



**ADDIS ABABA UNIVERSITY**

**ADDIS ABABA INSTITUTE OF TECHNOLOGY**

**SCHOOL OF CHEMICAL AND BIO ENGINEERING**

**STUDIES ON CLEANER LEATHER PROCESS OF AMMONIA FREE  
DELIMING, BATING AND DEGREASING SIMULTANEOUSLY**

BY

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A Thesis Submitted to the School of Chemical and Bio Engineering, Addis Ababa Institute Technology (AAiT), Addis Ababa University Presented in Partial Fulfilment of the Requirements for the Master of Science in Chemical Engineering (Leather Technology).

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This is to certify that the MSc thesis prepared by Tamiru Alemayehu, entitled: Studies on cleaner leather process of ammonia free deliming, bating and degreasing simultaneously and submitted in partial fulfilment of the requirements for the degree of master of science in chemical Engineering (Leather Technology) complies with the regulations of the university and meets the accepted standards with respect to originality and quality.

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**List of Acronyms**

- COD=chemical oxygen demand
- BOD=biological oxygen demand
- TS=Total solid
- TDS=total dissolved solids
- TSS=total suspended solids
- Peltec-BB= alkaline bating enzyme
- Peltec-BC-E-F=alkaline degreasing enzymes

ml=millilitre

mm=millimetre

l=litter

g= Gram

X= alkaline bating enzyme

Y=alkaline degreasing enzyme

IUP=international union of physical

SATRA=safety and technical rescue association

SLC=Standard Leather Chemical

SLP=Standard leather physical

APHA=America public health Association

IULTCS=international union of leather technology and chemist society

ISO= international organisation of standard

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## Abstract

The study presents the design of cleaner leather process of ammonia free delimiting, bating and degreasing to facilitate the production of leather. Ammonia salt bating and solvent degreasing are well known and adopted globally. Development of green chemicals and short coming of ammonium salts and organic degreasing solvent system of processes calls for a need for the development of cleaner leather process of bating and degreasing. Hence this research work focused on, the development of cleaner leather process of combining bating and degreasing in single bath using commercially available and cheap enzymes as an alternative bating and degreasing process.

Bating and degreasing in single bath system gives thin wet white pelts with high thumb impression. Among the selected enzymes and design process evaluated leathers obtained by alkaline bating and degreasing (peltec-BB and peltec-BC-E-F respectively) with in 1hr process were observed to be stronger, better general appearance and good run properties. In contrast acid bating and degreasing after pickling with 1hr process resulted poor organoleptic properties and less run properties. Physical testing and organoleptic properties of the matched pair leathers of the alkaline bating and degreasing system simultaneously were comparable to that of conventional bating and degreasing system of leather process. Most important is that it would not produce ammonia, reduce chemical consumption and produce very clean and wet white pelts, therefore alkaline bating and degreasing enzymatically in single bath good process for the manufacture of glove leather.



# **1. Introduction**

## **1.1 Background**

Leather making is a very long process and consists of many different chemical and mechanical process steps. The common raw materials of leather industries are skins/hides, chemicals, water. Other pre-requisites for leather manufacture are energy, machine, and labour. Leather industry has been categorized as one of highly polluting industries and there are concerns that leather making activities can have adverse impact on the environment.

Hides and skins constitute proteins, fats, carbohydrate, conjugate proteins and lipids. For the production of leather the leather making material is collagen and other components must be removed using different steps of unit operations. A limed pelt could be considered as calcium salt of ionized carboxylic acids contained in the protein molecule. For removal of calcium salts contained in the chemically and ionic ally bound form of calcium ions. Deliming process by using ammonium salts causes many problems both on the quality of final leather and the environments the commonly employed degreasing process is either before pickling and after pickling has its own drawback, too much water, chemical consumption and increase discharge load. In leather industries, there are a series of unit operations involved in the leather manufacturing. These are broadly classified as beam house, tanning, post tanning and finishing processes. In conventional leather process especially beam house operation contributes to high pollution load due to the use of huge amount of chemicals and undo after completing its contribution on the removal of non-collagenous materials results for high concentration of chemicals on liquid waste (Ramasami 1991).

Bio-based process is an alternative promising method to decrease the pollution load in pre tanning processes. In recent years, there had been several attempts to develop a bio-based pre tanning process using enzymes (Kamini, Hemachander, Mala & Puvanakrishnan, 1999). In such attempts significant reduction in pollution load has been observed (Dayanandan, Kanagaraj, Sounderraj, Govindaraju & Rajkumar, 2003; Thanikaivelan, Rao, Nair & Ramasami, 2004). Though options of enzymatic bating and degreasing exist, commercial practice of enzymatic degreasing is still eluding due to the inefficiency that occurs either in the stringent process controls or the efficacy of enzyme used for bating and degreasing. Hence there is an imminent need to design bating and degreasing enzymatically simultaneously after deliming by dry ice or after pickling for effective fibre opening and fat

removal. We hypothesized that fibre opening facilitate degreasing process and removal of fatty materials Hence we chose to use a protease (peltec-BB) and lipase (peltec-BC-E-F)simultaneously after deliming or after pickling process and determine its effect for the opening of fibres and removal of fat. In addition to this, green process wastes contain proteins and fats which are also less contaminated when we compare to conventional process wastes. Fleshing wastes is one type of solid wastes that contain useful chemical compound which is made major organic compound that obtained from beam house process. Pickled and salted skins with relatively low fat content are claimed to be degreased by enzymatic lipase treatment. For pickled pelt, the pH has to be raised to 10, to obtain optimum hydrolysis of the fats from the lipase. Additional calcium ions are also required to improve degreasing effect. Generated fatty acids by hydrolysis combined with calcium ions to produce (soaps), which physically remove the fatty acids away from the active site of the enzyme. However, nonionic detergents such as nonylphenol ethoxylate and alcohol ethoxylate inhibit lipase activity and will not have to be used at the same time of the enzymes.

## **1.2 Statement of the problem**

Conventional leather process especially, beam house operations needs to find alternative solutions for reduction of pollution loads to sustain in an environment of increasing pollution control regulations. Cleaner leather processing is an alternative promising method to minimize the pollution load in beam house processes. There had been several attempts to develop a bio-based beam house process using enzymes. In such attempts significant reduction in pollution load has been observed (Dayanandan, Kanagaraj, Sounderraj, Govindaraju & Rajkumar, 2003; Thanikaivelan, Rao, Nair & Ramasami, 2004). Most of Ethiopian leather industries manufactured leather products in conventional ways and conventional leather chemicals. Now days there are lots of green leather chemicals and designed process in the world.

### **1.3 Objective of the study**

#### **1.3.1 General objectives**

The overall objective of the study was to develop effective cleaner leather process of ammonia free delimiting, bating and degreasing simultaneously for the production of glove leather.

#### **1.3.2 Specific objectives**

The specific objectives of this research paper were:

- ❖ to develop and design enzymatic bating and degreasing process for efficient removal of fat and open up fibre matrix of collagen.
- ❖ To characterize and analysis of efficiency of the designed process and the compatible enzymes.
- ❖ To analysis the pollution loads of the designed process.

#### **1.4 Scope of the study**

The research focus on the development of cleaner leather processing in the beam house, especially focus on design of bating and degreasing simultaneously using commercially available and cheap enzymes with effective selection of compatible with required parameters. Optimize bating and degreasing process with effective fat removal, fibre splitting, minimisation of processing time and pollution load. one of the activities is delimiting with dry ice and optimize the bating and degreasing process simultaneously by changing the dosage of the protease and lipase respectively with the given parameters. Finally this project targets the design and development of cleaner leather process in the beam house (bating and degreasing) with green leather process and chemicals.

#### **1.5 Significance of the study**

In Ethiopian context, leather manufacturing process utilize different chemical that polluted the environment. Among them, Conventional beam house process contributes more than 60% of the pollution load in leather manufacturing process in the form of solid, liquid and gases where disposed to the environment. In order to reduce the pollution load from the environment, tanning industry looks new technology for sustainable environment and to achieve specific standard of requirement. Currently, the awareness of environmental issue increase time to time. Due to this reason, this work looks alternative option which is free from toxic chemicals that utilize for leather manufacturing. Cleaner leather process is one of

the effective strategies to address the requirement of environmental regulation by reduction of pollution. This study presents a road map for the development and design of cleaner beam house (bating and degreasing) process, cheap, new innovated green chemicals, processing time management process and pollution reduction by eliminating non-green chemicals and design new process.

### **1.6 Conceptual frame work of the study**

This study aims to compare the technical, environmental and economic aspects of conventional bating and degreasing of delimed pelt with an alternative system of alkaline bating and degreasing enzymes simultaneously using peltec-BB and peltec-BC-E-F respectively and to compare bating and degreasing of pickled pelt with alternative system of acid bating and degreasing enzymes simultaneously using peltec-AP (acid protease) and peltec-AL (acid lipase).The overall conceptual framework of the thesis work is shown in Figure 1.1; it describes the whole frame of the thesis work.

The technical issues of an alternative system of bating and degreasing were compared with the conventional bating and degreasing system as control taking the chemical parameters, fat content for raw skins as well as post tanned and the physical parameters such as tensile strength, tearing strength and run for the leathers made. Then, the environmental issues of an alternative system of bating and degreasing simultaneously were evaluated by comparing the conventional and an alternative bating and degreasing system with related to the pollution load parameters such as TS, TSS, TDS, COD, BOD and ammonia etc.

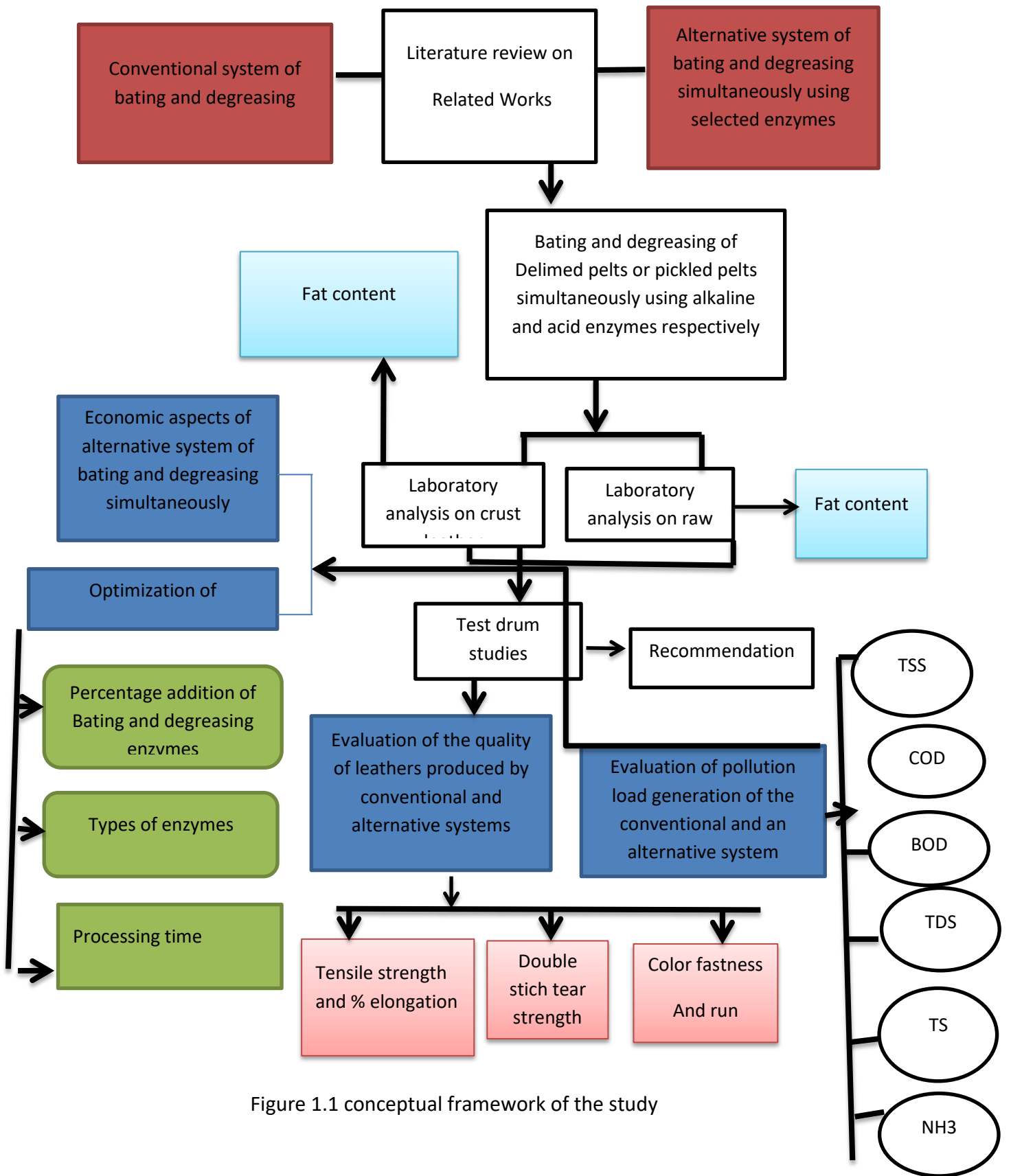


Figure 1.1 conceptual framework of the study

### **1.6.1 Conventional system of bating and degreasing**

The conventional leather process of bating and degreasing in leather industry were done in separate bath either in alkaline (before pickling) and acidic stage (after tanning).these two process of leather have their own drawback on the environment point of view and the processing time is too long.

### **1.6.2 Alternative system of bating and degreasing simultaneously using selected enzymes**

In conventional leather process there are two ways of bating and degreasing in separate bath, these are:

- Bating and degreasing before pickling in separate bath
- Bating and degreasing after chrome tanning in separate bath

The two process were used the conventional chemicals that have effect the environment .Based on the limitation of these process I tried to search alternatives system of bating and degreasing in single bath using the compatible bating and degreasing enzymes.

### **1.6.3 Bating and degreasing of delimed pelts or pickled pelts simultaneously using compatible enzymes**

In this project paper I tried to do alkaline bating and degreasing process after dry ice deliming was completed and the second process was done after pickling process the acidic bating and degreasing process was tried to process.

### **1.6.4 The laboratory analysis on raw skin**

For the production of glove leather the best raw material is sheep skin and has 25-33% of natural fat so, in this process the raw skin fat content has to be analysed by soxhlet fat extraction apparatus.

### **1.6.5 The laboratory analysis on crust glove leather**

At the end of the designed and developed system of bating and degreasing the physical and chemical properties of the final leather were determined depending on the given standard procedure.

#### **1.6.6 Economic aspects of alternative system of bating and degreasing simultaneously**

The alternative system of bating and degreasing process simultaneously were cost effective as compared to the conventional process because now days there are cheap enzymes and available on the market.

#### **1.6.7 Optimization of the process of enzymatic bating and degreasing simultaneously**

The designed and developed process of bating and degreasing simultaneously were optimized by varying the concentration of the bating and degreasing enzymes and the type of selected enzymes and the processing time.

#### **1.6.8 Evaluation of the quality of leathers produced by conventional and alternative systems**

the quality of final leather were evaluated and assed based on the tensile strength, tear strength and other general properties required for glove leather and compared to the conventional (control).

#### **1.6.9 Evaluation of pollution generation of the convention and alternative system**

The process of leather by ammonia free deliming, bating and degreasing simultaneously and the conventional bating and degreasing were compared in terms of wastewater analysis.

## **2. Literature review**

### **2.1 Ammonia free delimiting process in leather industry based on eco-benign products.**

Central leather research institute had developed simple procedure for dry ice delimiting process as an alternative delimiting agent for cleaner leather production. The delimiting process was studied on limed pelts processed from goat skins by varying the amount of dry ice. It was observed that 2% of dry ice was enough to delimit the pelt entirely within an hour. The latest method of using dry ice reduces the generation of ammoniacal nitrogen ( $\text{NH}_3$ ), total dissolved solid (TDS) content by 98 and 88 % respectively from delimiting process.

### **2.2 A cleaning and efficient approach to improve wet-blue Sheep leather quality by enzymatic degreasing**

Enzyme is a green efficient and easily degradable substance. The cleaner process of enzymatic degreasing was applied and replaces the organic solvent effectively. In this latest investigation 100-c enzyme instead of part of surfactants were used in degreasing process. The result indicates that the degreasing enzymes produce the wet blue leather treated by enzyme were much higher in quality than degreased by conventional organic solvents (Saravanan, P. et al, 2014; Song, J. et al., 2011).

### **2.3 Enzymatic technology applications in leather processing**

Failure to remove the non-collagenous protein during conventional leather processing initiates the enzymatic bating process using alkaline protease. The classical bating in the alkaline condition makes use of proteolytic enzymes, which are of pancreatic or bacterial origin, and the process of efficiency depends on the enzyme concentration as well as temperature, pH and time during the bating process. The bating in the alkaline condition today is universally recognized by the entire leather industry but the effectiveness of enzymatic process should be conducted 95-100°F and the pH parameter is at 7.5-8.5; otherwise the efficiency of the bating enzymes drops drastically. The effect of bating enzymes occurs through the diffusion of enzymes into the hide on the other side the too much concentration was found on the outer layers. On the unsplit pelts the penetration of bating enzymes to the inside of the hide is insufficient to digest unwanted globular proteins, this is particularly true in the neck and butt area of the hides. This latest research shows that the enzymatic bating is acceptable and produces good leather required by the

costumers and fulfilled the ISO standard in physical and chemical properties (Indian journal of chemical technology, vol.11, September 2004, pp.659-671).

#### **2.4 Analysis of the research gap**

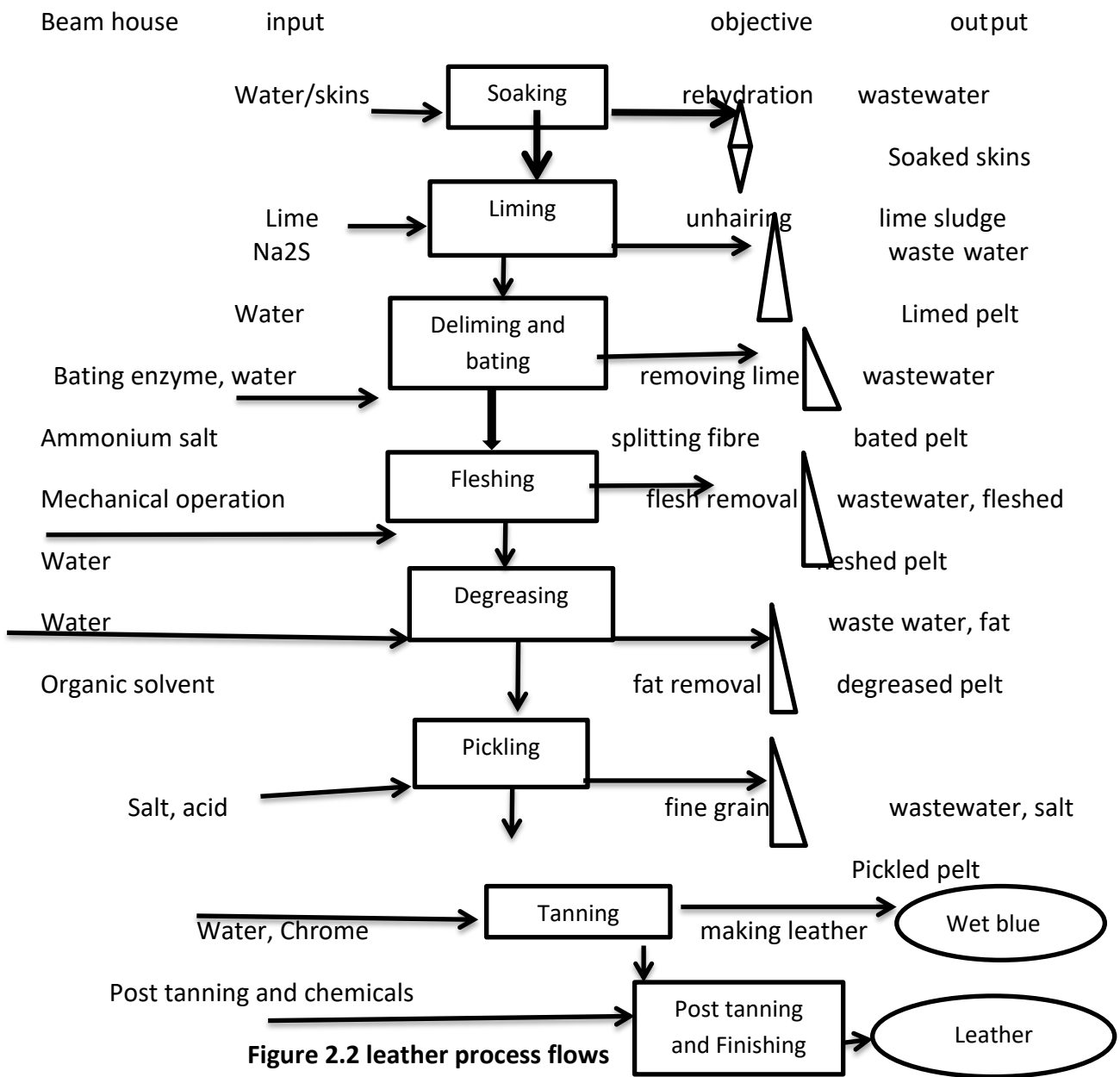
The above latest research in cleaner leather process designed enzymatic technology but the delimiting, bating and degreasing were done in separate bath as the result:

- Its limitation was long production process.
- Since enzymes are specific to the specific substrate, why not design simultaneous bating and degreasing enzymatically in single bath.

In my research work taking the dry ice delimiting as it is ,then I tried to design and develop bating and degreasing simultaneously using commercially available enzymes.

#### **2.5 Beam house operations**

Leather manufacturing is the process of transforming skins/hides into leather by sequential mechanical and chemical steps. In this process, skins/hides pass through four main consecutive stages which are beam house operations, tanning operation, post tanning operations and finishing. Beam house process is the first steps of operation section in leather processes which used for devoid unnecessary material from raw hides/skins. It contains serious operation viz., soaking, unhairing, and liming, delimiting, bating and pickling process. Hence our research concentrated on selected operation. Among of them, soaking, liming, delimiting, bating and degreasing were selected for study purpose which provides literature survey as follows.



### 2.5.1 Soaking

Soaking is the first process applied to the raw stock. This and all subsequent chemical steps are most commonly conducted in drums. Soaking is the primary stage and basic requirement in leather processing to precede the next process. There are two main objectives for the soaking process (Rao, Thanikaivelan, & Nair Ramasami, 2005):

- Remove dirty material from hides and skins such as blood, urine, soil, dung, salt and other extraneous substances.
- Rehydration of hides and skins to bring the original condition of fresh hides or skins after flaying takes place

In general, soaking process is carried out into two or three stages depend on the condition of raw materials, the first or second steps is called as dirty or pre-soaking, which perform for short period of time. The last step is known as main-soaking (IPPC, 2001). The amount of water needed for soaking per tonne dried hide can be as high 20m<sup>3</sup> water (Ludvik & Buljan, 2000). As usual it needs 5 to 24 hours to complete the soaking process depending on the status of raw materials. Alkalis such as sodium hydroxide or sodium carbonate, wetting agent, preservatives and protolytic enzymes are usually used as additives during soaking, and are depend on the condition of skins or hides, temperature condition affects (Heidemann, 1993; Thanikaivelan, Rao, 2005).

### **2.5.2 Unhairing and liming**

Liming as name indicates is an operation in which raw hide or skin is brought into contact with aqueous solutions of lime or calcium hydroxide. Understanding of physical and chemical changes undergone by raw hides and skins on being brought into contact with calcium hydroxide is important. Dissolution of calcium hydroxide in water is expected to release hydroxide ions and pH of an aqueous saturated solution of calcium hydroxide is expected to be in the range of 10.5 – 11.5. Under those conditions, carboxyl sites in protein would remain ionized and exist as COO<sup>-</sup>. Amino groups could exist partially as NH<sub>2</sub>. In other words, proteins in skin would be predominantly exhibit ionized behavior of a negatively charged semi permeable membrane. Whereas ionic mobility of calcium and hydroxide ions in solution are not restricted, mobility of ions bound to protein in the skin matrix is restricted. In other words one set of ions are free to move and others are not. There would be a build-up of calcium ions inside the skin matrix.

Donnan Equilibrium could be established under conditions of liming of skins. When two solutions containing charged particles (ions) are separated by a membrane that is permeable to one set of ions and not to others, Donnan Equilibrium could be established. It is an example of electrochemical equilibrium because electrical and chemical charges on either side of the membrane are equal and opposite of each other. (Thanikaivelan & Nair Ramasami).

Unhairing and liming are often linked because the traditional processes of hair dissolving and alkaline hydrolysis combine the process steps .however, strictly they ought to be thought of as separate processes and in modern processing, the steps are increasingly commonly conducted separately.as the term implies, unhairing is the process of removing the hair from the pelt. It is traditionally one of the dirtier aspects of leather processing, from the Point of view of the odour created (typically from the sulphide employed and the decomposed protein) and the polluting load generated.

### 2.5.3 Deliming and bating

The purpose of deliming is to remove lime by neutralizing with acids, acid-salt, ammonium salts or substances with an acid reaction. Numerous chemicals are available for this purpose. They are listed as follows:

<i>Acids</i>	<i>Acid-Salts</i>	<i>Ammonium Salts</i>
Hydrochloric acid	Sodium bisulphate	Ammonium chloride
Sulphuric acid	Sodium metabisulphite	Ammonium sulphate
Formic acid	(with bleaching effect as well)	Ammonium sulphamate
Acetic acid		Salts of aromatic and aliphatic acids and aliphatic dicarboxylic acid. (ammonium salts)
Lactic acid		
Sulphamic acid		
Boric acid		
Glycollic acid		
Naphthalene sulphononic acid		
Sulphophthalic acid		
Carbon dioxide gas		

#### 2.5.3.1 Conventional deliming bating process

The conventional deliming is using ammonium salts. The deliming reaction of such salts is very fast, because the whole offer of ammonium salt can be added at the beginning of the process step and the pH cannot fall below the value fixed by the equilibrium condition of the reaction products. Bating is an operation through which all internal and physically held

debris are loosened by enzymatically degrading the materials and substances that bind the unwanted materials to the skin matrix. Since it is an enzymatic process, it is extremely crucial that all collagen degrading enzyme activities should be scrupulously avoided.

There are two problems associated with using ammonium salts:-

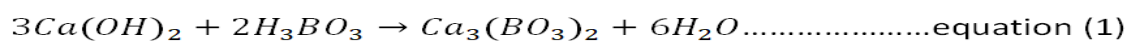
- Release of ammonia gas into the working environment, causing discomfort to workers though it does not create a serious toxicity hazard.
- The discharge of ammonical nitrogen in the effluent is poisonous to fish and other aquatic life.

### 2.5.3.2 Cleaner delimiting process

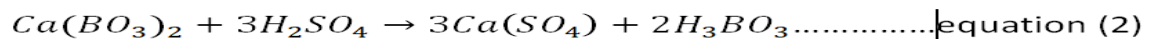
Weak acids would be safer than strong acids, because they would not cause the pH to drop low enough to cause acid swelling. However some weak acids can cause acid swelling too. Unionized carboxylic acids can cause lyotropic swelling, an exception is lactic acid. The problem of weak acids is too slow rate of reaction.

#### 2.5.3.2.1 Boric Acid

Since boric acid is very weak acid they do not swell the grain of the pelt to any appreciable extent. About 1.0-2.5% of the acid on the weight of the limed pelt can be used. The chemical reaction is represented as follows:-

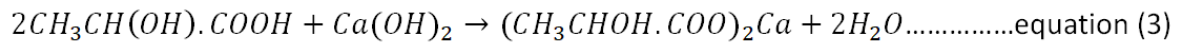


Calcium borate (i.e.  $Ca_3(BO_3)_2$ ) is soluble. It can be regenerated for reuse by adding calculated quantity of sulphuric acid to the used bath. The regeneration reaction is shown



### 2.5.3.2.2 Lactic acid

On account of its satisfactory result, lactic acid can be used for delimiting. It produces finer grain. It is available in the market in 40% or 80% strength. The chemical reaction is represented by the following equation:



Calcium lactate is soluble in water and is therefore washed out of the pelt. 1-2% lactic acid on the pelt weight can be used.

### 2.5.3.2.3 Acetic acid

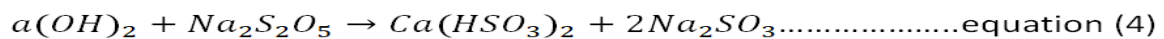
It is more expensive than boric or lactic acid and has no advantage over them.

### 2.5.3.2.4 Formic acid

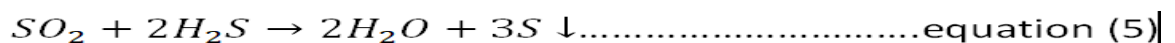
It is 10 times stronger than acetic acid. Its delimiting effect is similar to that of mineral acid. The reaction product calcium formate formed has buffering effect and may protect pelts from acid swelling action.

### 2.5.3.2.5 Delimiting with sodium pyrosulfite

The pH of sodium pyrosulfite is about 5.0. It can react with  $\text{Ca}(\text{OH})_2$  to form  $\text{Ca}(\text{HSO}_3)_2$  which is a soluble compound, and then the aims of delimiting can be achieved by washing:



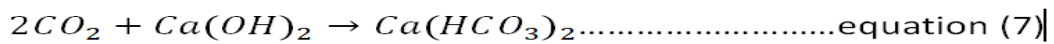
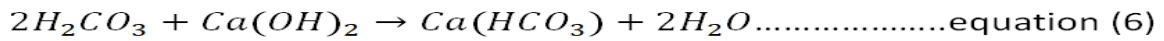
When sodium pyrosulfite is superfluous, it can produce  $\text{SO}_2$  and oxygenate the  $\text{H}_2\text{S}$  to form the simple substance S:



So it can avoid the toxic gas  $\text{H}_2\text{S}$  escaping during the delimiting process.

### 2.5.3.2.6 Deliming with Carbon dioxide

Solubility of CO<sub>2</sub> relates to temperature and pressure. Under low temperature and high pressure, the CO<sub>2</sub> solubility is large. If the volume of the CO<sub>2</sub> is enough during the deliming process, the CO<sub>2</sub> can react with Ca(OH)<sub>2</sub> to form soluble Ca(HCO<sub>3</sub>)<sub>2</sub>, finally the deliming can be achieved by washing:

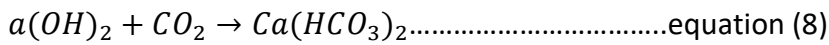


Because of the CO<sub>2</sub> solubility in water, in the end the deliming solution pH can realize buffering. The reason is that H<sub>2</sub>CO<sub>3</sub> and Ca(HCO<sub>3</sub>)<sub>2</sub> have formed the buffer system with weak acid and weak acid alkali salt. If the concentration of CO<sub>2</sub> is too low, CaCO<sub>3</sub> will form lime blast. There is H<sub>2</sub>S gas forming during the deliming, so some H<sub>2</sub>O<sub>2</sub> should be added to oxygenate. The final operation solution pH is stabilized at 7.0

<i>Process</i>	<i>Parameters</i>
Wash	
200 % Water, 35°C	
Switch on CO <sub>2</sub> gas	Pressure:0.5-1.0 Pa, 1L/min; Running time 10 min; PH=8.0
Switch off CO <sub>2</sub> gas	
0.125% H <sub>2</sub> O <sub>2</sub>	
CO <sub>2</sub> gas	0.3-0.5L/min, running drum for 2hrs till the end  Check pH = 6.5-7.0 and Cut = clear to phenolphthalein.

The CO<sub>2</sub> steel cylinder: commonly the CO<sub>2</sub> steel cylinder net weight is 25Kg, inner pressure is 60Kg/cm<sup>2</sup> (6.08×10<sup>-3</sup>GPa) , and boiling point is -78°C. The relative density of CO<sub>2</sub> is bigger than air's, it can be dissolved in water easily (solubility is 14mg/L), it can be used in any kinds

of drums. When the volume of CO<sub>2</sub> dissolved in delimiting liquor is large enough and the pH of delimiting liquor bellows 8.3, the insoluble CaCO<sub>3</sub> cannot be formed.

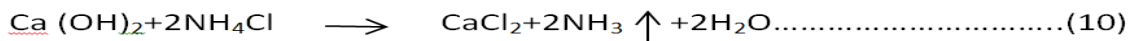
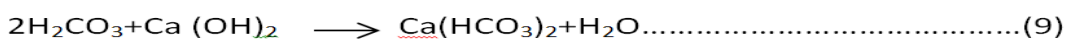


The solubility of Ca(HCO<sub>3</sub>)<sub>2</sub> is 1086mg/L, therefore, the purpose of CO<sub>2</sub> delimiting can achieve.

<i>Advantages of CO<sub>2</sub> delimiting</i>	<i>Disadvantages of CO<sub>2</sub> delimiting</i>
Reducing the pollution of the ammonia gas	it need a long time to delime the unsplit cow hides with CO <sub>2</sub> so it still need a little ammonium salt to assist in delimiting.

**2.5.3.2.7 Delimiting with dry ice**

Delimiting process was studied on limed pelts processed from goat skins, by varying the amount of dry ice, which is one of the cleaner processes of leather and produced good pelt with PH range of 6.5 to 8 ready for next process. The reaction mechanism of dry ice and ammonium chloride based delimiting process as shown from the reaction (9) and (10) respectively.



The new method of using dry ice reduces the generation of ammonia nitrogen (N-NH<sub>3</sub>), total dissolved solid (TDS) content by 98 and 88 % respectively from delimiting process. Release of ammonia is one of the major drawbacks associated with delimiting, which causes health hazards for the workers exposed after delimiting. The simple dry ice based method for delimiting could avert the ammonia release from the drum

#### 2.5.4 Cleaner process of delimiting ,bating simultaneously

Enzymes are used in the processing of different industrial raw materials for the preparation of various products. With the advancement of scientific and industrial developments enzymes have indispensable commodities in leather industries.

Raw hides and skins received in the leather industries for processing and it is composed of soluble and insoluble proteins. They are also called globular and fibrous proteins.

The bating and degreasing enzymes targeted to the removal of globular proteins during the process of bating and degreasing simultaneously at the selected processing parameters and the bating and degreasing enzymes are in the range of selected parameters as well as the bating and degreasing enzymes are compatible in the processing parameters. The bating and degreasing enzymes are selected based on

1. Compatibility of enzymes in the alkaline bating and degreasing process parameter's
2. Cost of enzymes
3. Compatibility of enzymes in the acidic bating and degreasing process parameter's
4. Availability of enzymes

The process of delimiting and bating simultaneously using commercially available enzymes, bating and degreasing enzymes are compatible for the delimiting process parameters.

The selected enzymes are

- ✓ Alkaline bating enzymes (peltec-BB)
- ✓ Alkaline degreasing enzyme ( peltec-BC-E-F)
- ✓ Acidic bating enzyme(peltec-AP)
- ✓ Acidic degreasing enzyme(peltec-AL)

After delimiting with dry ice processing bating and degreasing simultaneously with enzymes gives effective pelts with reduction of pollution load, bleached pelt

#### **2.5.4.1 Properties of bating and degreasing enzymes**

The properties of enzymes used in bating and degreasing are the process parameters and the mechanism of removal of globular proteins and fats respectively.

The enzymes are active at

- ❖ Alkaline bating and degreasing temperature of 25-37<sup>0</sup> c.
- ❖ Alkaline bating and degreasing at PH 5-8.
- ❖ Acid bating and degreasing are also active at PH 2.5-6.

#### **2.5.4.2 Chemistry of bating and degreasing enzymes**

Enzymes are biocatalyst, and by their mere presence, and without being consumed in the process, enzymes can speed up chemical processes that would otherwise run very slowly.

Enzymes are specific in their action and are active within a narrow range of temperature and pH. The bating enzymes acted upon the cementing substances and disintegrate the proteoglycans and the degreasing enzymes targets the adipose layers (fat) disintegrate fat is easily washed off simultaneously since enzymes are substrate specific. Bating agents are formulations of enzyme preparations. Production of industrial enzymes has now reached high levels of sophistication with the development of tools of modern biotechnology. It is possible now to ensure that activities of the desired enzyme formulations could be optimized and maximized. Specificity of the enzyme formulations could also be ensured. However, most bating agent formulations are not tested against the specific materials cementing the hair to hair bulb and other physically adhering substances. Their activity is tested against casein like substances. General proteinases with one assurance of the absence of collagenase like activity are selected.

Activity of enzymes is optimal at some pH conditions. Activities of the enzymes used for bating are optimized at the pH of the delimiting conditions. For bating, temperature of the bath is often adjusted to suit the activities of the enzyme formulations. Bating is essentially a clean-up operation.

At the end of bating operation, fibre bundles need to be opened up as completely as possible. A physical test of the completion of bating is to examine the extent of opening to pores. For this purpose, volume of air is deliberately trapped in a closed volume and

subjected to pressure from outside by pressing the bated pelt. Freedom with which trapped air is forced out of the matrix is an indicative of good bating effect. This test is feasible only for pelts from thin goat, sheep and pig skins.

#### **2.5.4.3 Advantage of alkaline bating and degreasing simultaneously**

Enzymatic process has its own advantage in leather process of bating and degreasing. It reduces the pollution load of organic solvent, disintegrated hair root, in terms of cost it is cheaper than organic solvent. It possesses bating and degreasing properties and bleached effect on the pelt especially for glove leather. The end product has good run properties and it imparts high tensile and elongation properties.

#### **2.5.4.4 Enzymatic acid bating and degreasing**

The process of acid bating is done after chrome tanning at pH of 4 for more and deep removal of root hair and opening up of skin matrix to the pent fibrils and more removal of fat, includes various process depickling repacking process. This process required too much amount of water and chemicals as well as common salts to prevent swelling acid

#### **2.5.4.5 A possible enzyme sources to design bating and degreasing simultaneously**

The sources of bating enzymes are from microbial:

1. bacterial , lactobacillus and
2. fungal , aspergillus

The sources of degreasing enzymes are from

1. bacterial , bacillus
2. fungal, aspergillus

Process of bating and degreasing simultaneously could give better run and bleaching, good elongation effect on the pelt etc. This is environmentally eco-friendly and has an effect on the workers and consumer's health. The PH of alkaline bating and degreasing which used for the experiment was 5.5-8 at 10% solution water.

Some drawback of alkaline bating and degreasing process simultaneously compared with other bating and degreasing processes

- process control is difficult
- the bating enzyme hindered the activity of degreasing enzymes ( if proper measurement is not taken)

#### **2.5.4.6 Properties of glove leather**

In this project, it is proposed to design glove leather processing using alkaline bating and degreasing simultaneously. The following are some of the important properties required for leathers to be used as glove leather.

1. run properties
2. percentage elongation
3. light weight
4. softness
5. Tensile and tear strength
6. Color fastness

#### **2.5.5 Pickling**

Pickling process is one of unit operations in leather industries .The pickling process is primarily conducted to adjust the collagen to the conditions required by the chrome (or any other) tanning reaction

The traditional recipe for pickling is as follows, based on limed weight of pelt:

- 100% float
- 10% salt
- 1% sulfuric acid

The timing of the pickling step is variable, depending on thickness of the pelt, for this experiment since the raw material is skin and the targeted end product is glove the pickling process is for an hour. Pickling is denoted as a process step in which the skin matrix is acidified. Acidification of the matrix is bound to protonate all groups which are capable of undergoing protonation. Carboxyl and amino sites of both main chain units of collagen as well as those of side chain residues are capable of undergoing protonation if the pH of the

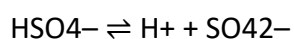
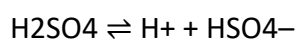
pickling medium is lowered below 2.0. Such a protonation of the protein residues of the skin serving as semi permeable membrane is expected to create an osmotic force as per Donnan Membrane equilibrium conditions.

Proton namely H<sup>+</sup> ions bound to carboxyl as well as amino residues of the protein would become non- diffusible once they are protein bound. For instance, if sulphuric acid, were used for pickling, diffusion of both H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ions inside the protein matrix would become necessary. Donnan Membrane equilibrium conditions would then apply. In order to match the osmotic pressure developing inside the protein matrix, imbibing of water leading to acid swelling is expected.

If acid swelling is not mitigated, breakdown of the entire skin matrix and acid hydrolysis leading to solubilisation of skin would be realized.

Acid swelling is easily mitigated by building up adequate concentrations of common salt inside the matrix. If the concentrations of ions namely Na<sup>+</sup> and Cl<sup>-</sup> inside the matrix are so large that they compensate for the osmotic pressure build up on acidification or protonation of all charged sites in the protein, acid swelling could be mitigated.

Physical chemistry of pickling demands that there is sufficient build up neutral salts inside the matrix prior to acidification. In other words pickling chemically is nothing but the addition of common salt and a mineral acid like hydrochloric or sulphuric. The addition neutral salt serves to dehydrate the matrix and prevent acid swelling by mitigating the build-up osmotic pressure inside skin. In this project the required end product is glove so extensive pickling was done. Mineral acids demonstrate pKa values much lower than those of carboxyl sites of proteins. If the acid used for pickling were to donate the proton to the protein site at the pickling pH values, the acid used remain ionized and release the proton for the protein to take up. Sulphuric acid elicits two pKa values as in the equations below.



Both pKa values for sulphuric acid are lower than 2. for this process since chrome salt is penetrate inside the skin matrix at pH of 2.8-3, so picking was adjusted to this pH range.

## **2.5.6 De-pickling-degreasing and re-pickling**

### **2.5.6.1 Disadvantage of De-pickling-degreasing and re-pickling**

- consumption of too much water and common salt
- chemical consumption
- generation of organic solvent in effluent (pollute the environment)

Conventionally to process acid bating and degreasing de-pickling and re-pickling is required during this process

- too much chemicals is needed
- the processing time is long
- Environmentally polluting

### **2.5.6.2 Advantage of De-pickling-degreasing and re-pickling**

- ✓ The process is simple
- ✓ The process step is can be controlled without any difficulty

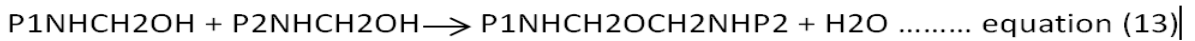
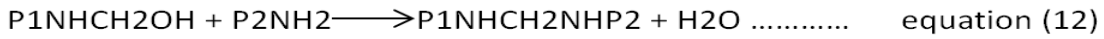
## **2.5.7 Tanning process**

In leather industry tanning is the basic unit operation of leather manufacturing. Tanning is also the chemical step through which the physicochemical properties are altered to suit the properties needed for a specific end use applications. Tanning is the most chemically complex step. During tanning, the skin structure is stabilised by crosslinking of collagen with complex ions of tanning agent. Depending on the compounds used the colour and texture of the leather changes. When leather has been tanned it is able to 'breathe' and to withstand boiling water, as well as being much more flexible than an untreated dried skin. In tanning operations there are reactions takes place between skin matrix and tanning materials.

Covalent interactions: Covalent binding involves sharing of electron and mixing of orbitals of atoms between the reactants. As a consequence, covalent binding associated with tanning should involve formation of bonds with interatomic distances of less than 2.5 Angstrom units. In the case of tanning, these modes of bonding are relevant to those based on small organic molecules like formaldehyde. It is known that formaldehyde could react with any free amino group as in the reaction given in eq, 11 below.



Reaction given in eq 1 would be considered as nucleophilic addition to carbonyl through covalent bonding. The NH2OH moiety could undergo reactions as in equation, 12 and equation 13 if they were in close proximity with suitable neighbouring groups.



.For covalent reactions as in equation 12 and equation 13 through covalent bonding, the interacting bonding sites in the neighbouring protein chains need to be positioned at right inter-nuclear distances.

### 2.5.7.1 Samming and shaving operations

Samming operation is a mechanical process in leather industry to the skin preparing for post tanning operations. Sammying is the process of removing excess water from wet blue skins to prevent damage during shaving. In the tanneries it is done by Sammying m/c or Setting m/c or Sam/Set m/c. The wet blue skins are well spread and squeezed between felts to reduce the moisture content to nearly 50-55%. This operation also helps in removal of folds and wrinkles from the wet blue hides and skins. Shaving was done for adjusting the thickness of wet blue for glove leather processing.

The main operational objectives of samming and shaving are:

- ❖ Reduce the moisture content of wet blue before shaving operations
- ❖ The objectives of shaving is adjusting the thickness of wet blue for glove leather processing before post tanning was done.
- ❖ The target of material segregation in terms of thickness before shaving is to get uniform substance, chemical uptake and desired properties that could be achieved through the retanning, dyeing and fatliquoring processes.

### 2.5.8 Post-tanning operation

Tanning does not always impart all the required physicochemical properties to suit the functional needs or specific end use applications of leather. Chrome tanned leathers are kept wet until the post processing to render it a useful commercial product is complete.

The raw material quality is dependent on several factors such as transportation system, slaughtering practice, breed, origin, preservation techniques etc. Especially in our country, Ethiopia all system of leather processing and farming as well as preservation of skins and hides are a great challenge for the quality of leather. The quality of leather enhancements are carried out in post tanning process. For aesthetic appeal and use as products, tanned leathers need to be further processed for imparting fibre compaction, softness and suitable colours. A set of operations known as wet finishing is applied for imparting the desirable properties for meeting the requirements of end use applications. Mechanical operations and chemical processing and physical conditions constitute together the body of wet finishing operations in leather manufacture. End-use properties of final leathers being processed would influence the design and selection of wet finishing strategies. However, mechanical operations like Sammying, setting, and shaving are carried out for all types of light leathers.

Chemical processing involves two steps namely neutralization of free acid and preparation of tanned leathers to receive retanning agents, fat liquors and dyes to meet the needs of final leathers. Several proprietary products of retanning agents, fat liquor formulations and dye mixtures are commercially available for designer choice of applications in leather making. At the end of wet finishing, chrome tanned leathers are ready for drying and conversion into the chosen types of finished leathers. Prior to drying, it is necessary for the leathers to be subjected to flattening of the grain and compactness of the matrix by subjecting them to mechanical setting operations and dry the materials under stretched conditions.

The main objectives of post tanning operations are shown below

- To produce various types of crust /finished/final leather from wet blue
- To achieve properties such as fastness, softness, run, drape, tensile and tear strength, light weight and desired shade through dyeing etc.
- To modify the properties of wet blue with the required characteristic chemicals.

Some of unit operations involved in post tanning process are mentioned as follows

### 2.5.8.1 Neutralisation & Washing of the wet back wet blue leathers

Chrome tanning is generally carried out under acidic conditions. Further coordinate covalent binding of chromium to the carboxyl groups of protein contained in the leather is expected to render the chrome tanned leather cationic and release free proton. The presence of mineral acids in chrome tanned leather is hence expected. Further, there is an imminent danger of iron contamination arising out of mechanical operations prior to wet finishing. Neutralisation process is required to neutralise the free acid components from chrome tanned leather and adjusting the wet blue for post tanning chemicals depending on the required end product. Most of the post tanning chemicals are anionic and they are reactive towards the cationic leather and crosslink on the surface of the wet blue rather penetrating through the cross section of leather, so the neutralisation is used to reduce the cationic nature of the wet blue by deprotonating the skin matrix this is done by rising the pH of wet blue from 3.8-4 to 4.8 to 6.5 depending on the types of leather to be produced.

As the objective indicates, the purpose of neutralization is only to neutralize free mineral acids in the leather matrix. Chemical principle involved is simple and the chemical reaction  $\text{PCOOH} + \text{Cr}^{n+} \longrightarrow \text{PCOOCr} + \text{H}^+$ ;  $\text{NaHCO}_3 \rightleftharpoons \text{Na}^+ + \text{OH}^- + \text{CO}_2$ ;  $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O}$

For processing soft and supple types of leathers like garment and glove, neutralization needs to be extensive and through and through for fat liquor emulsions to remain stable and access all potential surfaces of fibre bundles. Non filling types of retanning systems preferred. Ideally for garment leather, there is a weight limitation per square foot. Density of garment and glove leathers becomes an important parameter. Non loading types of wet finishing systems are preferred. After neutralization is complete, it is necessary to carry out washing of all the neutral salts formed during the operation. Neutralization is essentially a preparatory step for wet finishing and no storing of the neutralized leathers is planned and practiced.

### **2.5.8.1 Retanning**

Retanning is the process of filling the emptiness or filling the void space of the wet blue matrix. For manufacturing leathers which demand firm handle and tight grain, the use of vegetable tanning material as retanning system is essential. For such leathers, surface affinity of retanning systems is advantageous. Neutralization pH for such leathers is designed such that it is generally in the range of 4 to 4.8. The process sequence designed for such leathers is retanning, dyeing and fat liquoring. For tight and soft leathers like shoe upper, pH of neutralization is in the range of 4.5- 5.0 and retanning composition invariably includes vegetable tanning materials based on condensed tannins. The preferred process sequence in the design is retanning, dyeing and fat liquoring and retanning

On the other hand for soft and supple leathers (garment and glove), the use of vegetable tanning based on condensed tanning materials is avoided. The pH of neutralization is in the range of 5.0 to 5.5. Often high grade nappa and dress gloves are made from sheep skin based leathers. The process sequence is fat liquoring; dyeing, retanning and fat liquoring. Generally the order of post tanning processes are depends on the types of end product.

### **2.5.8.2 Fatliquoring**

Fatliquoring is done to impart softness, drape, run, flexibility and strength etc. to the final leather by reduction of internal fibre cohesion through lubrication for smooth bending of leather matrix. Depth of penetration of the oil formulation is a key step in optimal effect of lubrication. Particle sizes of emulsions are therefore are of high importance. In fatliquoring, oil in water emulsions penetrate into the leather matrix and break at the right time and location. Oils thus delivered as oil-in water emulsion is expected to coat the individual fiber bundles and keep them apart so that they slide over each other with reduced friction. Hence, it is important that the nature of fat liquor formulation is so chosen that it enjoys optimal stability as an emulsion and lubricating oils are delivered at the right location in the fibre matrix.

Coarse emulsions tend to penetrate through flesh layer while fine emulsions do not show much preference for grain or flesh side while they approach into the leather matrix. For upper leather production, fat liquor formulations based on Neat's foot oil are often preferred for this purpose.

In the case of soft and supple types of leathers where grain tightness is not essential, fat liquor formulations which are stable and consist of small size particles are preferred. Deodorized fish oil, sulphite sperm oil based formulations are preferred as base oil for fat liquor formulations.

### **2.5.8.3 Dyeing**

Dyeing is operations in leather process to give aesthetic appeal by way of colouring to the leather depending on the customers' requirement. Dyes used for leather processing are generally screened from those used in textile industry for applications in tanning sector. Dyes used commercially for dyeing of textiles and leather are mixtures or blends of differing molecular composition and rates of penetration into matrices undergoing dyeing. Each dye molecule displays characteristic affinity curve and rates of penetration into matrices like leather. It is extremely important that a dye formulator blends only those dyes with similar affinity curves and avoid differential shades across the cross-section.

Function of dyes is to impart colour to leather irreversibly. It should be so irreversible that it does not bleed on exposure to water, rubbing, chemicals and perspiration. Perspiration resistance of acid dyes used for leather processing is not often high. It is true that basic dyes offer high resistance to perspiration against bleeding. However, light fastness of basic dyes is poor. Hence only in the case of leather like hat band (unexposed to sun light) the use of basic dyes is even relevant. Light fastness of dyed shades is critical for many high end leathers.

There are primarily four kinds of dyes used namely acid, direct, metal complex and reactive groups. Choice from among all the four categories would need to be made on the basis of required level of intensity and uniformity of shades on the one hand and fastness properties of the dyed leathers on the other. In some cases, uniformity and through and through colouring would become essential and in some cases surface dyeing to match the shade of subsequent dry finishing would be sufficient. Grain finished leathers for shoe upper applications for instance need not receive through, and through dyeing whereas nappa and suede leathers not only require through and through dyeing but also uniformity of dyeing across the cross section. Glove leather and garment leather also required through and through dyeing.

#### **2.5.8.4 Fixation**

Fixing of leather at the end of post tanning is a basic step in leather process and obtained by cationised the leather matrix through lowering the PH by addition of acids to the process liquor typically formic acid followed by HCl for glove leather.

- ❖ To avoid bleeding of post tanning chemicals after completion of process and during rubbing
- ❖ To fix the post tanning chemicals permanently with the leather matrix

Then the post tanned crust is piled overnight and aged to drain out the moisture gradually for proper fixing and distribution of chemicals offered, to avoid after unloading and conditioning for the next setting out process of crust leather.

#### **2.5.9 Finishing process in leather industry**

Wet finishing operations focused on imparting desired bulk properties like softness, compaction etc. to the leather. Some of these properties relate to the touch and feel of the leathers. Visual impact of the leathers like colour, gloss and smoothness etc. become important properties. The purpose of finishing is to improve the use properties of the leather in general and to protect it from wetting and soiling, to level out patches and grain faults and to apply an artificial grain layer to split or corrected grain leather. Finishing modifies also the surface properties like shade, lustre, handle etc.

#### **2.5.10 Characteristic of waste water generation**

Leather industry generates too much wastewater and solid wastes that is why leather industry is a challenge for environmental problems. The volume of wastewater (effluent), its characteristic varies from tannery to tannery and from time to time. Wastewater in beam house operation such as soaking, liming and deliming, bating and degreasing are highly alkaline, containing decomposing organic compounds, lime, sulphide, high COD and BOD, organic nitrogen and hairs. The waste water from other beam house operations such as pickling and chrome tanning are acidic.

### **3 Materials and methods**

#### **3.1 Develop and design enzymatic bating and degreasing simultaneously**

##### **3.1.1 Materials**

The wet salted sheep skin and all leather chemicals were taken from CLRI model tannery and process in the conventional leather process steps as soaking, liming, delimiting (with dry ice), the medium size limed and delimited pelt were taken for preliminary bating and degreasing experiment simultaneously.

##### ➤ **Materials**

- Laboratory drum
- All leather making machine
- Weighting machine
- Cutter
- pH meter

##### ➤ **Chemicals**

- sheep skin
- alkaline bating and degreasing enzymes
- acidic bating and degreasing enzymes
- all leather making chemicals
- pholphthalien indicator

##### **3.1.2 Methods**

After delimiting with dry ice, enzymatic bating and degreasing were carried out simultaneously. Two different bating and degreasing process were practiced simultaneously. Bating and degreasing simultaneously at alkaline stage (after delimiting) and processed bating and degreasing simultaneously at acidic stage (after pickling).

###### **3.1.2.1 Simultaneous bating and degreasing process after (delimiting)**

The process were starting ammonia free delimiting process by using dry ice delimiting and adjusting delimiting PH 6.5-8.5, continued bating and degreasing enzymatically in the same bath in alkaline condition. Bating and degreasing enzymes could be compatible (in terms of

process parameters, pH, temperature).to optimised the amount of bating and degreasing enzymes, 9 trials were carried out with concentration of 0.5%,0.9% and 1.3% for both types of enzymes based on the fleshed pelt weight the concentration (amount) was measured.

Process: the limed pelt was taken to the dry ice delimiting process and further bating and degreasing experiment simultaneously. By varying the amount of bating and degreasing enzymes, 0.5%, 0.9%, 1.3% and 0.5%, 0.9% and 1.3% respectively by adjusting the dry ice delimiting PH 6.5-7.5 and run the process of bating and degreasing simultaneously for an hour. At the end of the process check the completion of bating and degreasing by checking the thumb impression test and air permeability. After the completion process of bating and degreasing process, the bating and degreasing enzyme carried out deactivating through cooling by washing and acidification process through pickling immediately otherwise the active enzyme could damage the grain (leather making collagen).Recipe for the dry ice delimiting process followed by enzymatic bating and degreasing simultaneously.

Table 3.1 recipe for alkaline enzymatic bating and degreasing simultaneously

Study area					CLRI(Chennai),India		
Type of article					Limed Sheep skin		
process					Bating and degreasing simultaneously		
% of chemicals used based on					Limed pelt		
operation	% water	Chemicals (%)		Time	temperature	PH	remark
Delimiting	100	Dry ice	2	40'	35	7.4	
Bating & degreasing		peltec-BB(bating) peltec-BC-E-F(degreasing)	(bating= X) Degreasing=Y)	1hr		7.4	
Drain/wash	2x100			10'		6.5	
Pickling	100	Salt(NaCl)	10	10'		2.9	
		HCOOH(1:5)	0.5	3x10'			

		HCl(1:5)	1	3x10'+30'		
Drain/pile	50					
Chrome-tanning	100	BCS	4	1hrs		
		BCS	4	1hrs		
	100			20min		
		sodium formate (1:5)	1	30min		
		sodium bicarbonate	1	3x10min+30min		3.8,check penetration
	Drain/pile					

Table 3.2 result of enzymatic bating and degreasing simultaneously.

process	bating and degreasing simultaneously							
% chemicals used based on	% water	Limed pelt wt.						
Bating & degreasing simultaneously X=bating enzymes For bating process Y=degreasing enzymes For degreasing process		Chemicals (%)			time	Temperature	PH	remark
	100	trials	X	Y	1hr	35	7.8	
	1	0.5	0.5					
	2	0.9	0.9					
	3	1.3	1.3					
	4	0.5	0.9					
	5	0.5	1.3					
	6	0.9	0.5					
	7	0.9	1.3					
	8	1.3	0.5					
9	1.3	0.9						

The primary objective of the present work was to develop and design enzymatic bating and degreasing process simultaneously to produce glove leather with good organoleptic and other physical and chemical properties of glove leather from sheep skin. Peltec-BB and peltec-BC-E-F have been chosen to act as bating and degreasing simultaneously to reduce chemical consumption, environmental challenge and to improve the properties of glove leathers bated and degreased by enzymes. The experiment were carried out in full limed pelt and the limed pelt was cut into left side and right side, the right side of the pelt were taken for the experiment and the left side of the pelt were taken as for the control process. The percentage of chemicals used was based on the weight of limed pelt. Two partial limed sheep skins were processed and from this one half were processed to final end product, one half left in crust stage and remain leather was used for chemical and physical testing.

For full limed pelt the pH of the liquor adjusted to 6.7-8 by the process of dry ice deliming. After the acidification (pH adjustment), by varying the amount of peltec-BB (bating enzyme) and peltec-BC-E-F (degreasing enzymes) was added to the liquor and the process was run for an hour with the RPM of drum was 4 generally from the enzymatic process and leather processing point of view one hour to give adequate time for opening up of collagen fibres and removal of fat, then the completion of bating and degreasing process was checked by thumb impression test, air bulb test. On the same way all(X=alkaline enzyme) and (Y=alkaline degreasing enzyme) concentration was done to check and optimized the simultaneous process of bating and degreasing enzymatically. The process of controlled leather was done through the common and well known process limed pelt was weighted and the deliming and bating process was done with the common bating agent and solvent degreasing process was followed in separate process by organic solvent degreasing agents. The limed pelt sheep skin was cut into right and left side, then for control process the left side was taken .after liming the weighted pelt was processed deliming with 3% of  $\text{NH}_4\text{Cl}$  and 1% of bating agents after completion of deliming and bating, the process was checked by measuring the removal of lime with phenolphthalein indicator (colour change) and opening up of collagen fibres .then after washing and drain the solvent degreasing was followed.

Table 3.3 control glove leather process recipe from limed sheep skin

process	% water	Chemicals (%)		Time	T(°c)	pH	remark
Long deliming	100	NH <sub>4</sub> Cl	3%	40'	35	8	
Drain 80% liquor							
Bating		Bating	1%	40'			
Drain/wash 2x100% water							
Degreasing		Solvent	1.5%	40'			
Drain/wash 2x100% water				30'		8	
Pickling	100%	Salt(NaCl)	10%	10'			
		HCOOH (1:5)	0.5%	3x10'			
		HCl(1:5)	1%	3x10'+30'		2.8	
Drain /wash	50%						
Chrome tanning	100%	BCS	4%	1hr			
		BCS	4%	1hr			
		HCOONa(1:5)	1%	3x10'			
		NaHCO <sub>3</sub> (1:5)	1%	3x10'+40'		3.8-4	
Drain and pile							

N.B: Further with reference to the recipe's presented in table 3.1 and 3.2 and the conventional glove leather process from limed sheep skin was to design and develop and find the optimal requirement of bating and degreasing enzymes simultaneously by using 9 trials of the selected concentration of enzymes.

Process 1: two left sides of limed sheep skins were processed with 3% NH<sub>4</sub>Cl and 1% of bating enzymes and followed by degreasing with 1.5% of organic solvent for control process.

Process 2: three right sides of limed sheep skins were processed after dry ice deliming with 0.5% for both peltec-BB (bating enzymes) and peltec-BC-E-F (degreasing enzymes) simultaneously

Process 3: two full limed sheep skins were processed after dry ice deliming with 0.9% for both peltec-BB (bating enzymes) and peltec-BC-E-F (degreasing enzymes) simultaneously.

Process 4: two full limed sheep skins were processed after dry ice delimiting with 1.3% for both peltec-BB (bating enzymes) and peltec-BC-E-F (degreasing enzymes) simultaneously.

Process 5: two right sides of limed sheep skins were processed after dry ice delimiting with 0.5% peltec-BB (bating enzymes) and 0.9% peltec-BC-E-F (degreasing enzymes) simultaneously.

Process 6: two full limed sheep skins were processed after dry ice delimiting with 0.5% peltec-BB (bating enzymes) and 1.3% peltec-BC-E-F (degreasing enzymes) simultaneously.

Process 7: : two full limed sheep skins were processed after dry ice delimiting with 0.9% peltec-BB (bating enzymes) and 1.3% peltec-BC-E-F (degreasing enzymes) simultaneously.

Process 8: two right sides of limed sheep skins were processed after dry ice delimiting with 1.3% peltec-BB (bating enzymes) and 0.5% peltec-BC-E-F (degreasing enzymes) simultaneously.

Process 9: two full limed sheep skins were processed after dry ice delimiting with 1.3% peltec-BB (bating enzymes) and 0.9% peltec-BC-E-F (degreasing enzymes) simultaneously.

Process 10: two full limed sheep skins were processed after dry ice delimiting with 0.9% peltec-BB (bating enzymes) and 0.5% peltec-BC-E-F (degreasing enzymes) simultaneously.

### **3.2 characterize and analysis the efficiency of the designed process and the compatible enzymes**

#### **3.2.1 Materials**

All the required materials and chemicals were sourced from CLRI model tannery.

##### **❖ Materials**

- Sheep skin before bating and degreasing
- Skin pelt after enzymatic bating and degreasing process
- Crust leather
- Standard Measuring Flask, Round bottom flask,
- Funnels, Crucible
- Filter paper
- Flasks
- Desiccators
- Dynamometer for tensile and tear as well as elongation at break
- soxhlet extraction apparatus
- Weighting machine

##### **❖ Chemicals**

- Hexane used for fat extraction

#### **3.2.2 Methods**

The characterization and analysis of the designed enzymatic bating and degreasing process simultaneously was done by measuring the required parameters of glove leather.

- ❖ fat content of the processed pelt and crust leather
- ❖ organoleptic properties of the end product
- ❖ physical properties of the post tanned leather

##### **3.2.2.1 Determination of fat content**

The fat content was determined by solvent extraction methods. Analysis of the fat content plays its role in designing the process recipe. The fat content of controlled process and experimental (bating and degreasing simultaneously) of crust glove leather was estimated by taking 5gm sample from the post tanned crust leather .the leather sample was accurately weighted by analytical balance and transferred into soxhlet thimble and extraction of oils

and fats is done with dichloromethane in a soxhlet extraction unit for 5 hrs. It is the Official method of fat extraction and standard soxhlet extraction method with dichloromethane.

In the soxhlet the fat was extracted, dried and the solvent was separated and collected in the soxhlet tank to recover. After recovering the solvent from the soxhlet tank, the extract in the round flat bottomed flask was dried at  $103\pm 5^{\circ}$  C to constant weight at the oven. The fat content was estimated as percentage (w/w) with respect to the input sample.

### **3.2.2.2 Organoleptic properties of crust leather**

The experimental and control glove leathers were assessed in terms of softness, run, elongation light weight and other general appearance by standard tangible evaluation technique. Experienced leather technologist rated the leathers in a scale of 0-10 points for each required properties of glove leather. The recorded values of the properties are the average of three leather technologist (scientist).the properties, run, softness, light weight, elongation, fastness properties of the experimental leathers (designed process) and the control leathers(Conventional process) were evaluated.

### **3.2.2.3 Physical properties of the post tanned crust leather**

In physical testing of leather conditioning and leather cutting test specimen is very important step in leather physical testing. The moisture content in the leather matrix is varied according to the relative humidity of the working place (environment).Temperature is also other well-known factor to influence the properties of matter. Hence it is an accepted procedure to conduct the test at pre-defined test environment. The samples for various physical tests were obtained as per IULTCS methods (ISO 2418:2005) from experimental and control crust leathers. The material is to be kept in a standard atmosphere (temperature  $23\pm 2$  C, humidity  $50\pm 5\%$  RH) for 48 hours prior to testing to bring it to natural condition. Tensile strength, % elongation at break and tear strength were examined as per the standard procedure [25].

#### **3.2.2.3.1 Measurement of tensile strength**

The leather samples were cut perpendicular and parallel to the backbone using dumbbell shape. The width and thickness of the samples were measured in the same position using a vernier calipers and standard thickness gauge, respectively (ISO 3376).

The specimens were cut as a rectangle 50 mm long and 10 mm wide using a press knife which cuts out the specimen. The jaws of the tensile machine were set 50 mm apart, and then the sample was clamped in the jaws, so that the edges of the jaws lay along the midline. The machine was run until the specimen was broken and the highest load reached was taken as the breaking load.

### **3.2.2.3.2 Measurement of elongation**

The percentage elongation of glove leather was done by measuring the initial free length between the clamps before the load is applied and the final free length between the clamps at the instant of break. The initial free length was set at 5 cm and the elongation calculated from the readout machine (ISO 3376).

### **3.2.2.3.3 Measurement of tear strength**

Tear strength test method is intended for use with any types of leather. the official method (SLP 2: IUP/2) measures the tear load on a specimen in which a slot has been cut and which is slipped over the turned-up ends of a pair of holders attached to the jaws of a tensile strength machine. The forces exerted during separation of the holders are recorded and the highest force is taken as the tearing load and expressed in newton. Tearing load can be expressed as the quotient of the load by the thickness of the sample. cut eight test specimen (four test specimen from along direction and four test specimen from across directions) using a cutting knife as a rectangle 100 long and 50 mm wide using a press knife which cuts out the specimen having a central slot in 1 operation (template machine). Conduct the test by operating the tensile tester at the rate of  $100 \pm 10$  mm/ minute speed until the test specimen is torn apart and the highest load reached during tearing was recorded as the tearing load. Continue the test in the same way for the other test specimens

### 3.3 Analysis the pollution load of the designed process

#### 3.3.1 Materials

The materials and chemicals required to analysis the wastewater pollution load were:

- **Materials :**

- ✓ Standard Measuring Flask, Round bottom flask,
- ✓ Funnels, Crucible
- ✓ Filter paper
- ✓ Flasks
- ✓ Desiccators
- ✓ soxhlet extraction apparatus
- ✓ BOD and COD meters(digester)
- ✓ Ammonia analyser
- ✓ phenolphthalein indicator
- ✓ Weighting machine
- ✓ Incubation Bottles

- **Chemicals used:**

- Potassium dichromate
- Sodium hydroxide solution
- Hydrochloric acid(HCl)
- Sulphuric acid( $H_2SO_4$ )
- Nitric acid ( $HNO_3$ )
- Ferrous Ammonium Sulfate ( $Fe(NH_4)_2(SO_4)6H_2O$ )
- Ferroin Indicator
- Mercuric Sulfate( $HgSO_4$ )
- Potassium hydrogen phthalate standard( $HOOC C_6H_4 COOK$ )

#### 3.3.2 Methods

##### 3.3.2.1 Total solid content in the waste liquor

The waste water was taken from both the control process of delimiting, bating, degreasing process and the enzymatic bating and degreasing (optimized) processes. The process was done based on the standard procedure (ISO).

Solid waste is generally used when referring to any materials dissolved or suspended in waste water than could be isolated physically filtration or evaporation. Analytically the total

solid content of a wastewater is defined as Total solids are the term applied to the material residue left in the vessel after evaporation of the sample and its subsequent drying in an oven at a definite temperature. Thus total solids are nothing but summation of total dissolved solids and total suspended solids. Suspended solids are part of total solids in wastewater that remain present on filter paper while filtration. Dissolved solids are part of total solids present in the filtrate while filtering the sample on filter paper. The measurement of total solid was based on the gravimetric analysis procedure and the various form of solid was determined by weighting the sample liquor for both experiment and control process after appropriate handling procedures. The total solid concentration of the sample is found by direct measuring the sample before and after drying in an oven at  $103\pm 3^{\circ}\text{C}$ . the remain solids (TDS and TSS) required further filtration process of samples and for liquid samples all measurement/solid levels are reported in mg/L.

The procedure to measure the total solids was

Procedure 1: done by taking clean crucible which has been washed and dried in hot air oven at  $105^{\circ}\text{C}$  for four hours.

Procedure 2: take the dried crucible into the desiccator to cool the crucible after cooling weigh the mass of the empty crucible with the analytical balance

Procedure 3: using pipet 50ml was measured from the experimental and control sample waste liquor into the crucible.

Procedure 4: dried the sample to get constant mass in an oven by evaporating the moisture for long duration (5hrs).

Procedure 5: after the drying process cool the sample in desiccator to avoid loss of mass since it is designed to provide an environment of standard dryness.

Procedure 5: finally weigh the crucible with dried sample and then repeat it till constant weight obtained then symbolized the sample, (A).

Calculation

$$\text{Total solid (mg/L)} = \frac{(A-B) * 1000}{\text{Volume of sample (L)}}$$

Volume of sample (L)

A= weight of dried residue + weight of crucible in mg.

B = weight of crucible in mg.

### 3.3.2.2 Chemical oxygen demand

Chemical oxygen demand is used as a measure of oxygen equivalent of organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. The aim of the test is to measure the pollution potential of wastewaters in terms of organic matter present in it. Samples of the liquor from various experiments and control process was taken and tested with the standard methods of open reflux (PITWELL, L.R. 1983. Standard COD. Chem. Brit. 19:907). The chemical oxygen demand (COD) test measures the oxygen required to oxidize organic matter in experimental and conventional control wastewater samples by the action of strong oxidizing agents under acid conditions in milligram per litre (mg O<sub>2</sub>/l) . Then the COD content is determined based on the standard test procedure. 10 ml COD digestion tubes (pre-washed with dilute H<sub>2</sub>SO<sub>4</sub>) to carried out the test analysis and add the required amount of dilution chemicals in sequence. Transfer 10 ml wastewater sample (Inlet). Then add 2.5 ml standard potassium dichromate digestion reagent slowly and mix. Next add 3.5 ml sulphuric acid reagent through sides of the tubes and let it go to the bottom. Cap and mix the contents. Transfer tubes to the pre-heated COD digester at 150 ° C and digest for 2 and half hrs. After this transfer the contents of the COD digestion tube in 150ml beaker. Add distilled water to make the volume to 50 ml. add 1-2 drops of Ferroin indicator and titrate against 0.05 M Ferrous Ammonium Sulfate solution.

$$\text{COD (mg/L)} = \frac{(B-S) \times N \times 8000}{\text{Volume of sample (L)}} \dots \dots \dots \text{eq. (15)}$$

Volume of sample (L)

B = ml Fe.Am.Sulfate consumed for blank

S = ml Fe.Am. Sulfate consumed for sample

N = Normality of Fe.Am. Sulfate.

### 3.3.2.3 Biochemical oxygen demand

Biochemical oxygen demand is amount of dissolved oxygen demanded by microorganism to decompose biodegradable organic matter under aerobic condition, at a certain temperature and over a specific of time. The sample is filled in airtight bottle and incubated at specific temperature for 5 days. The dissolved oxygen (DO) content of the sample is determined before and after five days of incubation at 20° C and the BOD is calculated from the difference between initial and final DO. Samples of the liquor from various experiments and control process was taken and tested with standard test method (*Sewage Works Journal*

Vol. 12, No. 3 (May, 1940), pp. 504-512 (9 pages).

### 3.3.2.4 Ammonia content in the waste water

The ammonia content in the wastewater is the discharge of ammonical nitrogen in the effluent and it is poisonous to fish and other aquatic organisms. The sources of ammonical nitrogen are decomposed proteins and conventional deliming chemicals and the determination of ammonia content in the wastewater is determined by kjeldahl nitrogen (International Journal of Advanced Research in Chemical Science (IJARCS)).

In the presence of  $\text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{HgSO}_4$  catalyst amino nitrogen of many organic materials is converted to ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$ , free ammonia and ammonium - nitrogen also are converted to  $(\text{NH}_4)_2\text{SO}_4$ . During sample digestion a mercury ammonium complex is formed and then decomposed by sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ). After decomposition the ammonia was distilled from an alkaline medium and absorbed in boric acid. Ammonia was determined by titrimetric method.

## 4 Result and discussion

The development and design of cleaner production of ammonia free deliming, bating and degreasing process gave the following results.

### 4.1 Fat content analysis

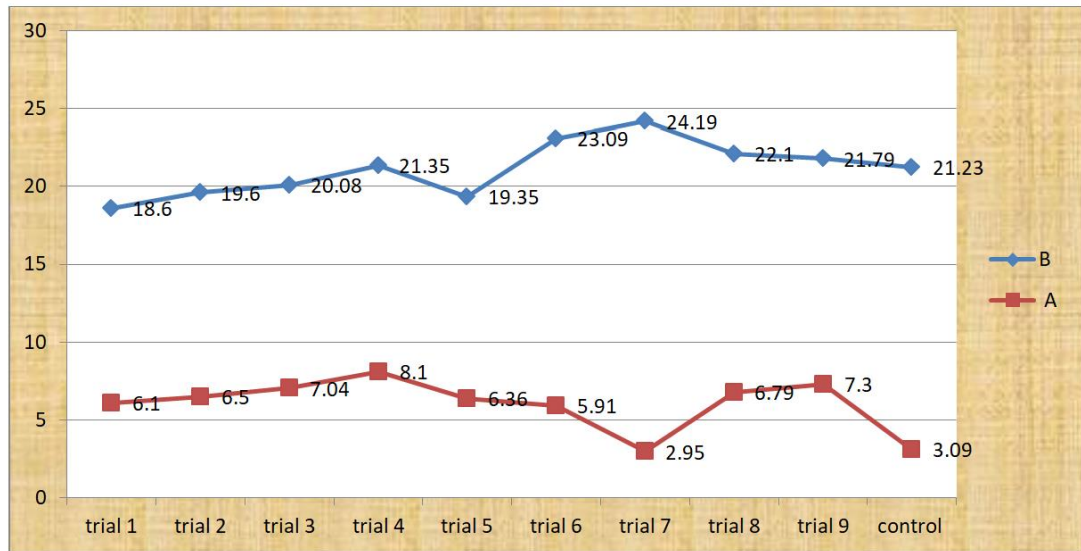


Chart 4.1 fat content of experimental and control process of glove leather

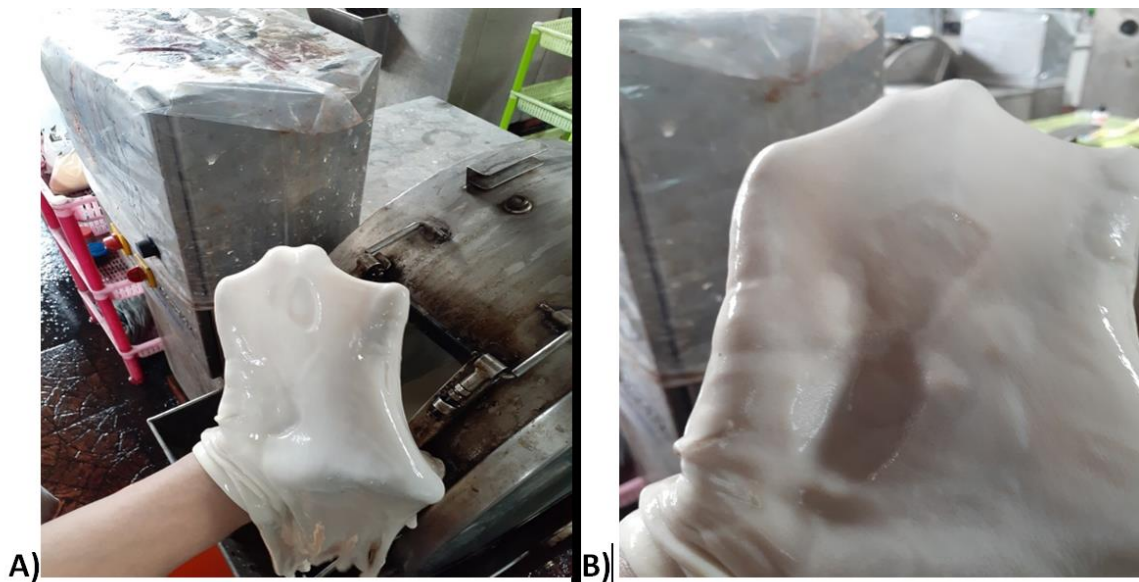


Figure 4.3 enzymatic bating and degreased pelt simultaneously and control  
A) Enzymatic bating and degreased pelt simultaneously B) control pelt

## 4.2 Organoleptic property analysis

Experimental and control glove leathers were assessed for light weight, softness, run, smoothness, general appearance and dye uniformity by hand and visual examination. Three experienced leather technologist rated the leathers on the scale of 0-10 points for each functional property, where higher points indicate better property and lower points indicates lesser properties. Based on the indicated evidence, run, dye ability, softness, and light weight of leathers bated and degreased by enzymes simultaneously comparable to conventional bating and degreasing system of leather process.

**Table 4.1 Visual Assessment of the organoleptic properties of control and experimental Post Tanned glove Leather**

parameters	T1	T2	T3	T4	T5	T6	T7	T8	T9	C
run	7	7.5	8	7.2	8	8.5	9.5	7	6.5	8
Light weight	7	7	8	7.5	7.5	7	8	7	7	8
softness	6	6.5	5	6.8	7	8	9	7.3	7.8	9.5
Dye-ability	5	6	7.5	7	7.2	6.8	8.5	7	8	9
General appearance	4	5	7	6	6.5	7.5	8.8	7	6	8.5
Color uniformity	3	4	5	6	6.5	7	9	7.5	7	9.5

## 4.3 Wastewater analysis

Based on the standard measurement and procedure the ammonia content, total solid, COD and the COD content of the control and experimental test result, the beam house liquor is explained as follows.

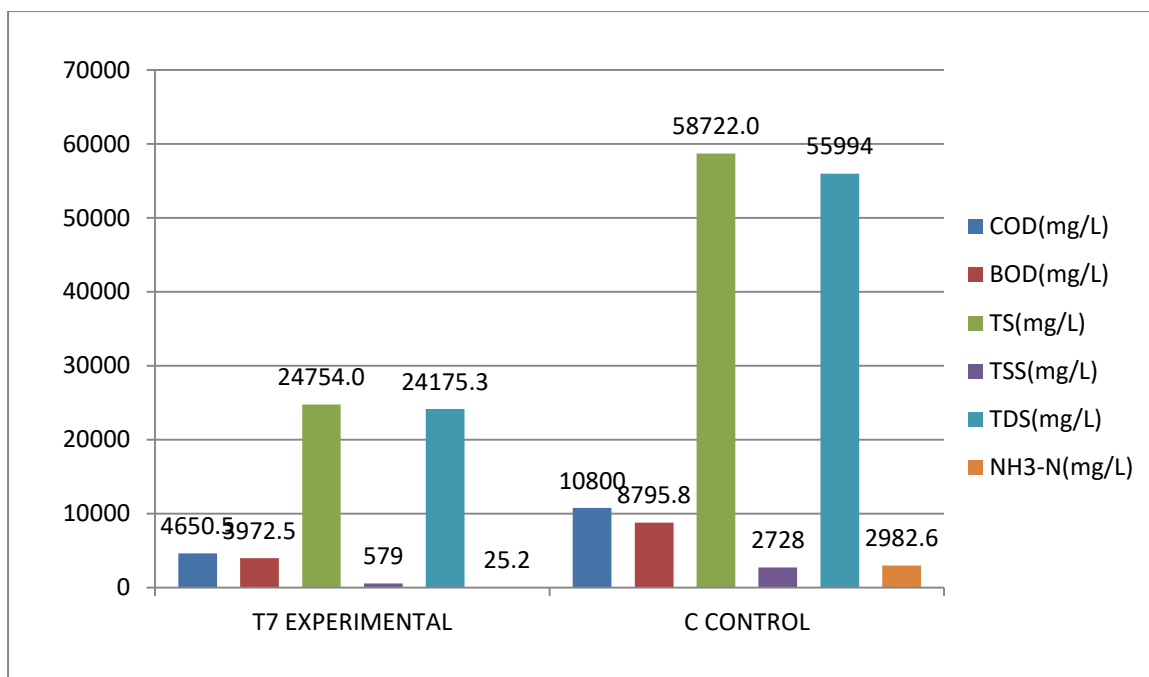


Chart 4.3 wastewater analysis for experimental and control process system

From the Chart 4.3, it is observed that the spent liquor results processed using both the experimental and the control in beam house wastewater liquors. The spent bating and degreasing liquor analysis from enzymatic bating and degreasing process simultaneously was carried out to evaluate the impact on the environmental pollution load. The biological oxygen demand (BOD), chemical oxygen demand (COD), ammonia, total solid(TS), suspended solid(TSS) and the dissolved solid(TDS) value for enzymatic bating and degreasing in single bath and for control process system are shown in Chart 4.3. It was seen from the Chart all the measured wastewater parameters were less in the enzymatic bating and degreasing process than the control process. On the other hand enzymatic bating and degreasing process has less waste load on the effluent compared to the control process system.

From the chart 4.3 the enzymatic bating and degreasing process waste water analysis gives 25.2mg/L of ammonia. Even though the process is ammonia free delimiting process the analysis result shows that there is presence of ammonia in wastewater so, this 25.2mg/L of ammonia in the wastewater come from the degradation or decomposition of globular protein in the skin matrix during bating and degreasing process of delimed pelt and from the other unit operation of beam house process.

#### 4.4 Chemical Analysis of Crust glove Leather

The fat content of both the experimental and control leathers were analyzed. The amount of fat content extracted indicated that, the amount of fat liquors which is fixed during fatliquoring as well as the natural fat.

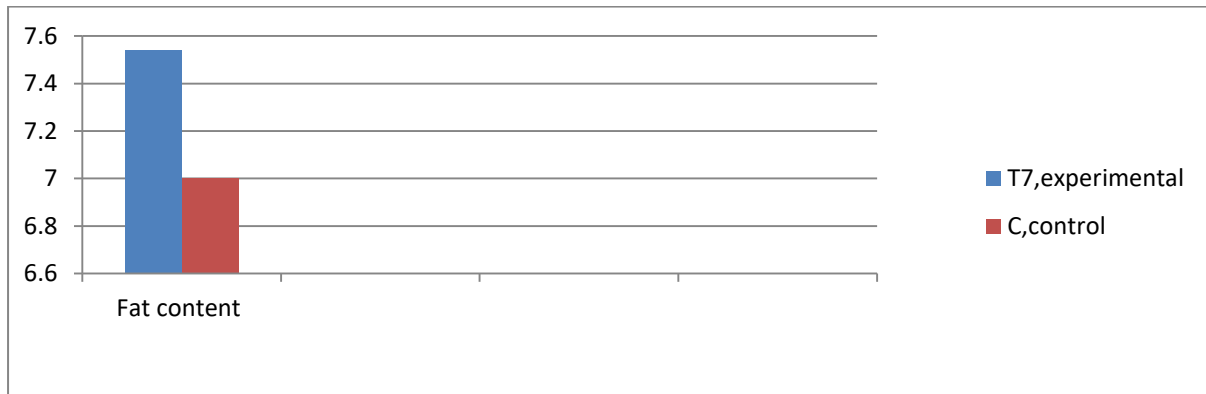


Chart 4.4 fat content analysis of experimental and control process system of crust leather

#### 4.5 Physical test analysis

The experimental leathers bated and degreased by enzymes in single bath and control leather processed in conventional way have been post tanned for glove leather. The physical characteristics of glove leather Processed by enzymatic bating and degreasing simultaneously and control process are shown in Chart.

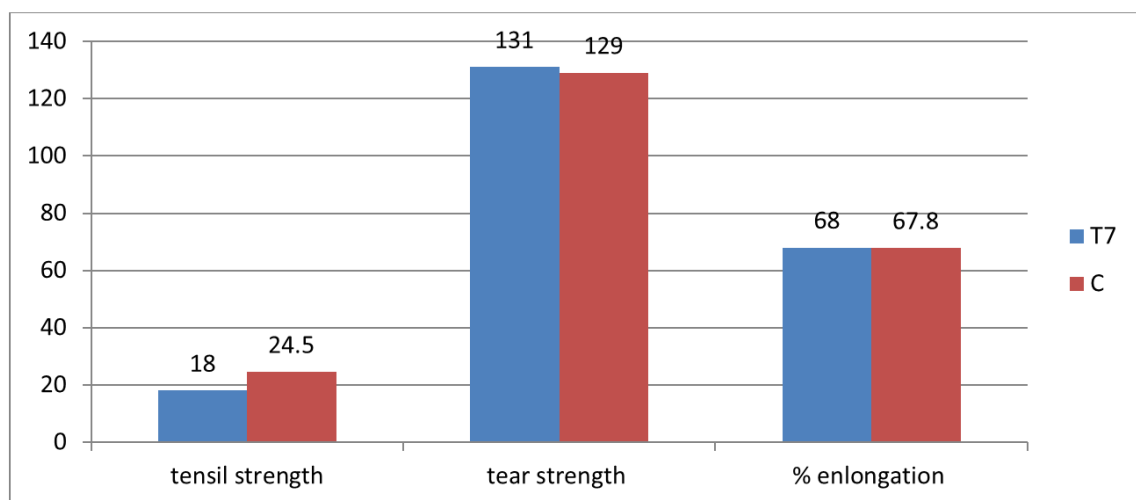


Chart 4.5 physical testing analyses of both experimental and control crust glove

#### 4.6 Colour fastness to circular rubbing for finished glove leather

Fastness can be judged by the effect on the sample material or the transfer of colour to the rubbing pad. The change in appearance of the finish and the colour transferred to the rubbing pad was assessed by reference to the standard grey scales and are presented in Table 4.2.

Table 4.2 fastness properties result for both experimental and control leather process

Test trials	Dry rub test		Wet rub test	
	Felt pad	Test piece		
T7	4/5	4/5	4/5	4/5
C	4/5	4/5	4/5	4/5

All the tests maintain greater results from the minimum grey scale standards. This indicates the enzymatic bating and degreasing process simultaneously did not affect the finishing process and finishing result. Matched pair comparison has also been performed to study the finishing characteristics of the developed enzymatic bating and degreasing processed crusts with that of the conventional bating and degreasing process in separate bath crust leathers. The wet and dry rub fastness measured for both control and experimental finished leathers process using the same composition and quantity of finishing components per unit area are shown in Table 4.10. From the table, it is observed that the fastness properties of both experimental and control leathers are very much comparable and the test results are much higher than the ISO standard minimum limit value, this indicates that the enzymatic bating and degreasing process in single bath system does not affect the finishing, which indicates that the enzymatic bating and degreasing in single bath system results in leathers with finishing characteristics similar to that of conventional bating and degreasing system of leather process tanned leathers.

## 5 Conclusion and Recommendation

### 5.1 Conclusion

Almost all tanneries in Ethiopia use conventional process of bating and degreasing process for production of good glove leather (bating with deliming and organic solvent respectively).these ammonia salt organic solvent and its derivatives are very perilous to the environment and human health. The detailed research study has been made on the development of new process of enzymatic bating and degreasing system simultaneously. The outcome of the research work clearly suggests that conventional bating and degreasing system can be replaced by enzymatic bating and degreasing system simultaneously so that the chemical consumption and the environmental impact on the environment and human being by organic solvent and ammonia deliming eliminated, and chemical consumption reduced by the enzymatic process of bating and degreasing in single bath.

In this project paper we have shown that enzymatic bating and degreasing system simultaneously greatly producing pelt with great thumb test, bleached pelt, and 68% elongation, 94% fat removal, good fibre opening, great run properties as well for glove leather and other physical and chemical properties of glove leather are fulfilled in this experiment. The selections of enzymes are concerned based on the processing parameters to be compatible with each other. The optimal process of enzymatic bating and degreasing system simultaneously were obtained 0.9% and 1.3 % ( w/w) of peltec-BB (alkaline bating) and peltec-BC-E-F (alkaline degreasing) respectively.

The organoleptic and other physical and chemical properties of experimental glove leather almost all comparable to the conventional process product glove leather and from the environmental point of view enzymatic process of bating and degreasing system simultaneously is green process and it is eco-friendly to the environment better than the conventional bating and degreasing process.

This enzymatic bating and degreasing system simultaneously presents the tanners the option of Producing ammonia and solvent free eco-friendly environments and good glove leathers. The major advantage of the enzymatic bating and degreasing system using peltec-BB and peltec-BC-E-F is the ability to produce good leathers ,reduction of chemical

consumption, reduction of environmental pollution and as well as design of green leather processing systems and , which is difficult in the case of other dominant bating and degreasing system existing at present. Both conventional alkaline bating degreasing and acid bating and degreasing system induce ammonia and organic solvent to the environment which leads to human health problem and incurred cost to treat the wastewater as well. The enzymatic bating and degreasing process simultaneously has great reduction of environmental pollution and chemical consumptions producing glove leather with comparable properties of glove leather to the conventional leather bating and degreasing system.

## **5.2 Recommendation**

Based on the conclusion and results of this study the following recommendations are listed

- As indicated from the fat content and other physical measurement results it should be clear that leather can be made with the process of enzymatic alkaline bating and degreasing system simultaneously but it needs careful selection of enzymes and control of process parameters.
- There is the scope to improve the tensile strength and other physical properties of glove leather made by enzymatic bating and degreasing system simultaneously.
- Glove leathers bated and degreased by peltec-BB and degreased by peltec-BC-E-F system simultaneously with careful control of process parameters is significant to reduce process defects.
- To see the practical application of alternative system of bating and degreasing, awareness creation for leather industries and the societies should be done so as to use alkaline enzymatic bating and degreasing system simultaneously instead of bating with deliming and organic solvent degreasing in different bath to reduce the chemical consumption and environmental impact due to organic solvent and ammonia.
- The replacement of conventional bating and degreasing system in separate bath by alkaline enzymatic bating and degreasing system simultaneously is one option to reduce the concentration of chemical discharge to the effluent, organic solvent elimination in the wastewater and elimination of emission of ammonia to the environment

- Leather industry development institute(LIDI) should initiate the Ethiopian tanneries to practice the green leather process and green leather chemicals
- Acidic bating and degreasing after pickling required deep research.
- The efficiency of bating enzymes for fibre opening I did not get the chance to do SEM, further histological study of the skin matrix should be done.

## 6 Reference

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## Annexes

### Annex 1

Properties	Target value	Method
Thickness	0.8-0.9mm	
Light fastness	≥3 blue scale	ISO 105-B02
Tear strength(KN/m)	≥15	ISO 3372-2
Tensile strength (Mpa)	≥15	ISO 3376
Elongation (%)	≥ 20% (@2N/mm <sup>2</sup> )	ISO 3376
Dry rubbing	≥grey scale 50 cycles	ISO 11640

Annex 2: Provisional standards for discharge of effluent by leather tanning and finishing industries

Table 1: Emission Limit Values for Discharges to Water Constituent Parameter	Emission Limit Value (mg/L)
Temperature	40oc
pH	6 – 9 pH units
BOD5 at 20oC	>90% Removal or 200 mg/l
COD	500
Suspended Solids	50
Mineral Oil (Interceptor)	20
Chromium (as total Cr)	2
Chromium (as Cr VI)	0.1
Oils, Fats, and Grease	15