

CHAPTER – I

➤ INTRODUCTION AND OBJECTIVE OF THE STUDIES

CHAPTER-I

I.1 Introduction

Leather processing is an ancient art; after all it is in existence since time immemorial, certainly for more than 5000 years¹. There are ample evidences that the ancient men prepared leather by fat tanning, smoke tanning, alum tanning and vegetable tanning etc². Technology of leather making proceeded even before the scientific methodology of leather making. All processing industries have impacts on the environment, as because the processing agents are derived from nature/synthetically prepared and the remnants after processing are also discharged to the environment and leather processing is no exception. Earlier there used to be practically no check on the use of natural resources, adoption of technology and discharge of effluents, but with the increased awareness of environmental degradation and also for cost competitiveness it is imperative that all these factors are taken into consideration for obvious reasons.

Raw hides and skins are temporarily preserved using common salt till it reaches the tannery from the collection centres/markets for the tanning operation, as otherwise, hides or skins from freshly slaughtered animals, generally get putrefied and become unsuitable for further processing. Thus temporary preservation is very essential for the intermittent period, especially for a tropical country like India. Temporary preservation of hides and skins by adding 40 – 60% (on green weight basis) common salt (NaCl) which is the most popular method world over, out of this about 50% of salt is lost during transportation and dusting operation, another 50% remains in the hides and skins. The salt dehydrates the raw hides & skins and thus prevents putrefaction.

Water a natural resource, is also used in leather processing, generally 30-35 L of water is used per kg of raw hides & skins in processing it to obtain usable finished leather. Processing of leather is a combination of some unit operations, of which soaking is the first one. In soaking, 6-9 L water is used per kg of raw hides & skins i.e. around 23% of the total water requirement in leather process.

In conventional soaking operation, 200 - 400% fresh water based on the weight of wet-salted hide and skins is used for 1st & 2nd wash and then nearly 400% water is taken in a drum with raw materials for 3rd part of soaking operation. Total time required for soaking is nearly 10-hours. The objectives of soaking are mainly to remove adhered salts, dirt, dung and some soluble organic matters present on the surface of wet-salted stock and to increase the moisture content of hides and skins almost to the level of green hides & skins.

Most of the adhered salts go into solution during soaking operation and in general, the soak liquor is discharged as effluent. The effluent from soaking operation is the major contributor of Total Dissolved Solids (TDS) and high value of conductivity in composite wastewater from tannery. It is due to high concentration of sodium chloride which comes from wet salted hides and skins through soaking operation. Though the NaCl is highly soluble in water, yet the soak liquor is not saturated after one soaking operation. Thus it is possible to recycle & reuse this water for several soaking operations before it becomes saturated. The possibility is studied with the aim of reducing consumption of water and also to reduce total dissolved solid in the effluent. The result will be reduction of operational cost.

As a result of present study, it has been found that consumption of fresh water can be reduced significantly by recycling & reuse of spent soak liquor without hampering any physical and chemical properties of finished leather. The results obtained in respect of finished leather properties both physical and chemical, from the studies are highly impressive, and the process, if, adopted by the industry, will change the conventional leather processing technology and will be of great advantage in many ways.

I.2 Leather processing – an over view

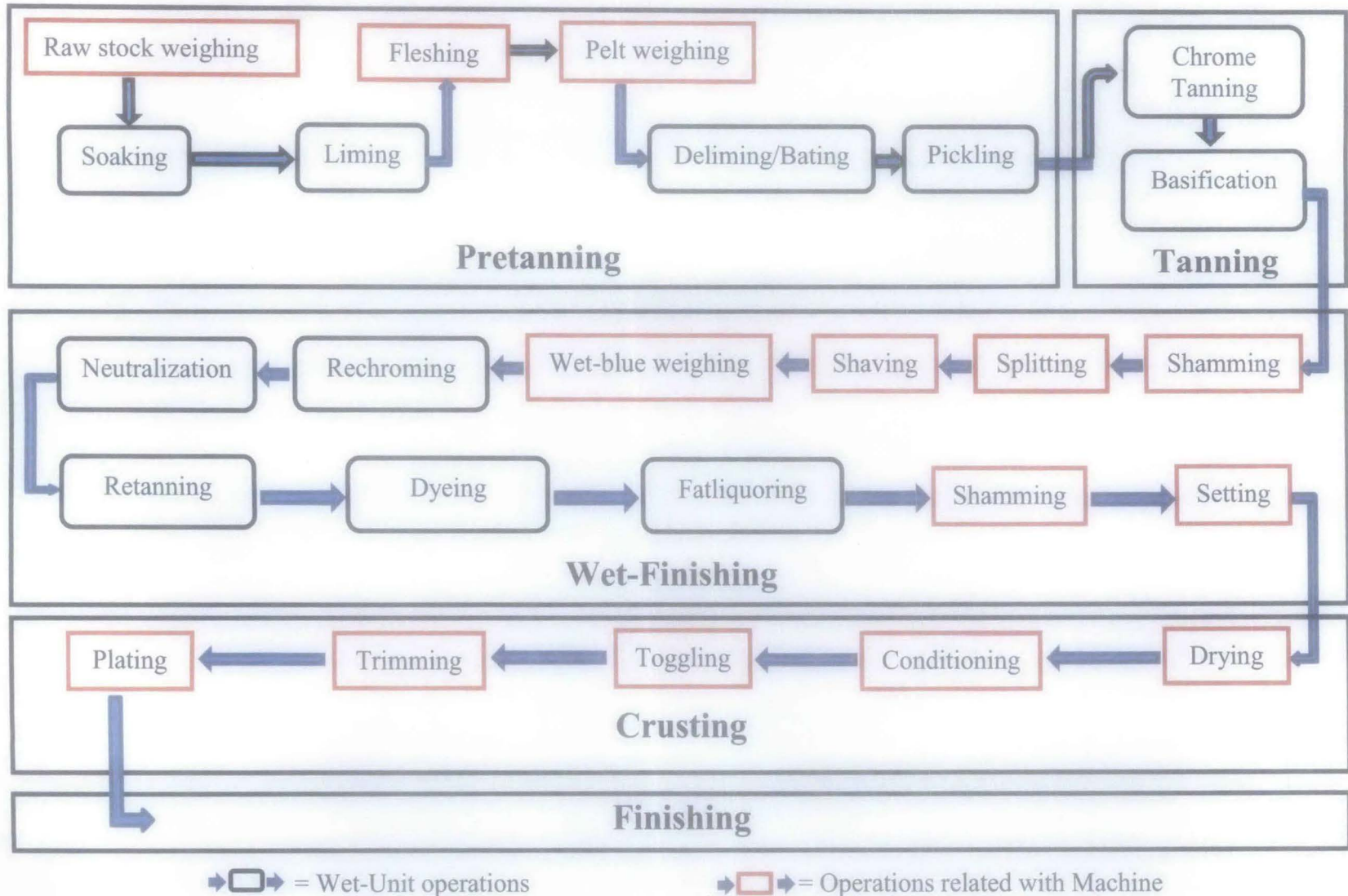
The whole operation can be divided into five groups viz;

1. Pretanning operation
2. Tanning operation
3. Wet finishing operation
4. Crusting operation and
5. Finishing operation

As all the above operations are carried out in the aqueous medium huge quantity of fresh water is consumed for processing. A brief description of each of these operations with their parts has been included in this section. The raw materials for leather industry, is the outer coverings of animals obtained by flaying either after natural death or after slaughtering. There is always some time lag between flaying and the processing. The maximum delay may be varying from two to three months for big and diverse countries like India. Thus the temporary preservation to prevent putrefaction of hides and skins during this period is most essential. There are many ways of preserving hides and skins, but wet-salting method is the most widely used as the process being very simple and is less costly compared to other available methods.

A flow diagram along with a brief description of the total tanning process is presented below with the Figure I.

Fig. I.1 Flow diagram presentation of leather processing



Soaking: Cured raw hides and skins are treated with water in a paddle or drum to clean and rehydrate it to the green condition. During soaking, the adhered salts are dissolved. Due to salting in effect, some of the globular proteins are also dissolved and discharged into soak liquor.

Liming: Soaked hides and skins are then treated with sodium sulfide and hydrated lime as reagents with water in a paddle or drum. The main objectives of the operation are to remove hair properly from the epidermal layer and to loosen the adipose tissue from the flesh side, saponify the natural fats and swell the derma properly for the splitting of the fiber bundles to make it suitable for chemical reactions in the next successive operations. Washing of the stock with fresh water immediately after liming is very essential. Fleshing is one vital mechanical operation after Liming.

Deliming and Bating: Lime pelts are treated with acid salts (sodium bi -sulphite, ammonium sulphate etc.) and some proteolytic enzymes (like trypsin) as reagents with water in a drum. The main objectives are to neutralize the lime inside the derma and remove short hair roots from the pelt surface and also some coagulated proteinous matter from inside the pelt. After deliming & bating, some considerable amount of water is also required for washing.

Pickling: Delimed pelts are treated with common salts and concentrated sulfuric acids with water in a drum to bring down the pH of the pelt around 3.0 which is very much conducive for the starting of the chrome tanning operation. Common salt is used here to suppress the acid swelling of the pelt.

Tanning: Pickled pelts are treated with Basic Chrome Sulphate Powder as reagent in the 50% pickle floats to give hydrothermal stability and stop putrefaction by bacterial action to hides and skins.

Basification: Such chrome treated leathers are treated with Sodium bi carbonate in the same chrome bath in the drum to increase the astringency of the basic chrome salts which favours unipoint or bipoint linkages by the way of ligand exchange. The unipoint and bipoint linkages of Cr(III) complex by replacing ligands (L) with free carboxylates of protein are shown with the following **figure I.2 (a) and (b)** respectively³. It also favours creation of cross links between two adjacent polypeptide chains by di or tri nuclear- μ -bridged Cr complexes, conferring thermodynamic stability of Cr-collagen matrix. After basification, a considerable amount of water is consumed for washing purpose.

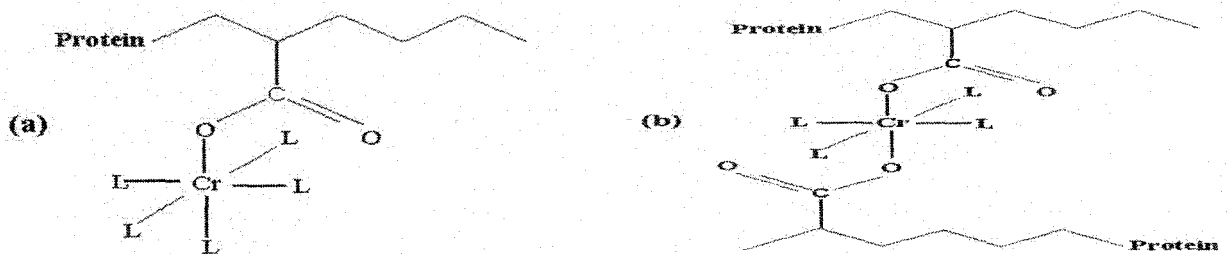


Fig. I.2 Unipoint and Bipoint Linkage of Cr(III) with Carboxylates of Protein

All unit operations up to pickling can be clubbed together as pre-tanning operation. The chrome tanned hides and skins are called Wet-Blue. Some mechanical operations are performed on the wet blues depending upon the conditions and as per requirement of different finished leather. These mechanical operations are shamming, setting, splitting, shaving and trimming. The brief description of different wet unit operations in the Post Tanning section is given bellow:

Rechroming: Wet-blues are treated with again Basic Chrome Sulphate powder and some organic salts with water in a drum to enrich the chromium content in wet-blue and make stocks suitable for the next neutralization operation. Most of the cases, washing are essential after rechroming.

Neutralization: Rechromed materials are treated with inorganic and organic basic salts and some neutralizing syntans as reagents with water in a drum. The objective of the operation is to neutralize the excess acids & reduce the gradient of charge in the cross section of the leather so as to become conducive for the differential fixation of anionic dyes and fat liquors within the cross section. In general, the remaining unit operations are completed in the neutralizing bath so in those cases require no further washing.

Dyeing-Retanning & Fatliquoring: The sequence of these three unit operations may vary depending upon the type of leather is to be processed and also the tanners' personal experiences. All these operations are done in drum using water as a vehicle, but water may change for each unit operation or may carry forward for the next operation. It is also depended on those above stated factors. In dyeing operation, the leather is treated with suitable dyes (anionic, direct or basic) for colouration as required in the final product. In retanning, the leather is treated with some vegetable tanning stuffs and/or synthetic tanning agents to impart fullness as required in the final product. In fatliquoring, the leather is treated with suitable fatliquors (anionic, cationic and amphoteric in nature) to make it soft and pliable as required in the final product. Some organic acids (formic acid or acetic acid) or some dye fixing chemicals are used to fix dyes (anionic or direct), Retanning materials (mainly vegetable tanning stuffs)

and fat liquors (mainly anionic) with leather fibers. This acid fixation may be done after individual unit operation or at the end of these three unit operations. After fixation, thorough washing of leather is essential, in spite of that intermediate washing after each unit operation may be done depending upon process. Then the following operations are carried out sequentially.

Shaming → setting → drying → conditioning → staking → toggling → trimming → plain plating → buffing (if necessary).

A brief description of all these operations has been given under sections III.2.2 and III.3.7 in Chapter III. Wet finishing operation covers all the machine and wet unit operations after basification to setting before drying and after that up to before finishing all operations termed as crusting. Then the leather is ready for finishing operation.

Finishing: The objectives of finishing operations are mainly to improve the properties and add aesthetic value of leather. Finishing is the final chemical and mechanical treatment of leather before manufacturing leather goods like bags, clothes, shoe etc. Finishing is not necessary for all variety of leathers; it depends on the requirement of final product. The major ingredients are used for the finishing purposes generally as follows: pigments, binders and fillers, feel modifiers, preservatives, lacquers, organic solvent etc. and also water. Polymer materials are used as film former and also binder in leather finishing. The film holds the pigment particle which gives the colour. Although there is no definite structure of finishing technique, yet the skeleton of that can be expressed as: ground/base coat, intermediate coat and top coat. The main function of ground coat is to hold the intermediate coat with leather surface. The

function of intermediate coat is to hold mainly the coloured pigment particles and the top coat gives the protection of finish layers.

I.3 Objective of the study

It is well known that the leather processing industry is one which consumes huge quantity of water. The main objectives of the study are to reduce fresh water consumption and also to reduce pollution load by reducing the discharge from soaking operation. This is possible by recycling the water from the soaking operation a number of times and finally the water from the last cycle may be processed to recover salt and possibly some amount of water also. Adopting the proposed repeated use of soaking water tanning industry can be transformed into more ecofriendly and cost efficient technology. The objectives are summarized as follows:-

1. Reduction of fresh water consumption.
2. Reduction of TDS value in the composite wastewater from tannery.
3. Prevention of soil and water pollution.
4. Recovery of salt from the soak liquor.