CHAPTER 6

LEATHER PROCESSING: METHODS, ENVIRONMENTAL CHALLENGES AND CLEANER TECHNOLOGY OPTIONS

6.1 RAW MATERIAL

Technically, leather is a natural protein polymer treated with tanning agents to make it resistant to enzymatic attack and putrefaction and to improve its several physical properties. Leather is made from hides and skins, which are by-products of slaughterhouses. Hides and skins are obtained from fallen animals too.

The outer covering of a small animal like sheep, goat etc. is referred to as skin while that of the bigger animal like cow, buffalo, etc is hide. These raw materials are obtained from a variety in size, shape, substance and structural characteristics depending upon the animal, its age, sex, breed, food, climate and the care of the live animals. The raw skin readily putrecises but not the processed leather. Leather is more resistant to heat, hydrolysis and micro-organisms.

The raw hide or skin is composed of about 60% water, 35% proteins (fibrous as well as non-fibrous) and the rest lipids, carbohydrates and mineral salts (Buljan et al 1997). The fibrous protein collagen is the leather making material. The various components of the animal skin
except the fibrous network of collagen are no more useful and often detrimental to the making of good quality leather. These unwanted components are therefore removed and skin brought into a condition by suitable processes when it can resist bacterial, thermal, chemical and hydrolytic influences. The protein collagen is retained with minimum of physical alterations while its reactivity is suitably modified by tanning agents.

In the conversion of hide or skin to finished leather about fifty different operations are involved each affecting the previous and the next step. They are washed, depilated, fed in various liquor, oiled, given massages, coloured and painted, decorated and even scented. Unlike other finished materials/products, which are normally made from standard raw material, leather needs careful and meticulous control during processing in order to obtain a finished product of acceptable quality and requirements.

6.2 STAGES IN THE LEATHER PROCESSING

The processing of leather involves three distinct sets of unit operations. These are

i. beamhouse or pre-tanning operations
ii. tanning process and
iii. post-tanning operations including finishing.

The process flow diagram of raw to finishing operation is given in Figure 6.1. In the beam house operations, the skins and hides received mostly in the wet salted conditions in the tannery are processed to remove
Figure 6.1 Leather process flow diagram
unwanted materials such as hair, flesh and other proteinous materials and conditioned suitably for the tanning process.

Tanning process is the operation in which the skins and hides are converted into semi-finished leather. In other words, the tanning process imparts resistance to the putrescible skins and hides against bacterial degradation. Apart from this basic function, the tanning materials also impart specific characteristics to the leather, many of which are unique to the nature of the tanning materials used.

In the post-tanning operations, the tanned semi-finished leathers are dyed to give a colour determined by the fashion demand and fatliquored to impart the degree of softness needed in the final leather and retanned to impart the filling, grain tightening and improve the uniformity in substance. Before doing these basic post-tanning operations, it might become necessary especially in the case of mineral tanned leathers to condition them by adjusting the pH to suitable level in neutralisation process to get uniform results in dyeing, retanning and fatliquoring. Each process under these three distinct sets of unit operations is detailed in this chapter.

6.3 PRE-TANNING OPERATIONS
6.3.1 Soaking

The skins and hides are received mostly in the wet salted conditions in the Indian tanneries. So, the first operation performed in the tanneries is the soaking operation in which the salt is removed and the goods are rehydrated to their original condition. In this process, the adhering blood, dung and other soluble protein such as albumin and globulin are also removed. Soaking is normally performed either in pits or
paddles. In the case of pits, the skins and hides should be trampled in order to remove the salt and other adhering materials and hence the first change of water is usually referred to as dirt soaking. Two or three changes of water are necessary to bring back the raw material to the original condition. Wet salted goods soak back easily whereas some difficulties may be encountered in the case of dry salted and dried skins and hides. 300-400 % water is used in each stage and it is a common practice to use a non-ionic wetting agent to accelerate the process of soaking and a bactericide to prevent bacterial damage. Sometimes, an alkaline soaking aid such as soda ash or sodium sulphide might also be used in soaking process. Duration of soaking may vary from 3 hours to overnight depending on whether the material is skin or hide and nature of curing the stock has undergone. Still longer soaking may be necessary in the case of sun-dried stock.

6.3.2 Liming

Primary objectives of the liming process are
i. to remove the hair and flesh and
ii. to open up the fibre structures of the skins and hides by suitable plumping and swelling.

Apart from these, a part of the natural fat or grease and other unwanted proteins such as sweat glands, blood vessels, nerve tissues etc. are also removed during the liming operations. The important properties expected in the final leather can better be controlled in liming process. This fact is emphasised by the saying that the leather is made in the liming yard. The liming process is carried out in two stages. In the first stage, which is called unhairing process, the soaked stock is treated with a mixture of lime and sodium sulphide. This is performed either in pits or
paddles for hides whereas a paint liming system is employed for sheep and goatskins as a hair shaving method.

In the pit or paddle unhairing process, 300-400% water is employed whereas in the case of paint liming, only 10-15% water is used to make a paste of suitable consistency. In the traditional pit method, a part of the old lime liquor is recycled in the unhairing bath for the subsequent lot.

After the removal of the hair, the goods are relimed in order to open up the fibre structure suitably depending upon the type of finished leathers to be made from them or the type of tanning system to be employed.

Reliming is carried out either in pits or paddles mostly with 300-400% water and lime. Soda ash or sodium hydroxide may be used in small quantities to improve swelling to obtain better opening up of fibre structure in shorter duration. After the reliming, the goods are fleshed and scudded to remove short hair and dirt. The fleshing operation is shown in Figure 6.2.

6.3.3 Deliming

After washing of the limed pelt to remove lime from the surface, they are delimed with mostly ammonium salts viz. chlorides or sulphates to bring down the pH to 8 - 8.5. Usually a complete deliming is performed for soft types of leathers whereas in the case of heavy and firm types of leather like sole leather, it is customary to leave a streak of lime in the middle. This process is carried out in drums with about 100% water and the subsequent operation, bating is continued in the same bath.
Figure 6.2: Fleshing operation
6.3.4 Bating

The important objective of this unit operation is to purify the pelts by removing the unwanted components consisting of the proteinous products, epidermis, short hair and the scud. Interfibrillary proteins are also removed during the process to obtain proper grain texture and achieve softness and flexibility in the finished leather. In bating, the proteolytic enzymes based on mostly trypsin are used. After the deliming and bating, the pelts are thoroughly washed to remove the salts formed during the process. They are then scudded and washed.

6.3.5 Pickling

Pickling is carried out to bring down the pH to 2.5-3.0 so as to get quicker penetration and more uniform distribution in chrome tanning. In the case of rapid method of vegetable tanning, a partial pickling is done to a pH 4-4.5. The pelt is treated with a mixture of formic and sulphuric acids, and sodium chloride is used to suppress the acid swelling due to drop in pH and 10% salt concentration is considered necessary to suppress the swelling. 80% water based on pelt weight is used in pickling process.

6.3.6 Degreasing

Though part of the fat and natural grease is removed during the liming process by saponification, with skins like wool sheep skins which contain lot of fats, it might become necessary to carry out degreasing process separately. The process may be carried out either after deliming or after pickling, though it would be more effective after pickling. Due to washing, the pH of pickled pelt increases and hence repickling is done to bring down the pH to 2.8 before commencing chrome tanning.
6.4 TANNING PROCESS

Tanning process is the most important unit operation involved in the leather processing not only because it imparts the resistance against bacterial degradation and improves the durability but because of the fact that it imparts specific characteristics to the leather like hydrothermal stability, fullness, the charge characteristics and hence the affinity for post-tanning chemicals and auxiliaries.

The materials that are used for tanning of skins and hides are chrome, vegetable tanning materials, aluminium and zirconium salts, aldehydes like formaldehyde and gluteraldehyde, oils such as fish oil etc. The most popularly used materials are chrome and vegetable materials. Chrome tanned leathers and vegetable tanned leathers form the important raw materials for the manufacture of different types of finished leathers.

6.4.1 Chrome Tanning

The chrome tanning is done using wooden drums as shown in Figure 6.3. The process is continued in pickle bath itself after draining the float. 8 - 10% chrome in the form of Basic Chromium Sulphate (BCS) is offered along with a cationic or multicharged fatliquor. Now acid and electrolyte stable fatliquors (Rajamani et al 1998) are also employed in place of cationic fatliquors. Chrome tanning is started at a pH around 2.8 and finally after ensuring complete penetration, the pH is raised to 3.8-4.0 during basification to complete chrome tanning. A mixture of sodium formate and bicarbonate is used for basification. Total float volume at the end of chrome tanning is about 100-150% and total duration of tanning process is about 6-8 hrs.
6.4.2 Vegetable Tanning Process

In vegetable tanning, the pelts are treated with extracts of bark, nuts, leaves or heartwoods of certain plants. The most commonly used tanning materials are wattle, avaram, konnam, myrobalan, babul, quebracho, cutch, etc. The vegetable tanning materials are polyphenolic compounds and form colloidal dispersions in water.

In the conventional method, the tanning used to be carried out in a series of pits containing the liquors in the increasing order of concentrations and the goods used to stay in each pit for 2-3 days and the total duration of the vegetable tanning alone used to take around 30-60 days for completion.

Today, mostly the rapid method is followed by many tanners. A short pre-tanning at a pH 4.2 for 6 days followed by drum tanning is the usual tanning method followed nowadays. Some tanners also follow only drum tanning method to cut down the time and drudgery. In the rapid method, a treatment with phenolic pre-tanning syntan is given before commencing vegetable tanning to quicken the penetration and it is also customary to use sulphated vegetable fatliquor during tanning (Chandra Babu 1998).

In the case of drum tanning method, the float employed is very minimal ranging from 20-40% whereas in the case of pit tanning it may go upto 300-400% on the pelt weight. In the EI making, the vegetable tanned leathers are given a bleaching with oxalic acid and a bleaching syntan to remove the iron stains and to impart uniform colour and treated with an infusion of myrobalan nuts to obtain a light colour and light fastness characteristics. Oiling with pungam oil or groundnut oil is carried out.
before drying to avoid grain crackiness and imparting lightfastness. Epsom salt and glucose are used to increase the weight of the EI leathers.

6.5 POST-TANNING OPERATIONS

Wet blue leathers and EI leathers are the raw materials for the production of many finished leathers. Vegetable tanned leathers possess many good qualities but lack in hydrothermal stability and affinity for dyes and fatliquors. So usually a retanning with chrome is carried out before they are processed into different finished leathers. This is called semi-chroming.

The unit operations involved in semi-chroming are as follows:

1. Stripping to remove unfixed or unwanted tannins from the leather and also to remove oils and greases from the leather using alkalis such as borax or sodium bicarbonate with sodium sulphite and degreasing agent. Float employed is about 500% of the dry EI weight basis.

2. Stripping is followed by a thorough wash with about 600% water and bleaching with oxalic acid and bleaching syntan with about 300 to 400% float to remove iron stains formed during the shaving operation and to get a uniform colour. Washing with 600% water is done after bleaching.

3. Souring to pH 3.0 - 3.3 with 300% water and formic acid is carried out and the chrome tanning is commenced in the same bath. Cationic or multicharge fatliquors are also used along with chrome and the tanning is completed at pH 3.8.
4.0 using sodium formate and sodium bicarbonate mixture during the basification stage.

6.5.1 Rechroming of Wet Blue Leathers

The chrome tanned semi-finished wet blue leather is split into two parts. The grain part is used for quality leather and the split is used for lining purposes. These splits also are further shaved and trimmed before wet finishing operations. The double width shaving machine used for big hides is shown in Figure 6.4. The wet blue leathers, after splitting/shaving are rechromed again for equalisation of chrome in a pack of leather and in different layers of the same leathers before the post-tanning operations. The sequence of unit operations for wet blue and semi-chrome leather would be the same.

6.5.2 Neutralisation

The primary object of neutralisation is to neutralise the excess acid present in wet blue/semi-chrome leathers, which interferes with subsequent operations like dyeing, fatliquoring and retanning. The extent of neutralisation would depend on the desired properties of the finished leathers. The agents commonly used for neutralisation are sodium formate, sodium bicarbonate, sodium sulphite, ammonium bicarbonate, neutralising syntan, etc. Float employed is 100-150% on the shaved weight.

6.5.3 Retanning

Retanning is done to impart

i. filling of the loose portions
Figure 6.4 Double width shaving machine
ii. fullness, round feel and body to the leather and
iii. tightness of the grain.

The main retanning materials are

i. vegetable tanning materials
ii. phenolic syntans
iii. acrylic and other resin tanning materials
iv. protein based tanning agents
v. whitening syntans and
vi. polyurethane syntans.

6.5.4 Dyeing

Leathers are dyed to impart colour as demanded by the fashion. The
dyes used in leather can be classified into

i. acid dyes
ii. direct dyes
iii. basic dyes
iv. metal complex dyes and
v. reactive dyes.

The most commonly used dyes are acid, direct and metal complex
dyes. Sometimes basic dyes are used for darker shades like blacks and
some browns. Reactive dyes are seldom used in leather processing. The
leather dyes are recently coming under close scrutiny of the environmental
authorities. Germany has recently come out with a ban on use of
benzedine and related aromatic amines based dye stuff.
6.5.5 Fatliquoring

Fatliquoring of leathers are performed to impart softness, flexibility, feel, drape, run, etc. The strength properties are also improved by fatliquoring. Fatliquors are oil in water emulsions. The oils and fats are converted into emulsions by a process of sulphation, sulphonation, sulphitation or sulphochlorination.

The fatliquors, based on their charge characteristics are classified into

i. anionic
ii. cationic
iii. non-ionic and
iv. multicharged fatliquors.

They are also classified based on the origin of the oils as

i. vegetable oils
ii. animal oils which include marine based oils and
iii. synthetic oils based on long chain hydro carbons, long chain fatty esters and long chain fatty alcohols etc.

All the three unit operations are carried out together in the same bath mostly and the dyes and fatliquors will have to be fixed by the addition of formic acid. The float volume employed is about 100%. After these unit operations, the leathers are dried.
6.5.6 Finishing

Finishing of leather consists in the application of a firm forming material to the grain to provide aesthetic appeal and to improve the sale value of the leather. It also provides surface protection against rubbing, abrasion and staining. The defects of the grain are covered by the protective coat and hence the cutting value is also very much enhanced.

Finishing formulations contain pigments and dyes for colouring, binders based on casein or acrylates or polyurethane for binding, wax emulsions for feel modification, fillers for readjustment in optical property and nitro cellulose or cellulose acetate butyrate or other hard resins for surface coat protection. Formaldehyde is used for fixing for casein based finishes.

6.5.7 Chemical Consumption Pattern in Leather Industry

The chemicals used in leather processing are classified as bulk and performance chemicals. Bulk chemicals are sodium chloride, lime, sodium sulphide, ammonium salts, formic acid, sulphuric acid, sodium formate, sodium bicarbonate, ammonia etc., which are used in many other industries as well. On the otherhand, tanning materials, formulations of fatliquors, retanning, finishing agents etc., are performance chemicals. These are used to add to the performance of leather in usage and limited to use in leather sector alone.

The consumption pattern of chemicals in leather processing per ton of hides or skins is presented in Table 6.1
Table 6.1

Consumption pattern of chemicals in leather processing

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Chemical</th>
<th>In Kg per ton of hide/skin process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Soaking aids</td>
<td>1.0 - 2.5</td>
</tr>
<tr>
<td>2</td>
<td>Preservative</td>
<td>2.5 - 5.0</td>
</tr>
<tr>
<td>3</td>
<td>Lime</td>
<td>80-200</td>
</tr>
<tr>
<td>4</td>
<td>Sodium sulphide</td>
<td>20-30</td>
</tr>
<tr>
<td>5</td>
<td>Sodium chloride</td>
<td>80-100</td>
</tr>
<tr>
<td>6</td>
<td>Ammonium salts</td>
<td>10-15</td>
</tr>
<tr>
<td>7</td>
<td>Sulphuric acid</td>
<td>12-20</td>
</tr>
<tr>
<td>8</td>
<td>Sodium formate</td>
<td>5-12.5</td>
</tr>
<tr>
<td>9</td>
<td>BCS</td>
<td>60-120</td>
</tr>
<tr>
<td>10</td>
<td>Al (Al₂O₃)</td>
<td>1-20</td>
</tr>
<tr>
<td>11</td>
<td>Zr(ZrO₂)</td>
<td>0-15</td>
</tr>
<tr>
<td>12</td>
<td>Vegetable tannins</td>
<td>10-220</td>
</tr>
<tr>
<td>13</td>
<td>Synthetic tanning agents</td>
<td>20-60</td>
</tr>
<tr>
<td>14</td>
<td>Fatliquors</td>
<td>25-100</td>
</tr>
<tr>
<td>15</td>
<td>Dyes</td>
<td>2.5 - 20</td>
</tr>
<tr>
<td>16</td>
<td>Binders</td>
<td>20-45</td>
</tr>
<tr>
<td>17</td>
<td>Pigments</td>
<td>10-25</td>
</tr>
<tr>
<td>18</td>
<td>Top coats</td>
<td>20-45</td>
</tr>
<tr>
<td>19</td>
<td>Wax emulsions</td>
<td>2.5-5.0</td>
</tr>
<tr>
<td>20</td>
<td>Feel modifiers</td>
<td>1-2</td>
</tr>
</tbody>
</table>
6.6 ENVIRONMENTAL CHALLENGES

Pollution prevention by adopting cleaner technologies is the best option for tannery waste management problems. Selection and implementation of cleaner technologies, water management, waste minimisation, recovery and reuse of chemicals in the tanneries are very important for sustainable growth of leather industry. In leather processing, a large quantity of water, as much as 40 to 50 litres of water per kilogram of raw material is used. It is also known that the amount of pollutants discharged in the tannery effluent arises to a greater extent from the beamhouse operations. Leather processing employs the complex principles of biotechnology and inorganic chemistry for achieving the desired technical objectives. Over 80% of organic pollution load in BOD is generated in beamhouse of which 10% is derived from soak liquors, 60% from unhairing/liming, 5% from deliming and bating and 25% from the rest of the processes.

The soak water provides 60% salinity and the rest comes from pickling and other operations. Even though the conventional practices do allow tanners to achieve satisfactory leather quality, they suffer from disadvantages like longer processing times and large working space and environmental problems. These conventional practices are based on techniques standardised prior to the recognition of their impact on environment. Waste minimisation/low waste concept is the underlying principle for resource conservation and inplant control to achieve production consistency and reduction in pollution problems (De 1993). In leather processing, chrome tanning is an important step, which has raised serious ecological concerns in leather sector.
The international regulation stipulates concentrations of 0.3 to 2.0 ppm of chromium in treated industrial wastewater (Rajamani *et al.* 1985). So several technological options have been developed to render chrome tanning eco-friendly. Among the options developed, one is high exhaust chrome tanning system, the second option is chrome recovery and reuse and the third is replacement of chrome partially or completely with ecologically acceptable tanning compounds. Similarly in post-tanning operations, the conventional practices require a total reappraisal in the light of current environmental regulations (Bosnic *et al.* 1997). The general characteristics of tannery effluent before and after treatment are presented in Table 6.2. These figures can be compared with the norms specified by Pollution Control Board and Bureau of Indian Standards, which are set out in Table 6.3 (Pollution Control Acts 1995).

### 6.7 CLEANER TECHNOLOGY OPTIONS

The emerging cleaner technology options in leather processing are detailed as follows.

#### 6.7.1 Curing

Common salt (sodium chloride) is the most economical and efficient curing agent known so far. But continuous use of salt has led to severe soil erosion and pollution of ground water. Since cost for removing salt from water streams is prohibitive, alternatives for salt have emerged. The advantages and disadvantages of these methods are given below.
Table 6.2
The general characteristics of effluent before treatment and after treatment

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Parameters</th>
<th>Before treatment</th>
<th>After treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>pH</td>
<td>6.0-10.0</td>
<td>6.5-8.5</td>
</tr>
<tr>
<td>2.</td>
<td>Total suspended solids</td>
<td>2000-5000</td>
<td>10-100</td>
</tr>
<tr>
<td>3.</td>
<td>Total dissolved solids</td>
<td>11000-16000</td>
<td>8000-12000</td>
</tr>
<tr>
<td>4.</td>
<td>Chlorides as Cl</td>
<td>6000-9500</td>
<td>2000-6000</td>
</tr>
<tr>
<td>5.</td>
<td>Sulphates as SO₄</td>
<td>2400-4000</td>
<td>800-2000</td>
</tr>
<tr>
<td>6.</td>
<td>BOD</td>
<td>1000-3000</td>
<td>30-150</td>
</tr>
<tr>
<td>7.</td>
<td>COD</td>
<td>3000-5000</td>
<td>200-500</td>
</tr>
</tbody>
</table>

All values except pH are expressed in mg/l
Including segregation of saline streams and evaporations in solar pans
### Table 6.3

Pollution Control Board and BIS norms

<table>
<thead>
<tr>
<th>S. No</th>
<th>Parameters</th>
<th>Discharge into inland surface water</th>
<th>Discharge into land for irrigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>pH</td>
<td>5.5-9.0</td>
<td>5.5-9.0</td>
</tr>
<tr>
<td>2.</td>
<td>Total suspend solids</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>Total dissolved solids</td>
<td>2100</td>
<td>2100</td>
</tr>
<tr>
<td>4.</td>
<td>BOD</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>5.</td>
<td>COD</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>6.</td>
<td>Oils &amp; grease</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>7.</td>
<td>Chromium as Cr(III)</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>8.</td>
<td>Chromium as Cr(VI)</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>9.</td>
<td>Percent sodium</td>
<td>-</td>
<td>60</td>
</tr>
</tbody>
</table>

All values except pH are expressed in mg/l
6.7.1.1 Air drying

By air drying method, the raw hides and skins are dried in the air. This method is very economical but it is difficult to wet back the flint-dried goods, which are horny and crumpled (Ramasami et al 1998). This method may also cause damage to the skins in subsequent processing.

6.7.1.2 Frame drying

In this method, the raw hides and skins are stretched and tied/nailed on frames and dried in the air. Though this method is economical, this will also pose similar problems as in the case of air drying.

6.7.1.3 Freezing

This technique has been studied extensively by some researchers and the trials were carried out in 1953. The formation of ice-crystals inside the fibre network may cause micro-damage to the substance, which in turn may produce looser leather. This method is not economical to put into practice.

6.7.1.4 Chemical methods

There are alternative chemical methods by which the raw hides and skins can be preserved. They are as follows

1. Application of zinc chloride and preservative on the flesh side of the stock. This method requires effective control over the system for success.
2. Immersing the raw hides and skins in 20% soda ash solution for 8 hours. This method also requires effective control over the system for success.

3. Application of 3% sodium bisulphite on the flesh side and folding into bundle and keeping in sealed polythene bags. This may not be practicable, as the stock requires to be kept in sealed polythene bags to prevent reinfestation.

4. Immersion of stock in a solution consisting of 1% sodium sulphite + 1% acetic acid + 50% water + 0.03% preservative. This also requires to be sealed in a polythene bag, which may not be practicable.

5. Application of 1% sodium bisulphite on the flesh side and followed by the application of 1% sodium chloride + 1% acetic acid + 20% water. The stock is to be sealed in the polythene bags and put into the drum for agitation.

6. 1% sodium bisulphate is applied on the flesh side and 1% sodium bisulphite is applied on the grain side and immediately the hide/skin should be put into the sealed polythene bags before $S_0$, evolves.

6.7.1.5 Biocides for curing

There are certain biocides, which can be used for a shorter period preservation. Several biocides were investigated of which biocides based on bigunanidine hydrochloride and benzothiazole derivatives along with
boric acid are found to be effective. Even though these methods are comparatively less polluting, there are certain limitations such as cost effectiveness, not being effective for longer duration etc. which make the salt indispensable as curing agent till today (Ramasami 1997a).

6.7.1.6 Control drying

If the stock is dried in a controlled manner by maintaining the optimum temperature and relative humidity, it may become an alternative method for salt curing. The first operation in leather processing in the tannery is soaking. The hides and skins are soaked in 3 changes of water normally in the tanneries in order to rehydrate the stock and to give them freedom from dirt, dung and salt. In the conventional system the rawhides and skins are cured by using 30-50% of common salt on the weight of the stock. If the salted stock is taken directly for soaking, the wastewater will contain 80-90% of the salt applied, which will create environmental problems due to high salinity. On account of this, the presence of chloride level in the soak liquor is in the order of 30,000-40,000 mg/l. In order to reduce the salinity in the soak liquors, partial removal of salt prior to soaking is essential which is known as desalting process.

6.7.2 Desalting

Desalting is the removal of salt from the salted stock by gently beating the hide on a specially constructed masonry platform of two feet height with a curved surface on top to prevent mechanical damages during manual desalting operation in the conventional process. Now the system has been mechanised by CLRI, which has designed a perforated drum to remove the salt mechanically from the hides/skins.
By drumming the salted goods in the specially designed drum, it is possible to remove the salt to an extent of 30% on the total salt used. Mechanical desalting has long range implications in preventing environmental degradation of ground water and soil. After mechanical or normal desalting, the hides and skins are sorted on grade wise basis. The sorted materials are taken for wet process.

6.7.3 Soaking after Desalting

Normally for soaking in the conventional system, three changes of water are given at 300% per soak, which lead to larger consumption of water. To reduce the consumption of water in soaking, counter current soaking system can be followed. By this method, the spent liquors of the second soak and third soak can be used for first and second soak respectively for the next batch of raw stock. By adopting the counter current method, it is possible to reduce 60-65% water in soaking operation (Viswanathan 1998). It is also found by adopting this system of soaking, there is no deterioration in physical or functional properties in the resultant leathers.

Another important step in the cleaner technology is the green fleshing. Green fleshing helps to reduce the consumption of chemicals because it reduces the weight of the stock by 10%. Apart from reduction in the consumption of chemicals, green fleshing facilitates better penetration of chemicals in the subsequent operations. By green fleshing, the consumption of chemicals gets reduced and thereby the load on the effluent also gets reduced. The green fleshing has got better market demand than the fleshing after lime sulphide process.
6.7.4 Liming

After soaking in the sequence of operations, liming is done. Liming is done in the conventional system by hair destructive method using sodium sulphide and lime. Hair destructive method not only increases BOD and COD levels in effluent but also interferes with the biological oxidation process. So, it is very important to adopt hair shaving process to reduce BOD and COD levels in the effluent (Ravindranath et al. 1999). Hair shaving method can be followed by employing enzyme alone if possible or combination of enzyme and sulphide or sulphide alone in the liming process for dehairing (Reeder 1998).

6.7.4.1 Advantages of sulphide free unhairing system by using dehairing enzyme process

1. Less toxic and less polluting unhairing system
2. Hair/wool gets removed with epidermal layer
3. Free from stains and cleaner pelt
4. Strength properties are better
5. Wool/hair better, cleaner and not contaminated with sulphide
6. No odour during unhairing
7. Better scope for assortment, as the pelts are cleaner
8. Energy cost for the treatment of effluent is lesser.

6.7.4.2 Advantages of less sulphide enzyme unhairing system

1. Pollution reduction due to use of reduced amount of sulphide
2. Lesser stains on the pelt
3. Lesser odour during unhairing
4. Energy treatment cost of effluent is lesser compared to conventional hair destructive method.

6.7.4.3 Advantages of sulphide-lime unhairing system

1. Pollution reduction compared to hair destructive method
2. Hair loosening effect is faster
3. Better alternative to hair destructive method
4. Energy cost of effluent treatment is lesser compared to the conventional hair destructive method.

Of the above three methods, order of preference from pollution angle is as follows:

1. Sulphide free enzymatic unhairing
2. Combination of enzyme and sulphide
3. Sulphide-lime method

There are certain conditions to be maintained while using dehairing enzymes for unhairing. They are as follows:

1. Strict control is required over the process with regard to temperature, pH of both skins and the enzyme paste, concentration of enzyme paste, etc.

2. Addition of disinfectant to the enzyme paste is required where enzyme alone is used for unhairing.
3. The raw hides/skins are to be treated with alkali before the application of enzyme to raise the pH of the hides/skins to 8.5-9.5.

After unhairing, the hides/skins are relimed with fresh lime and water in a specific proportion to achieve the other objectives of the liming process. In the conventional systems, the lime is mixed with water either in pits/paddles/drums, which causes dust problem in the tannery.

So, it is advantageous to have a lime-slurry system (mixing of lime with water in different proportions) and charge the units i.e. pit/paddle/drum as desired. Lime slurry system helps to have dust free, cleaner environment in the tannery and also reduces the consumption of lime and water and wastage. An overall saving of 10-15% in lime can be achieved due to better management and supervision in weighing, mixing, homogenisation and distribution. It also results in consistency in leather quality, reduction in labour and time. After liming operation, the goods are fleshed, scudded, weighed, washed and delimed.

6.7.5 Deliming

Deliming with ammonium salts results in pollution problems because of the oxidation of ammonium contaminated wastewater into nitrates and nitrites through the activity of aerobic micro-organism referred to as nitrifying bacteria. In the ammonia form, it may be directly toxic to aquatic life. Nitrogen can seep through ground and contaminate the drinking water. Exclusive concentrations of nitrates in drinking water have been associated with public health problems. Nitrogen can exist in several forms in the aquatic environment. Transformation can occur from one form to another and the transformations are biochemical in nature.
and therefore occurrence and the speed with which the transformations occur are affected by a vast array of factors and thus making the nitrogen cycle complex one. Therefore to avoid these kinds of problems, carbon dioxide deliming has been developed as a cleaner technology.

6.7.5.1 Advantages of carbon dioxide deliming

1. Reduced ammonia odour in the tannery
2. Reduction in BOD level upto 50%
3. Easier handling
4. Easy adaptability to automation
5. Reduced risk of acid shocks in the pelt and achievement of gradual reduction in pH, which is very much desirable.
6. Improved qualities in terms of refined and cleaner grain improvement in degreasing action.

However, there are limitations in 100% replacing ammonia salt with carbon dioxide in deliming particularly for thick hides.

6.7.6 Chrome Tanning

Nearly 80% of total finished leathers produced is processed by adopting chrome tanning. Normally BCS with following characteristics is used in the powder form for tanning process:

\[
\begin{align*}
\text{Cr}_2\text{O}_3 & : 25\% \ (\text{min}) \\
\text{Basicity} & : 33\% \\
\text{pH of 10\% Solution} & : 3.0 \ to \ 3.5
\end{align*}
\]
Generally about 8% of basic chromium sulphate on pelt weight is used for effective tanning in practice. But the present chrome tanning methods employ the commercially available tanning salts, which exhibit exhaustion levels of only 50-65%, and the rest gets discharged into the effluent. Apart from material loss, which is very significant, such poor exhaustion leads to an alarming environmental problem. The residual discharge of chrome into the effluent on physico chemical end of pipe treatment generates chrome-bearing sludge and also liable for chocking of drainpipes through which it is discharged. In the absence of viable utilisation technologies for chrome sludge, disposal becomes a serious problem. The chromium present in the tannery effluent is believed to behave as a hazardous pollutant. Currently used chrome tanning salts and methods employed lead to a discharge of chromium concentrations in the range of 1500-4000 mg/l in the spent chrome liquor. But the permissible level of chrome in the wastewater is in the range of 0.3-2.0 mg/l as per the environmental regulatory agencies in many countries. These stipulations are difficult to comply with the present levels of exhaustion of chromium in the tanning process. Chrome tanning also contributes significantly to TDS to an extent of 25-35% (both pickling and chrome tanning put together). There are quite a few viable options to overcome these problems. They are as follows:

i. Chrome recovery and reuse

ii. Partial replacement of chrome tanning agent by other tanning agents

iii. High exhaust tanning systems.

Therefore the solution to the problem rests in the reduction of discharge of chrome in the effluent by better chrome management systems.
6.7.7 Chrome Management Options
6.7.7.1 Chrome recovery and reuse

In this process, the spent chrome liquor is collected separately and chromium present in the spent chrome liquor is precipitated as chromium hydroxide by using suitable alkali (Rajamani et al. 1991) and the supernatant is decanted. The precipitated chromium hydroxide is then regenerated as basic chromium sulphate by redissolving with calculated amount of sulphuric acid. Chrome tanning generates a significant amount of total dissolved solids in the form of sodium chloride, sodium sulphate etc. (Rajamani et al. 1993).

6.7.7.2 Partial replacement of chrome tanning agent by other tanning agents

The usual practice in chrome tanning is to offer 8% BCS of which only 50-65% exhausts and the rest gets transferred into the effluent which increases the level of TDS and also leads to chrome bearing sludge during the treatment of effluent. In order to reduce the problems generated by using higher percentage of chrome, it is possible to replace chrome to an extent of 50% with other mineral salt like aluminium. After the pickling process, instead of using 8% chrome, 4% chrome can be offered and run for some time. The 6% aluminium is added to the same drum and run for sometime and then basified to a pH of 3.8 - 4.0.

6.7.7.3 High exhaust tanning systems

There are different methods of effecting the higher exhaustion levels of chrome into the leather. Of which chrome exhaustion by the use of additives is one of the methods. This is done by modifying the affinity of
chrome tanning salt and/or by introducing more reactive sites for the chrome to reach. There are three different categories of chrome exhaust aides as follows (Catherine Money 1998).

1. Compounds that are held by the substrate (hide/skin) chemically/physically, possessing suitable reactive groups i.e. creation of additional sites for the chromium to react.

2. Compounds, which can precipitate or form insoluble complexes with chromium inside the hide/skin matrix thereby enhancing the uptake of chromium from the tanning bath.

3. Compounds with multi-functional groups of sufficient molecular sizes capable of bridging an unipointly fixed chromium with another chromium molecule in the tan liquor.

6.7.7.4 Closed loop tanning system

High exhaust chrome tanning system with near zero discharge of chrome, which is called closed loop tanning system, is also being tried by research institutions like CLRI.

This has advantages, which are

i. considerable amount of water saving
ii. material economy
iii. near zero discharge of chrome and
iv. reduction in neutral salt discharge leading to better environment.

Most of these processes are in developmental stage.

6.7.8 Wet finishing operations
6.7.8.1 Rechroming

The next step in leather processing after chrome tanning is the rechroming process. In this rechroming process chrome is again used for incorporating better hydro thermal stability, better strength properties, better dyeability, better light fastness, better fullness, tightness, and softness without much stretch. Usually 4-5% of BCS is used in rechroming process. The exhaust level of chrome in rechroming process is only 40-50% in the usual process where BCS is used. To minimise the chromium present in the wastewater in rechroming process, it is better to use a high performance mineral (chromium-aluminium) based syntan in place of BCS. These mineral syntans are capable of effectively fixing 90% of aluminium and chromium present in them irreversibly unlike conventional basic chromium sulphate. In case of upper leathers, in rechroming, BCS can be replaced to an extent of 75% by mineral syntans and in the case of softy and garment leathers, 100% replacement of chrome can be done with desired results (Michel Aloy 1998).

6.7.8.2 Neutralisation

The next step after rechroming is the neutralisation. The rechromed leathers are neutralised by using a blend of sodium formate and sodium bicarbonate in equal proportion to a pH of 4.0-5.0 in the case of uppers, lining etc and to a pH of 5.5-6.0 in the case of garment leathers.
Neutralisation is done essentially to neutralise the free acid present in the chrome tanned leathers to raise the pH to a desired level depending on the end use and also to condition the leathers for effecting better distribution of chemicals used in the post tanning operations such as retanning materials, fatliquors and dyes. This process of neutralisation with neutralising salts generates total dissolved solids significantly.

6.7.8.3 Retanning

After neutralisation and washing, the leathers are usually retanned with a mixture of synthetic tanning agents and vegetable tanning agents to get the required tightness, fullness etc. As many of the synthetic tanning materials are not biodegradable, one has to choose such a blend for retanning process, which are biodegradable. Since the requirements in the final leather are quite demanding, it is not possible to achieve the results by using only vegetable tanning materials alone. The next alternative for preventing the chemicals (retanning agents) from going into the effluent and causing environmental problems, is to exhaust the chemicals to a very great extent by optimising the amounts offered and by controlling certain critical parameters such as float, temperature, pH and drumming period.

6.7.8.4 Dyeing

The next important post tanning operation is the dyeing process. Before the ban was imposed on use of benzidine and other arilamine based dyes, the pollution problems were much more. It is essential to use the dyes free from these compounds due to carcinogenic problems. The exhaustion of other dyes also needs to be improved, so that effluent does not contain any unused dyes in the wastewater.
6.7.8.5 Fatliquoring

This is another very important post tanning process. This is essentially done to lubricate the leather fibres in order to get the required degree of softness in the final leather. Before the advent of synthetic fatliquors, people in the leather industry were using only fatliquors based on vegetable and animal base. Though they were cheaper there were certain disadvantages associated with those fatliquors such as speew forming, bad odour, poor light fastness, heaviness, rancidity etc. Since the requirements in the finished leathers have become very much demanding, the synthetic fatliquors were developed to overcome most of the problems associated with non-synthetic fatliquors (Jean-Marie Gigante 1998b). Since it is found that most of the synthetic fatliquors are non biodegradable, this poses problems in treating the effluent containing these fatliquors. To reduce the problems posed by the synthetic fatliquors it is necessary to blend fatliquors based on vegetable/animal and synthetic origins in a suitable proportion to avoid the pollution problems. Even by creating the favourable conditions for the leathers by adjusting the float levels, temperature, pH of the leather, drumming time etc. the uptake can be improved to near zero discharge levels.

6.7.8.6 Finishing

After carrying out all the wet operations and mechanical operations, the leathers are finished in order to give protective coat to the leather to prevent penetration of excessive moisture, dirt and also to protect the leather from damages caused by rubbing, scuffing apart from giving a decorative coat. The finish should maintain its original beauty as long as the articles made out of such leathers last. The season of the finish consists of several finishing ingredients like dyes, pigments, resin binders.
protein binders, fillers, plasticizers, ammonia, waxes, water etc. The finishing is broadly classified into two major categories. One is aqueous finish and the other non-aqueous finish. The aqueous finish is eco friendly (Adams et al. 1998) and the non-aqueous finish is eco unfriendly because of the solvent used in the finish. Now the leather industry prefers eco friendly aqueous finish. (Jean Marie Gigante 1998a) Further, these two categories of finish are sub-categorised as protein finish and resin finish. Since the protein is a biodegradable one, the effluent is treatable, whereas the resin binders are not biodegradable. In the resin finish, nitro cellulose lacquer emulsion is used as topcoat, which causes pollution problems because of the use of solvents in nitro cellulose lacquer (Wenzel 1998).

As it is well established that the conventional system of leather processing generates enormous amounts of pollution problems discharging toxic materials, TDS, TSS, Cl, Cr etc into the effluents making the treatment more expensive, complicated and the standards unattainable, the implementation of cleaner technologies is the only way of tackling the environmental problems (Michel Aloy 1997d). By introducing in-process control systems, (Niaz Ahmed 1998) segregating the soakliquor, introducing chrome recovery/reuse systems and adopting high exhaust chrome tanning systems, it is possible to reduce the pollution problems (Mohammed Ali 1998) to a great extent. Further by integrating the in-plant process control systems and end of pipe treatment systems, it may be possible to attain the environmental standards stipulated by the authorities concerned.