TANNERIES

A. PROCESS DESCRIPTION

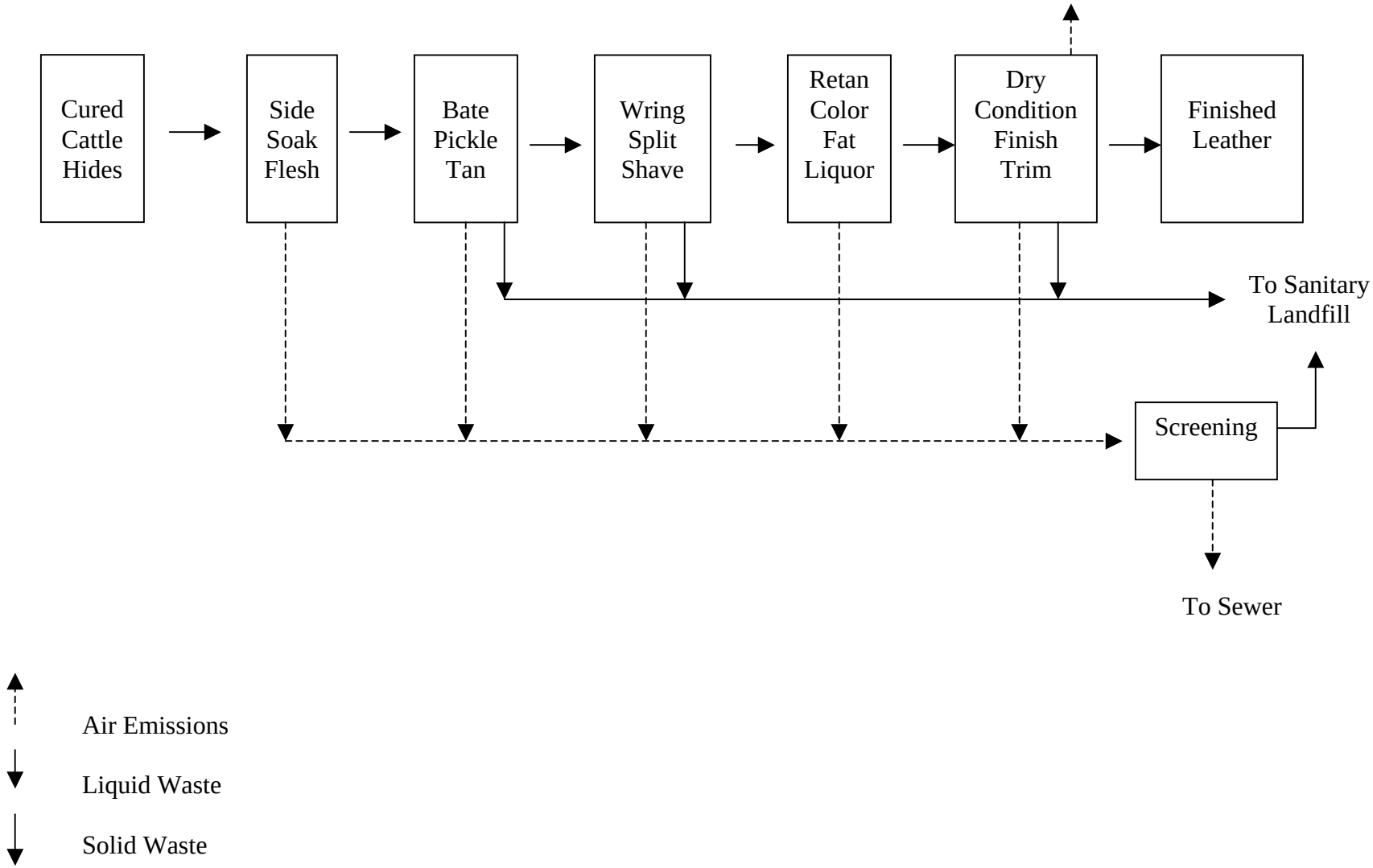
Tanning involves a complex combination of mechanical and chemical processes. The heart of the process is the tanning operation itself in which organic or inorganic materials become chemically bound to the protein structure of the hide and preserve it from deterioration. The substances generally used to accomplish the tanning process are chromium or extracts from bark of trees, such as chestnut. These tanning agents give rise to the two predominant types of tanning operations - chrome and vegetable tanning.

1. Chrome Tanning

Most leather produced is chrome tanned. Chrome tanning produces leather better suited for certain applications, particularly for the upper parts of boots and shoes, and requires less processing time than traditional vegetable tanning. The general steps required for chrome tanning of leather are shown in Exhibit 1 and described briefly below. No two tanneries are identical; each has its unique characteristics and subprocesses; some perform only some of the processes shown and ship their goods to another tannery to complete the processing. Hides and skins are received from meatpacking plants by truck or railroad car. Each cattlehide is tied in a bundle weighing approximately 25 kg. The bundles are cut open and the hides unfolded, inspected, and usually split along the backbone, producing two sides from each hide. Next follows a sequence of wet operations. The sides are soaked in water to return some of the lost natural moisture. The remaining flesh or fatty substance adhering to the inside or flesh surface of the side is removed; these fleshings are usually either rendered in the tannery or sold. The cattlehides are then soaked in a lime and sulfide solution which either loosens or dissolves the attached hair. In some operations, the hair is only loosened through the caustic action of the lime, with the hair removed mechanically, followed by washing, drying, and sale as a by-product (for carpet pads and similar uses). However, the more common approach for hair removal is to completely dissolve the hair and discharge it to the wastewater stream. Following hair removal, the hides are ready to be prepared for the actual tanning operation. The hides are placed in large rotating drums and treated in turn with an enzyme solution and then a salt-acid solution. These operations (respectively called bating and pickling) prepare the hide for the tanning process. While still in the drum after discharge of the pickling solution, the hides are tanned. A chromium sulfate solution is added to the drum and the hides and chrome solution are mixed for periods of up to 24 hours.

Following chrome tanning, all hides have a characteristic blue color caused by the chrome tanning solution. Upon removal from the tanning drums, excess moisture is removed from the hides through a wringing operation.

EXHIBIT 1: Process Flow Diagram of a Typical Chrome Tannery



Cattlehides are too thick for most purposes so the tanned hides are split using a machine similar to a horizontal band saw. The splitting operation produces a grain side of more or less uniform thickness. One surface of this grain side is the original outer surface of the cattlehide and retains the natural grain. The splitting operation also yields a thin, inner portion of the hide known as a "split" or "blue drop." Splits have no graining and are often used for suede garments. Both the grain side and the split may be further processed to form a piece of material of uniform thickness. This operation is called shaving and results in the removal of small pieces of leather with a consistency similar to very coarse sawdust.

Another series of wet operations gives the leather the color and other properties desired in the finished material. The tanned hides are placed into another drum for retanning, coloring, and fatliquoring. Retanning is a second, shorter tanning operation normally using a tanning agent other than chromium. After the retanning solution is discharged from the drum, a pigment is added in order to dye the leather to the desired color. The coloring solution is also discharged from the drum and the hides are taken out and wrung to remove excess moisture. Next a mixture of oils is added and the hides and oil are rotated in the drum. This operation, called fatliquoring, helps to produce the desired softness.

After removal from the retan, color, and fatliquor drum, the leather is dried and physically conditioned. The two most common approaches to this conditioning are staking and buffing. Staking is a form of massaging which makes the leather more pliable. Buffing is a light sanding operation applied to either the grain surface or the underside of a piece of leather. It is used to improve the nap of the underside or to smooth out surface imperfections on the grain surface.

One or more of several possible finishing steps give the leather the required pattern gloss or waterproof qualities. Usually all leather receives at least one coat of a liquid finish material. Finishes are either rolled or sprayed onto the leather. Often three or more coats of finish are applied to leather, each one followed by a drying cycle. Other finishing operations include embossing, in which patterns are pressed into the leather surface. Finally, the surface area of each piece of leather is measured electronically and the area stamped on the underside. The leather is then packaged and stored for shipment.

2. Vegetable Tanning

Vegetable tanning employs the use of extracts from the bark of various trees as the tanning agent. Since the introduction of chrome tanning, vegetable tanning has decreased in importance. Soles of shoes have been traditionally vegetable tanned; however, since the introduction of synthetic materials for shoe soles, vegetable tanning has further decreased in importance. Vegetable tanning is also used to produce leather used in crafts.

Many of the basic steps used in the chrome tanning process are also present in vegetable tanning. The sequence in which these steps are employed is somewhat different, and there are few finishing operations associated with vegetable tanning. The processing of hides prior to vegetable tanning begins with a soak in lime to loosen the hair. Hides are then removed from the lime solution and the hair is removed mechanically. The hides are then soaked and rinsed, and

the fleshing operation is accomplished. Note that in the chrome tanning process, fleshing preceded the hair removal operation. After fleshing, the hides are trimmed into a roughly rectangular shape and then passed through a bate and pickle operation similar to that used in the chrome tanning process. Coloring, the next operation, is often done utilizing a weak tanning solution. Normally vegetable tanned leather is not highly colored. After coloring, the hides are placed into vats containing the bark extract tanning solution and moved from a strong tanning solution to a slightly weaker one, then rinsed and partially dried.

True splitting is not usually a part of the vegetable tanning process; however, an operation called leveling is used to produce a uniformly thick piece of leather. Leveling removes only the thickest portions of the underside of the hide, and no "split" is produced. Next, the hide is oiled, which is a process similar to the fatliquoring in chrome tanning. Following oiling, the hide is dried and then mechanically conditioned.

Virtually no finishing is done at vegetable tanneries. Few, if any, spray finishes are applied and often the only finishing process employed is pressing to yield a smooth grain surface. Finally, the hides are measured, packaged, and stored prior to shipment.

B. SOURCES OF POLLUTION

Typical sources of emissions include (1) solvent receiving, (2) mixing vault, (3) supply drum, (4) spray chamber, (5) dryer, (6) receiving recycled solvents, (7) cleaning operation, (8) waste solvent storage (See Exhibit 2 for air emissions and solid waste generation points).

C. POLLUTANTS AND THEIR CONTROL

1. Air Emissions

Typical pollutants (either solid or gaseous) from a tannery include chlorine, formaldehyde, sulfuric acid, glycol ether EB, glycol ether PMA, methyl isobutyl ketone, toluene, xylol, phosphoric acid, methanol, manganese sulfate, chromium III, ethylene glycol, lead, copper, and zinc. See Exhibit 2 for a sample listing of toxic air pollutants and their amounts.

Air pollution control methods can include the use of a water fall (efficiency = 50% for particulates and 10% for VOC), a fume incinerator for spray booth exhausts, and process modifications (using more water-based processes and less solvent-based ones).

Exhibit 2: Emissions of Toxic Air Pollutants From a Typical Tannery

Emission Point	Pollutants	Emission Rate kg/hr	Control Methods
Solvent Receiving	Methyl Ethyl Ketone Methyl Isobutyl Ketone Toluene Xylol	22.58 1.67 10.04 1.17	Incineration Process Modification (e.g., water-based process instead of solvent-based process)
Mixing Vault	Methyl Ethyl Ketone	0.52	
Supply Drum	Methyl Ethyl Ketone	0.52	
Spray Chamber	Diacetone Alcohol Glycol Ether EB Glycol Ether PMA Methyl Ethyl Ketone Methyl Isobutyl Ketone Toluene Xylol	1.89 11.85 7.6 75.72 59.05 95.78 33.38	
Dryer	Diacetone Alcohol Glycol Ether EB Glycol Ether PMA Methyl Ethyl Ketone Methyl Isobutyl Ketone Toluene Xylol	1.89 11.85 7.6 75.72 59.05 95.78 33.38	
Receiving Recycled Solvents	Acetone Methyl Ethyl Ketone Toluene	0.61 0.98 0.61	
Cleaning Operation	Less than 1 kg/hr of each pollutant		
Waste Solvent Storage	Less than 1 kg/hr of each pollutant		

2. Process Liquid and Solid Wastes

Pieces of leather (containing 10 to 50% moisture) in various stages of processing, and wastewater treatment sludges constitute the bulk of the process solid waste from tanneries. In order to produce the quality products required by leather consuming industries, tanneries trim off inferior portions of hides at many steps in processing. Smaller pieces of leather wastes are produced in shaving and buffing operations. Approximately 35% of all tannery solid waste is trimmings and shavings of various types.

Another source of tannery wastes is the finishing department. Finishes are sprayed or rolled onto leather and the residue is considered to be a solid waste since it is land disposed. Finish residues are usually slurries containing 10 to 50% solids. Waste finishes account for about 2% of tannery solid waste.

Wastewater treatment is the single largest source of process solid waste. Almost all tanneries screen their wastewater. Direct dischargers and some discharging wastewater into municipal sewers have some form of primary or secondary treatment (only direct dischargers use secondary treatment). The screenings and sludges from these operations contain lime, chromium compounds, pieces of leather, hair, and other protein-like substances which are land disposed. Wastewater screenings and sludge account for about 60% of tannery solid waste.

Floor sweepings are the final source of process solid waste. These include twine used to tie bundles of hides, salt used to preserve the hides prior to handling, and general plant debris. Approximately 3% of tannery solid waste is floor sweepings.

Wastewater pretreatment is accomplished through sludge dewatering. Sludge dewatering is performed using gravity (sequential settling) or mechnical means. Three mechanical methods of sludge dewatering are used by tanneries - vacuum filters, centrifuges, and filter presses. All three are effective; however, there seems to be a preference for filter presses due to the slightly drier (40% solid) filter cake produced.

See Exhibit 3 for solid wastes, their amounts, and methods of disposal.

Exhibit 3: Hazardous Wastes From a Typical Tannery

Waste Source	Pollutant	Concentration Range[a] (wet weight in mg/kg)	Disposal Method
Chrome trimmings & Shavings	Cr^{+3}	2,200 - 21,000	Landfill
Chrome fleshings	Cr^{+3}	4,000	
Unfinished chrome leather trim	Cr^{+3} Cu Pb Zn	4,600 - 37,000 2.3 - 468 2.5 - 476 9.1 - 156	
Buffing dust	Cr^{+3} Cu Pb Zn	19 - 22,000 29 - 1,900 2 - 924 160	Dewater sludge; all waste disposed in certified hazardouswaste disposal facility
Finishing residues	Cr^{+3} Cu Pb Zn	0.45 - 12,000 0.35 - 208 2.5 - 69,200 14 - 876	
Finished leather trim	Cr^{+3} Pb	1,600 - 41,000 100 - 3,300	Landfill with leachate collection
Sewer screenings	Cr^{+3} Pb Zn	0.27 - 14,000 2 - 110 35 - 128	
Wastewater treatment residues (sludges)	Cr^{+3} Cu Pb Zn	0.33 - 19,400 0.12 - 8,400 0.75 - 240 1.2 - 147	

[a] Range not shown when only one sample was analyzed for the constituent

D. REFERENCES

1. All information on air emissions for this report was taken from Assessment of Information Available Through State & Local Air Pollution Control Agencies to Support NESHAP Development presented by VíGYAN Inc. to the U.S. EPA on February 26, 1993.

2. All other information for this report was taken from Assessment of Industrial Hazardous Waste Practices in Leather Tanning and Finishing Industry presented by SCS Engineers to the U.S. EPA in November 1976.