

9.15 Leather Tanning

9.15.1 General¹⁻⁴

Leather tanning is the process of converting raw hides or skins into leather. Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable. The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep, and pigs.

Tanning is essentially the reaction of collagen fibers in the hide with tannins, chromium, alum, or other chemical agents. The most common tanning agents used in the U. S. are trivalent chromium and vegetable tannins extracted from specific tree barks. Alum, syntans (man-made chemicals), formaldehyde, glutaraldehyde, and heavy oils are other tanning agents.

There are approximately 111 leather tanning facilities in the United States. However, not every facility may perform the entire tanning or finishing process. Leather tanning and finishing facilities are most prevalent in the northeast and midwest states; Pennsylvania, Massachusetts, New York, and Wisconsin account for almost half of the facilities. The number of tanneries in the United States has significantly decreased in the last 40 years due to the development of synthetic substitutes for leather, increased leather imports, and environmental regulation.

9.15.2 Process Description^{1-2,5-6}

Although the title of this section is "Leather Tanning", the entire leathermaking process is considered here, not just the actual tanning step. "Leather tanning" is a general term for the numerous processing steps involved in converting animal hides or skins into finished leather. Production of leather by both vegetable tanning and chrome tanning is described below. Chrome tanning accounts for approximately 90 percent of U. S. tanning production. Figure 9.15-1 presents a general flow diagram for the leather tanning and finishing process. Trimming, soaking, fleshing, and unhairing, the first steps of the process, are referred to as the beamhouse operations. Bating, pickling, tanning, wringing, and splitting are referred to as tanyard processes. Finishing processes include conditioning, staking, dry milling, buffing, spray finishing, and plating.

9.15.2.1 Vegetable Tanning -

Heavy leathers and sole leathers are produced by the vegetable tanning process, the oldest of any process in use in the leather tanning industry. The hides are first trimmed and soaked to remove salt and other solids and to restore moisture lost during curing. Following the soaking, the hides are fleshed to remove the excess tissue, to impart uniform thickness, and to remove muscles or fat adhering to the hide. Hides are then dehaired to ensure that the grain is clean and the hair follicles are free of hair roots. Liming is the most common method of hair removal, but thermal, oxidative, and chemical methods also exist. The normal procedure for liming is to use a series of pits or drums containing lime liquors (calcium hydroxide) and sharpening agents. Following liming, the hides are dehaired by scraping or by machine. Deliming is then performed to make the skins receptive to the vegetable tanning. Bating, an enzymatic action for the removal of unwanted hide components after liming, is performed to impart softness, stretch, and flexibility to the leather. Bating and deliming are usually performed together by placing the hides in an aqueous solution of an ammonium salt and proteolytic

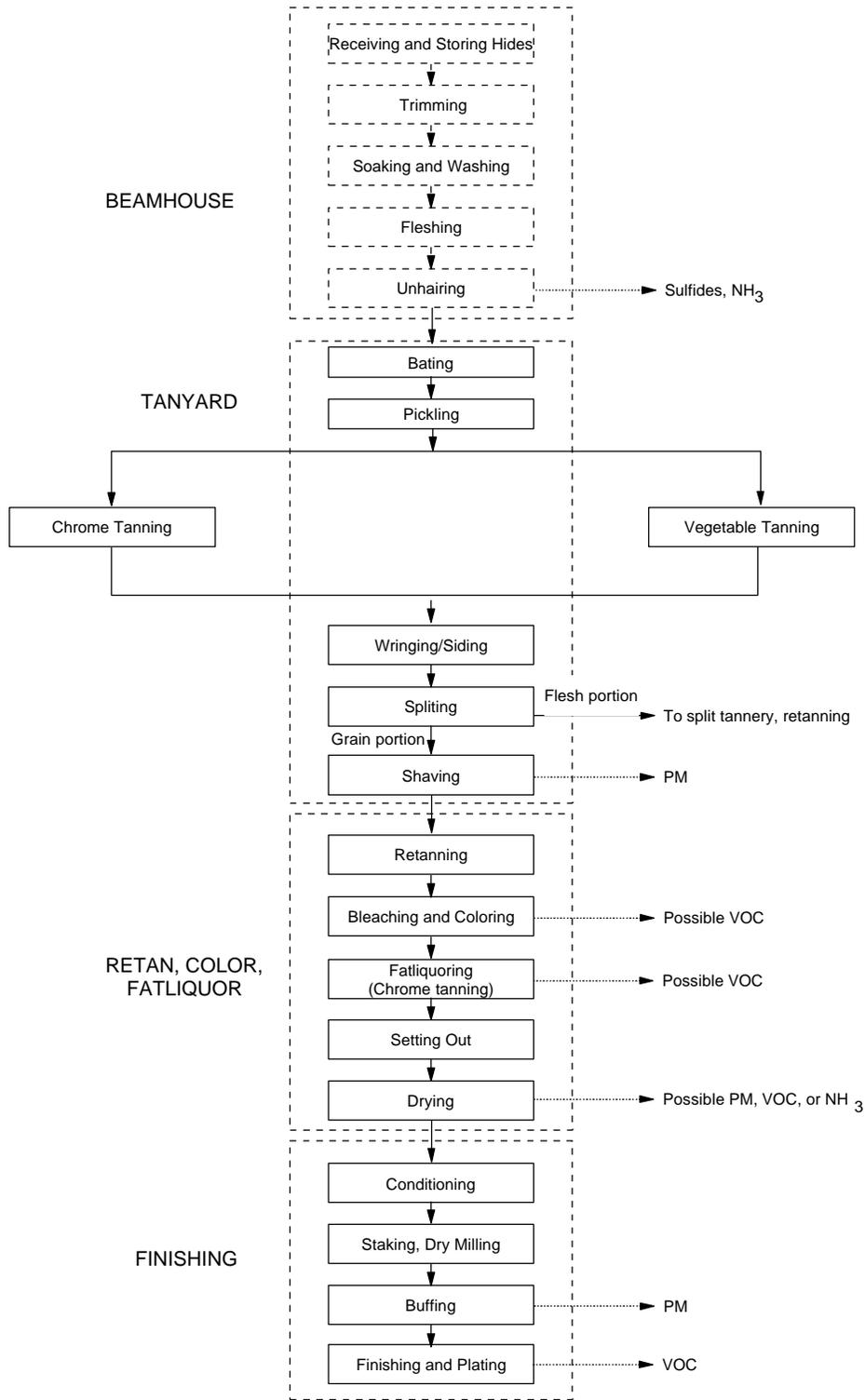


Figure 9.15-1. General flow diagram for leather tanning and finishing process.

enzymes at 27° to 32°C (80° to 90°F). Pickling may also be performed by treating the hide with a brine solution and sulfuric acid to adjust the acidity for preservation or tanning.

In the vegetable tanning process, the concentration of the tanning materials starts out low and is gradually increased as the tannage proceeds. It usually takes 3 weeks for the tanning material to penetrate to the center of the hide. The skins or hides are then wrung and may be cropped or split; heavy hides may be retanned and scrubbed. For sole leather, the hides are commonly dipped in vats or drums containing sodium bicarbonate or sulfuric acid for bleaching and removal of surface tannins. Materials such as lignosulfate, corn sugar, oils, and specialty chemicals may be added to the leather. The leather is then set out to smooth and dry and may then undergo further finishing steps. However, a high percentage of vegetable-tanned leathers do not undergo retanning, coloring, fatliquoring, or finishing.

Leather may be dried by any of five common methods. Air drying is the simplest method. The leather is hung or placed on racks and dried by the natural circulation of air around it. A toggling unit consists of a number of screens placed in a dryer that has controlled temperature and humidity. In a pasting unit, leathers are pasted on large sheets of plate glass, porcelain, or metal and sent through a tunnel dryer with several controlled temperature and humidity zones. In vacuum drying, the leather is spread out, grain down, on a smooth surface to which heat is applied. A vacuum hood is placed over the surface, and a vacuum is applied to aid in drying the leather. High-frequency drying involves the use of a high frequency electromagnetic field to dry the leather.

9.15.2.2 Chrome Tanning -

Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. Almost all leather made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned. The first steps of the process (soaking, fleshing, liming/dehairing, deliming, bating, and pickling) and the drying/finishing steps are essentially the same as in vegetable tanning. However, in chrome tanning, the additional processes of retanning, dyeing, and fatliquoring are usually performed to produce usable leathers and a preliminary degreasing step may be necessary when using animal skins, such as sheepskin.

Chrome tanning in the United States is performed using a one-bath process that is based on the reaction between the hide and a trivalent chromium salt, usually a basic chromium sulfate. In the typical one-bath process, the hides are in a pickled state at a pH of 3 or lower, the chrome tanning materials are introduced, and the pH is raised. Following tanning, the chrome tanned leather is piled down, wrung, and graded for the thickness and quality, split into flesh and grain layers, and shaved to the desired thickness. The grain leathers from the shaving machine are then separated for retanning, dyeing, and fatliquoring. Leather that is not subject to scuffs and scratches can be dyed on the surface only. For other types of leather (i. e., shoe leather) the dye must penetrate further into the leather. Typical dyestuffs are aniline-based compounds that combine with the skin to form an insoluble compound.

Fatliquoring is the process of introducing oil into the skin before the leather is dried to replace the natural oils lost in beamhouse and tanyard processes. Fatliquoring is usually performed in a drum using an oil emulsion at temperatures of about 60° to 66°C (140° to 150°F) for 30 to 40 minutes. After fatliquoring, the leather is wrung, set out, dried, and finished. The finishing process refers to all the steps that are carried out after drying.

9.15.2.3 Leather Finishing

Leathers may be finished in a variety of ways: buffed with fine abrasives to produce a suede finish; waxed, shellacked, or treated with pigments, dyes, and resins to achieve a smooth, polished surface and the desired color; or lacquered with urethane for a glossy patent leather. Water-based or solvent-based finishes may also be applied to the leather. Plating is then used to smooth the surface of the coating materials and bond them to the grain. Hides may also be embossed.

9.15.3 Emissions and Controls^{2,4,6}

There are several potential sources of air emissions in the leather tanning and finishing industry. Emissions of VOC may occur during finishing processes, if organic solvents are used, and during other processes, such as fatliquoring and drying. If organic degreasing solvents are used during soaking in suede leather manufacture, these VOC may also evaporate to the atmosphere. Many tanneries are implementing water-based coatings to reduce VOC emissions. Control devices, such as thermal oxidizers, are used less frequently to reduce VOC emissions. Ammonia emissions may occur during some of the wet processing steps, such as delimiting and unhairing, or during drying if ammonia is used to aid dye penetration during coloring. Emissions of sulfides may occur during liming/unhairing and subsequent processes. Also, alkaline sulfides in tannery wastewater can be converted to hydrogen sulfide if the pH is less than 8.0, resulting in release of this gas. Particulate emissions may occur during shaving, drying, and buffing; they are controlled by dust collectors or scrubbers.

Chromium emissions may occur from chromate reduction, handling of basic chromic sulfate powder, and from the buffing process. No air emissions of chromium occur during soaking or drying. At plants that purchase chromic sulfate in powder form, dust containing trivalent chromium may be emitted during storage, handling, and mixing of the dry chromic sulfate. The buffing operation also releases particulates, which may contain chromium. Leather tanning facilities, however, have not been viewed as sources of chromium emissions by the States in which they are located.

References for Section 9.15

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