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CLEANER PRODUCTION GUIDELINES IN LEATHER INDUSTRIES

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BACKGROUND OF THE LEATHER INDUSTRY

Leather was one of the first manufactured materials, and the Leather Technologist can claim to be a member of an ancient profession. Leather has long outgrown in its practical purpose and today is regarded more as a luxury than a necessity, particularly in the affluent West.

The global industry is valued at about Rs.3964.4 billion (71.27 Billion Euro). Most of the producing countries are developing countries, yet China and Italy are the leading producing and exporting nations in the world with exports worth Rs. 886.16 billion (15.93 billion Euros) and Rs. 606.32 billion (10.901 billion Euros) respectively. The industry is buyer –driven, with producing countries manufacturing in line with specifications, guidelines and technical advice provided by the buyer countries.

The leather industry occupies a prominent place in the Indian economy in view of its substantial export earnings, employment potential and growth.

LEATHER INDUSTRY IN INDIA

The leather industry occupies a place of prominence in the Indian economy in view of its massive potential for employment, growth and exports. There has been an increasing emphasis on its planned development, aimed at optimum utilization of available raw materials for maximizing the returns, particularly from exports. The exports of leather and leather products gained momentum during the past two decades.

- The Leather Industry holds a prominent place in the Indian economy. This sector is known for its consistency in high export earnings and it is among the top ten foreign exchange earners for the country. This industry is an employment intensive sector, providing job to about 2.5 million people.

- With an annual turnover of over US$ 7.5 billion, the export of leather and leather products increased manifold over the past decades and touched US$ 3.84 billion in 2010-11, recording a cumulative annual growth rate of about 5.87% (5 years).

- India has abundant raw material - India is endowed with 21% of world cattle & buffalo and 11 % of world goat & sheep population. Added to this are the strengths of skilled manpower, innovative technology, increasing industry compliance to international environmental standards, and the dedicated support of the dedicated support of the allied industries.

- Major markets for Indian leather products are Germany with a share of 14.34%, UK 12.80%, Italy 11.52%, USA 8.72%, Hong Kong 8.11%, France 7.07%, Spain 6.31%, Netherlands 3.98%, Belgium 2.02%, U.A.E.1.92%, Australia 1.30%. These 11 countries together accounts for nearly 78.09% of India's total leather products export.

Strengths of Indian leather sector

- Abundant raw material source- 2 billion sq ft of leather produced annually.
- Varieties of goat/calf/sheep skins which command premium position.
- Strong and eco-sustainable tanning base
- Modernized manufacturing units
- Trained/Skilled manpower at competitive wage levels
- World-class institutional support for design & product development, HRD and R & D.
- Presence of support industries like leather chemicals, components and finishing auxiliaries
- Presence in major markets - long European experience
- Strategic location in the Asian landmass.

Major Production Centers of Leather and Leather Products

Southern Region	
▪Tamil Nadu	Chennai,Ambur, Ranipet, Vaniyambadi, Trichy and Dindigul
▪Andhra Pradesh	Hyderabad
▪Karnataka	Bangalore
Northern Region	
▪Punjab	Jallandhar
▪Delhi	Delhi
Eastern Region	
▪West Bengal	Kolkata
Central Region	
▪Uttar Pradesh	Kanpur and Agra
Western Region	
▪Maharashtra	Mumbai

THE LEATHER MANUFACTURING PROCESS

Animal skin consists of epidermis, a layer of fatty tissue called areolar and inner corium. The semi-soluble protein, called 'collagen' present in corium is converted into highly durable leather through tanning operations. Skin of cows and buffaloes is called hide. Skin of goats and sheep is called skin. In India, 80% of hide available is from animals that died naturally due to ban on cow slaughter in many parts of the country. Goat and sheep skins, however, are by products of meat industry. Hides are 1-3 square meter (m2) in size and weigh about 10-20 kilograms (kg). Skins are smaller in size, 0.4 – 0.5 m2 and lighter in weight around 1-2 kg. Slaughter hides and skins contain 60-70% of moisture, which make them liable to bacterial attack, which in turn decomposes the hides and skins.

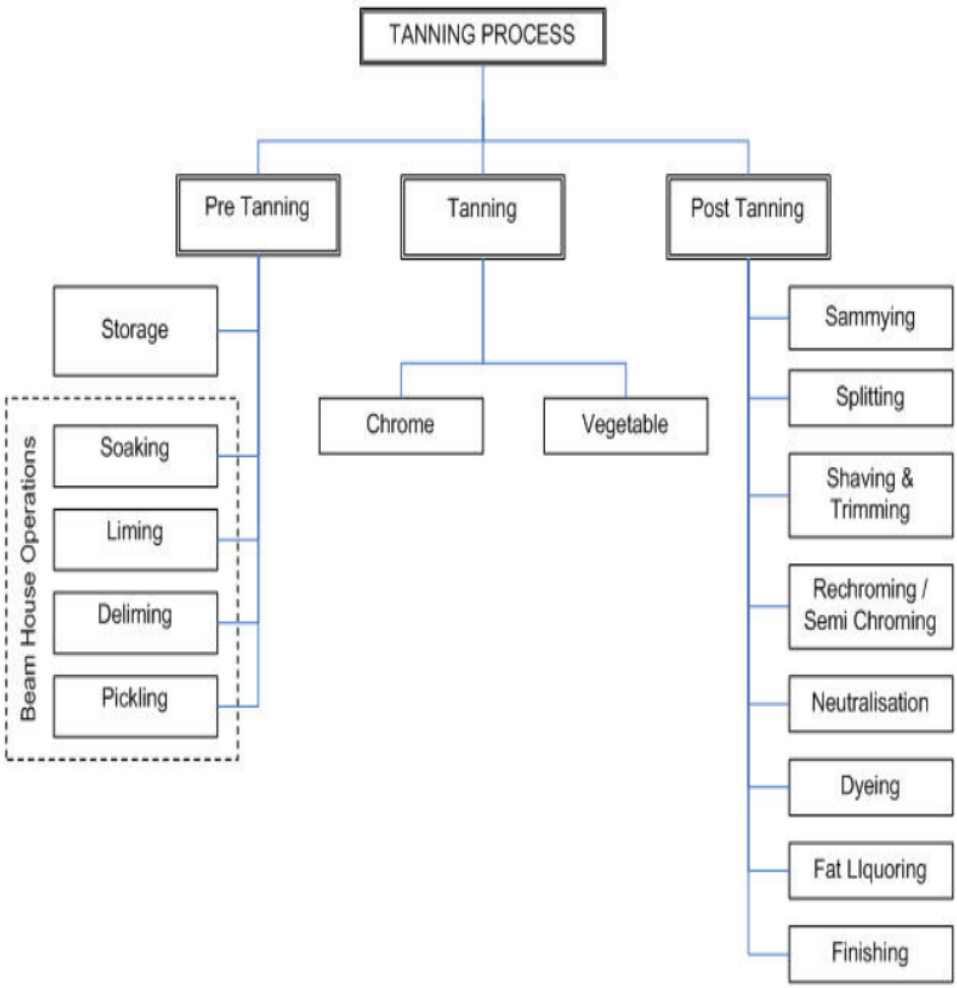
The preservation of hides and skins in a tannery can be split into following four main categories:

- Preservation of hides and skins storage
- Beam house operations
- Tanning operations
- Post-tanning and finishing operations

Furthermore, tanneries employ abatement techniques for the treatment of wastewater, solid waste and air emissions generated during these processes. Operations carried out in the beam house, tanyard, and post-tanning areas are often referred to as wet processes, as they are performed in processing vessels such as drums. After post-tanning, the leather is subjected to dry finishing operations.

Processes employed in each of the above categories change depending on the raw materials used and the final desired products. Hence the environmental impacts vary from tannery to tannery and a more detailed assessment is necessary at each unit/sit

Process of Tanning



Brief process description of each step is discussed in the sections below:

RE-TANNING OPERATIONS

- **Raw hides/skins**

Usually, the hides/skins consist 65% of the water and 30-35% proteins and fat. Because of the high amount of moisture in the hides/skin, there will be bacterial degradation. In order to prevent this bacterial activity, the moisture content should be brought down to less than 30%. This dehydration is usually done by applying common salt (i.e., Sodium Chloride) to the hides/ skins to the tune of 30-45% by weight.

- **Sorting**

Hides and skins are sorted into several grades by size, weight, or quality.

- **Trimming**

Trimming is generally carried out during the sorting process. Some of the edges (legs, tails and heads, etc.) of the raw hides and skins can be cut off. Usually this is done in the abattoir, but it can also be carried out in tanneries.

- **Curing and storing**

Curing is a process that prevents the decomposition of hides and skins from the time they are flayed in the abattoir until the processes in the beam house begin. Whenever a raw material cannot be processed immediately (green), it must be cured. Popular methods of long-term preservation are salting and drying. Methods for short-term preservation (2-5 days) are cooling, using crushed ice or refrigerated storage, and biocides. Curing is done in the abattoir, at the hide market, or at the tannery. In certain cases it might be necessary to repeat the step in the tannery, e.g., chilled hides can be salted for longer storage or if salting was not efficient enough. Hides and skins are generally stored on pallets in ventilated or air- conditioned and/or cooled areas, depending on the method of curing chosen. From storage the hides and skins are taken to the beam house.

- **Soaking**

The main purpose of this process is to remove the salt used during curing, re-hydrating the material and to get rid of unwanted materials such as dung, blood, soil, etc. The duration of soaking may range from several hours to a few days. Depending on the type of raw materials used, soaking additives such as surfactants, enzyme preparations and bactericides can be used. The process of soaking can be classified into three stages Dirt Soaking – In dirt soaking, 300-400 % of water is used to remove the unwanted materials Main Soaking – The purpose of main soaking is to re-hydrate the material. In this operation, water, non-anionic wetting agent (0.2 % concentrated Soda ash (0.2% concentrated) and preservatives (0.05% concentration) are used. Final soaking – Only water is used for the washing purpose in this operation Major part of salt associated with preservation of skin/ hides is removed during the soaking operation.

- **Liming**

The purpose of this operation is to facilitate the removal of hair, flesh, fat (partially), inter-fibrillary protein and to open-up the fibrous structure for osmotic swelling. The process of liming can be broadly classified into two parts i.e. dehairing and re-liming Dehairing – Lime (8-10 %) along with Sodium Sulphide (3 %) is applied to the skin to remove hair Re-liming – To open up fibrous structure, lime, soda ash, caustic soda, etc., are applied. The pH of the skin being processed will rise to 12- 12.5.

- **Fleshing**

The excess fleshing is removed manually or by using fleshing machines. The quantity of wet fleshings is in the range of 10-15% of the weight of raw hides/skins

- **De–liming**

This is a process to adjust the pH in between 8-8.5 in order to enhance the enzymatic activity, which converts some of the proteins into soluble forms. pH correction i.e., from 12-12.5 to 8-8.5 are done by using ammonium chloride in case of soft leather and ammonium sulphate in case of hard leather.

- **Pickling**

Pickling is a process of correcting the pH suitable to the tanning operation and to prevent swelling of the leather i.e. dehydration of the leather. In this process, water (80%), salts (8-10%), formic acid (0.28-0.3%), sulphuric acid (0.75 – 2% based on thickness) are applied.

- **pH correction**

For vegetable tanning, a pH in between 4 and 4.5 is maintained whereas; pH in between 2.5 and 7.3 is maintained in case of chrome tanning.

- **Prevention of swelling**

The salts to the tune of 8-10% are used in this process, to prevent the swelling. Thus the dehydration takes place.

TANNING OPERATIONS

The tanning process is of two types i.e., chrome tanning and vegetable tanning. Of the total leather production in India, more than 80% is based on chrome tanning and the rest is based on vegetable tanning.

a) Chrome tanning

Basic chromium sulphate [$Cr_2(SO_4)_3$] (7-10 %) containing 25% Cr_2O_3 and sodium sulphate (25- 30%) is used in chrome tanning. Part of the pickle bath is used for chrome tanning operation. The pH is increased to 3.8-4.0 at the end of chrome tanning process which is called basification. The semi-finished leather after chrome tanning is called wet blue.

b) Vegetable tanning

Plant extracts are used for the purpose of tanning in this process. The pH falls down from 4- 4.5 to 3-3.5. Though this process is free of any heavy metal use, the leather developed from this process has comparatively weaker capacity of heat resistance and dye-holding.

Post-tanning operations

Post-tanning operations comprise of re-chroming of semi-finished wet blue leather, neutralization, dyeing, fat liquoring and finishing. In case if post-tanning of vegetable tanned semi-finished leather, the operations involved are semi-chrome tanning, neutralization, dyeing, fat liquoring and finishing. However the operations vary depending upon the final product.

- **Sammying**- It is a mechanized process followed to remove excess moisture in the wet blue.
- **Splitting**: After sammying, the material is split into required thickness using splitting machine
- **Shaving and Trimming**: The semi-finished leather is leveled using the shaving machine.
- **Re-chroming**: Depending on the quality of wet blue, re-chroming is carried out to improve the chromium content in the leather.
- **Semi-chroming**: Incase of vegetable tanned semi-finished leather, chrome tanning is given depending on the final leather quality.
- **Neutralization**: pH is adjusted to 4.5-6.5
- **Dyeing**: The leather is colored using dyes such as anionic dyes, acid dyes, direct, metal complex compounds and basic dyes.
- **Fat-liquoring**: Natural/synthetic oils are applied for fat liquoring, thereby imparting softness to the leather
- **Finishing**: Phenolics, melamine, acrylics, polymers, naphthalene, etc., are used for finishing to impart fullness to the leather

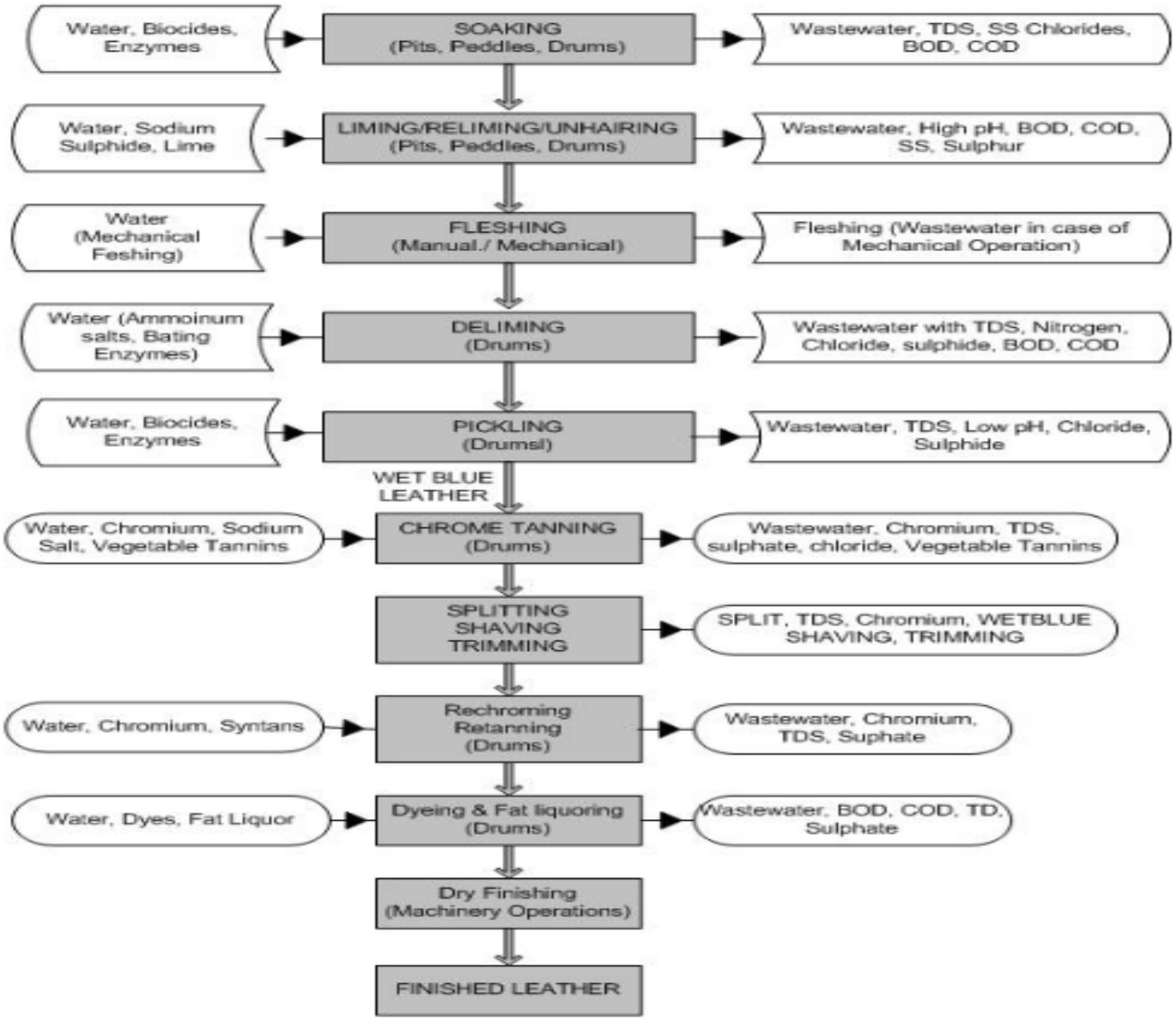
INPUT VS OUTPUT IN THE TANNERY PROCESS

- The major inputs such as water, chemicals in each sectional operation starting from soaking, liming, fleshing, deliming, pickling, vegetable/chromium tanning, etc., till finishing are shown as a part in the process flow diagram in Figure.

- The mode of operation and equipment used such as pits, paddle, drums, type of machine operations are also indicated as a part in the process flow diagram in figure.

- The waste discharges from each sectional operation such as wastewater fleshings, waste trimmings and the major constituents in the wastewater in terms of TDS, COD, BOD are also given in Figure.

Input Vs Output Tanneries



ENVIRONMENTAL ISSUES AND PREVENTIVE METHODS

Environmental issues associated with tanning and leather finishing include the following

- Wastewater
- Air emissions
- Solid waste
- Hazardous materials

Wastewater

A. Water usage

Water plays a vital role in tannery operations. Approximately 30-40 liter (L) of water is used for processing one kilogram (kg) of raw hide/skin into finished leather. Most of the Indian tanneries which are located near the riverbanks or natural water bodies draw surface water. Ground water from their own open wells/tube wells existing within their premises is also used by some tanneries. Most of the traditional tanneries store water in open cement lined pits and ground level tanks. Water from these storage tanks would be pumped directly to the process zones.

B. Wastewater generation and characteristics

Volume of wastewater (effluent) and its characteristics vary from tannery to tannery. They may also vary within the same tannery from time to time. The wastewater from beam house process viz. soaking, liming, deliming, etc., are highly alkaline, containing decomposing organic matter, hair, lime, sulphide and organic nitrogen with high BOD and COD. The wastewater from tanyard process viz.pickling, chrome tanning are acidic and colored. Effluent from vegetable tanning contains high organic matter. The chrome tanning wastes contain high amounts of chromium mostly in the trivalent form. The characteristics of combined wastewater before treatment and after treatment are given in Table

Characteristic of Wastewater

SL No.	Parameters	Average concentration in mg/litre (Before Treatment)	Average concentration in mg/litre(After Pre-treatment)
1.	BOD	1850	700
2.	COD	4500	3000
3.	Chloride	5500	1200
4.	SS	3750	1500
5.	Total Cr	165	38
Source: Minimal National Standard for Tanneries: COINDS/35/1991-92, CPCB, Delhi			

Fig- The pollution load per tonne of hides and skins process is given in Table as below

S.No.	Pollution Parameter	Pollution Load (kg)
1	Volume (m^3)	40
2	BOD	70
3	COD	180
4	Chlorides (Cl)	270
5	Dissolved Solids	600
6	Suspended Solids (SS)	100
7	Sulphides (S)	4
8	Chromium (Cr)	30
Note: Composite Wastewater (no Segregation)		

Pollution load per tone of Hides/Skines Processed

(source: Central Leather Research Institute, Tamil Nadu)

Process-wise generation of wastewater and their characteristics are explained in Table as below

Characteristics of Tannery Effluent

Parameter	Soaking	Beam House Operation (Liming, Reliming, Fleshing , Deliming)	Pickling & Chrome Tanning	Wet finish - Rechroming Dyeing & Fat Liquor	Composite (Including Washings)
Volume of the effluent in litres /ton of hides/skins	6000 - 9000	6000 – 10000	1500 – 3000	3000 – 5000	30000 – 40000
pH	7.5 - 8.0	8 - 12	2.2 – 4.0	3.5 - 4.5	7.0 - 9.0
BOD 5 day at 20°C (Total)	1100 - 2500	2000 - 8000	400 - 800	1000 – 2000	1200 – 3000
COD (Total)	3000 - 6000	3000 – 15000	1000 - 3000	2500 – 7000	2500 – 8000
Sulphide (as S)	-	50 – 200	-	-	30 – 150
Total Solids (TS)	35000 - 55000	6000 - 20000	30000 - 60000	4000 – 10000	15000 – 25000
Dissolved Solids (DS)	32000 - 48000	5000 – 15000	29000 - 58000	3400 – 9000	13000 – 20000
Suspended Solids (SS)	3000 - 7000	3000 – 15000	1000 - 2000	600 – 1000	2000 – 5000
Chlorides (as Cl)	15000 - 30000	3000 – 6000	15000 - 25000	500 – 1000	6000 – 9500
Total Cr	-	-	1500 - 3000	30 – 60	80 – 200
▪ All values except pH are expressed in mg/L ▪ Volume of wastewater applicable for hides (cow & buffalo) and goatskins and not for wool sheepskins					

(Source: Central leather research institute, Tamil Nadu)

EFFLUENT TREATMENT

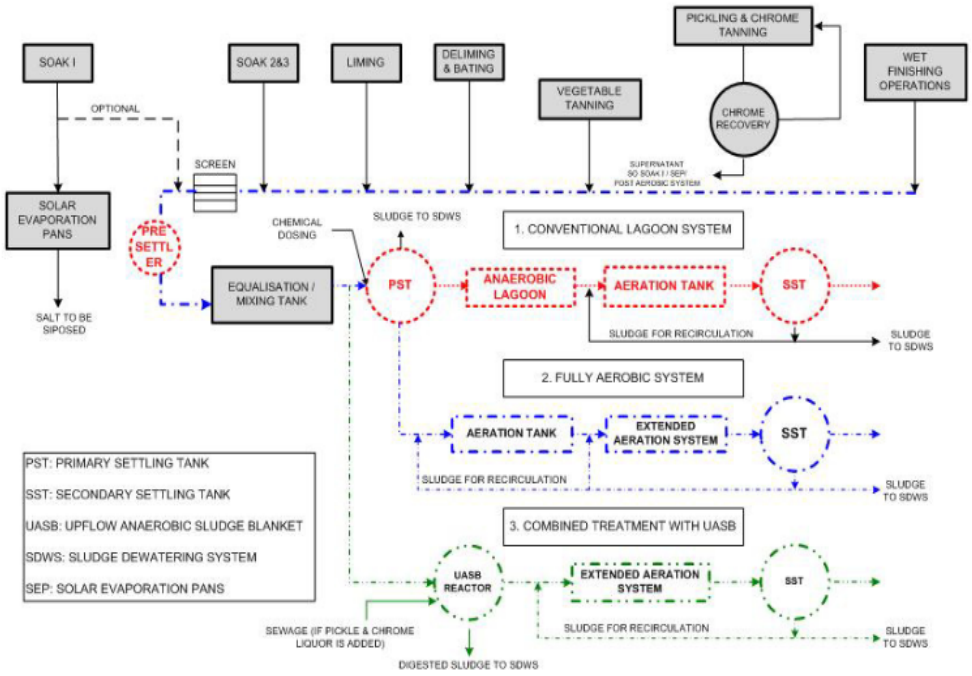
Techniques for treating effluent from tanneries include source segregation and pre-treatment for removal/ recovery of chromium; grease traps, skimmers or oil water separators for separation of floatable solids; filtration for separation of filterable solids; flow and load equalization; sedimentation for suspended solids reduction using clarifiers; biological treatment, typically aerobic treatment, for reduction of BOD; biological nutrient removal for reduction in nitrogen and phosphorus; chlorination of effluent where disinfection is required; dewatering and disposal of residuals in designated hazardous waste landfills. The typical wastewater treatment process flow diagram is shown in Figure below. The following additional engineering controls may be required in addressing the specific pollution control parameters

- Advanced metal removal using membrane filtration or other physical/ chemical treatment technologies.

- Reduction in effluent toxicity using appropriate technology (such as reverse osmosis (RO), ion exchange, activated carbon, etc.).

- Reduction of TDS in the effluent using RO or evaporation.
- Containment and neutralization of odour nuisance.

Management of industrial wastewater and examples of treatment approaches are discussed in the General EHS Guidelines. Through use of these technologies and good practice techniques for wastewater management, facilities should meet the Guideline Values for wastewater discharge.



Tannery Effluent Treatment System

Air emission

Air emissions from tanning facilities include the following.
Sources of Air Emissions and Preventive Methods

Emission to Air	Source Operations in Tannery	Suggestive Methods of Prevention
Organic Solvents	Degreasing Finishing	▪ Usage of water-based formulations for spray dyeing ▪ Usage of roller coating techniques or curtain coating machines wherever applicable ▪ Usage of spraying units with economizers and high volume / low-pressure spray guns ▪ Avoid usage of internationally banned solvents ▪ Usage of wet scrubbers, activated carbon adsorption, bio-filters (to remove odors), cryogenic treatment, and catalytic or thermal oxidation.
VOCs	Spray-finish Machines Dryers	
Sulfides	Beam house and Effluent treatment	▪ Maintain a basic pH over 10 in the equalization and sulphide oxidation tanks. ▪ Avoid breeding anaerobic conditions in sulphate containing materials. ▪ Add manganeese sulphate to treated effluent. ▪ Use adequate ventilation
Ammonia	Beam House Deliming Dehairing Drying after dye-penetration	▪ Adequate ventilation followed by wet scrubbing
Dust	Storage handling of powdery chemicals Dry shaving Buffing Dust removal machines Milling drums, Stalking	▪ centralized system ▪ employing cyclones ▪ Usage of scrubbers/bag filters, as needed.

Emissions of sulfur dioxide may occur during bleaching, post-tanning operations, or carbon dioxide (CO_2) deliming, but they are not typically a significant source of emissions.

ODOUR EMISSIONS TO AIR

Odorous Emissions to Air	Source Operations in Tannery	Suggestive Methods of Prevention
NH_3	Beam house operations	▪ Prompt curing of raw hides ▪ Reduce the time that sludge remains in the thickener, dewater thickened sludge by centrifugation or filter press, and dry the resulting filter cake. Sludge
H_2S	Beam house operations ETP collection tanks ETP Primary Treatment Units	
	ETP Sludge Dewatering System ETP Anaerobic Lagoons	containing less than 30 % solids may generate especially strong odors ▪ Ventilate tannery areas and control exhaust from odorous areas (e.g., where wastewater sludge is thickened and dewatered), through use of a biofilter and / or a wet scrubber with acid, alkali, or oxidant
VOCs	Finishing Operations	
CH_4	ETP Anaerobic Lagoons	

(Source draft report of expert committee on odour pollution and its control july 2007 CPCB)

Solid waste

Solid waste includes salt from raw skin / hide dusting; raw skin / hide trimmings; hair from the liming /dehairing process, which may contain lime and sulfides; and fleshing from raw skins / hides. Other solid waste from tannery industry includes wet-blue shavings, containing Cr2O3; wet-blue trimming, which is generated from finishing processes and contains Chromium oxide (CrO), syntans, and dye; and buffing dust, which also contains CrO, syntans, and dye. The reducing characteristics of tannery sludge stabilize Cr (III) with respect to Cr (VI), due to the presence of organic matter and sulfides.

Prevention and control measures for solid waste include the following:

- Reduce inputs of process agents (particularly precipitation agents in wastewater treatment) to the extent practically applicable.

- Segregate different waste / residue fractions to facilitate recovery and re-use (e.g., to manufacture pet toys, pet food, leather fiberboard).

- Recycle sludge as compost / soil conditioner or in anaerobic digestions for energy generation. Process sludge may be used for composting / agriculture after appropriate assessment for contaminants and potential impacts to soil and groundwater
- Fleshings could be degraded through bio-methanation process – CLRI research findings are encouraging

Hazardous materials

Tanning and leather finishing processes involve the use of a variety of hazardous chemicals. Guidance on the management of hazardous materials, including handling, storage, and transportation, shall be adopted as provided in the General EHS Guidelines

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