be rewetted completely. Thus, the drying operation must be carefully controlled. A criterion of good tannage is a leather that is soft when dry. The extent of softness depends on the tannage, retannage, and fat liquors used. Even so, drying must be done under carefully controlled conditions of temperature, humidity, and air circulation.

The oldest method is air-drying by hanging the hides and skins on supports in drying chambers in which the temperature and humidity are kept relatively constant to control moisture removal. Since the hides and skins are not held taut, they shrink. This can be minimized by mechanically stretching the hide and holding it in place by tacking it flat to a board or on a screen with toggle clamps. The frames containing the wet hides and skins are then placed in drying units. In another method, the hides or skins are pasted, grain-side down, to plates of glass or porcelain. The plates are mounted on tracks that move into and out of large drying units. The leather dries from the flesh side only and a smoother, flatter grain is achieved.

A more recent method is vacuum drying. The hides and skins are spread out, grain-side down, on a smooth, highly polished, heated, stainless steel plate that is carefully temperature-controlled. A cover is lowered and sealed over the plate and the space between is evacuated. This method permits rapid drying with few problems of product quality because the moisture content can be controlled much more accurately than by other methods.

Finishing. Uniformity is of prime importance in any leather product. Individual skins vary in thickness, angle of fiber weave (95), and natural defects, not only from animal to animal, but from area to area in one piece of skin. The leather manufacturer minimizes these differences by splitting and shaving the leathers to uniform thicknesses, tanning and filling the voids in looser-structured flanks, and using mordants to obtain level dyeing. However, it is the finishing process with its application of natural or synthetic polymers and of colorants, within and on the surface of the leather, that produces the uniformity, appearance characteristics, and resistance to scuffing and abrasion required for a commercial product.

Leather coatings function both as decoration and protection. They must have enough flexibility and extensibility to function under rigorous conditions, such as in the vamp of a shoe where the leather is folded and straightened with each step for hundreds of thousands of flexes. Because of its fibrous network, leather stretches multidirectionally and thus exerts extreme local extensions and stresses

in the coatings. The leather finish must undergo such stretching even at subzero temperatures without breaking or checking under the strain.

The ability to meet these demanding requirements for uniformity, flexibility, and extensibility depends to a large extent on primer coatings that are similar in formulation to those of latex house paint. They are made with specially developed emulsion polymers, mostly of the polyacrylate type, although butadiene copolymers also are employed. The latex polymers for leather base coats must be of exceptionally high molecular weight and exceedingly low glass-transition temperature T_g (96). Unfortunately, latex coatings of this type offer little protection against abrasion and scuffing. Higher modulus polymers (97) are required, and are provided in upper coats applied from solvent solutions. Nitrocellulose or vinyl chloride copolymer lacquers are commonly employed. Polyurethanes are used increasingly, but their principal application has been in patent-leather coatings where thermoplastics, followed by a moisture-cured polyurethane, have replaced the previously used linseed-oil varnishes (98).

If the high modulus polymer topcoats are applied directly over the low modulus base coats, the difference in modulus results in intercoat failure during flexing. Multiple coatings are required with gradually increasing modulus in each coat from bottom to top. This prevents a stress buildup within any particular coating. No less than 3–5 coats are employed. The leather is passed through an oven between each coat to volatilize the solvent. To preserve the long-term flexibility achieved in the base coats by high molecular weight emulsion polymers, the polymers in the upper coats are of as high a molecular weight as practical, but with limited solubility. For this reason almost all upper coats for leather finishing contain a maximum of 10% solids, and 90% of the weight of the coatings enters the environment as volatile organic compounds (VOC). The EPA is limiting VOC emissions for a group of industries (99) and is expected to do so for leather coatings. Consequently, emphasis is being placed on potential utilization of water-based upper coats, including vinylidene chloride–acrylate copolymers (96), water-based polyurethanes (100,101), and tough water-based acrylics (102–104). These water systems do not yet provide all of the characteristics obtained by the current solvent-system upper coats. Early reports of radiation-curable, 100% active leather-coating systems may avoid this problem and reduce energy costs as well (105,106). Such radiation-curable systems use vinyl or acrylic monomers as the solvent. The leather and its wet coating are passed under a beam of electrons or strong uv light; polymerization occurs in seconds and, instead of evaporating, the monomer solvents become part of the coating. The coatings have good gloss and clarity, and solvent is not emitted to the environment. The energy and space requirements for this process are much lower than those of drying in conventional ovens.

A commercially important treatment for corrected grain leathers was introduced during the 1960s (107,108). A penetrating polymeric precoating system was applied that migrated rapidly into the grain layer of the leather to reduce scuffing and improve handling in the shoe factories. It also improved the breaks or fine folds that appear on the leather surface after repeated flexing. The acrylic impregnant filled the grain surface, in effect replacing the enamel, to provide a suitable substrate for finishing. This greatly improved the appearance so that the coarser grain surfaces of shoe-upper leathers made from steer and cowhides

could rival or even surpass the appearance of fine calfskin leathers. Special polymers of acrylic (109–110), polyurethane (111), and acrylic–urethane copolymer (112) types were developed. Because of greater ease in handling, lower cost, and better break improvement, acrylics have been favored.

The process of making leather–polymer composites in conjunction with the normal wet-processing operations prior to finishing has been receiving considerable attention both in the U.S. Department of Agriculture's Eastern Regional Research Center (113–116) and in the Central Leather Research Institute at Madras, India (117–118). The addition of monomers onto the leather protein structure to form new chemical entities has been studied extensively. The actual degree of grafting is still in question, but, whatever the mechanism, the modification of leather is sufficient to introduce new combinations of properties. An example is the development of shearling and garment leathers whose polymer retanning agents, fat liquors, and dyes were not extracted by dry-cleaning solvents.

By-products. The weight of finished grain leather constitutes only 20–30% of the weight of the raw hide, depending on the thickness of the leather and the hide selection (119,120). The remaining 70% consists of by-products that can be sold or waste requiring disposal. Over the years, as markets have changed, some wastes have become by-products and various by-products have become wastes. The largest by-product by weight is the "split," which may account for 30–50% of the incoming hide. If the hide is split after liming, the split can be used to make collagen casings and for other potential food uses (121), cosmetics, and medical materials such as burn dressings and sutures (26). If the hide is split in the blue, its use is limited to split leather manufacture. Although this market fluctuates, the split is almost always a salable by-product.

Another 15% of the raw hide appears in the effluent as dissolved and suspended organic matter, consisting largely of the protein that was dissolved in the beam house processes. Some potential exists for obtaining this protein in a form that could be used for animal feed. However, this is generally not done and the protein is considered a waste requiring disposal. There is not enough protein in the effluent of a single tannery to make recovery economically worthwhile.

About 5% of the weight of an unfleshed hide coming into the tannery ends up as raw material for a renderer. The value of fleshings is lower if they contain salt. Most fleshing is now done by the packer prior to salt curing. The remaining 7% of the hide is composed of solids free of chrome, primarily the trim that sometimes can be sold along with the fleshings to the renderer; otherwise it is considered a solid waste.

The cattle hair markets disappeared with the advent of hair-burning or dissolving processes. Hair that was once a salable by-product has become an effluent-treatment problem.

Of the raw hide substance, 18% ends up as solids containing chromium other than grain or split leather; 60% of these solids are in the form of chrome shavings; and the remainder consist of blue trim, buffing dust, and leather trim. These solids can be used in a leather fiberboard product. However, if a tanner does not produce enough of a material to economically convert it from a waste into a by-product, he must pay to have the chromium-containing solids hauled away to a landfill.

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LIVING POLYMER SYSTEMS

- Living cationic ring-opening polymerization, 380
- Living cationic polymerization, alkenyl, 399
- Epoxides and lactones, new developments, 412
- Olefin metathesis, 420
- Radical polymerization, 429
- Ziegler-Natta polymerization, 437

The term living polymers is often used to describe systems in which active centers remain after complete polymerization, so that a new batch of monomer subsequently added will add to the existing chains and increase their degree of polymerization (qv). These systems are well-documented in anionic polymerization (qv). Indeed, in the Volume 2 article living polymerization is treated as a normal feature of ANIONIC POLYMERIZATION. In living polymerization the mechanism is comprised of chain initiation and chain propagation with no termination reactions [or chain transfer (qv)]. Each initiator molecule produces one growing chain, so that the degree of polymerization at the end of polymerization will simply be M_0/I_0 if initiation occurs by addition to the monomer, or $2M_0/I_0$ for radical anion initiation, where M_0 and I_0 are the initial monomer and initiator concentrations. If the rate of chain initiation is rapid compared to that of chain propagation, then all chains start at the same time and, apart from a small statistical factor, add monomer equally. Highly monodisperse polymers (qv) with a Poisson distribution of molecular weights form.

More recently, living systems other than anionic have been developed. This article presents various living polymerizations, classified largely according to the nature of the propagating species. The first section begins with a brief discussion of the requirements for a truly living system.

LIVING CATIONIC RING-OPENING POLYMERIZATION

According to the original Szwarc definition (1) several criteria must be met simultaneously in order for a system to be called living. In the living system, active species are formed relatively fast (compared to their further propagation) and most of these species stay active until the monomer is consumed. This description, translated into the language of measurable quantities, requires that

1. $k_i \geq k_p$, ie, the rate constant of initiation is at least as large as the rate constant of propagation;
2. $[C^*] = \text{constant}$, ie, the concentration of active species is constant; the rate constants of termination and transfer are close to zero ($k_t, k_{tr} \sim 0$).

These requirements, if simultaneously met in the studied system, have the following consequences:

1. $\ln [M]_0/[M]_t = k_p[C^*]t$, ie, the polymerization follows first-order kinetics with respect to monomer concentration;
2. $\overline{DP}_n = ([M]_0 - [M]_t)/[C^*]$, ie, the number-average degree of polymerization is proportional to the monomer conversion;

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