# *Leather Processing*

## *GENERAL USE OF FATS AND OILS IN LEATHER*

Although most of the 20-odd steps of leathermaking use fats and oils as detergents, by far the majority of these materials are used as additives to soften leather. Oils are usually applied in aqueous emulsions while the leather is still wet from tanning. Several oils are conventionally used, often made self-emulsifying by partial sulfation or sulfonation by treating with sulfuric acid. These oils are called *fatliquors.* Heavy grades of leather are also softened by the addition of neat melted fat after the leather has been dried. This "hot stuffing" process involves softening the leather by milling it in the presence of the warm molten fat. While the milling by itself is sufficient to soften the leather, the fat dispersed among the fibers allows the leather to remain soft if it is dampened and dried again.

The amount of these materials that are used annually has not been compiled. It can be estimated as $22 \times 10^6$ lb/yr from the average content in leather, 15%, and the production of leather, $15 \times 10^7$ lb/yr. Alternatively, the Leather Industries of America estimated it as $40 \times 10^6$ lb/yr in 1971, when leather production was $23 \times 10^6$ lb/yr. Since leather production is now down to $15 \times 10^6$ lb/yr, the amount of fats and oils used is on the order of about $30 \times 10^6$ lb/yr. Therefore, from 22 to 30 million pounds per year of fats and oils are used in the leather industry.

Besides for softening, a smaller amount of oils and fats as detergents is also used in preliminary cleaning of the raw skins and hides; to suspend lime particles, buffer the alkaline solution that removes the epidermis and hair, and suspend these materials when they come off; to remove grease; to tan certain types of leather; and to control the penetration of dyes.

## *SOFTENING OF LEATHER*

### Drying Skin or Hide

The skin or hide of an animal is an organ whose complex structure can be simplified for purposes of analysis into two layers: a thin (<1 mm) epidermis and a thicker (up to 1 cm) dermis. The epidermis, bearing the hair, is removed early in the steps of leathermaking. The dermis comprises very long fibrils, 100 nm in diameter, composed mostly of the protein collagen type I. The fibrils are organized into interwoven bundles. Among the fibrils is a concentrated solution or network of glycoproteins and, immediately after slaughter, blood plasma. There are also blood vessels and nerves, which are removed during leathermaking before the tanning (collagen crosslinking) step, which is the last step before the addition of fatliquor.

If skin or hide is dried, even minus the hair and epidermis, it becomes a hard material, like horn. If the skin is thin, this product can be used as a tough parchment, but little else. This behavior is attributed to the proteins and proteoglycans found among the fibers of the hide, which act as a glue when they dry.

If the skin is agitated with lime-buffered water (pH = 12.5), it swells enormously, and most of the gluelike material is extracted. On neutralization, however, the fibers become flaccid and, on drying, stick together to again form a hard mass. Before being dried for leather, however, the extracted skin is tanned: the collagen protein of the fibers is crosslinked to make them stiffer. The resulting product can be dried to a leathery material that is stiff, but much more flexible than that dried without tanning. To soften tanned skin, one can mill it by lifting and dropping it in a large rotating drum or in a staking machine, which pounds it with small hammers. The result is not satisfactory, however, for a number of reasons, including the effect on the integrity of the surface of the leather and the inability to rewet the leather without making it become stiff again.

### Use of Oil or Fat

If, after tanning, a soluble resin is added and the leather is dried and milled in the presence of melted grease, a flexible but resilient product is obtained that can be rewet, within limits, and dried again to the same esthetically pleasing product. This hot-stuffed leather is actually a commercial product used for the upper parts of shoes. The product is not stable, however, to dry cleaning, which removes the grease. The grease removed from this dry-cleaned leather must be replaced.

It is not necessary to depend on mechanical milling to make soft leather. Usually after the hide is tanned it is tumbled in a drum with an oily emulsion (fatliquor). On drying, the emulsion droplets coalesce among the fibers, pro-

ducing a soft leather containing 10–15% oil on basis of dry weight. Although this leather can be wet again and dried without becoming stiff, the organic solvents used in dry cleaning can extract the oils as they do to the fats in hot-stuffed leather.

There are other drawbacks to conventionally fatliquored leather. When it is used in automobile upholstery, it is often heated by sunlight in the unstirred air of the parked vehicle to temperatures high enough to sublime or distill the fat or oil onto the windows. This deposited material is troublesome to remove and causes some lots of leather to be rejected by the automobile manufacturer. Another drawback is flammability, which can be obviated by a judicious choice of oil in the emulsion. Further, the oil sometimes tends to migrate to the surface of the leather, causing an unpleasant film, or spew, to form. Under some conditions it can cause separation of the finish or coating from the leather substratum.

## *SOFTENING WITH FATLIQUOR*

### 3.1 Physical Mechanism

It is not clear exactly why oil, added as a fatliquor emulsion when the leather is wet, causes the leather to dry to a soft product. The most cogent hypothesis derives from the observations of von Fuchs (1), who noticed that the oil could be removed from the dried leather with solvent without causing it to become stiff. One concludes that the fatliquor prevents the fibers from sticking together during the drying but afterward is not needed. There is uncertainty, however, about what comprises a fiber. We have evidence that it is a bundle of the unitary 100-nm collagen fibrils, perhaps 10 $\mu$m in diameter (2) (Figure 8.1).

The emulsion of a fatliquor should not be too stable. The leathermaker wants to control its depth of penetration into the leather by the tendency of the surfactant to adsorb to the protein of the hide. This adsorption depletes the micelles of surfactant, causing the emulsion to break before it permeates the interior of the hide, releasing the oil somewhat superficially. The untreated interior thereby retains its stiffness, but with only a small mechanical moment. The product is then firm but resilient (not like cardboard). The released oil, with the surfactant tightly bound to the fibers, also resists being washed out of the leather by water. Suede leather, on the other hand, requires full penetration of the fatliquor and therefore an emulsifier that does not bind tightly to the protein.

As noted, when a leather is dried without fatliquor, the fibrils adhere and form irregular fiber bundles with a linear cross-sectional dimension of about 100 $\mu$m. When the leather is still wet in the fatliquoring step, however, the emulsion is distributed among the fibrils. As the fatliquored leather dries, the fibrils still tend to adhere to each other but with weakened adhesive force because of the presence of the oil. We believe that the lateral forces, due to

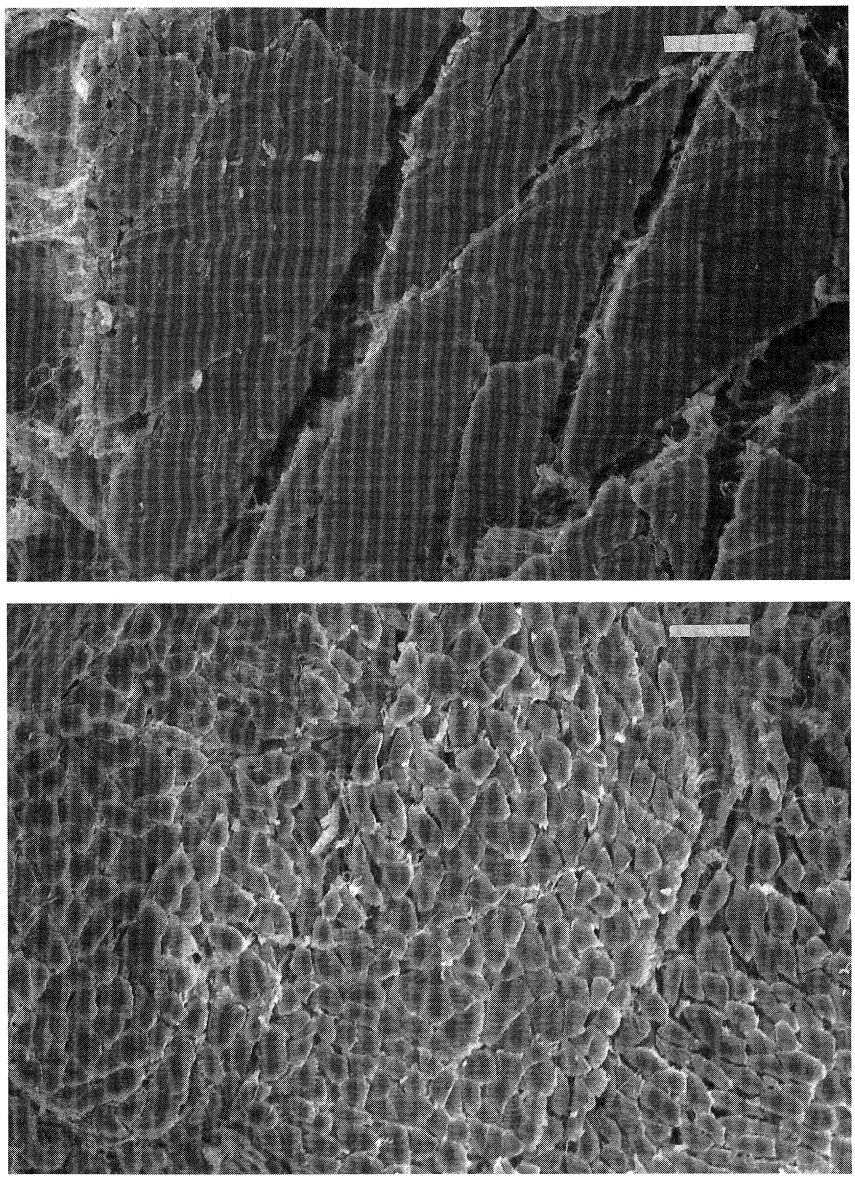

**Figure 8.1** Effect of fatliquor on the structure of fibers in leather after drying. (Top) The 100-$\mu$m fiber bundles in the leather dried without fatliquor are intact. (Bottom) They are broken into fragments when dried with fatliquor, making the leather compliant. Bar = 10 $\mu$m.

shrinkage of the bundles of fibrils as water evaporates, causes them to rupture into the 10-$\mu$m fibers; at this writing this is still under investigation. What is important is that the eventual softness of the leather would depend on the topology of the fragments rather than directly on the rheological or chemical properties of the oil. The same geometric effect should be achieved by mechanical milling of the dried leather in the presence of grease or oil, as in hot stuffing.

## 3.2 Components and Formulation

In formulating a fatliquor, one is concerned with the chemical interactions with the substance of leather fibers, the dyes, and the tanning agent, mostly hydrated chromic oxides. Mostly, these interact with the emulsifier. With the likely introduction of substitutes for chromium, such as aluminum or vanadium, the reactions of the emulsifiers will have to be adjusted. The surface charges of the new inorganic materials will be different from that of chromium, affecting the tendencies of various emulsions to coalesce. This chemistry can be adjusted by changes in pH and perhaps will lead to other requirements on lengths of the fatty chains.

The neutral portion of the fatliquor can be almost any oil. Triglycerides are most common, but wool grease and mineral oil are also used. The oil is chosen to be nonvolatile (for permanence and to prevent the fogging effect described above), minimally soluble in water, and liquid at about 40°C (and so emulsifiable). Longer carbon chains (above 14) are better: Heidemann (3) attributes this to retention of the oil among rather than within the fibrils. Mixtures of different oils are usually used. Esthetic properties are resistance to discoloration and hardening and lack of unpleasant odor. An important chemical property for an oil is that it should be easily sulfonated, sulfated, or oxidized so that it can be the starting material for its own emulsifier. In fact, the most commonly used fatliquors are partially sulfonated oils, adjusted to the correct degree of sulf(on)ate by addition of more base oil. One of the most common oils is castor oil, which can be both sulfated and sulfonated. Others commonly used are fish oils, especially from cod, neatsfoot oil, rendered from the bones of cattle, rice bran oil, soy oil, coconut oil, linseed oil, and rapeseed oil.

Sulf(on)ation is not the only method used to prepare fatliquor from oil. Simple oxidation of fish oil with air or nitric acid is another, again causing a portion of the oil to become amphipathic. The products are often referred to as "moellons" or "degras."

Leather softeners that are technically satisfactory can also be made from jojoba oil (4) and even butadiene rubber (5). Waste animal fat obtained from scraping the flesh from the fresh hide, before the leathermaking process is begun, can be used after sulfation or ethoxylation.

Although neat fats and greases can be added to the leather after it has been dried, oils must be emulsified if they are to be used during the wet end

of the leathermaking process. Fortunately most oils can usually be sulf(on)ated or oxidized easily, making them amphiphilic; the usual degree is 50% of the triglyceride molecules, so that an oily emulsion can be prepared with excess neutral oil. By artful formulation, the properties of the emulsion are carefully controlled with regard to the viscosity and size of the particles and their affinity for the leather fibers and the chromic oxide tanning agent. These properties affect the ability of the emulsion particles to penetrate the leather. Castor oil, unlike fish oil, yields the sulfated as well as the sulfonated product when it is treated with sulfuric acid; its emulsions have a greater tendency to break in the presence of electrolytes. When used as fatliquors, its emulsions tend to break in the superficial regions of the leather, releasing their oils there rather than deeper inside. This allows the leathermaker a means to control deposition of oil "stratigraphically." As already described, this permits adjustment of the mechanical properties and leather esthetics.

A balance of properties of the product can be obtained by formulations based on natural oils to which sulf(on)ated oils are added. The mixtures can then be optimized statistically with respect to the mechanical properties (6).

Besides sulf(on)ates, carboxylates (soaps) and phosphates can also be used in the surfactant. An emulsion based on alkyl phosphate emulsifier is reported to give an especially soft leather (7). Phosphates are reviewed by Fricke and Haeussler (8). There is also experience with sulfosuccinic acid amides (9) and other surfactant formers.

Before the growth of organic chemistry and techniques for sulfonating fats and oils, tanners emulsified oils for leather softeners with soap and protective colloids. These mixtures were prepared as water-in-oil emulsions, called "mayonnaise" in the trade and added to the water in the drum with the leather. They are still used but not nearly as frequently as sulf(on)ated oils. On the other hand, salts of naphthenic acid are used with hydrocarbon oils (e.g., 10) to make the reverse forms of these.

Egg yolk was once commonly used, probably because of its lecithin, to emulsify oils in leathermaking. Lecithin itself is effective as a fatliquor emulsifier (11). Nonionic emulsifiers have the advantage of forming emulsions that are stable to electrolytes, so they do not interact electrostatically with the chromium or aluminum tanning ions. Nonionic–anionic combinations (e.g., 1% nonionic–99% anionic) are now used to suppress the accumulation of fatty deposits or extrusions at the surface of the leather. These systems are under active development.

Cationic surfactants are used mainly to treat the surface of the leather, making it waxy. These are typically C-16 to C-18 alkylbenzyl quaternary ammonium compounds (e.g., Ref. 12). Also effective are cationic fatliquors from aminated and quaternized castor oil; other vegetable oils are also used (13).

Oils are frequently chlorinated in addition to being sulf(on)ated or oxidized. The reaction is extended to both the neutral oil and the surfactant, to make them less volatile and more flame resistant. Fish oil is the usual substrate for

this treatment, but it has been extended to fatliquor from mineral oil and paraffin wax (e.g., Ref. 14).

## *OTHER SOFTENING MATERIALS*

Leather is also softened, after it is dried, by the addition of grease at temperatures at which it is fluid. These "stuffing compounds" are made from wool grease or high-melting (230–266°C, 110–130°F) mixtures of mineral waxes and fatty acids. For reasons that are not understood, they must be used at much higher levels than fatliquors—usually about 30% of the weight of the leather, instead of 10–15%.

The development of new softening materials is considered to be a high priority by the international leather industry. Research to find materials that give softer leather for garments without the drawbacks of greasy feel, odor, and cost that attend increasing the amounts used is proceeding in many laboratories in many countries. There have been 10 patents per year over the period 1988–1990. Nearly all of these have been issued to investigators in Eastern Europe and China, which are also the main sources of published investigations in the area. Research on leather softeners is driven by the same considerations everywhere: the need to find new sources of oils and greases that are of constant quality, inexpensive, convertible to emulsifiers, color-fast, and preferably colorless, odorless, fixed well in the leather, and ecologically acceptable.

Examples of such developments are sulfation of transesterified rapeseed oil phosphatides (15) and the use of bicontinuous microemulsions obtained by the addition of aliphatic alcohols (16,17). The stability of these systems promises to be more reliable than those in present use. Oils from wood (tall oil) can be sulfonated for self-emulsifying fatliquors (18). We expect more progress on the use of high polymers, such as the already commercial alkyl acrylate esters developed by Hodder and co-workers (19,20), and material based on elastomers (5). We anticipate the development of novel systems to be encouraged by the demand for leather in washable garments and automobile upholstery.

## *EVALUATING EFFECTS OF FAT IN LEATHER*

The amount of residual natural fat and added fatliquor is usually determined by chemically analyzing hexane extracts, following ASTM Standard D-3495 (21). The leather is extracted in a Soxhlet apparatus and the amount dissolved in the hexane is determined gravimetrically. Analyses for specific fatty components are described in Ref. 22.

Fatliquor affects mostly the mechanical properties, measured also by a collection of ASTM methods given in Ref. 21. In addition, the sounds emitted

by leather when it is deformed are greatly suppressed by the presence of fat, supporting a method of assay by means of the acoustic emission test (23).

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