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pta Pakistan tanners association

DRAFT FINAL REPORT

IN-HOUSE ENVIRONMENTAL IMPROVEMENT PROGRAM FOR TANNERY CLUSTERS IN PUNJAB

APRIL 13, 1995

Prepared by:

National Management Consultants (Pvt) Ltd.

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PROJECT BACKGROUND

1.1 INTRODUCTION

Environmental Management, over the past years, has focused on end-of-pipe waste treatment, design of waste treatment plants and installation of pollution abatement equipment for preventing/abating industrial pollution.

However, recent years have seen a progressive shift from waste treatment to in-house modifications. These modifications are mostly in the "process stream design" for achieving resource optimization, improving performance, reducing processing costs and overall reduction in the pollution load. These in-house modifications are commonly known as "Clean Technologies". Such technologies involve the continuous application of an integrated preventive environmental strategy to processes and products to reduce risks to humans and the environment. These result in conserving raw materials and energy, elimination of toxic raw materials, and reduction in the quantity and toxicity of all emissions and wastes before they leave a process.

Cleaner production serves the dual function of avoiding waste generation on the one hand, and minimizing the use of raw materials and energy on the other. The In-house Environmental Improvement Program for Tannery Clusters in Punjab aims at achieving the same goal.

Leather industry is one of the oldest industries in Pakistan, with leather exports reaching a figure of US $ 650 million for the year 1991-92. The tanning industry is famous for the generation of enormous amount of obnoxious liquid, solid and gaseous waste. Poor practices and use of old conventional methods for leather processing are the main reasons behind the greater intensity of pollutants generation. These pollutants are not only environmentally hazardous but also their loss is an economic loss. Heavy metals can be recovered, trimmings can be used for making by-products, and after treatment the effluent can be used in down stream agriculture activities. For improving the situation, it is necessary for tanneries to minimize these hazardous wastes by adopting environment friendly or clean technologies and modern practices for leather production.

The purpose of this study is to carry out a literature review of the use of cleaner methods, recycling concepts and modern practices for leather production currently being adopted by developed countries and then comparing them with old conventional methods which are still being practiced in Pakistan, with special emphasis on their environmental impacts. In this study only Punjab tanneries are covered.

Punjab is the most populated province of the country. In the province, 66 % of the total number of tanneries of the country are located in different cities including Multan, Kasur, Sheikhupura, Gujranwala and Sialkot. In this context, surveys were conducted for the purpose of collecting necessary information regarding existing processes, operations and practices in the tanneries of these cities. This information has then been analyzed to evaluate the possibilities for the introduction of cleaner technologies and modern practices in the local tanneries which would ultimately help in minimizing the extent and nature of pollution.

1.2 OBJECTIVES

Specific aims and objectives of the study/program include:

- To investigate methods and practices for reduction in processing costs.
- To study the current in-house methods and practices of tanning industry and recommending better and modern methods and practices for reducing the pollution at source.
- To determine ways and means to improve quality of final products through better technologies and practices.
- To suggest improvements of quality of final products through better technologies and practices.

1.3 ACTIVITIES

The major activities envisaged to achieve the above listed objectives include:

i) Review of good modern processing practices used by the progressive tanners in Pakistan and in other parts of the world.

ii) Formulation of an Action Plan for In-house Environmental Improvement Program for the tannery clusters in Punjab.

iii) Identification of in-house pollution abatement equipment at different processing stages.

iv) Proposals for better In-house leather processing practices.

v) Preparation of a communication and extension plan for the dissemination of better in-house processing practices.

1.4 METHODOLOGY

A four step methodology was developed and applied for conducting this study. Following are the step specific details of the methodology:

1.4.1 STEP-1: LITERATURE REVIEW

A comprehensive literature review of tannery processes and practices being adopted in developed countries of the world was conducted. General and processing specific inferences were drawn. While drawing these inferences, it was specifically considered that these should remain relevant to local processing techniques being used by tanneries in Punjab.

1.4.2 STEP-2: FIELD SURVEY

In order to asse the existing conditions in Punjab tanneries with respect to in-house processing technologies and practices a case study type of survey was conducted. The tanneries in each cluster of Punjab were divided into three categories, i,e., Small, Medium, and Large.

- Small size tanneries were producing below or equal to 3000 sq. feet leather/day, the smallest tannery, visited was producing 350 sq. feet/day of leather.
- Medium size tanneries were producing around 5000 sq. feet/day of leather.
- Large size tanneries were producing above or equal to 10,000 sq. feet/day of leather. The largest tannery, visited was producing about 25000 sq. feet/day of leather.

One tannery from each category at each cluster was selected and surveyed.

A comprehensive questionnaire was prepared. This questionnaire was field tested in Korangi-Karachi tanneries. Required changes were made as the results of the field testing. Questionnaire is attached as Annexure 1.1.

The questionnaire based survey was carried out in each cluster. The major parameters, covered by questionnaire are as follows:

- Processing technology
- Working Practices
- Physical conditions (Plot size, construction, layout etc.)
- Environmental conditions
- In-house occupational health and safety issues.

1.4.3 STEP 3: ANALYSIS OF THE SURVEY FINDINGS

Findings of the survey about the general conditions of the Punjab tanneries were analysed at the general level. The next stage includes a process-wise review of the Beam House and Tann House Operations in detail, special consideration was given to their environmental impacts. On the basis of this analysis appropriate clean technologies suitable for adoption in the local context have been recommended for each process keeping in view the modern practices being adopted globally.

Health problems in tannery workers have also been discussed in the light of questionnaire survey findings. Appropriate safety measures have then been proposed with regards to equipment/machine and handling of the chemicals used in the tanneries.

1.4.4 STEP 4: ACTION PLAN

Based on the analysis carried out in the sections as discussed above, an Action Plan has been formulated and recommendations have been made for the implementation of the In-house Environmental Improvements, some recommendations have also been emerged communication and extension for better in-house practices.

CHAPTER - 2

TANNERIES IN - HOUSE ENVIRONMENT : STATUS AND OPTIONS

2.1 GENERAL : TANNERY PROCESSES AND PRACTICES

The production of leather is a long and complicated process, it is comprised of a complex combination of processes and operations of different characteristics. A schematic diagram of tannery operations and processes is shown in figure.1.

Hides and skins differ in their structure, depending upon the habits of life of the animal, season of the year, age, sex, and breeding. Tanners define the skins of large animals, such as full grown cattle and horses, as hides; whereas, the term skin is refered for small animals, such as sheep, goat, and calves.

Hides and skins are seldom processed directly into leather. These are first kept in a state of preservation and later they undergo a series of tannery processes and at the end are ultimately transformed into leather.

The tannery processes are classified into two main stages; Beamhouse and Tannhouse processes. The term beam house refers to the processes in the tannery between the removal of the skins and hides from a state of preservation and their preparation for tanning. This includes soaking, trimming, fleshing, unhairing, liming, deliming and bating. Whereas, the tanning process converts the proteins of the raw hides and skins into a stable material, which does not putrefy, is resistant to heat and abrasion, and is suitable for a wide variety of purposes.

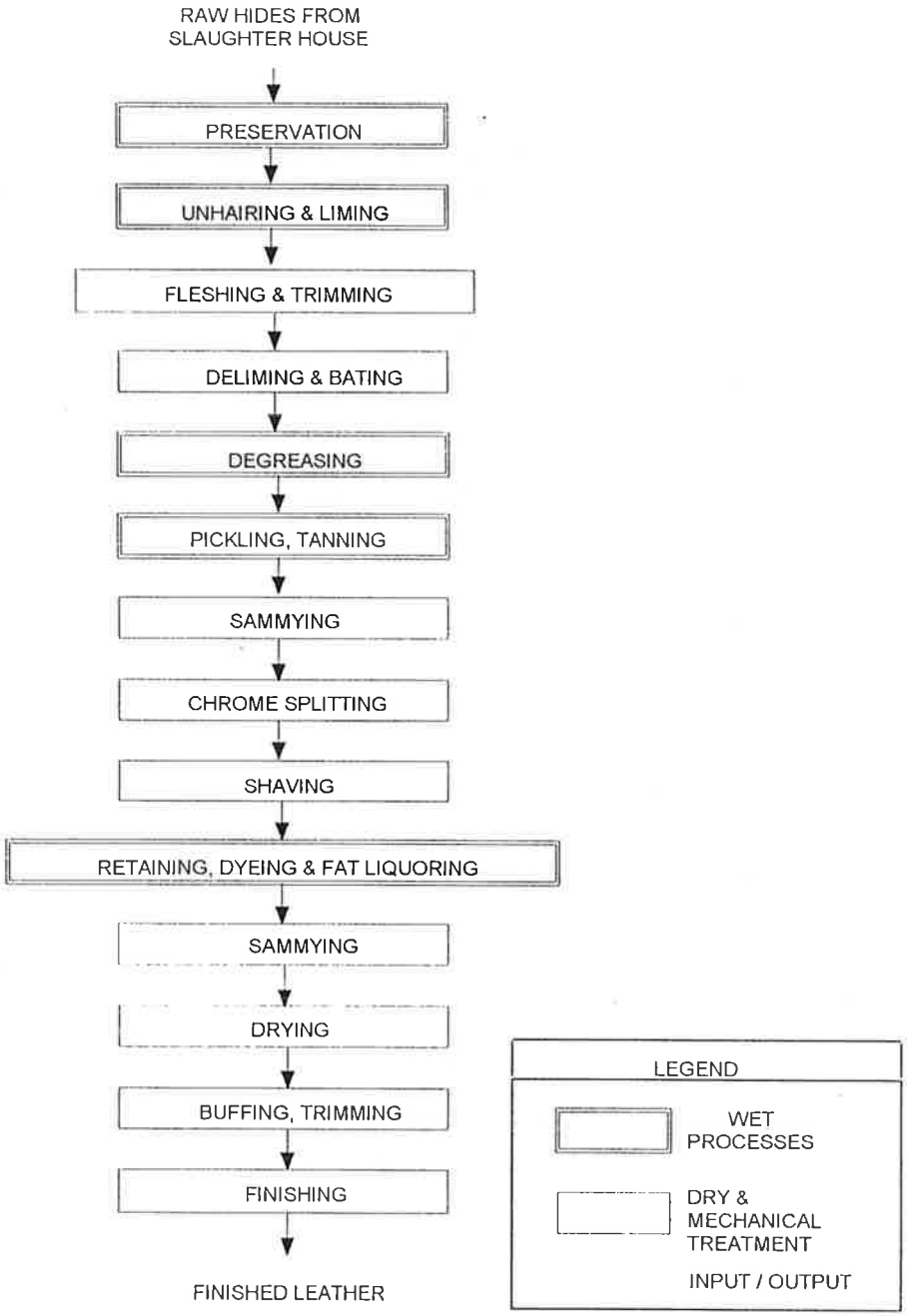
2.1.1 EVIDENCE FROM LITERATURE

This section is based on the findings of literature review done for this study. The bibliography of the documents reviewed is attached as Annexure-2.

Leather is produced from hides and skin in the following stages:

FIGURE - 1

GENERALIZED PROCESS FLOW OF LEATHER PRODUCTION



a) **Pre-tanning or Beam House Operations: (the removal of constituents such as hair, flesh, fat and some interfibrillary material, leaving a concentrated network of high-protein collagen fibres, greatly dispersed and softened with water)**

In the beamhouse, the hide or skin is processed to prepare it for tanning, and this stage is therefore primarily concerned with the production of a properly conditioned network of collagen fibres in water. Hides that have been cured with salt or brine are received, stored, trimmed, and soaked to restore moisture and to remove salt. Wash waters from this operation contain dirt, salt, blood, manure and proteins. Fleshing, the removal of fatty tissue and meat from the hides, is accomplished on a fleshing machine, through the use of operating blades. Cold water, necessary to keep fat congealed, generates a fatty wastewater. Fleshings are recovered and sold to plants for rendering or for conversion to glue.

Unhairing is then carried out by chemical dissolution of the hair and epidermis, generally using an alkaline-sulphide medium; typically lime and sodium sulphide are employed. The alkali also dissolves non-collagen inter-fibrillary proteins. This makes the hides swell for easier splitting and to assure complete hair follic removal. The liming and unhairing processes are among the principal contributors to the waste effluent.

Deliming & Bating are the steps for preparing the hides for the tanning process. Since residual lime would interfere with the subsequent tanning process, deliming is done to remove lime. Hides are placed in vats or drums which contain a solution of ammonium salts and enzymes, which delime the skins, reduce the swelling, peptize the fibers, and remove protein degradation products. The final beamhouse operation is pickling, which is the adjustment of pH of the hides prior to tanning. Pickling is carried out typically by using brine solutions and dilute sulphuric acid. it is possible to store pickled stock for several months with the appropriate selection of salt and acid concentrations.

The beamhouse wastes include; aqueous effluent containing suspended and dissolved organic matter, curing salt and grease in addition to unused process chemicals, and will have high oxygen demand. The solid and semi-solid wastes are hide trimmings and fleshings.

b) **Tanning: (treating the hide with an agent that displaces the water and combines with the collagen fibres, greatly increasing resistance to heat, hydrolysis and micro-organisms)**

After the hides have been soaked, fleshed, unhaired, delimed, bated and pickled, these leave the beamhouse and enter the processing area of the tannery. In the tanyard, the tanning process chemically stabilizes the collagen network. Tanning turns a hide into a non-putrescible material, one that is resistant to bacterial degradation. Tannin is the compound that joins with the skin protein to form

leather. Chromium salts are the most widely used tannins, although vegetable and synthetic tannins are also used. Vegetable tannins are obtained from the bark of trees and the pods of a vast number of bushes. Spent vegetable tanning solutions are responsible for a major portion of the organic content and almost all of the colour-causing material in the tannery effluent.

Majority of the leather is now tanned with solutions of basic Chromium (III) Sulphate. The major advantage of chrome tanning is that it shortens the tanning time to less than one day, and produces a leather with more resistance to heat and abrasion. However, Chromium salts are of particular concern as they are toxic in the hexavalent form. Financially viable solution for chrome recovery are applied in many countries. Chrome recovery plants are simple in design and operation.

c) Mechanical Operations

A number of mechanical operation are applied to the leather for different purposes including the removal of the excess water, adjustment of the thickness, spliting. The waste generated by mechanical operations include Chrome split sheets and shavings.

d) Post-tanning

This involves further processing of the stabilized collagen network, and may comprise a further tannage where a high degree of perspiration resistance is required. Retaning, colouring, stuffing and fatliquoring imbue the leather with the softness, flexibility, water repellence, hue and other qualities required. No solid wastes are produced and the aqueous effluents do not generally contribute to the overall pollution load.

e) Finishing

Finishing operations are comprised of; drying, conditioning, staking, buffering and finishing, further prepare the leather for sale. The surface coatings consist of dyes or pigments dispersed in a binder, typically casein or acrylic polymer, and are applied by padding or spraying. Most of these are basically dry processes, and the solid wastes produced from these finishing operations include buffing dust and finished leather trimmings. Pasting and wash-up generate a high strength, low volume wastewater.

2.1.2 SURVEY FINDINGS FOR PUNJAB TANNERIES

The findings of the survey and the general observations during the visit of the tanneries cluster in Punjab are discussed in this section.

In Punjab, tanneries plot sizes vary from one Kanal to 5 acre or more. The tanneries located on the small plots are very congested. Some small residential units have been converted into tanneries with only few modifications in the construction. Most of the processes and operation are being performed in these small tanneries. As a result the overall in-house conditions are poor. Generally it is very difficult to develop solutions for small tanneries in Punjab. The tanneries located on the big plots, however, have a lot of unused space. Options for the installation of pollution abatement equipment and changes in lay out are possible in case of big tanneries.

Some small mechanised tanneries and most of the bag tanneries are poorly constructed. In these tanneries most of the tannery work is carried out on unpaved land under ordinary shade which can only provide protection against sunlight. Spilled chemicals on unpaved land can not be recollected.

It is observed that irrespective of tannery size, ventilation system was found to be in the range of poor to fair quality. Very few tanneries have provision for good ventilation.

Proper layout in the industry is an important parameter to attain optimum efficiency. In general, tanneries have not taken this factor seriously and therefore poor layout was observed in most of the tanneries. However, in some of the tanneries particularly large ones, layout was considerably good.

Occupational health and safety practices for leather processing were found different from tannery to tannery. It is generally observed that in tanneries that hazourdous chemicals are handled carelessly. Use of gloves, apron, goggles, and masks during the handling of chemicals is not common. However, some tanneries provide these items to their workers. Workers also do not pay much attention for using these accessories during the work. It may be due to the obliviousness and ignorance of these workers about the hazards of these chemicals. Information boards about safety and health regulations are not installed in the working place of the tanneries. Dumping of the empty bags of chemicals is very common. Moreover, dumping of excess lime-sulphide paste (used for unhairing purpose), salt (curing), etc., was also observed. Loading and unloading of the skins/hides during processing, is normally carried out manually without using gloves and proper clothes for protection. Moreover, clothes of the workers during working become completely wet with the float of different tanning processes. Irrespective of tannery size, hand fleshing of cow and buffalo hides is very common in Punjab. During this operation the body of the worker is frequently exposed to the water containing lime and sulphide. However, the use of a fleshing machine and use of water repellent aprons or cloths can improve this situation. Irrespective of the size of the tanneries, pits are not provided with the railing and covering. Drums are not equipped with shield or cover for the gear drive. The railing around the drums to ensure certain distance from the drum are also not installed. Floors have not been kept dry. No measures have been taken for reducing the machines and drums noise in the tannery.

The volume of aqueous effluent produced from the tannery is not only dependent on the volume of the float used in various stages of the tanning process, but it is also a function of the amount of water used for washing the hides or skins at different process stages. In Punjab tanneries, the rinsing and washing is carried out by using a continuous stream of fresh water, which is responsible for the increase in the total volume of the effluent. If tanneries adopt batch washing, a considerable reduction in volume of effluent is possible. Punjab tanneries are using ground water, and a record of the daily water consumption is not maintained. Draining out of the untreated effluent is common practice.

In Punjab tanneries, all types of raw material i.e. sheep/goat, and cow/buffalo is used for producing finished leather. The general tannery operation and processes used are of the conventional type. A lot of improvement is required to upgrade and update the existing practices. The following section contains a description of each tannery operation and process, the present status of the process in Punjab tanneries, modern clean technologies being adopted worldwide for in-house modification within the process itself, followed by concluding remarks about improvement options recommended for Punjab tanneries.

2.2 SPECIFIC PROCESSES: STATUS, ENVIRONMENTAL IMPACTS, CLEAN TECHNOLOGY OPTIONS, AND RECOMMENDATIONS

This section contains a process wise description of the conventional processes as well as modern clean technologies being adopted in the various stages of the tanning processes, including curing, soaking, unhairing & liming, deliming and bating, pickling & tanning, wet finishing, drying and finishing. The associated environmental impacts are then reviewed. Keeping in view the status of Punjab tanneries as evident from the survey findings, improvement options are discussed in the local context and recommendations for adoption of cleaner technologies are made.

2.2.1 PRESERVATION (CURING)

(a) Process Description

When the hide or skin is removed from an animal, the outside of the skin is covered with the dirt of animals surroundings. The inside of the hide or skin of living animal's contains bacteria and other micro -organisms held in control by the metabolic defence of animals. When the animal is killed, the process of decay starts immediately. Proper curing methods, therefore, need to be applied to minimize both bacterial decomposition and biochemical changes in the hide, so as to maintain good leather-making qualities.

Preservation, although not performed in tanneries has a direct effect on the composition of tannery effluent. The preservation agents are washed out during the first production step in the beam house, mainly with the soak effluent. The conventional methods used for preservation are **air drying, salt curing and Brine curing.** In Pakistan salt curing method is widely used and therefore only salt curing is discussed in detail.

- **Salt Curing**

  This is the most common method of preserving cattle hides in Europe, North America, and other countries of temperate climates. In this methods the freshly flayed hides are spread out, flesh side up, on a concrete floor and well sprinkled with salt (Sodium Chloride). Coarse or round-grained salt is preferred to fine salt, as the former spreads better, whilst the latter forms patchy wet cakes. The second hide is placed on the first one and is also sprinkled with salt. This is repeated until stacks reaches the height of 5-8 feet, the top hide is well overlaid with salt. The stack is left in this condition for many days. During this storage period salt is dissolved in the moisture of the skins and the brine permeates the pile. The amount of salt used is normally 25-30 % of raw hide weight.

  During salt piling, the skins drain, lose some moisture, and therefore lose some weight. In the case of hides this may amount to 10 % of the drained flayed weight. Drained salted hides contain about 50 % water. A merit of salting is that the salt fully penetrates the hide structure and by the dehydration effect on the fiber structure, together with the coagulation of the inter-fiber proteins, renders the hides more porous to subsequent processes such as soaking.

  In **Punjab tanneries,** it was found that the large, medium, and small tanneries receive salted skins from the local market. However imported skins/hides (air dried) are also utilized as raw material. Sea salt and rock salt are both applied to the skins for curing purpose. Red salt is also used for curing but there were complaints among the tanner that it damages the raw skins. However, for hides it does not effect much.

  In some tanneries salt that falls from the cured hides is dumped into open land. However, in one tannery it was noticed that this salt is collected by the qulfi (ice cream) maker for lowering the temperature of ice used for facilitating freezing. One of the tanneries visited during survey revealed that in order to reduce the quantity of salt in soaking effluent, shredding of the cured skins was carried out for some time. As a result a large quantity of the salt gathers in the tannery and the tanner fails to find its further use. However, this salt may be used for recurring purpose. In the tanneries usually no curing is performed as raw hides/skins are not kept in storage for a long period. However, if long time storage is required, then skins/hides are treated with some antibacterial agents.

(b) Environmental Impacts

The main environmental issue of the preservation of raw hides and skins is the use of salt (sodium chloride) as a preservant. High concentrations of chloride in the effluent of the curing plants and in the first steps of the beamhouse operation cause high salinity of natural water bodies, which has to be avoided, since there is no economic way of removing salt from effluent.

(c) Clean Technologies

As inferred from literature, it is recommended that the following procedures need to replace the conventional salt preservation process:

- **Processing of Fresh Hides and Skins**

  Processing of the fresh hides and skins is the best alternative from the point of view of the chloride load of the effluent. No use of any chemicals and bactericide results in a better quality effluent. Soaking process can be replaced by washing procedure. Fleshing is possible just before the liming-unhairing processes, hence results in reduction of the quantity of chemicals. Fleshing by product will be of better quality. However, time elapsing between slaughtering and further treatment (e.g. beamhouse processing) must not exceed a few hours, mainly when the temperature of air is high. In hot climate of the Punjab province to make arrangement for the supply of fresh hides and skins from slaughter house to the tanneries in a short time to avoid putrefaction seems impossible.

- **Air Drying**

  This is one of the oldest methods of skin preservation. It is the standard method of preservation of most reptile, goat, and fur skin and of a very large percentage of the hides and skins obtained in the tropical areas of Central and South America, Africa, and Asia.

  This technique is a simplest form of preservation. Most practical in areas where salt is expensive and a small number of skins are to be cured. Particularly useful in dry, tropical climates and in rural areas of some under-developed nations. However, some of the disadvantages of this technique are also very important and described here. The rate of drying is of great importance, If it is too slow, putrefaction may begin in the hide before the moisture level can be decreased to the point where bacteria can longer be active. If drying is too fast, the outer surfaces of the hide may become hard and dry while the inner parts still have enough moisture to support bacterial growth. This " case hardening" of the hides may rot

out from inside. Upon soaking for processing, the hide will have a blistered appearance and eventually holes will appear. Skins may get damaged from the permanent fold marks of hanging, and direct sunlight may cause case hardening of the upper surface. In case of spreading on ground, supported on sticks or stones, it will be necessary to prevent the skin to be damaged by insects.

As many difficulties associated with this technique and common salt is also not expensive in the Punjab cities therefore to replace the salt curing with this curing technique looks unjustified and impractical.

- **Chilling of Raw Hides and Skins**

This process permits the long preservation time as compared to the processing of raw hide and skins depending upon the temperature applied, which can last up to three weeks without problems.

The most substantial question concerning chilling preservation is the time between flaying and the freezing of the hides. It has to be as short as possible.

Each piece has to be frozen separately to assure that a fast cooling can be reached before putrefying processes begin to damage the hide tissue.

Chilling is done with shredded ice, cold water and cold air.

Chilling with ice requires about 5 kg ice to chill one hide. It is spread on the flesh side of each hide piled inside a box. The raw hides can be sent to the tanneries, while a temperature not higher than 8°C has to be maintained for a maximum of three weeks.

Chilling with cold water requires cold water spray or batch to reduce the hides's temperature rapidly just after flaying, and thus, facilitate further refrigeration by other systems.

Chilling with cold air is carried out in a refrigerated store. Each hide has to be hung and stretched, without coming into contact with others, to permit the freezing of the entire surface. Temperature between -2 and +5°C, storage up to 3 or 4 weeks without any other auxiliary agent.

Some of the disadvantages includes, energy consumption, necessity of freezing equipment and cold storage, additional efforts to maintain equipment and installations and to control the operation are required. To meet these requirement for country like Pakistan looks impossible at present.

- **Hide Preservation Using Bactericides**

  At present, bactericides can be used for short time preservation only. As bactericides have severe ecological impacts if released to nature (water, soil, food, food chains), the use has to be controlled effectively.

  For the selection of biocides the following points should have to be taken into consideration.

  - In case of leather export, the regulations of the country where the leather is sold have to be recognized.
  - If there is a choice of more than one product, less toxicity and high biodegradability should be the criteria for the selection of one.
  - Instructions for the use of bactericide have to be followed strictly.
  - Personnel using biocides have to be trained, and safety equipment should be used effectively.

  As this technique can only be environmental friendly if the above mentioned precautions should be adopted strictly. The cost of the biocide as it will be imported from the foreign countries, in any case, will be higher as compared to the locally available common salt. In Pakistan the curing is carried out by the untrained persons, widely spreader in different parts of the country and generally unaware about the hazards of the biocides. Moreover, to train these people in this regard will be a very difficult job. Therefore it will not be possible to apply this technique instead of the salt curing.

- **Salt Recovery and Minimization**

  Salt curing still remains the mostly widely used method for preservation of hides and skins. Although not considered a clean technology, and despite intensive research work, no alternative process of comparable economic and ecological efficiency could be found. Due to low cost, easy application and long-term effect, it seems that, salt preservation will be used world wide for the years to come.

  However, the adoption of cleaner technologies for recovery and minimization of salt concentration in the soaking effluent is possible. Options available includes:

- To pre-flesh the hides before salt application to reduce the weight and consequently the amount of salt to be used.

  In pre-fleshing, it will be necessary to bring the raw hides/skins in the tannery as soon as possible after flaying from the slaughter house. Otherwise, putrefaction of hides/skins may occur due to the high temperature and humid climate. The problems same as processing of fresh hides and skins are also associated with this technique.

- To shake the salted hides in a sieve drum or a similar device, or manually prior to the soaking process, to take off part of the salt adhered on the hides's surface. The recovered salt can be returned to the curing process again.

- Introducing a washing step prior to the soaking step after the removal of adhered salt as described above. The washing should be carried out with little quantity of water. This washing will dissolve most of the salt from the hides and skins. The effluent resulting from this washing step may be collected and subjected for sun drying in open dishes. After water evaporation, salt can be reused for curing purpose.

(d) Improvement Options for Punjab Tanneries

As the curing process is performed out side the tannery therefore it will not be possible for the tanneries to bring any change in the curing process. Due to easy availability, simple application and very low cost of the common salt, presently seems difficult to replace the salt curing by other methods like air drying, the use of bactericides and chilling of the raw hides and skins. The processing of fresh hides and skins is possible. If an efficient collection and transport system will be available to bring the raw skin from slaughter house or collection points into the tannery in a short interval of time to avoid any bacterial action on the skin/hides. Due to long distances, poor transportation system and warm climate, it will be difficult to manage this option. However, adoption of clean technology for recovery of the salt from cured skins to minimize the salt concentration in soaking effluent is possible. Salt recovery techniques can easily be adopted in the large tanneries.

2.2.2 SOAKING

(a) Process Description

Hides and skins, when received by the tannery, are usually in a condition of preservation based on dehydration. The skins must be wet back and brought to a flaccid condition for subsequent operation. Soaking is generally accomplished by placing the skins in water which may contain an additive. The time required for soaking depends on the nature of curing of hides and skins.

Irrespective of the raw material the **tanneries in Punjab** widely use pits for soaking purpose. Use of paddle and drum is rare. Wetting agent is commonly used whereas, bactericide is only used in hot season. Wetting agent and bactericidal agent are imported from Germany/Switzerland. Use of PCP (Penta Chloro Phenol) as anti-bacterial agent is avoided. For hides, small quantity of sodium sulphide is also used. Cured skins (salted) are directly subjected to the soaking process. Usually no efforts are made to remove the salt from cured skins. However, in Kasur efforts are being made, on an experimental basis, to recover the salt for minimization of chloride in the soaking effluent. Prior to soaking, the salted skins are manually shaken to detach the salt adhered to the skins. The salt is collected and stored in the tannery, however the tanners have not found any further use of it. In some tanneries, the soaking and liming process is carried out simultaneously.

Before soaking hides/skins are trimmed in order to remove nose, eyes, ears, mouth, hooves, horns, and tails. Quantity of waste material generated in trimming process is 120 kg/ton of hide (Leather, August 1993) . However, during the course of the field survey conducted for Punjab tanneries it was found that tanneries do not have a specific figure for the quantity generated during this process. Approximate values as mentioned by the tanneries range from 150- 400 Kg/ton of hides. **The trimmed material is sold to the glue and poultry feed manufacturers.**

(b) Environmental Impacts

The environmental impact of the soaking process depends to a great extent on the characteristics of the processed raw hides and skins, fresh, salted, or preserved by any other method. Moreover, the use of surfactant, bactericide, alkali and sulphide in the process are the important contributing factors alongwith the load of solids and soluble proteins which are washed out of the hides during the concomittant cleaning procedure.

(c) Clean Technologies

Enzymatic products are considered to be less toxic and can be a good replacement of sulphide. Surfactants, if used, should be selected with respect to their biodegradeablity. Alcohol ethoxylate based products are preferable.

If bactericide is used properties like less toxicity and high biodegradability should be considered. Most of these products are more expensive than traditionally used PCP (upto 5 times more) and may not have the same long -lasting effect. The banning of PCP in leather, shoes and leather goods imported in Germany has accelerated the withdrawal of this product in Asia and South American countries.

If hides are not pre-fleshed neither in the slaughter house nor in the preservation plant, green fleshing work just after deep soaking is a suitable procedure to obtain a by-product at pH close to neutral, which can then easily be processed to recover fats and proteins with good marketing possibilities and to save liming-unhairing chemicals.

The use of pits or paddles for soaking operations results in a higher consumption of water, mainly for the washing phase which are much less efficient than when using drums. Even for drums, it can be recommended to operate with sequential washing instead of continuous rinsing which leads to the saving of enormous amount of water at this stage.

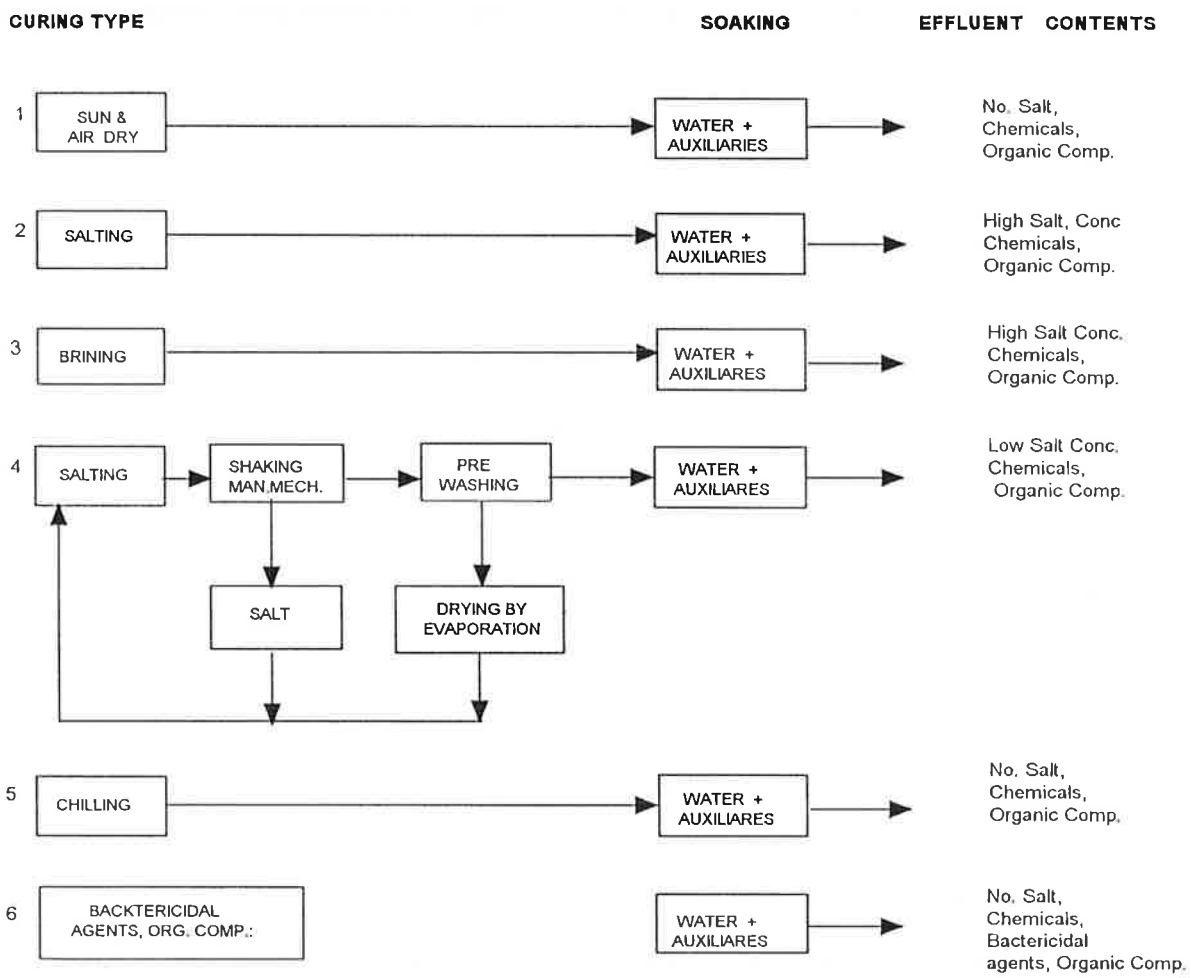
To reduce the volume of effluent possibilities should be investigated to perform soaking and unhairing in a single stage. This approach could reduce the volume of effluent for this stage to 4 - 5 l/kg raw hide. Although such savings do not directly reduce the pollution, however they can lead to reduction in the water consumption in a tannery and reduction in the size of the effluent treatment plants. A comparison of pollution load with respect to different curing processes is given in figure 2.

(d) Improvement Options for Punjab Tanneries

Tanneries are generally taking care of using the bactericidal agent. However, the use of paddle for soaking is very common. As mentioned above use of drum for soaking purpose can reduce the volume of water for washing. Enzymatic product is not available frequently, therefore it can not be replaced by sodium sulphide. Many tanneries are doing soaking and unhairing process in the same float. However, the option of green fleshing just after deep soak can be adopted in the local tanneries.

FIGURE - 2

POLLUTION IN SOAKING EFFLUENT WITH RESPECT TO DIFFERENT CURING AND SOAKING PROCESSES: A COMPARISON



2.2.3 UNHAIRING AND LIMING

(a) Process Description

Unhairing and liming are usually performed in one single operation in order to remove hair, fats, and unwanted proteins. Liming action due to the alkaline pH also produces a swelling effect on hide proteins or on hide collagen, which is called the "opening up" of the fibers. The action of this prolonged swelling has a definite practical effect on the hide with respect to its leather making properties. To facilitate this process, a number of other chemicals are also used with the lime, which are sodium sulphide, arsenic sulphide, sodium cyanide, sodium hydrosulfite, diethylamine sulfate.

Many unhairing systems in practical use are based on a balance between these chemicals to produce rapid, efficient unhairing system with controlled swelling.

In Punjab tanneries, most commonly, a painting system is used for unhairing of small skins, particularly those with large quantities of hair such as sheepskins and many goatskins. Painting is conducted with a solution of lime and sodium sulphide, sodium sulphide alone, or sodium sulphide plus caustic soda. The strong reducing agent is painted on the flesh side of skins and skins are piled in such a manner that the sulphide paint is sealed in. Care should be taken so that the wool does not come in direct contact with the strong sulphide painting solution. The skins are piled in a cool place, or folded along the backbone, after some time the hair become loose and are removed by manually. Some tanneries are also using machines fot unhairing. The unhaired skins or hides are then placed in an additional liming solution, usually overnight or more depending on the desired quality of leather, and then it is followed by deliming, bating and pickling.

The painting system is not effective for heavy cattle hides due to their thickness. The painting system is time consuming and laborious, and its use is justified where the value of the hair is very high. This process is commonly used for the sheep skins and some time for the goat skins.

Hair removal of hides and goat skins is commonly carried out in pits and drums. The sodium sulfide, sulfhydrate, and lime are introduced into the pits and drums. In drums, the hair destruction takes place within a very short interval of time (fifteen minutes) and the hair loses most of its fiber structure. The hair-destruction system (pits or drum) is quite common in production of all types of leather in **Punjab tanneries.** The hair destruction system requires a strong sulfide solution (3 % by weight of hides & skins) with about 1 or 2 % hydrated lime. After this process the hides are washed by flow-through water to remove the sulphide, and then hides are treated with additional lime for liming purposes.

(b) Environmental Impacts

The unhairing-liming process only consumes 40 to 45 % of lime and 50 to 55 % of sodium sulfide or sodium hydrosulfide in the treatment float.

Unhairing & liming process is responsible for 55 % of COD, 70 % BOD_5, 40 % of nitrogen and 76 % of the toxicity in tannery effluent. In addition to this, a large amount of settleable matter also comes from this process in the effluent. Hair destructing system produces 122 % , 58 %, and 157 %, more suspended solids, BOD_5, and COD respectively as compared to the hair saving system.

Sodium sulphide and sodium sulfhydrate used for unhairing process are most dangerous materials. Upon acidification, solution containing sulfides, even in trace amounts, will release hydrogen sulphide gas into the atmosphere. The gas is heavier than air and may accumulate in sewers or wherever solutions from acid processes and sulfide unhairing system come together. Hydrogen sulfide at very low levels, has a noxious odour and at high enough levels it could be fatal, paralyzing the nerves, and fatality may result without warning. A comparison of pollution load in effluent with respect to the different unhairing processes is given in figure 3.

(c) Clean Technologies

There are two major possibilities for the improvement in the unhairing process, these are;

1. Pollution reduction in conventional methods.
2. Use of alternative methods.

- **Pollution Reduction Possibilities in Conventional Lime Sulphide Method**

(i) Hair Saving Methods

Hair saving systems use smaller quantities of sulphide as compared to hair destruction system, and allow an easy separation of the proteins constituted by the undissolved hair and hence imply less pollution than the hair destruction process. In this process, the hair is loosened and removed from the hides but not pulped or dissolved in the float. The installation of a screen is required to remove the hair from the unhairing liquor. The procedure results in a significant reduction of COD, BOD, nitrogen, sulphide, total and suspended solids in the wastewater, besides a decrease of sulphide consumption. Hair recovered through this process can be reused, at least, as nitrogen source in agriculture, or for making brushes, mats, ropes, and felt production.

(ii) Recycling of liming liquor

Some of the liming unhairing techniques permit a direct reuse of the spent liquors after decantation and /or filtration to separate the sludge containing lime, fat, and proteins, and then recharging with chemicals according to the recipes. The number of recycling steps depends on the efficiency of the clean-up process for the spent liming liquor, and on the desired leather quality. The liquor may be regenerated and reused many times, which may even be upto 30 times. The procedure permits saving of water, sulphide, and lime. The sludge recovered through this process may be used in agriculture. Only the pH of the soil and the application dose have to be considered.

(iii) Recycling of unhairing liquors

For several years, experiments and practical processes have been performed to re-use unhairing liquors after separation of insoluble substances by sedimentation. Important savings are claimed. Experimental processes at CTC in Lyon, France show that the following reduction is theoretically possible:

Process water upto 60 %,
Sodium sulphide upto 50 %, and
Lime upto 40 % of its initial value.

However, according to experiments of the German Leather Institute in Reulingen shows that almost twice the initial concentrations of sulphide are necessary to obtain an effective unhairing in very polluted recycled bath.

A second consequence of the high degree of pollution of the waste water is that more water is needed to wash the unhaired hide. Another drawback is that the hair proteins are strongly destructed, because the proteins are exposed to the sulphide for a very long time.

(iv) TNO Proteins separation method

The main pollutant in beam house effluent is dissolved proteinous material. The minimum solubility of proteins is found at pH value between 3 and 4. Low solubility at pH 3 and 4 is the basis of the TNO method. However, before the pH can be lowered, the sulphide in the unhairing liquor must be removed, to avoid the development of gaseous hydrogen sulphide. This is done by the

aeration of the liquid in the presence of divalent manganese (50 g Mn/M^3). Soaking, unhairing and eventual deliming liquors are collected in the wastewater pit. After addition of manganous sulphate, the mixture is kept homogeneous by means of the circulation pumps and is aerated for some hours. After complete oxidation, bicarbonate (1 kg $NaHCO_3$) is added. Subsequently, the aerated mixture is introduced into the protein separator and a measured amount (10-20 l/M^3 wastewater) of concentrated hydrochloric acid is added through the different injection points to obtain an end pH of 3.5. After this, several pulses of compressed air are injected to get a smooth floatation of the insoluble proteins within half an hour. After removal of the clear liquid, under the proteins layer, a fresh quantity of wastewater can be introduced and the earlier procedure described before may be repeated. After some 5 or 6 charges and removal of the clear liquid, the protein cake can be driven out, using the screw. In case of optimum unhairing processes about 80 % of the organic pollution present can be separated as a liftable sludge, with a composition, Water 80 %, Proteins 12 %, Fat 4 %, Salt 4 %.

Amino acid composition of the protein-fraction of the sludge is comparable to that of the feather meal. In case of working with fresh hides of known origin, this sludge may represent a valuable additive to animal fodder. In case of salted hides of less known origin, the likely presence of preservatives may only leave open their application as fertilizer.

(v) TNO unhairing method for destruction of proteins during unhairing.

Long unhairing time and high sulphide concentrations contribute to higher solubility of the proteins formed. Moreover, the sludge formed in these cases after acidification becomes much less coarse and more strongly hydrated. For this reason, these sludge are much more voluminous and have a worse filterability. To improve protein separation, unhairing procedures were worked out in which the process is split up into a 2-7 hours lasting unhairing phase and a liming phase which may last 5-40 hours or even longer. In this way any opening of the hide structure by lime can be realized, while the hair destruction is always very moderate, so that the protein separation can take place very efficiently. As the lime liquor is hardly polluted, it can be re-used several times in the liming process or recycled through the unhairing process.

(vi) Sulphide Oxidation

A separate pre-treatment of the toxic sulphide salt and organic sulphide compounds formed during liming-unhairing is the oxidation to non-toxic sulphate. Further this procedure helps to avoid the formation of toxic and smelly hydrogen sulphide gas, and contributes to a higher and better economy of the final effluent treatment.

- **Alternative Unhairing Methods**

Quite a lot of research is going on to find satisfactory alternative to the use of sulphide or to minimize its quantity for unhairing purpose.

(i) Dimethylamine sodium hydroxide system

This method is proposed by the Rohm & Hass Chemicals Company. Dimethylamine has long been known as an effective unhairing agent when used in lime systems. The proper maintenance of a balance of caustic soda in the system is of great importance. As a result of this work, a 24 hours hair saving procedure employing dimethylamine sulfate (DMAS) and caustic soda has been used on calf skins and cattle hides to make both light weight leathers and heavy sole leathers. One of the main drawbacks of the system is that the stock is quite slippery due to caustic soda, which makes it more difficult to handle. In the interest of economy, and also to decrease the strong action of the caustic soda. The system has been modified to incorporate DMAS, lime, soda ash. and sodium sulfhydrate. By using a balance of these materials, the harshness of the caustic soda is overcome by a buffering action attributed to the lime.

(ii) Oxidative System

The unhairing systems discussed so far have been based on the alkaline hydrolysis of the keratin after the action of reducing agent to break the disulfide linkage or the action of dimethylamine on the sulphide bonds of cystine in the hair protein.

To eliminate the sulphide and lime from the effluent of unhairing process, a new method was introduced by Germany in which the unhairing is done by strong oxidizing medium and under acid conditions.

The active ingredient in oxidative unhairing is chlorine dioxide which reacts with the sulfur-sulfur bonds of keratin to produce a keratin sulfonic acid and free chlorine. The keratin substance of the epidermis is then converted into water soluble materials, and in the weakly acid medium the hair and the epidermis are removed by the mechanical action of the drum itself. The chlorine liberated from the reaction, is absorbed by the collagen. It is claimed that a large quantity of the natural fat is saponified and a loosening of the fiber structure of the hides is achieved so that the unhaired hides can be pickled and made ready for tanning operation, in about twenty four hours. The medium used is glycol acid, which maintains a buffered pH value between 3 and 3.5. In order to maintain the proper pH value, sulfuric acid is added. The temperature is maintained below 40°C in order to prevent any hydrolytic decomposition of the collagen, and slowly rotating drums (4-6 rpm) are used to prevent the generation of the heat. The strong oxidizing action of the chlorine dioxide and chlorine results in the bleaching of the hair, and there is no dark scud left on the hide. After completion of the unhairing, the excess oxidizing agent is decomposed with thiosulphate in order to prevent the strong oxidizing agent from being carried over into the chrome tanning bath. The strongly oxidizing chlorine dioxide would oxidize the trivalent chromium tanning agents to dichromate. It is also claimed that the absorption of the chlorine by the hide proteins has the advantage of giving a fine grain and making a somewhat firm leather. The excess oxidizing agent must be reduced with thiosulphate prior to the use of vegetable tanning, in order to avoid excessively rapid fixation of vegetable tanning agents. Chrome tanning can, however, be conducted in the usual manner.

The oxidative system has drawbacks in the high cost of materials and the necessity of shifting production from an alkaline system to an acidic system, which would mean a complete readjustment of the subsequent process of tanning, coloring, and fat-liquoring etc.

(iii) Enzymatic Unhairing

Enzymatic unhairing may be considered to be one of the newest and yet one of the oldest practical methods. A wide variety of the enzymes can be used for this purpose. However, a Keratin selective enzyme that does not attack collagen has yet to be found for the use on commercial scale. There are different ways to carry out unhairing with enzyme, as described below.

Enzymatic treatment system, except for small skins that are processed through sweating is a partial substitution of sodium sulfide. Such a process could not result in a 30 % to 50 % reduction in pollution for this phase of the tannery process.

- **Sweating process**

  This system is applied by dipping the skins in water and hanging them in a moist room for a period of time until the hair slip took place by natural wild bacterial growth. The system is resulted in a clean unhairing system, but if the skins are left too long, more often excessive damage to the hide collagen resulted and pits and holes were found in the leather. Therefore, higher level of skills are required to handle the sweating process.

- **Enzymatic unhairing at neutral pH.**

  This system produces very tight leather. Due to the absence of swelling of the collagen, during tanning through conventional procedure; fine grained, tight leather with a tendency to be tinny, hard and thin is produced. Extensive modifications of the subsequent tanning, coloring and fat liquoring procedure are necessary to compensate for these draw backs. The simplest way of correcting the disadvantages is to introduce an alkaline swelling bath of either lime or caustic soda prior to the pickling and tanning operation.

- **Enzymatic unhairing in combination with lime and sulphide.**

  The cost of the enzyme has been a draw back in some instances. In a low cost enzymatic unhairing a mixture of sodium sulfide, sodium bisulfite, and ammonium hydroxide, a buffered medium at a pH of about 9.5-10 was obtained in the presence of strong reducing agents. The enzyme, papain, introduced into this system exhibited very strong unhairing action. Excellent unhairing results were obtained , but it was necessary to modify the tanning process by intermediate alkaline treatment, and also to modify subsequent tanning processes.

(vi) Molescal System

The BASF Corporation has developed a new system called the Molescall system. This is a Proprietary Product which has the property of being an active sharpening agent, at the same time, it is easily oxidizable and very little sulphide will remain in the system. The Molescall system can be used with or without the addition of a small quantity of sulphide to aid in the unhairing and can be used for both hair destruction (burning) and hair save leathers. This greatly reduces the sulphide effluent which is attractive to tanners, particularly with effluent problems. The leather quality is equivalent to that from a lime sulphide unhairing system.

(vii) Lime Splitting and Trimming

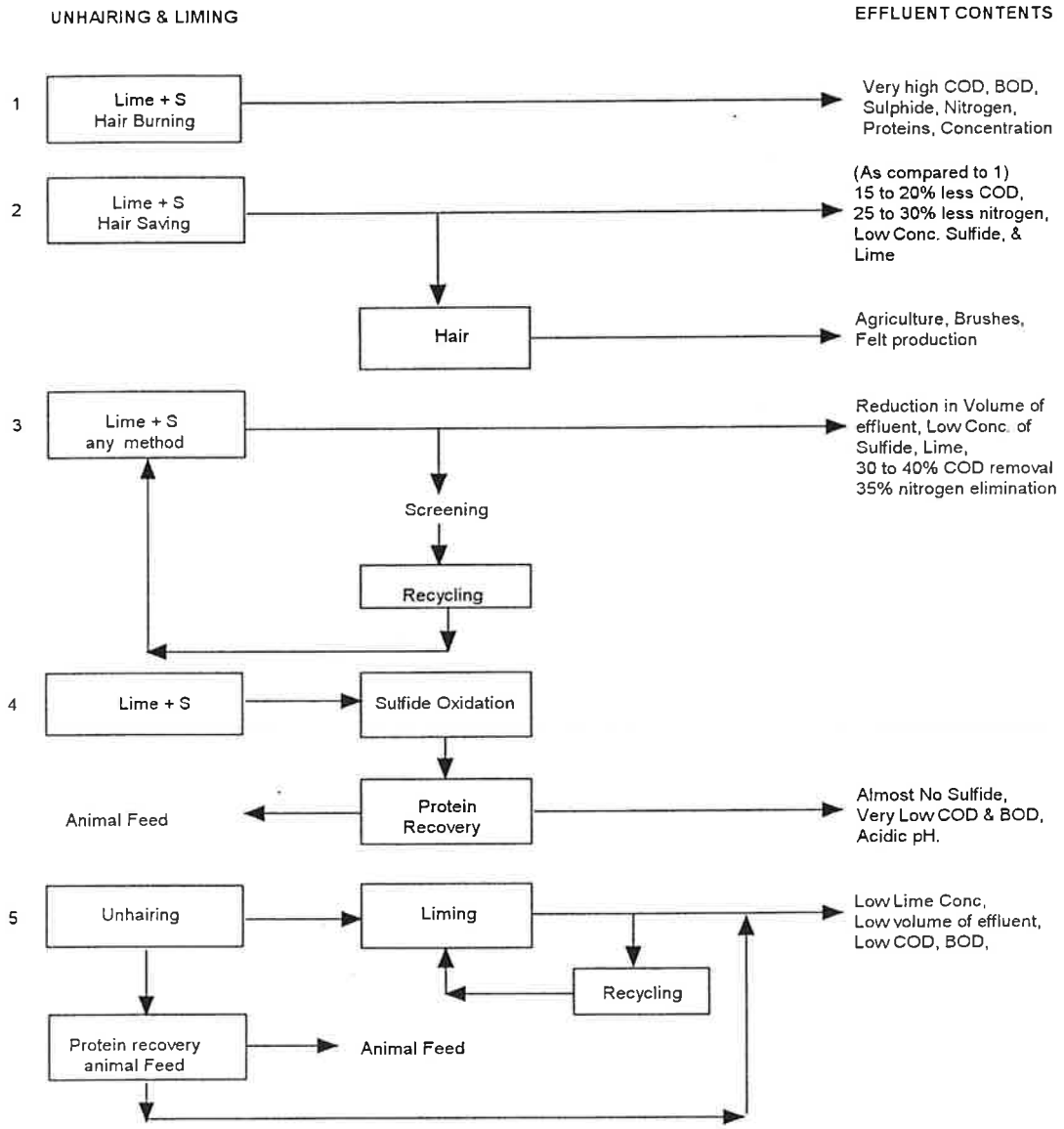
Lime Splitting and trimming is usually carried out after tanning which results in by-products of low quality containing chromium in it. If these procedures are carried out with the pelt, the produced by-products can be sold easier in the market than those resulting from splitting and trimming of wet-blue (tanned hides). This will result in a reduction in the quantities of chemicals used for deliming, pickling, tanning, and consequently the load of the pollutants in wastewater will be considerably reduced. A relime process may be necessary after the lime splitting to get a uniform opening-up of the hides. To conduct the lime splitting successfully, tanneries have to train the beamhouse workers well to perform proper work under lime conditions, and correct adjustment of the split machine is necessary. The non-tanned by-product will be a good raw material for the manufacturing of gelatin or animal feed stuff.

(d) Improvement Options for Punjab Tanneries

The alternative technologies of the lime sulphide process are not locally available for practical use. Therefore the change in the process at present will not be possible. However, the options for pollution reduction can be adopted in the tanneries. Hair saving system, recycling of liming liquor, sulphide oxidation, lime splitting and trimming are the possible options for Punjab tanneries in order to improve the inhouse environmental conditions. However, these options can only be seen with respect to the size of the tanneries. For all tanneries (small, medium, and large) the hair saving system must be adopted. Whereas sulphide oxidation, recycling of lime liquor, lime splitting and trimming can be adopted by medium and large tanneries, as these tanneries have enough space for this purpose and are also capable of adopting this option.

FIGURE - 3

POLLUTION IN EFFLUENT OF UNHAIRING & LIMING PROCESS: A COMPARISON



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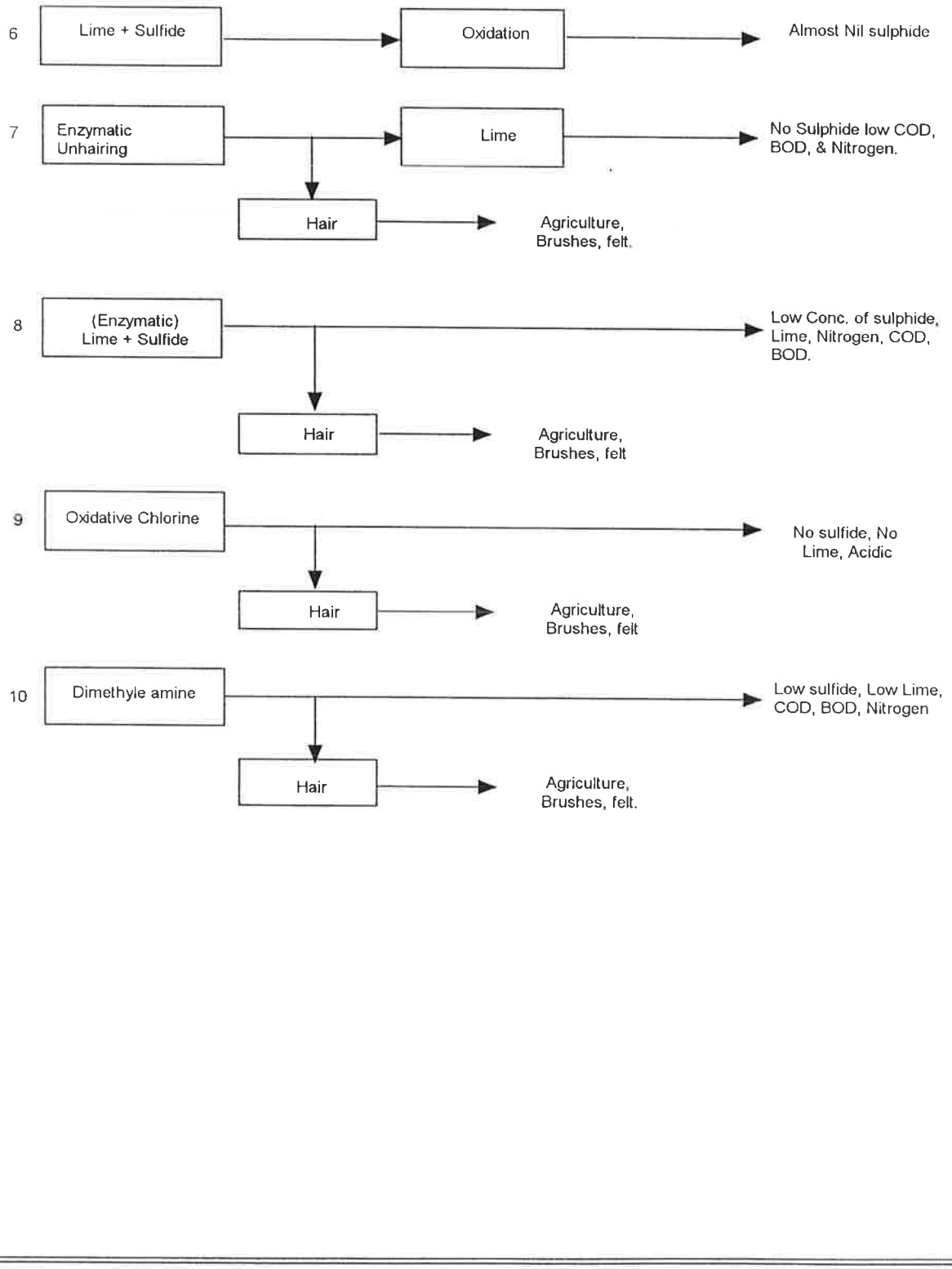

6
Lime + Sulfide
Oxidation
Almost Nil sulphide
7
Enzymatic Unhairing
Lime
No Sulphide low COD, BOD, & Nitrogen.
Hair
Agriculture, Brushes, felt.
8
(Enzymatic) Lime + Sulfide
Low Conc. of sulphide, Lime, Nitrogen, COD, BOD.
Hair
Agriculture, Brushes, felt
9
Oxidative Chlorine
No sulfide, No Lime, Acidic
Hair
Agriculture, Brushes, felt
10
Dimethyle amine
Low sulfide, Low Lime, COD, BOD, Nitrogen
Hair
Agriculture, Brushes, felt.

2.2.4 DELIMING AND BATING

(a) Process Description

The purpose of deliming and bating is to prepare the unhaired hides, chemically and physically, for tanning. Deliming is the removal of absorbed calcium salts and the adjustment of pH for bating. Bating is an enzymatic action for the removal of unwanted hide components.

Limed hides and skins are blue-white, swollen, rubber like, semi-translucent mass containing sulphide and calcium salt. The deliming process, therefore, must be one that will solubilize the absorbed calcium and bring the skin to the desired pH level.

Calcium has good solubility in ammonium sulfate or ammonium chloride. The natural buffering pH of the ammonium sulfate is about 5. In the presence of calcium hydroxide and ammonium salts the solution pH is buffered between 7 and 8; good solubility of the lime results. The lime is gradually removed from the skin by diffusion, and the swelling effects on the hide during this operation are kept at a minimum. This is also the pH range of maximum enzymatic action during bating.

Bating is a further step in the purification of the hide prior to tanning.

Some of the chemically resistant, fibrous protein must also be removed in order to obtain proper grain texture and leather softness. Bating refers to the action of enzyme on these components.

By the time the bating has proceeded to the desired point, the differential swelling effects have been overcome and the skin can stand the mechanical action. It is desirable to wash out the chemicals and the degradation products from the bating application and to lower the temperature to stop the reaction of the enzyme. Cold water is added and these skins are run, with a continual flow of the water, through the drum or paddle until the wash becomes clear and the temperature reaches the desired level, which is usually about 18 ^{oC}.

Deliming process in **Punjab tannereies** is carried out in a similar way as described above with the ammonium salt. For bating purpose enzyme based bating agents, usually products of German firms, are used most commonly. Imported wetting agent is also used. Usually no efforts are made to avoid the formation of hydrogen sulphide gas due to the decrease in pH during the process. After completion of the deliming and bating, washing is carried out by continual flow of the water through the drum.

(b) **Environmental Impacts**

The deliming phase using ammonium salts, brings about considerable nitrogen pollution, estimated to be as much as 40 % of the total discharge. Moreover, there is a risk of formation of toxic hydrogen sulphide gas during this process.

(c) **Clean Technologies**

- **Oxidation of Sulphide**

  To avoid the formation of hydrogen sulphide during the acidification of the deliming float, the oxidation of the sulfide present in the liquor by using hydrogen peroxide or sodium hydrogen sulfite is required.

- **CO_2 Deliming**

  The use of carbon dioxide seems to provide quite a few advantages as far as pollution is concerned. In practice, the only difficulties are related to the required distribution equipment of CO_2 from storage. This technology avoids the use of nitrogen salts. Further more it helps to avoid an increase of the COD value caused by the use of organic acids. From a technical point of view, the results obtained are very favorable for light pelts (Thickness lower than 3 mm). The CO_2 is injected directly in the axle of the drum. The application rate is 1 to 1.5 % of the weight of pelts. For thicker hides, diffusion remains rather slow and requires much greater CO_2 amount, and it is necessary to increase float temperature (upto 35°C) and/or process duration, and/or to add small amount of deliming auxiliaries. A large amount of H_2S appears at the beginning of the reaction requiring pre-treatment with hydrogen peroxide.

  Since the pH of CO_2 deliming float is lower than that used in common procedure, special ammonium free bates should be used.

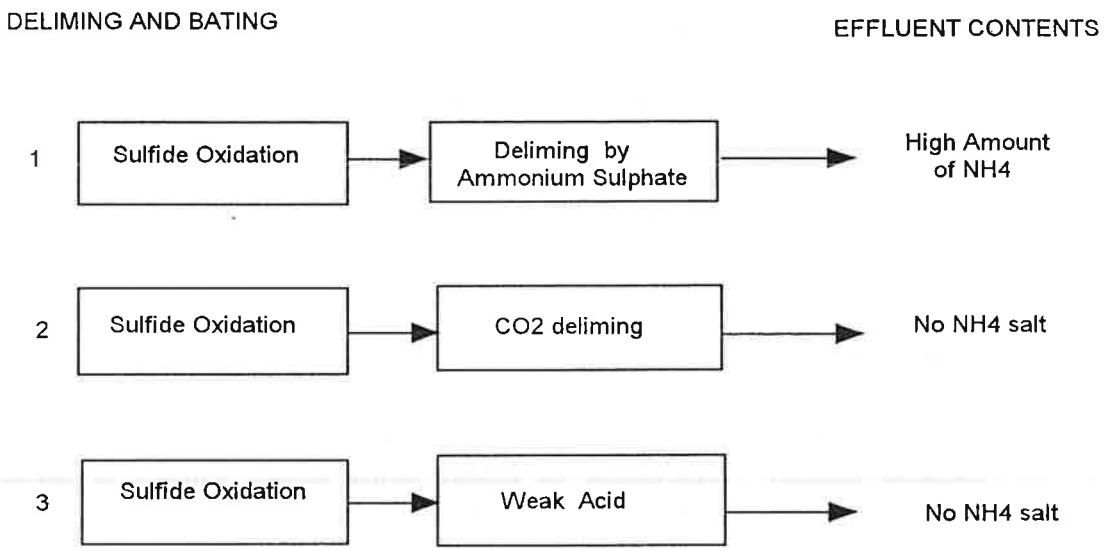
  Currently, more than 100 European and American firms are using this technology, and the advantages of the process should ensure its rapid development. The cost of chemicals is slightly higher than those used in the conventional scheme.

- **Weak Acid (Organic) deliming**

  It is useful to mention the use of the weak acid in deliming operations (Lactic acid, acetic acid, etc) but their cost limits their application to specific cases. This cost is 50 to 100 % greater than the conventional scheme, although the application rate is not more than 0.5 to 1 % of the pelt weight.

FIGURE - 4

POLLUTION IN EFFLUENT OF DELIMING AND BATING PROCESS: A COMPARISON



(d) Improvement Options for Punjab Tanneries

Use of sodium bi sulphite or hydrogen peroxide before addition of the deliming chemicals, would help in oxidation of sulphide. Use of weak acid could be a useful method for small, medium, and large tanneries. In Karachi, a large tannery processing sheep and goat skins is using weak acid (organic) for this purpose. As far as carbon dioxide deliming is concerened, the process requires precise technical control and investment in special injection piping. Therefore for small and medium tanneries, adoption of this technique will be difficult. Large tanneries can investigate this option. There are ammonia free bating agents available for the subsequent bating process.

The continual flow of water for washing should be changed into batch washing. This practice would result in a volume reduction of 50 % or more.

2.2.5 DEGREASING

(a) Process Description

Some sheeps and other skins which are particularly greasy are required to be degreased at this stage.i.e., before tannage. Excessive amounts of tan or dye, cause difficulties in finishing processes, and show as dark greasy patches in the finished leather. Degreasing of greasy skins before tannage is particularly important before chrome tannage, where chrome salt can react with some grease to produce chrome soap. These are, subsequently, very difficult to remove and usually accentuate the above grease problems.

For degreasing purpose solvents or surfactants are used as main degreasing agents. Both procedures have their own advantages and disadvantage. Enzymes and hot water may be applied as auxiliary agent in some recipes.

Solvent based *Degreasing* method is more commonly used in the European tanneries. Paraffin, kerosine and white spirit are the main solvents used for degreasing purpose. In addition to the solvent small amount of wetting agent is also added to facilitate the process.

In **Punjab tanneries,** the surfactant is widely used for degreasing purpose. This procedure involves the emulsification of the grease which becomes water soluble and is removed from the skins. Literature shows that more widely used surfactants are etoxylated allylphenols based. The surfactants used in the Punjab tanneries are imported from the European countries and tannery people do not have any idea about the composition of these wetting agents.

(b) **Environmental Impacts**

Oil and grease effects the receiving water by limiting oxygen transfer and thus reduces dissolved oxygen levels, which in turn may also affect the gills of the fish and plumage of water fowl. Emulsified oil which settles on the bottom of water courses has the same affects as other suspended solids.

The degreasing agents commonly in use are organic solvents, which release a greasy residue after recovery. Parts of the solvents may be emitted as vapor to the air during the process.

Surfactant if used instead of solvent, leads to a higher value of COD and BOD in the effluent because of the presence of dissolved greases and surfactants in the stream.

(c) **Clean Technologies**

- **Recycling of Degreasing Solvent**

Adequate equipment for storage, recovery and regeneration of solvent has to be provided to permit the correct handling of solvents and to avoid their release to the environment. If the extract brines are recycled, grease is recuperated, and solvent vapors are controlled, the occupational exposure are minimized. Such a system may be considered as environmentally sound, depending on the available technical possibilities. However, investment costs for the implementation and operation are higher than those for the methods using surfactant. Furthermore it is imperative to avoid solvents containing halogenated hydrocarbons.

In recycling procedure the degreasing float and the three extraction pickling brines have to be collected in a vertical tank. Three phases are obtained:

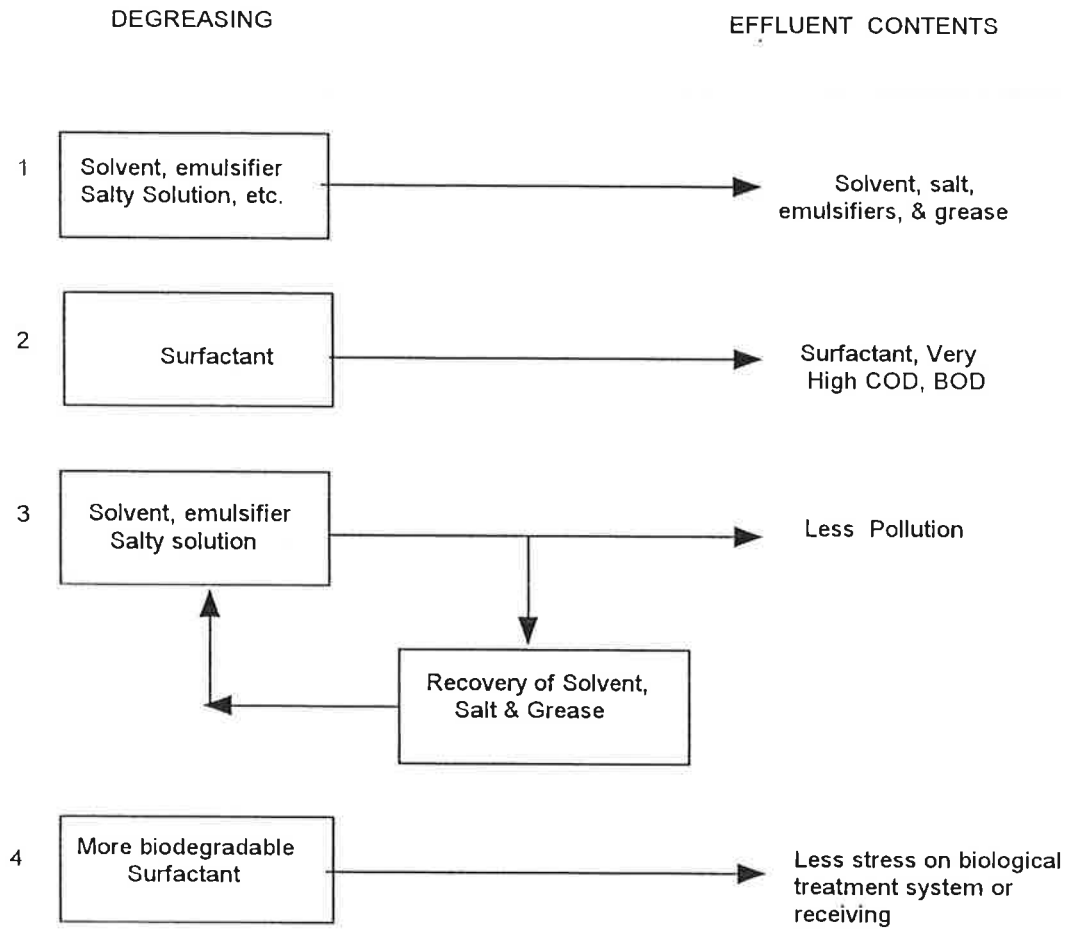
i) A salty aqueous phase, which is perfectly reusable for a new extraction. The sodium chloride solution reaches 90 % of its initial concentration. The required concentrations of water and sodium chloride are adjusted before recycling.

ii) An organic phase rich in solvents and combined fat solvents, which may be regenerated through steam-stripping.

iii) An intermediate emulsifying phase, which can be controlled by using little emulsifier and bringing the temperature of that phase to 50°C.

FIGURE - 5

POLLUTION IN DEGREASING EFFLUENT: A COMPARISON



All in all, 50 to 70 % of the solvent may be recovered, and distillation residues may occasionally be upgraded. This upgrading may only take place if large volumes are involved. Residues such as tallow may then be upgraded.

- **Degreasing with surfactant**

  This procedure contributes water pollution (COD, BOD). Many suppliers offer products based on alcohol ethoxylate, which are considered to be more biodegradable than the traditional nonylphenol ethoxylate based products, and therefore they should be preferred. A comparison of the pollution in the effluent of the degreasing processes is given in figure 5.

(d) Improvement Options for Punjab Tanneries.

In Punjab tanneries the use of raw material hides and skins changes with the season and demand. This change is very common in small and medium tanneries. Whereas, the change in the large tanneries is not very common. Therefore, the small and medium tanneries may continue the use of surfactant for degreasing purpose. However, alcohol ethoxylate based surfactant should be selected. For large tanneries the solvent based degreasing system with the option of the recovery of solvent for reuse purpose will be suitable.

2.2.6 PICKLING

(a) Process Description

Pickling refers to the treatment of the hide with salt and acid to bring the skin to the desired pH for either preservation, for some time, or for tanning. At the end of the pickling operation, the skin is theoretically a purified net work of the hide protein. Pickling will give a pH of 1.0 - 2.0 to the skins. Ample salt need to be present not only to prevent dangerous acid swelling, but to cause some decrease in thickness of the skins. As a result skins and hides become white, soft and flaccid. Normally 3 % salt on the total volume of the water present prevents dangerous acid swelling.

Pickling due to the use of organic acids which gives chrome masking ions, e.g. formates or lactase are well known. Non swelling acids such as 1% sulphothalic acid are also used. In this case the salt may be greatly reduced.

Vegetable tannage may be done on pickled skins. Where pickling is undesirable, the bated and delimed hides and skins may be further acidified down to pH 4.0 4.5.

In **Punjab tanneries** the chrome tanning process is commonly used, therefore, pickling needs to be essentially carried out. For this purpose, tanneries are using organic and inorganic acids in addition with common salt. After pickling, the chrome salt is added into the same pickling float and tanning begins. Sometime tanneries keep the pickled skins in storage before the tanning process. In this case the float of pickling process is drained out. Use of fungicides is not common. The pickling process is carried out in wooden drums.

(b) Environmental Impacts

Spent pickling float contains very high amounts of chloride due to the use of salt as non - swelling agent. Residue of the fungicides, if applied, will also be present in the pickling stream. Pickling is usually carried out with the tanning. Therefore environmental impact is usually seen with respect to both processes. However, if pickling and tanning processes are performed in separate float a pickling effluent will arise from the beam house operation. The same environmental impacts that lead to a lowering of the quantity of salts during soaking process are associated with the pickling process.

(c) Clean Technologies

- **Recycling of Pickling Float**

  Today recycling of pickling floats is a common practice in many tanneries of the world to reduce the salt pollution. After collection, the used float is sieved and its acidity (Mainly from formic and sulfuric acids) is controlled by laboratory test. After readjustment to initial pH value, the float is reused for the following cycle. In practice, salt savings are about 80 % and reduction in acid consumption is estimated to be 25 %.

(d) Imrovement Options for Punjab Tanneries

The pickling and tanning process in Punjab tanneries is carried out simutaneously. Therefore the improvement options are described along with the tanning process.

2.2.7 TANNING

(a) Process Description

Tanning may be defined as the treatment of hides and skins for preservation and conversion into useful articles of commerce. Many ways to achieve this target are mineral tannage, vegetable tannage, aldehyde tannage and oil tannage, etc. Among these mineral tannage is widely used. In mineral tannage, chrome tanning took its place in the commercial world shortly after its discovery and became the most common method of tanning of light leather and shoeupper leather. Other agents like aluminum, titanium and zirconium salts are also available for tanning at the moment they represent only a very small part of the tanning agents used in the world.

The origins of vegetable tanning are lost in pre-historic times. Primitive people in all parts of the globe and from all the ages of the past have developed vegetable tanning systems based on the local materials. Vegetable tanning and vegetable tanned leathers remained the "Standards Leather" until the fairly recent development of the chrome tanning industry. However, the production of some special type of leather is still achieved through vegetable tanning process. The leathers made by full vegetable tannage are used for soles, belting, saddler, upholstery, lining, and luggage. In addition to these, handicraft and some fancy leathers are also produced by vegetable tannage. The retannage of chrome tanned leather with vegetable tanning extracts is very common.

(a.1) Process Description of Chrome Tanning

The bulk of the chrome tanning is carried out with chromium sulphate, a green salt more usually produced by reduction of the dichromate in the presence of acid. A number of reducing agents like glucose, molasses or sulphur dioxide are employed for this purpose. Increasingly, today the preparation of chrome liquor and powder is carried out by specialist firms and chrome is thus available in the form of closely controlled standard products.

Hexavalent chromium compounds are also used for the tanning purpose. In this process skins are first impregnated with chromic acid and then treated in a second bath of hypo and hydrochloric acid. During these processes the chrome is converted into basic chromium sulphate (the actual tanning material) and sulphur is liberated. The objective of the second bath is complete reduction of all the chromic acid in the skins and the formation of a chromium salt of the correct basicity in the leather. This is achieved by the use of an excess of hypo (sodium thiosulphate).

This is probably the oldest commercial chrome tannage method and has largely been superceded by one bath tannage, except in certain cases where the older method is thought to give a particularly uniform tannage and a deposit of colloidal sulphur in the leather.

Now-a-days the chrome tanning method employes the use of prepared trivalent chromium compounds both in liquid and solids form. Practically chrome tanning is conducted in paddles and drums. Paddle tannage employs liquor ratios of approximately four parts of the solution to one part of the hide, and under these dilute solution conditions the tannage proceeds more slowly as compared to the drum tannage. In many countries, this system has been replaced by drum tannage. In drum tanning system handling of hides/skins and liquor is easier as compared to the paddle tanning system.

In **Punjab tanneries** wooden drums are used for tanning purpose. At present, trivalent basic chromium sulphate salt is the most common material used for tanning purpose. In the past, hexavalent chromium salt was also in use for tanning purpose. The use of trivalent and hexavalent salts of chromium depends on the cost of these salts, the cheaper salt obiviously being prefered. Restriction on the import of leather containing hexavalent chromium in European countries has compelled the tanners to use trivalent chromium salt. Vegetable tanning is also carried out but in combination with chrome tanning.

Trivalent basic chromium sulphate salt is available locally in powder form, produced in a factory situated in Sindh. Some tanneries are using imported chrome salt. Tanneries also claim that 90 % exhaustion of chromium take place. However, literature shows that 70 - 75 % exhaustion takes place in normal chrome tanning process. The effluent is drained out after completion of the process. For vegetable tanning process extracted material (Quebracho, Mimosa) is used. These are imported from European countries.

For saving chromium salt, only about 4 %, of this salt is applied for wet blue production. To give full tannage, rechroming is carried out after shaving, splitting and trimming. Similarly, pre-tanning is carried out with about 2 % chrome salt before vegetable tanning. After shaving and trimming the vegetable tanning process is carried out.

Unbleached vegetable tanning material is used. Bleaching is carried out during the process. The bleaching process produces sulphur oxide gases that effect the worker very badly, as the eyes and respiratory tract of workers get affected by these gases. The combination tanning is observed in large tanneries, whereas small and medium tanneries are using only chromium tanning.

Shaving material generated during the thickness adjustment operation is sold to the leather board manufacturer. They collect this material from the tanneries. Split material from wet blue of cow and buffalo hide is sold mainly to the leather glove manufacturer.

(b.1) Environmental Impacts

The principal environmental concern of the tanning techniques originates mainly from the excess of tanning agents. Significant quantities of the offered chemicals are not fixed in the collagen, and thus, either remain in the "spent float" and are squeezed off during the sammying operation or are washed out by the wet finishing float. Another part of the offered tanning agents is washed within the solid residue produced by some mechanical works which are performed after tanning(shaving, trimming, buffing).

As in "one bath tanning" method basic chromium sulphate is applied in an acid medium under which conditions only trivalent chrome (Cr^{+3}) can be released. This is much less toxic than hexavalent chrome (Cr^{+6}) which is toxic to bacteria at a concentration of 2 mg/l. Hexavalent chrome will only enter in tannery effluent streams following spillage or incomplete reduction of hexavalent in tanneries which prepare their own tanning solutions (two bath method). For humans, hexavalent chromium, or chromate is extremely hazardous inducing lung cancer, tumors and kidney inflammation at very low concentrations.

Besides the environmental factors there is also an economical loss due to the drainage of unused chromium salts in the effluent, which is almost 25-30 % of total chromium applied during the tanning process.

In the case of bleaching process in the tannery the generation of sulphur oxide gases creates hazards for the workers by affecting their eyes and respiratory track.

(c.1) Clean Technologies

Compounds of trivalent chromium are the most widely applied tanning agents and no significant changes are to be expected in the near future. During the last few years, some improvements in chrome tannage have been developed, tested and evaluated with respect to their operational difficulties, efficiency, economic viability, safety and effects on the leather quality. The use of such procedures permits tanneries to reduce the chromium discharge to the environment and improve the efficiency in the use of chemicals.

- **Direct recycling of chrome tanning float**

  Direct recycling of tanning floats remains the easiest method to apply for recovery and reuse of chromium salts from tanning operations. After collection and sufficiently fine screening, the float are controlled and the chromium amounts used in the previous cycle are replaced by chromium salts. Depending on the tanning technology in use, the degree of exhaustion reached for each cycle may vary. In a conventional bovine tanning process, it is estimated that the direct recycling technology can save about 20 % of the chromium used in the conventional process.

  On the other hand, for the treatment of wooly sheep skins (especially double face), this direct recycling makes it possible to reuse almost 50 % of the chromium introduced in the process, since tanning floats do not reach exhaustion rates. This recycling method may be repeated several times on the same float. However, it is limited by the occurrence of quality problems with delicate hides, and by the need to control residual floats (acidity and chromium concentration).

Many bovine and sheepskins tanneries have experimented with this technology and used it for several years. This technology is specially adopted by small firms and is widely used throughout Europe.

Although the system does not completely eliminate the chromium being discharged through the effluent or sludge, it can be seen as a part of a general environmental plan of a tannery, because it reduces the necessary amount of chromium being discharged to the environment, thus facilitating the treatment and disposal of a small amount of chromium containing sludge.

- **Recycling After Precipitation**

This is the oldest and most conventional method. It allows collection of the tanning float along with the rinses, that sometimes occur at the end of the tanning, and the effluent from various post-tanning stages (Washing, dripping, sammying, etc). After collection, screening and storage, the floats are precipitated with different types of coagulants including sodium hydroxide, sodium carbonate, magnesium oxide, and even lime when recycling is not possible. A flocculation with polyelectrolyte may follow.

The re-use of sludge after simple settling and acidification has been experimented and practiced. However the normal process consists of settling the chromium sludge, and treating it on a filter-press or vacuum filter.

Large plants have operated under this scheme for many years in Germany, Italy, South America and France.

Only large plants treating significant amounts of chromium can justifiably use the technology of recycling after precipitation and dewatering of the sludge. As a result, tanners collect their tanning residual bath for a common treatment. Small scale tanneries are using magnesium oxide precipitation and direct redissolution of the settled sludge for reuse as a tanning residual bath for a common treatment.

Besides, the recycling after precipitation method can also be practiced as a treatment of chromium containing floats. Both systems, if conducted properly, can meet the limits demanded by most of the actual legislation for trivalent of chromium in effluent. However, most chemicals used in the process increase the salinity of the effluent.

Chromium recycling is not recommended for effluent containing residues of surfactant, fat liquors and tanning agents other than chromium. So retanning floats can not be treated by chromium recycling. In the case of treatment of more complex chromium containing floats, for example of retanning floats, chromium containing floats can be precipitated with calcium hydroxide and flocculants, followed by a separation and sludge drying by filter press or remaining overnight in a tank. The separated liquid phase can be discharged to the effluent and the remaining chromium sludge can be disposed of. It is therefore very important to avoid mixing of floats.

- **Tanning Products that Improve the Exhaustion Rate**

  For the past few years, tanning and basification products have been available in the market which enable a tanning cycle inducing only small chromium wastes. These products are developed with the aim of bringing about the complete fixation of the chrome on to the protein fibers so that the exhausted chrome tanning float contains little or no chrome. It has the great advantage that no chrome losses are incurred by chrome liquor left in the tanned hide to be removed by subsequent machine squeezing or washing. Chrome take up of over 90 % with exhaust of less than 1 g per liter is possible. It is therefore possible to reduce the initial chrome oxide offer to about 1.8 % on the fleshed weight and still obtain the same amount of chrome fixed on the fibre.

  Tanning with such products can only be performed on split hides. Since the molecules are too large to penetrate adequately in the hide close to the grain side. When hides are split, the hide's reduced thickness make this operation easier.

  Tanning with high exhaustion chromium salts requires extensive monitoring and is rather difficult to control. Care must be taken so that the chromium penetrates deeply in the hide before fixing, otherwise marks may appear on the grain side.

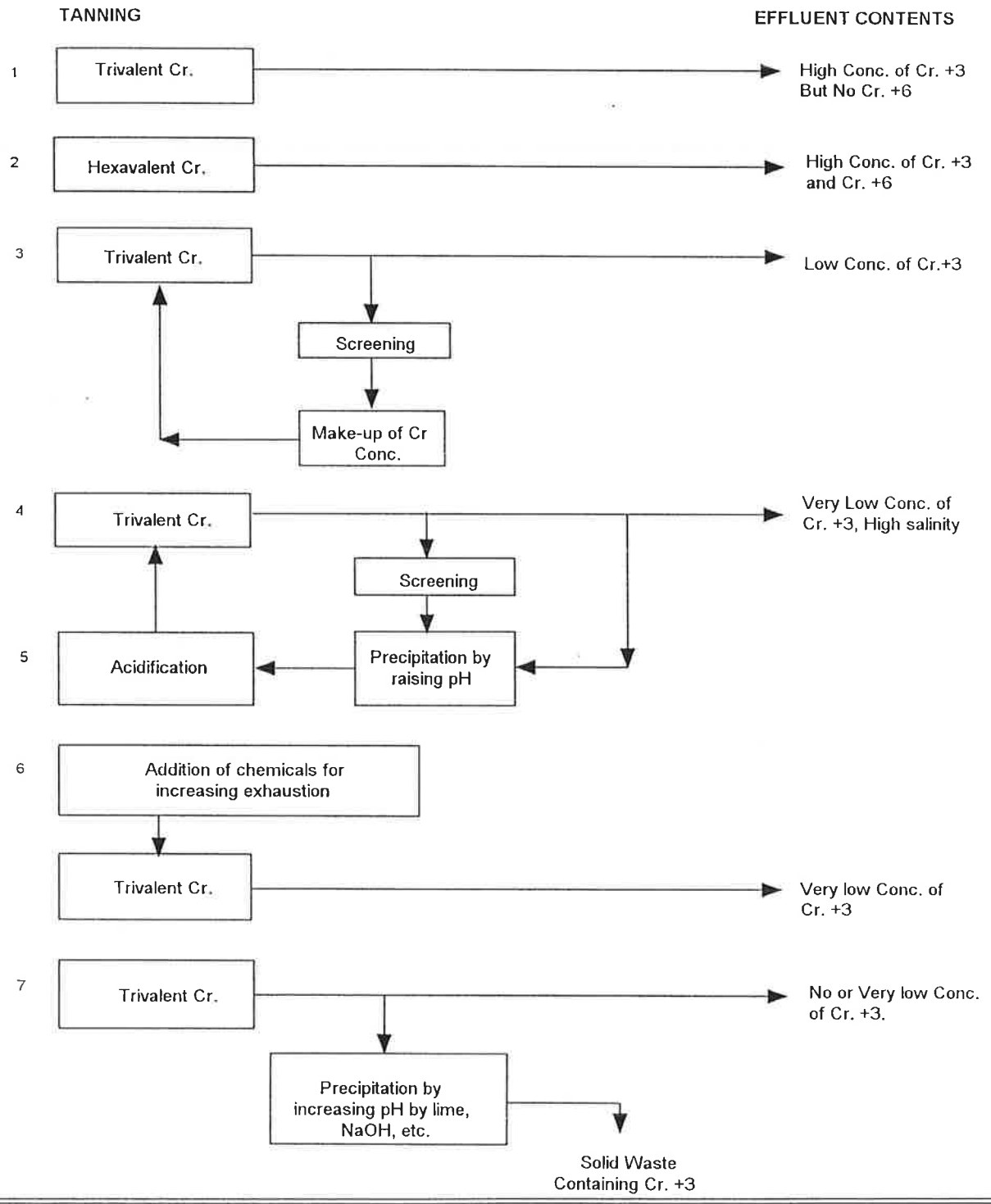
  A comparison of the pollution load in effleunt of the tanning process with and without clean technologies is given in figure 6.

(d.1) Improvement Options for Punjab Tanneries

As the tanneries in Punjab carry out pickling and chrome tanning simultaneously, therefore, no separate float of pickling process exists. Effluent of the tanning process contains considerable quantity (25 - 30 %) of chromium. The claim of 90 % exhaustion looks unwise as tanneries are using ordinary processes which may not be able to exhaust 90 % chromium in the skins/hides.

FIGURE - 6

POLLUTION IN EFFLUENT OF CHROME TANNING PROCESS: A COMPARISON



The recycling of spent chrome liquor and improved exhaustion of chromium are most suitable for small and medium tannereis. However, for large tanneries the recycling of chromium after precipitation is most suitable options.

The use of hexavalent chromium salt for tanning purpose must be banned.

The bleached vegetable tanning material should be used in vegetable tanning process.

(a.2) Process Description of Vegetable Tanning

The vegetable tannins come from a wide variety of plants, and may be found in wood, leaves, nuts, twigs, and bark. The extract of a particular plant consists of a broad range of substances, and there is no such thing as a single tannin from a particular plant source. The material extracted from the wood not only contains many different tannins, but also starches, gums, and other material. The extract is not a true solution but will contain suspended insoluble materials.

The techniques employed by tanners to produce different leathers are based on controlled penetration of the vegetable tanning materials into the hide or the skin. In the vegetable tannage of **light leather**, particularly in a drum, the chemical aspect is most important. In this case the tanner tries to obtain a full, soft tannage with a minimum amount of material. **In heavy leather**, where filling action and weight increases are important a rocker system is employed. In the manufacture of **sole leather**, vegetable tanning is the predominant process for two reasons; the first is that it imparts to **sole leather** the property of moldability, and the second function of vegetable tanning in sole leather manufacture is the build up of solid materials inside the hide to give more physical weight and greater wearing characteristics. Vegetable tanning for light leather is already discussed in the section of the chrome tanning process. Here vegetable tanning for sole leather will be discussed.

Sole leather is produced by vegetable tanning of hides. These hides are given a long liming period to open up the structure and make them more suitable to receive the vegetable tanning components. The bating and deliming process brings them to the slightly acidic pH range, and they are then introduced into the vegetable tannage rocker system. The initial vegetable tanning liquors are quite dilute and consist of the spent liquors from previous tannages. Normal vegetable tannage by the tradional method is in a rocker system, where the hides are hung on racks in pits containing the vegetable tanning materials. A gentle rocking keeps the hides in constant motion in the tanning solutions without folding or flexing. The vegetable tanning process continues for approximately three weeks, during which the leather is placed in solutions of gradually increased strength. This is done by shifting the hides from pit to pit of increasing concentration of

tanning materials, or by pumping the solution from one pit to another. The vegetable tanning process, as employed here, is a counter-current take-up of vegetable tannins. At the end of the tanning time the tannin is thoroughly struck through the skin and the skin is tanned.

In the other sole leather processing, more vegetable tanning material are introduced by treating the skins with very concentrated liquors, thereby building up the concentration of the solids in the void of the skin. The increase in fixation of the vegetable tannins near the end of the tanning period is accomplished by lowering the pH.

Before the days of proper knowledge of pH control it was customary to allow the souring of the vegetable tannins to process through natural fermentation of the sugars (in the extract) to acids. This controlled fermentation was very difficult to keep in proper adjustment, and quality control of this system was a matter of luck.

In **Punjab tanneries** sole leather is produced in the tanneries called "Desi" or bag tanneries. These tanneries are not mechanised and use traditional method for production of sole leather. In these tanneries all processes including vegetable tanning is carried out in pits and the hides are shaked from time to time manually during the process. The extract of the bark of locally availble plant called babul is used as tanning material. The extraction is carried out inside the tannery by soaking the ground babul bark in the large pits for 4-5 days. The solid material left after the extraction is sold to the bricks maker. They use this material as fuel in their furnace.

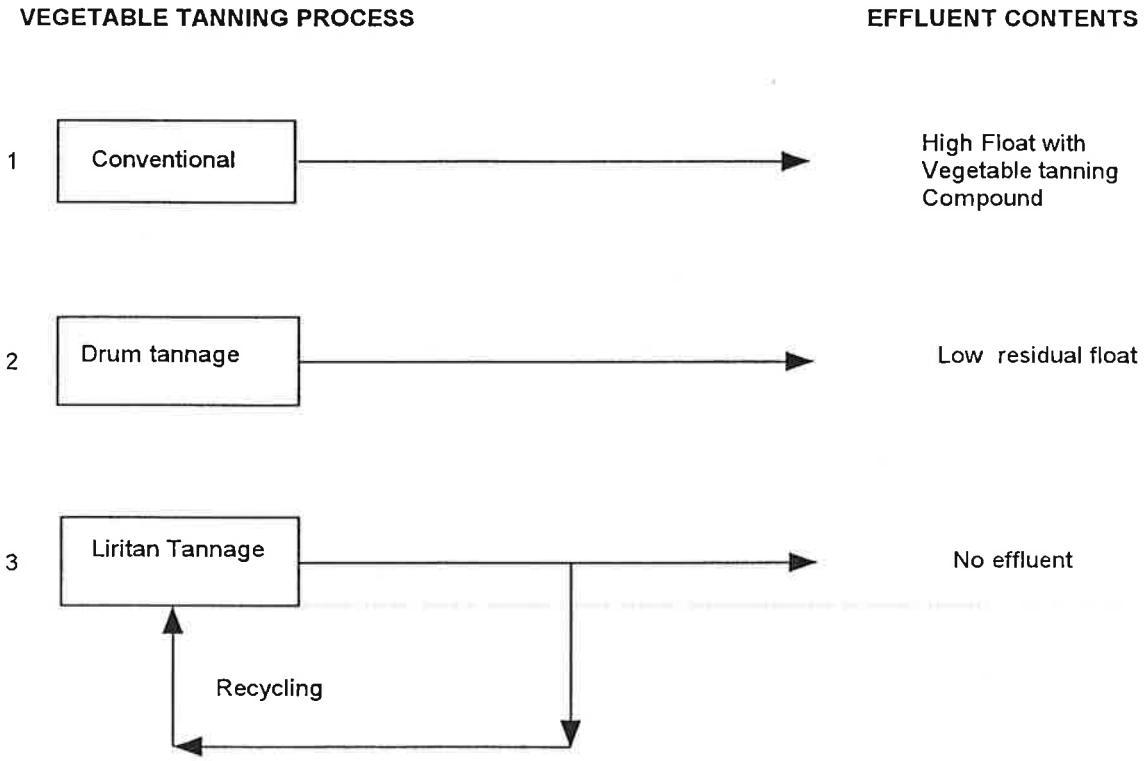
(b.2) Environmental Impacts

The vegetable tanning agents produce a higher pollution load than chrome tanning agents although the latter have particular problems of their own (as described above). Spent tannin liquors cause very high COD value and persistently colored effluent. Furthermore, the degradation of tannin in conventional wastewater treatment is a slow and costly process.

5% Calgon and the limed pelt is delimed at pH 2.8 to 3.0 by an addition of sulfuric acid. An open pit pickle is usually necessary to ensure pH near 3 and equilibrium. The spent pickle liquor is kept and refortified by the addition of approximately 2.25 Calgon on limed weight and about 1-1.5 % sulfuric acid. These quantities are finalized by the tanner to best suit his individual preferences.

FIGURE - 7

POLLUTION IN VEGETABLE TANNING PROCESS: A COMPARISON



Drained pickled pelt is transferred to a warm vegetable tan with a pH of between 3.2 and 3.5 and a density of approximately 1.1 or 100° barkometer. The temperature is kept at about 35°C. Tannage was originally developed for mimosa, but since then it has been adapted to a number of different tanning materials. The vegetable tanning liquor maintains its strength by refortifying with the addition of more vegetable tanning material. The solutions stabilize on each repetitive bath. The quantity of Calgon in the tanning bath will be maintained at slightly less than 1 %. The pH will stabilize between 3.2 and 3.5 as desired.

In some cases, it has been found convenient to use three steps. Between the Calgon pickle bath and the warm vegetable tanning bath, a vegetable tanning step is added, using a coloring vegetable bath of about 20° barkometer. This step produces slightly better leather, and is easier to control. However, it will result in some effluent, since the intermediate stage may not be refortified and maintain consistent concentration in low strength liquors.

(d.2) Improvement Options for Punjab Tanneries

"Desi" or bag tanneries tanneries need a lot of improvement in their present status. The most important is the updation of these tanneries with the modern knowledge and technologies. Use of drums for tanning purpose should be applied instead of pits. New system should be adopted that offers very close control of pH, temperature, and rapid penetration of vegetable tanning material. As a result high speed production with low labor cost will be attained.

2.2.8 WET FINISHING: RETANNING, DYEING AND FATLIQUORING PROCESS

(a) Process Description

Usually retanning, fatliquoring and dyeing is carried out in the same float. However, owing to their different significance, the processes are described here separately.

- **Retanning**

  Many Chemicals combine with, or affect, skins and cause resistance to putrefaction and imparts a number of desirable properties. These include salts of heavy metals, products of aromatic substances(e.g. cresol, phenol, naphthalene) treated with formaldehyde and sulfuric acids. Other material including urea, di-cyanamide, Bisphenol A, trephenylnapthalene sulfonic acid, benzyl alcohol, oxazolidone and polyamide are also used as retanning agents. Vegetable tanning materials are also applied as retanning agents. Retanning is also carried out with the salt of basic chromium sulphate. The syntans or retanning materials available to leather industry are constantly in a state of change. The exact nature of these proprietary products is seldom revealed for competitive reasons.

There are various ways to apply the retanning agents. Most commonly after splitting or shaving, pH adjustment is carried out according to the suppliers instructions and then in presence of retanning agents with 30-100 % float, drumming is carried out for 30-60 minutes. The leather is then processed normally for dyeing and fatliquoring.

- **Dyeing**

In conventional dyeing processes the dye is dissolved in water and the leather is treated with this solution. During dyeing the color fixes chemically to the leather, leaving the water colorless. Under ideal conditions all the dye offered is fixed to the leather and subsequent washing of the dyed leather with water should not remove any color. The dyeing is then said to be 100 % wash fastness.

The application of leather dyes is done in a batch process and is conducted in a drum. The dye drums are considerably smaller than those used for chrome tanning. The liquor ratios employed are about three pounds of water per pound of blue shaved weight. Even higher liquor ratios may be necessary to maintain even coloring.

Brush dyeing is a method of applying dyes to a leather where it is desired to color only one side. It has the advantage of being very economical in dye and is adaptable for obtaining special effects or evenness of dying, depending on the skill of the operator.

Tray dyeing may be employed for the dyeing of small skins. With this system a shallow pan, large enough to take the spread-out skins, is used. Two skins are usually placed flesh to flesh and are lowered into the solution. When the desired depth of penetration of the dye on the grain side is obtained, the skins are removed, placed grain to grain, and dipped again to get the desired depth of penetration on the flesh side. Due to high labor cost, the method is satisfactory for limited production only. Like brush dyeing, dyes are needed which have good solubility at low temperature and which attain fixation without close pH control.

- **Fatliquoring**

The preliminary processes of unhairing and bating remove most of the natural oil from the skin. Whatever the course of the pretreatment and the tannage, the leather at the time of the completion of the tannage does not contain sufficient lubricants to prevent it from drying into a hard mass.

Therefore, proper lubrication of the leather fibers is one of the most important factors in determining the characteristics of the leather, both from a utilitarian and an aesthetic point of view. Proper lubrication or fatliquoring, greatly affects the physical properties of break, stretch, stitch tear, tensile strength and comfort of leather.

Leather particularly chrome tanned leather, is acidic and has a pH at which soap emulsions are too near the precipitation point. For proper control greater solubility at low pH is desired for most applications.

In modern practices, the sulphonated or sulphated oils are by far the largest category of fatliquoring materials presently being used. Another most popular of the modern fatliquoring systems uses bisulfited oils. The bisulphited oils have application in the manufacture of chrome tanned leather. For light and soft leather, such as garment or glove leathers greater penetration of the oil into the centre of the leather is required. This can be achieved easily with the application of the bisulfited oil.

Fat liquoring products are classed as An-ionic emulsion (as in the case of soap & the sulfonic acid, since they introduce negative charges to the droplet) Cationic emulsion (quaternary amines, imparts plus charges on the droplets) and Non ionic emulsion, e.g. polyhydric alcohols, such as polyethylene glycol or methyl cellulose.

Application of the fat liquoring material depends on the nature of oil, and the nature of the leather, that determines the type and extent of the lubrication of the leather fibers.

In a fatliquoring system using an ionic oil such as a soap or a sulphated oil, the oil droplet is introduced into the drum as an emulsion at a pH value where the emulsion is reasonably stable. Once it is in the drum the oil droplets gradually begin to penetrate the leather. The pH in the leather is lower than needed for maintaining the stability of the oil, and the oil will be deposited on the leather. The attraction of anionic oil group to the leather filter brings about a stable bond upon drying and the leather may have a fixed oil.

Cationic oil have found limited application in the fatliquoring of most leather. since the positive charge of the droplet does not permit much penetration of the fatliquor into the leather.

In **Punjab tanneries** the retanning, fatliquoring and dyeing processes are caried out in the same float. Wooden drums are used for these process. Phenol, nephthelene, and resin based retanning agents are widely used. For dyeing purpose, dyes containing benzadine are not used. Mixture of suphonated, sulphited, and chlorinated oils are used in fat liquoring process. Tanners claims more than 90 % exhuastion of these materials.

(b) Environmental Impacts

Usually retanning, and wet finishing (Dyeing, fatliquor) are conducted in a single float and result in an effluent containing residue of dyes, fatliquors and retanning agents. Chromium may be present in the float due to the presence of unfixed chromium in the wet-blue stocks. The use of very harmful chemicals for retanning fatliquoring and dyeing processes does have unavoidable impacts on the environment. For example; chromium, lead and cadmium salts can still be found in some types of older dyes and pigments. Unused phenol based retanning agent if discharged in the water containing fish can cause the tanning of sensitive protein of fish. Some azo-dyes, containing carcinogenic amino-components like benzidine are also in use in some countries. Fatliquoring oils used in the tannery are often composed of chlorinated alkane sulphonate and fatty acid methylester sulphonate that are now questionable because of the organic halogens quantities they can generate.

(c) Clean Technologies

It can be seen from above mentioned processes description the proper penetration of the material used in these processes is very important factors for the proper utilization of the chemicals and also for avoiding their serious environmental impacts. The process has to be performed in a manner that assure the highest possible exhaust of the float. Metal complex dyes, which contain restricted heavy metals and benzidine based dyes, must be replaced. Handling of dyes in dry powder form demands protective equipment to avoid inhalation or skin contacts during the preparation of the formulation. The absorbable organic halogens, the chlorinated fatliquoring products will be replaced. Various substitutes are available commercially for this purpose. Some of the products have been developed which must be added to the fatliquoring oils. The oils are then converted into micro emulsions producing a significant reduction of COD in fatliquoring wastewater.

The use of classic wood drums for dyeing is unsuitable. This is why stainless steel drum with three compartments like washing machine appeared 15 years ago. The continuous mechanical action on the hides, the changing of the drums's rotation, the constant temperature and recycling of the bath from the bottom to the top, improve the efficiency of the chemicals's penetration into the hides. This

type of equipment has proven to be particularly interesting from environmental points of view, as they permit dye savings (heating the bath at the end of the process increases the exhaustion for 15 or 20 %). In addition, they enable dyeing in a very short float and require lower quantities of water for rising. The rate of water in the float is only 100 % of the wet blue weight, whereas, it is 400 % in classic drums. Thus, the discharge load is reduced by 50 % and the product exhaustion rate reaches 90 %. Finally, controls are eased during the rather complicated process of dyeing.

The cost of three compartment drum is very high, but the duration of the whole process can be shorten, compared to a classical drum.

(d) Improvement Options for Punjab Tannereis

Change of the wooden drum with the stainless steel drum would be difficult even for the large tanneries. The use of haloginated fatliquors, benzidine based dyes etc., should be avioded. The high exhaustion process for these material is most important and is an unavoidable factor. Polymeric auxiliaries, availbale in the market, that can ensure high fixation. Moreover, these auxiliaries can also function as retanning and fatliquoring agents, hence reduces the pollution load also. The processing of dyeing and fatliquoring involves acidification of the float in order to fix these material, but the lowering the pH below 4 has the effect of releasing chromium into the solution. Therefore care should be taken in this regard.

2.2.9 DRYING OF LEATHER

(a) Process Description

Drying is more than the simple removal of the moisture to bring the leather to a practical, usable form; it also contributes to the chemical reactions of leather-making. The drying of leather is one of the most important steps in practical leather quality.

Practically many techniques are used for drying the leather.

- **Air drying**

  It is the earliest method of drying of leather, and the one which is probably still in greatest use. The skins are hung on hooks or sticks or placed on horizontal racks. The leather is dried by the natural passage of air around it. If the conditions of temperature and humidity are such that the leather dries slowly, case hardening is avoided and good uniformity will result. Air drying has the advantages of (1) low capital investment,

(2) no heat input, (3) little chance of case hardening, and (4) simplicity of operation. The drawbacks of the system are its low productivity and low area yielded.

- **Tacking**

A variation of the air drying technique is tacking, where the leather is stretched out on boards and tacked. As the leather dries, the fibers tend to draw together and area loss results; this is avoided by tacking. The tacking has the advantages of (1) low capital investment (but more than air drying), (2) no heat input, (3) no case hardening, (4) simplicity of operation, and (5) good area yield. The drawbacks are its low productivity (less than hanging) and higher labor costs.

- **Toggling**

A toggling unit consists of a number of clamps(toggles) that hook into the screens. Toggling has the advantage of drying large quantities of leather in a relatively small space; in addition, it provides for stretching the leather during drying. Toggling has the disadvantage that constant temperature and humidity conditions are difficult to maintain and control.

- **Tunnel drying/Pasting or Hanging**

In a pasting unit leather is pasted on large sheets of the plate glass, porcelain, or metal. By this means the leather can be fully extended and the grain fibers so oriented as to give maximum smoothness and area yield; also, better grain characteristics can be obtained than with the air-drying and toggling techniques. The pasting plates are sent through a tunnel dryer consisting of a number (4-8) of zones of controlled temperature and humidity, which result in the controlled rate of evaporation and avoids the overheating. Paste drying units are the most expensive single pieces of equipment inside the leather tannery. Tunnel drying is also used for drying the skins. For this purpose skins, instead of pasting, are hung in hooks and then pass through the tunnel in a similar way described for paste drying.

- **Vacuum Drying**

The most significant advancement in the drying technique applied to leather is the development of the vacuum dryer. In this technique, the leather is spread out, grain down, on a smooth, usually a chrome plated, polished steel surface. Heat is applied to this surface by a built-in heat exchanger under the table. This temperature is maintained by thermostatic

control of circulating hot water and a hood is placed over the plate and then evacuated to aid in dying the leather. The vacuum-drying technique, which has the advantages of being independent of weather conditions, can be used equally effectively anywhere in the world. The temperature and drying conditions are maintained by the equipment itself and are independent of outside influence. Vacuum drying units are competitive in cost as compared to paste dryers but are more expensive than toggling or other less sophisticated systems.

In **Punjab tanneries** air drying is the most popular method for light leather. Skins are hung in shades or are spread on the open land or on the floor of roofs of the tannery building till drying. Toggle drying is carried out after air drying at temperature 50 - 60 °C. The purpose of toggle drying is to increase the area of leather. Pasting and Vacuum drying is used for the hides in medium and large tanneries. In small tanneries paste drying is carried out by pasting the leather on metal sheets. These metal sheet with the help of stands are kept inclined at about 45°. These metal sheets with pasted leather are placed in open space under sunlight for drying and tunnel dryer is not used in these tanneries.

(b) Environmental Impacts

No environmental impacts are reported in the literature for drying operation.

(c) Clean Technologies

The air drying system is the cleanest methods, weather conditions in most parts of Pakistan permit the use of air drying system.

(d) Improvement Options for Punjab Tannereis

Punjab tanneries availing the advantage of the weather are already using the air drying system. This practice saves energy and produces good results.

2.2.10 FINISHING

(a) Process Description

Finishing is concerned with imparting suitable physical properties to the leather for the particular end use in mind, together with applying a decorative surface finish. In addition to this, finishing imparts durability and beauty of leather and must be an integral part of the process.

There are several methods used for the application of finishing material on leather. Hand finishing, seasoning machine, flow coater, spray finishing, Roll Coating, Embossing, and Boarding Machine are commonly used for this purpose.

Buffing, it is also an important finishing process. It consists of grinding the leather surface with an abrasive, and is akin to sandpapering. It is used on the grain to remove surface blemishes and thus provide a more uniform surface, to which pigment and other finishes can be applied.

In **Punjab** the small tanneries are using hand spray for application of finishing material. Exhaust system used in finishing room do not work properly. The whole working become affected with the vapors of finishing material. Workers mask their nose and mouth with ordinary clothes. After finishing, the leather is subject to air drying. Medium and large tanneries are using the automatic spray plant with drying chamber. The water circulation system in many modern plants is also provided. However, in one tannery automatic spray plant was installed without the water circulation system. The water circulation system captures unused finishing material and hence provides better environmental conditions. Large tanneries use water based finishing material. Whereas, small and medium tanneries use both solvent and water based finishing material.

In some large tanneries, buffing dust is ejected outside the tannery into the drain directly from the buffing section. In some tanneries, the buffing dust is collected by automatic dust collection system in the bags. This dust is sold with the chrome shaving material to the leather board manufacturer. In some tanneries automatic dust collection system is not installed. Buffing is not carried out in all tanneries.

(b) Environmental Impacts

The environmental impact of finishing operations is mainly related to the finishing chemicals (e.g. dyes and pigments dispersed in binder) which can reach effluent water or are emitted to the air, like solvent vapors or formaldehyde, which also causes occupational health problems.

(c) Clean Technologies

Halogen containing hydrocarbons have to be replaced by water based finishers. Metal complex dyes which contain restricted heavy metals have to be avoided, as well as aziridine based cross linking products. Formaldehyde should be controlled well or replaced by other kinds of preservatives with lower environmental and occupational implication, like the use of ammonia in finishing solutions.

Roll coating results in reduction of VOCs in the work place and financial savings.

Filters for dust control in the buffing units, aerators in the finishing working rooms and activated carbon filter in the exhaustion of the finishing equipment are recommendable procedures for keeping finishing air emission under control. The buffing process generates dust in the dry form. This dust can be used as a flocculating agent in sedimentation tanks or as a filer in the manufacture of certain plastic articles. If the dust is from chrome-tanned leather, it may be treated with other chrome containing solid waste.

(d) Improvement Options for Punjab Tanneries

The water based finishing material should be used in finishing operation in all tanneries. Care should be taken in the selection of the finishing chemicals like crosslinking agent, pigment dispersion, etc. Environment friendly chemicals must be chosen. Knowledge of the people working in finishing must be updated in this regard. Small tanneries using hand spray system should use the proper exhaust system. Workers should be provided with proper accessories for protection against the hazards of the chemicals.

Conventional spray equipment is wasteful. Between 30 and 50 % of finish is usually lost, whereas, with the use of a roll coating machine, losses may be reduced to as low as 5 %. Large tanneries and some of the medium size tanneries may be able to change the conventional spray equipment.

Exhaustion from spray plants and drying tunnels, which are in use, can be improved by efficient scrubbing to clear the air emission. Plants without scrubbing system should instal this system.

2.3 HEALTH PROBLEMS IN TANNERY WORKERS

Result of the questionnaire survey about the general health problems in tannery worker is given in the following table.

Response Recieved	% of tanneries responding	Inferences and Remarks
1. No Health Problems are observed in the workers	67 %	This response could be due to the reason that tannery people do not want to mention it or it is also possible that no case has actually been reported.
2. Following Health Problems are observed in the workers. - If new worker starts beam house work, some of them face the problem of skin allergy. Whereas in workers, where tanning is their family profession, no health problems are observed. - Some of the workers of the beam house operation face problem of skin allergy. - Workers involved in bleaching process of the vegetable tanned leather face severe problem of irritation in their eyes and respiratory system. - Workers of finishing operation face eye irritation problem.	33 %	These problems are very relevant with the tannery operations and processes. However, these problems can be overcome by adopting the measures described under the section of " General Safety Conditions"

These reply has been made by the people of the supervisory grade including the owner of tanneries.

2.4 GENERAL SAFETY MEASURES IN TANNERIES

Safety conditions are generally associated with the protection from machine operations handling of hides and skins, chemicals used in the tannery, and hazards of chemicals generated during different tannery processes. In **Punjab tanneries** following measures are necessary to be adopted in order to improve the overall working environment:

(a) Equipment and Machinery

If machinery and equipment of the tannery are being operated by two workers, both have to release the start button for operation, but switch off must be possible by releasing one button only. Moving parts of the cylinder machine (fleshing, unhairing, stretching, smoothing and sammying machine) must be protected in such a manner that parts of the body do not come in contact with these parts. Splitting machine must be equipped with sufficient shielding for knifes. Sharpening, buffing and brushing machine must be equipped with an efficient exhaust device to withdraw dust. In case of machines for spraying, care should be taken that hands should not be put into the spray device. Pits must be equipped with complete railing and covering. Drums must be equipped with shields or covers for the gear drive and in general, a railing to ensure a certain distance should be provided. A mechanical device to fix the drums safely during filling or cleaning procedures must be present.

Movable machine parts (like drums and mixers, gear wheels, conveyor belts or cylinder machine must be shielded and provision should be made for the machine to operate only if the shield device is closed. Same safety precaution is associated with the machine performing movements with force and the machines working with heat. In addition, these machines must be equipped with an emergency switch. If the procedure is performed with both hands, releasing of the switch must be possible with another part of the body. Hot surface on the machine must be protected against contact.

Floors have to be kept clean and dry, thus reducing the hazards of stumbling or slipping. A high degree of noise level during short or long periods may lead to defective hearing and functional defects of the brain. Measures for noise abatement have to be taken as much as possible, like shielding of engines and machines.

(b) Handling of Chemicals Used in the Tannery

As described earlier the handling of the chemicals in most of the **tanneries of Punjab** is poor, therefore the following suggestions are made which will be helpful in the improving of the in-house practices and in reducing the health hazards for the worker

A number of different chemicals are used in the tannery. These chemicals are different in nature and characteristics, therefore, their handling, collection, and disposal must be performed with respect to their specific characteristics and hazards. Empty vessels or containers must not be dumped since they still contain small amounts of chemicals which need to be disposed off properly.

Workers must be provided with protective devices depending on the working places (gloves, protective clothing, protective goggles, etc).

Material for cleaning and skin protection (protective cream, special soap) must be available. Parts of the body, specially eyes, contaminated with chemicals, have to be cleaned thoroughly with clean water.

Following precautions against fire and explosion risk have to be taken:

- Inflammable chemicals should not be stored at the working place, but in the store room.
- Places involving fire risks must be so indicated by symbolic signs.
- Open fire or any other sources of ignition are prohibited at working places where inflammable substances are used.
- Inflammable wastes and material must be kept away from working places.

General Chemicals Used in Tanneries and Their Handling.

- **Acids and bases**

  This group contains calcium hydroxide and alkali hydroxide (used for soaking and unhairing), sulfuric acid, hydrochloric acid, formic acid (pickle), and other organic acids.

  Acids and bases irritate skin and eyes and are more or less caustic. Their vapors irritate mucous membranes and respiratory tract.

  Precautions against any direct contact have to be taken (gloves, resistant clothing, efficient ventilation etc.).

  Due to inflammable nature of formic acid, any fire in the working area must be prohibited.

  Pouring of water into an acid for dilution must be avoided. Dilution is always carried out by pouring acid into water.

- **Sodium Sulphide, Sodium Hydrogen Sulphide**

  Both compounds are caustic. They should never come in contact with acids, because the reaction generates highly toxic hydrogen sulphide.

  Precautions against any direct contacts have to be taken for which gloves, resistant clothing, efficient ventillation are required.

- **Tanning Agent (Chrome Tanning)**

  Basic Chromium sulphate, chromium (III) oxide salt is used for tanning purpose. Care must be taken to avoid risks of explosions of dust and toxic hazard if the dust is inhaled. Therefore, it will be better to use suspensions of chromium salts.

  Careful handling is essential, direct skins contact should be avoided. Chromium (VI) compounds are highly toxic and cause cancer. The use of these compounds must be stopped in the tanneries.

- **Tanning Agent (Vegetable Tanning)**

  This group contains a variety of complex organic molecules. As in general, direct contact with the skins has to be avoided. Any handling must be performed carefully.

- **Chemical used for finishing**

  This group of chemicals includes dyes, polymers, preservatives and other groups of compounds. The agents used for the various steps of finishing are often combinations of several organic compounds or solution in water or in organic solvents.

  In general, precautions against skin contact must be taken.

  Efficient exhaust devices must be provided to minimize the concentrations of organic solvents or dust from powders in the working environment.

  It is recommended to use the agents in accordance with the instructions given by the producer.

  Smoking must be prohibited in this area.

- **Dyes**

  Dyes must be handled carefully, with due consideration being given to characteristics and hazards. After skins contact, thorough cleaning with water and soap must be performed. Especially eyes have to be cleaned intensively and doctor must be consulted.

  It is very important to store dyes in perfectly closed containers. If dyes are spilled, they have to be collected dryly and filled into closed containers.

  It is highly recommended to cease the use of benzidine dyes because they are highly carcinogenic.

- **Formaldehyde**

  In many cases formaldehyde is emitted during finishing processes especially during drying of finished leather. In higher concentration, it is a strong acute toxin, causes skins allergies, leads to coughs, spasms of the respiratory tract. chemicals induced pneumonia and sensibilisation of the respiratory tracts. Furthermore, it is under suspicion to cause cancer.

- **Pentachlorophenol**

  The use of PCP for preservation is forbidden in Europe and many other countries and must be ceased in the local tanneries.

(c) Chemical Generated in Tanning Processes

As a result of the present practices and absence of any remedial measure in the Punjab tanneries many hazourdous gases are produced. To reduced their hazards and their complete elimination is only possible after the adoptation of the clean technologies in the tanneries. Sections below explain the remedial measures for each gas:

- **Hydrogen sulphide**

  The generation of hydrogen sulphide is basically due to the use of sodium sulphide and sodium hydrogen sulphide during unhairing. It starts at a pH below 10. If washing after unhairing is not performed properly, the risk of hydrogen sulphide generation starts even in the deliming process, but at least during pickling due to the addition of the acids.

  It is possible that high amount of this toxic gas is present within drums or mixers and it is distributed in the plant through the hollow axis or the opening of the drum. Besides, the gas might be generated in pits, effluent channel and effluent collection basins.

  Hydrogen sulphide and air are highly explosive in mixture from 4.3 to 45.5. vol% therefore open fire or other source of ignition must be avoided.

  In addition, the gas narcotizes the sense of smell even in low amounts. This means, that the worker is after a short time, no longer aware of being exposed to this toxic compound and might be poisoned to a high degree.

  The following measures are recommended to avoid the possibility of hydrogen sulphide formation.

  (i) Application of low sodium sulphide unhairing processes.

  (ii) Thorough washing of pits with water (2-# times water: 200 %, 30 °C).

  (iii) Use of manganese sulphate/oxygen, sodium sulphite or sodium hypochlorite during deliming in order to oxidize hydrogen sulphide.

  (iv) Efficient ventilation of the plant.

  (v) Thorough washing after deliming/bating.

- **Ammonia**

  The generation of ammonia is possible during deliming. This gas is very caustic, toxic if breathed in and inflammable.

Precautions need to be taken to avoid the generation, like change in the deliming agents.

- **Gases from Bleaching process**

  Bleaching process after vegetable tanning process is a major cause of producing very corrosive gases like SO_2, and SO_3. The workers may be effected badly with these gases. Use of bleached vegetable tanning material can help to avoid the formation of these gases. Otherwise workers should be provided special masks, capable of providing protection against these gases.

CHAPTER - 3

ACTION PLAN

Detail analysis of the inhouse conditions presented in the chapter-2 further validity the facts that tanneries in the cities of the Punjab are generating enormous amount of pollution. The analysis also establish that there is a substantial scope for in-house improvement in the tanneries operations. Most important improvement are needed in the following areas.

(a) Improvement in practices
(b) Improvement in processes and technologies
(c) Improvement in management and monitoring.

Following sections summarize the improvement required by each element of the improvement area.

3.1 IMPROVEMENT IN PRACTICES

(i) Washing process should be changed from continual flow of water to the batch washing process in order to reduce the volume of the effluent generally by the tannery.

(ii) Maintenance of the record of the water consumption in the tannery.

(iii) Maximum exhaustion of the chemicals in tanning and finishing process.

(iv) Lay out of the tanneries should be improved, wherever it is possible.

(v) Arrangement of the proper clothes and safety devices for the workers.

(vi) Abatement of the noise pollution.

(vii) Proper ventilation system in the tannery.

(viii) Proper handling of the chemicals, hides and skins.

(ix) Training of the worker about the hazards of the chemicals.

(x) Installation of the information boards about safety and health regulation at working place in the tannery.

(xi) Maintenance of the safety conditions in the tanneries.

(xii) Use of harmless chemicals

3.2 SPECIFIC IMPROVEMENTS IN THE PROCESSES AND TECHNOLOGIES

Though there are a number of clean technologies described in the chapter-2 for each tannery process and operations, however in this section emphasis has been given to the technologies which look best applicable in the local conditions of the tanneries in the Punjab.

3.2.1 BEAM HOUSE OPERATIONS

(a) CURING

- Salt recovery from the cured skin to minimize the concentration in the soaking effluent.
- In case of curing in the tannery, if any, biodegradable bectricidal agent should be used instead of salt.

(b) SOAKING

- Avoidance of the use of PCP (Penta chlorophenol) as bactericidal.
- Less toxic and more biodegradable Bactericidal agent should be used.

(c) UNHAIRING AND LIMING

- Pollution reduction in conventional methods.
  - ► Lime splitting and trimming should be adopted.
  - ► Sulphide Oxidation in the effluent of this process.

(d) DELIMING AND BATING

- Use of Sodium bi sulphite or hydrogen peroxide for sulphide oxidation.
- Use of the organic acids for deliming purpose.
- Use of the batch washing.

(e) DEGREASING

- Use of environmentally friendly surfactants, as indicated in the study, (alcohol ethoxylate based surfactant) for degreasing purpose in the case of the surfactant degreasing. Tanners should be very conscious in selecting this material.
- Use of the recovery and recycling systems of the solvents in the solvent based degreasing systems.

3.2.2 TANN HOUSE PROCESS

(f) PICKLING/TANNING

- In separate pickling system the pickling float should be recycled.
- In mineral tanning the use of hexavalent chromium salt must be stopped.
- In case of trivalent chromium salt direct reuse, improved exhaustion and recycling after precipitation are applicable to improve the situation.
- In case of vegetable tanning process the bleached vegetable tanning material should be used.

(g) WET FINISHING (dyeing, fatliquoring and dyeing)

- Use of the benzidine based dyes should be stopped.
- Use of the halogenated fatliquors should be avoided.
- Exhaustion of the dyes, fatliquors, and retanning agents should be monitored by continuous laboratory test.

(h) FINISHING

- Proper ventilation system in the finishing area.
- Use of water based finishing material.
- Use of efficient scrubbing systems in the spray plant.
- Use of the environmentally friendly chemicals in the finishing process.

3.2.3 IMPROVEMENT IN MANAGEMENT AND MONITORING

Tanning industry has emphasized very little on the management and monitoring system with regard to the in-house environmental improvement of the tannery. Consequently, the overall in-house conditions in the tanneries are not good. To improve the situation it is necessary to include in-house environmental improvement activities in their existing management and monitoring system, which at present only deals with the production. In this regard technical guidance to the staff through an extension program involved in the management and monitoring is needed.

3.3 INSTITUTIONAL ARRANGEMENT FOR IMPLEMENTATION

Implementation of the in-house environmental improvement program for tanneries requires specific institutional input with well defined responsibilities. Following action should be taken:

3.3.1 IMMEDIATE ACTIONS TO BE TAKEN BY INDIVIDUAL TANNERS

In the light of this study individual tannery should prepare specific inventory data showing the problems of the tannery. However, improvement work on the following area can be started immediately:

- Arrangement of the proper clothes and safety devices for the workers.
- Installation of the information boards about safety and health regulation must be installed at working place in the tannery.
- Proper ventilation system in the tannery.
- Maintenance of the record of the water consumption in tannery.
- Maintenance of the safety conditions in the tanneries.
- Abatement of the noise pollution.
- Arrangement segregated discharge of the beam house and tann house effluent to avoid the generation of hydrogen disulphide gas inside the tannery.

3.3.2 ACTION TO BE TAKEN BY PTA AND LOCAL ASSOCIATIONS

PTA and Local Associations should collectively prepared dissemination material. Substaintial amount of extension material can be developed on the basis of the findings and recommendations of this study and distribute it to all its members . Following are the other tools through which dissemination can be ensured:.

- Group meetings with tanners
- Lectures by the leather technologists, progressive tanners, environmental engineers, community development experts, etc.
- Video shows and poster exhibition

3.3.3 ACTION TO BE TAKEN COLLECTIVELY BY PTA AND OTHER ORGANIZATIONS LIKE PROVINCIAL EPA, PROVINCIAL GOVERNMENT, LOCAL RESEARCH INSTITUTES AND UNIVERSITIES

- Short term training course for tannery staff.
  - ▸ Arrangement of the short term training courses about the occupational health hazards and preventive measures.
  - ▸ Arrangement of the short term training courses for the technical people of the tanneries about the modern tannery processes and practices.
  - ▸ Adaptation of recycling and reuse technologies.

    In collaboration with EPA's, Research and Educational Institutes, and private consultants PTA should arrange the demonstration of recycling and reuse technologies as recommended by this study. These demonstrations should explain the practicality, and relevancy of these technologies with the local tanneries conditions and at the same time implementation mechanisms required for implementing these technologies should also be explained.

- Adaptation of clean Technologies.

  PTA in collaboration with international counterpart technologists and research institutions should arrange the demonstration of clean technologies. The most suitable forum for such demonstration will be PTA'S leather show, general body meeting, management committee meetings and other such relevant events.

- Process control system in tanneries.

  Process control in the tannery is only possible if a proper chemical laboratory will be available. In most of the tanneries this facility has not been arranged yet. This may be arranged with the help of local research institutes and universities. The combined chemical laboratory may be arranged collectively by the tanneries of small cluster.

- Legislation to stop the use of hexavalent chromium salt.

  Use of the hexavalent chromium compounds in tannery must be banned legally to avoid any use of it in the future even in the case of the reduction of its cost as compared to the trivalent chromium salt. In this regard, PTA should co-operate with provincial EPA for the formulation of such legislation.

- General safety measures in the tanneries.

  - The knowledge of the general safety measures should be disseminated by the PTA with the collaboration of provincial EPA.

  - One of the condition for the membership of the PTA must be that the tannery will carry out the proper implementation of the safety measures.

3.3.4 MONITORING AND EVALUATION PROCEDURE FOR THE ACTION PLAN

- PTA and Local Associations will carry out the continuous monitoring and evaluation of the implementation of the Action Plan.

- EPA Annual Monitoring.

  Committee consisting the members of the PTA or Local Association and members of the provincial EPA should be formed for this purpose.

ANNEXURES

ANNEXURE 1

QUESTIONNAIRE SURVEY
IN-HOUSE ENVIRONMENTAL IMPROVEMENT PROGRAMME FOR TANNERIES

QUESTIONNAIRE SURVEY
INHOUSE ENVIRONMENTAL IMPROVEMENT PROGRAMME FOR TANNERIES

Date :_____

Name and address of Tannery :_____
_____
_____
_____

Type of Skin/Hide : [] Sheep [] Goat [] Cow [] Buffalo [] Mixed_____
: _____

End product (leather) : [] Garment [] Upper [] Sole [] Other_____
Chemicals : [] Local [] Imported [] Mixed _____
_____

Total Production/year :_____

Working Pattern : [] Single shift [] Double shift [] Triple shift

Sources of Water : [] Govt. [] Well [] Tankers [] Mixed_____
_____

Quantity of Water being consumed :_____

Quality of Water tested : [] yes [] No
if yes, when and what are the results.
_____
_____
_____

Any effect of water on quality of Leather. : [] Yes [] No
: If yes, what are they _____
_____
[] By well water_____
: [] By tanker water _____

Operations and Processes

Nature of skins/hides coming in tannery
: [] Uncured (Fresh)
: [] Cured (Salted [] Sundried [] Dried [] Brined [] Others)
: if salted, what are the ingredients of salting, detail about quality and combination of ingredients.
_____
_____
_____

(a) Curing in Tannery : [] Yes [] No (if Yes answer the following)
: [] Type of curing (o Dry salting. o Wet salting. o Brining. o Freezing. o Drying in shades).

(b) Trimming : Use of trimmed pieces
[] Sale [] Waste
Use of other waste (if any) _____
: Quantity of waste:
: Remarks _____
: _____

(c) Soaking : [] Pit [] Paddle [] Drums [] Rocking frames [] Other
: [] Without Bactericides [] With Bactericides:
: [] % of Float _____
: Use of Aids [] yes [] No
(If yes answer the following)
: [] Temperature _____ [] Time _____
: [] Chemical Addition [o Acid o Alkali o Ammonia (Liquor) o Salt o Wetting Agent o Other_____]
Proportionate combination of chemicals _____
_____
Remarks_____
_____
_____
_____

(d) Unhairing : [] Liming (-Hair Saving - Hair Destruction)
Painting; [] Manual [] Machine [] Drum [] pit/pits
[] Other method_____
[] Source & Grade of lime _____
[] Quantity of float unit per unit weight of skin
_____
Hair Removal; [] Manual [] Machine
[] Other method _____
Remarks_____
_____
_____
_____
_____
[] Non liming (- Sweating - Chemical - Enzymatic)
Remarks_____
_____

(e) Fleshing : [] Trimming (if any) [] Use of trimmed pieces_____
[] Manual [] Machine
[] Quantity of fleshings/unit weight of skin
_____
[] Use of fleshed Material _____
_____
[] Splitting (if any)
[] Use of splitted material _____

(f) Deliming & Bating : [] Amm salt [] Mg salt [] Other salt _____
[] Use of detergent [] Other Method _____
[] Bacterial [] Enzymatic
[] Cold [] Hot
[] Quantity of float _____
[] Washing water (o Draining o Reusing)
[] Quantity of washing water _____
_____
Remarks_____
_____
_____

(f) Pickling : Pickling & Tanning; [] simultaneous [] separate
Pickling float (if separate); [] reuse [] drain

(g) Tanning : Type of tanning;
[] Chrome [] Vegetable [] Aldehyde
[] Combination_____ [] Oil [] Other _____

In case of Cr;

[] Paddle [] Drum [] Dry tanning [] Other_____
[] Using trivalent chromium salt available in market
[] Trivalent chromium salt prepared in Tannery.
[] Two bath system
[] Used float of tanning; [] Draining [] Recycling

In case of vegetable;

[] Using barks nut etc for tanning
[] Using extracted (powder) available in market
Used float of tanning; [] Draining [] recycling
Remarks_____
_____

(e) Fleshing : [] Trimming (if any) [] Use of trimmed pieces_____
[] Manual [] Machine
[] Quantity of fleshings/unit weight of skin
_____
[] Use of fleshed Material _____
_____
[] Splitting (if any)
[] Use of splitted material _____

(f) Deliming & Bating : [] Amm salt [] Mg salt [] Other salt _____
[] Use of detergent [] Other Method _____
[] Bacterial [] Enzymatic
[] Cold [] Hot
[] Quantity of float _____
[] Washing water (o Draining o Reusing)
[] Quantity of washing water _____
_____
Remarks_____
_____
_____

(f) Pickling : Pickling & Tanning; [] simultaneous [] separate
Pickling float (if separate); [] reuse [] drain

(g) Tanning : Type of tanning;
[] Chrome [] Vegetable [] Aldehyde
[] Combination_____ [] Oil [] Other _____

In case of Cr;

[] Paddle [] Drum [] Dry tanning [] Other_____
[] Using trivalent chromium salt available in market
[] Trivalent chromium salt prepared in Tannery.
[] Two bath system
[] Used float of tanning; [] Draining [] Recycling

In case of vegetable;

[] Using barks nut etc for tanning
[] Using extracted (powder) available in market
Used float of tanning; [] Draining [] recycling
Remarks_____
_____

(m) Buffing : Automatic Dust Removal system: [] Yes [] No
If yes,
Detail _____

(n) Finishing : [] Hand (o Brushing o Padding o Spraying) [] Machine
Remarks _____

(o) Other Processes and Operations : _____

(p) Remarks: _____

QUESTIONNAIRE SURVEY
ABOUT GENERAL HEALTH CONDITION OF TANNERY WORKERS

Diseases	Workers: Beam House		Tann House		Finishing		Remarks
(a) Irritation							
Skins :	yes	No	yes	No	yes	No	
Eyes :	yes	No	yes	No	yes	No	
Mucous membrane :	yes	No	yes	No	yes	No	
Respiratory Tract :	yes	No	yes	No	yes	No	
(b) Headache							
Temporary :	yes	No	yes	No	yes	No	
Permanent :	yes	No	yes	No	yes	No	
(c) Chronic Diseases:	yes	No	Yes	No	Yes	No	
(d) Stomach problem :	yes	No	yes	No	yes	No	
(e) Difficulty in Breathing :	yes	No	yes	No	yes	No	

(f) Other Observation : _____

_____

_____

General Conditions in Tanneries	Beam house	Tannhouse	Finishing	Remarks
(a) Ventilation	A B C D	A B C D	A B C D	
(b) Lighting	A B C D	A B C D	A B C D	
(c) Floor condition	A B C D	A B C D	A B C D	
(d) Equipment	A B C D	A B C D	A B C D	
(e) Chemical Handling	A B C D	A B C D	A B C D	
(f) Layout	A B C D	A B C D	A B C D	

(g) Age of plant: _____

Other Observation : _____

_____

A: Excellent **B: Good** **C: Fair** **D: Poor**

Name of Tannery: _____ Name of person : _____

Age of person (Interviewed): _____ Tannery Experience: _____

Residence : _____ Date: _____

ANNEXURE 2

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Ing. M. T. Van Vliet, Wastewater treatment, Institute for leather and Shoe Research , TNO, Waalwijk, Holland.

2. J. H. Sharphouse, Leather Technician's Hand Book, 1983, Leather Producers's Association, King's Park Road, Moulatn Park, Northampton NN3IJD.

3. Michael Aloy, UNIDO Consult, Introduction of Cleaner Leather Production Methods, Prospects and Constraints, 1993.

   Eleventh Session of the leather and Health production industry Panel, Nairobi, Kenya, 29 November - 3 December 1993. UNIDO.

4. Porst Consult, Hand book of Environmental Sound Production and Processing of Leather & leather Boards, Leather goods. (unpublished)

5. Thomas C. Thorstensen, Practical Leather Technology, 4th Edition 1993, Krieger Publishing Company, Malabar, Florida.

6. Urwick technology Management Ltd, Environmental Impacts and Polices for the EEC Tanning Industry, 1977, Published by Graham & Trotman Limited for the Commission of the European.

7. Razina Bilgrami, Research and Assessment of Leather Tanning Industry's Liquid and Solid Waste Treatment and Disposal Techniques, 1993, Research Project, Imperial College, London.