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STUDY ON THE SPECIALITY OF ETHIOPIAN HIGHLAND HAIR SHEEP SKIN TO MAKE GLOVE AND CABRETTA

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A Thesis

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DECLARATION

I declare that this thesis is my original work and has not been presented for the award of a degree in any university.

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ACRONYMS

FAO	Food and Agriculture Organization
ICT	Information and Communications Technology
UNIDO	United Nations Industrial Development Organization
ILRI	International Livestock Research Institute
Ecbp	Engineering Capacity Building Program
Sq.ft	Square fit
UV	Ultra Violet
PDAB	Para Dimethyl Amino Bezaldehyde
ISO	International organization for standardization
SLC	Standard Leather Chemical
IUC	International union of Chemical test
IUP	International union of physical test
H_2SO_4	Sulphuric Acid
NaOH	Sodium Hydroxide
ASTM	American Society for Testing and Materials
OD	Optical density
RH	Relative Humidity

Abstract

Ethiopian highland hair sheep skins have a wide importance mainly as a source of foreign exchange to the country from the leather industry. The consumption of these products is high for reasons of high quality to make glove, cabretta as well as for sport goods leathers.

The present work describes the study on characterization of the Ethiopian highland hair sheep skin by carrying out histological analysis using light microscope and scanning electron microscope (SEM). Indian hair sheep skin has been used for comparing the characteristics features. Various features of the Ethiopian highland sheep and Indian red hair sheep skins such as thickness distribution of the skin, layers in the epidermal area, fibre size, fibre orientation and the interweave in the dermal area, the hair pore count and grain to corium ratio have been determined.

In addition to this physico-chemical characteristics of hair sheep skins have been analyzed using different equipment and procedures. From the result of physical and chemical characteristics it could be inferred that tensile and tear strength of the leathers from Ethiopian highland hair sheep skin is higher than Indian hair sheep skins. Chemical characteristics such as the hydroxyproline content, collagen, nitrogen, glycoprotein, hide substance of the skins have been determined and in all result Ethiopia highland hair sheep skins are better compared to Indian material.

From the histological, physical and chemical characteristics of the Ethiopian sheep skins, it could be inferred that the inherent character of these skins make it suitable for making of glove and cabretta leathers.

CHAPTER ONE

1. Introduction

1.1. Background

The world livestock population was approximately 1.62 billion for bovine animals, 1.08 billion for sheep and lambs, and 0.91 billion for goat and kids [1]. Out of this about 80.3% are found in developing countries for bovine, 70.4% for sheep and lambs and 95.7% for goat and kids. [1]

The world production of bovine hides was approximately 321.30 million pieces (approximately 65.59% for the developing countries), sheep and lamb skins of 543.40 million pieces (approximately 67.54% for the developing countries), and goat and kid skins of 427.60 million pieces (approximately 95.86% for the developing countries) in 2010 [1].

Ethiopia's livestock population is estimated at 53.3 million cattle, 25.5 million sheep and 22.8 million goats. Ethiopia is well-endowed in livestock resources, ranking first in Africa and occupying the tenth position in the world and providing a strong raw material base for the leather industry, As a result of this, leather has been at the core of Ethiopia's economy since many centuries. Around 8.5 million pieces sheep skin, 7 million pieces goat skin and 1.2 million pieces hides are supplied to the tanneries per annum. It has been estimated to recover 96%, 93% and 36% of sheep skin, goat skin and cattle hides respectively and the rest being uncollected or consumed by rural tanners [1, 2].

Ethiopia highland crop- livestock mixed farming system covers around 40 % of the total land surface and is located 1500 m above sea level (a.s.l.). The highlands are situated in the Northern, North-eastern and central part of the country. It is featured by a mixed farming system where crop cultivation and livestock production are undertaken side-by-side complementing each other. The highland, agricultural based system of livestock production includes some 80% of cattle, 75% of sheep and 30% of goats' population. About three-quarters of the total sheep flock is in the highlands, whereas lowland pastoralists maintain about three-quarters of the goat herd. The highlands are a major source of sheep for slaughter in the cities [3].

This highland hair sheep skins is known in the international leather market for its sovereign qualities in particular retain a high reputation for some natural characteristics of clarity, thickness, flexibility, strength and compact texture which makes them especially suitable for high quality gloves, sports equipment and garments and the goat skins are equally acknowledged to be the finest for suede making for garments and footwear. In fact, the international leather market has coined special names for these two varieties of skins after two Ethiopian provinces – Selallie (highland sheep skin) and goat skins Bati Genuine. The sheep skins are referred to as Selallie Genuine and which are offered premium prices over all others. [4, 5]

The government of Ethiopia puts developing the leather sector among its top four priorities. Its initial step towards fostering the development in this sector is to create a conducive business environment for the private sector to take over the lead. This involved the deregulation and liberalization of the goods and factor markets maintaining a stable and predictable macro-economic environment, revision of the investment code to widen the scope and areas of investment, additional incentive schemes that add to the profitability of private investments, etc. The country has also signed the World Bank's multi-lateral agreement to protect private investments and several bi-Internal agreements with many countries around the world [6].

The Tanning Industry: The Ethiopian leather industry is backed by this considerable support and has gained momentum of growth over the last several years. The number of tanning industries that were handful ten years ago have now rose to twenty seven with more under formation. All of them are of considerable size with the smallest having a soaking capacity of 3000 skins per day of eight working hours. A national leather sector master plan has been drawn as a common strategy document to accelerate the industry's growth to a well integrated and vibrant sub-sector of the national economy. As a result, thirteen of them can finish leather to any specification required including custom-made recipes. Many are vertically integrating themselves so that their respective capacities can have full control on the critical components of the supply chain [6]

This thesis work is focus on the special characteristics of highland hair sheep skin that get world class raw material of high value glove and cabretta.

1.2. Problem Statement of the research

In Ethiopia, significant potential lies in the leather value chain. Ethiopia is home to one of the largest livestock populations in the world and Ethiopian sheep skins are known for their superior quality. Yet Ethiopia's share in world trade of leather and leather products is tiny. For example, in 2010, Chinese exports of leather products were estimated at US$8.3 billion while Ethiopian exports were estimated at only US$3.7 million. Formal Chinese firms employed almost 3 million workers; while Ethiopia's formal firms employed a mere 7,600 workers [8]. It is not surprising that the Ethiopian government has been actively involved in the promotion of industrialization in the leather value chain. To promote indigenous manufacturing, the Ethiopian government has generally not allowed foreign investment in tanneries (up to crust level) or in the marketing of hides and skins. However, due to local tanneries not advanced enough to process up to the crust level, the government suspended the ban on new foreign investment in tanneries for several years. As a result of relaxing these controls, [7]

Notably, government policy to date has focused almost exclusively on leather processing. Very little attention has been paid to upgrading and commercializing the livestock sector

As we know highland sheep skin has gain an international belief by its high quality but until now there is no scientific data to validate the superior quality of the sheep skins. Hence, this paper develops and gives scientific information to validate the speciality of Ethiopian highland hair sheep skin.

1.3 Objectives

1.3.1 General objective

- The main objective of this study is to develop valuable scientific data on Ethiopian highland hair sheep skin

1.3.2 Specific objectives

- To analyse histological characteristics of Ethiopian highland hair sheep skin with the comparison of Indian hair sheep skin.
- To analyse chemical characteristics

- To analyse physical characteristics to make cabretta and glove
- To identify the properties that makes Ethiopian highland sheep skin is best for producing good quality cabretta and glove
- To compare the quality of cabretta and glove leather produced from Ethiopian highland hair sheep skin and Indian hair sheep skin
- To give essential information about speciality of Ethiopian highland hair sheep skin for the foreign investors and Ethiopian leather processing industries or to develop a data base.

1.4 Significance of the Research

Ethiopia actively promotes foreign investments, exports, private sector development and an Agriculture Development-led Industrialization (ADLI). While an increasing number of western firms of all sizes are now looking at doing business in Africa. Ethiopia is one of the countries from Africa giving high priority for the leather sector due to large live stock population and high quality hair sheep skin for making glove leather. From the western country one big glove industry was established in Ethiopia named Pittards. One of the reasons for this industry is that Ethiopia banded export of any raw skin and semi finished leather. Like this it is expected in the future both external and internal investors would come and work in this area and this work forms a basis for good scientific information about our sheep skin.

Cognizant of the potentials this renewable resource has for the development of the country, the government of Ethiopia puts developing the leather sector among its top priorities. Its initial step towards fostering the development in this sector is to create a favourable business environment for the private sector to take over the lead.

It is hoped this study will explain the unique properties of highland sheep skin and develop essential scientific data on this area; this gives reliable information for the investors those needs to invest on leather sector and used to encourage private investment and promote the inflow of foreign capital and technology into Ethiopia.

CHAPTER TWO

2. Literature survey

2.1 Introduction

The tannery operation involves converting the raw skin, a highly putrecible material, into leather, a stable material, which can be used in the manufacturing of a wide range of products. The whole process involves a sequence of complex chemical reactions and mechanical processes.Conventional leather processing involves four important operations, viz., pre-tanning, tanning, post-tanning and finishing. It includes a combination of single and multi-step processes that employs, as well as expels, various biological, organic and inorganic materials.

Liming and re-liming processes employ lime and sodium sulphide. These two processes purify the skin matrix by the removal of hair, flesh and other unwanted materials to produce pelt. The de-liming process employs quaternary ammonium salts for neutralizing the alkalinity. The bating process purifies the skin matrix further by using pancreatic enzymes. The pickling process prepares the skin for subsequent tanning. The tanned skin matrix may be further re-tanned to gain substance; fat liquored to attain required softness and dyed to preferred shades and finished to customer requirements. [8, 9]

2.2 Description of leather processing

a) Soaking

Soaking is the first process applied to the raw stock. The main purpose of this process is to remove the salt used during curing, re-hydrating the material and to get rid of unwanted material such as dung, blood, soil, etc. The duration of soaking may range from several hours to a few days. Depending on the type of raw materials used, soaking additive such as surfactants, enzyme preparations and bactericides can be used. [9, 10]

b) Liming

The purpose of this operation is to facilitate the removal of hair, flesh, fat (quality), inter fibrillary protein and to open-up the fibrous structure for osmotic swelling.

The process of liming can be broadly classified into two parts i.e. Un-haring and re-liming. [11]

c) Unhairing

Unhairing is a process of removing the hair from the pelt. The traditional method of dissolving the hair is to dissolve it, called 'hair burning'. Hair removal in alternative ways, 'hair saving', keeping the hair intact while removing it; each technology requires a different degree of process control. [10, 11]

d) Enzyme-assisted chemical unhairing

Conventional hair burning can be accelerated by the presence of so-called 'alkali stable' proteolytic enzymes, obtained from bacterial fermentation. [10]

- **Painting**

For the special case of woolskins, the technology of painting has been developed. The idea is to drive the un-haring agent from the flesh side of the pelt. In this way, the chemicals do not make contact with the wool and devalue it. The paint is applied to the flesh side of the pelt: the pelts are then stacked, flesh to flesh for several hours. The hairs are 'pulled' by hand or machine. [11, 12]

e) Fleshing

The excess fleshing is removed manually or by using fleshing machines.

f) Deliming

The functions of deliming are: - removing the lime, lowering the pH in preparation for bating, and reversing the swelling. It can be carried out by using:- Weak Acids, Acidic Salts, Ammonium salts (In industry it is common to use either ammonium sulfate or ammonium chloride) and Carbon dioxide.[10,11]

g) Bating

Bating refers to the use of enzymes; its purpose is to break down specific skin components: usually the non-structural proteins are the target. [10]

h) Pickling

The pickling process is primarily conducted to adjust the collagen to the conditions required by the chrome tanning reaction. The traditional recipe for pickling based on limed pelt weight is 100% Float, 10% salt, 1% Sulphuric acid. [11]

i) Tanning

Tanning is the conversion of a putrescible organic material into a stable material. It may have three part mineral tanning, vegetable tanning and Combination tannage. [12]

- **Mineral Tanning**:

Chromium (III)

The use of chromium (III) salts is currently the commonest method of tanning perhaps 90% of the world's output of leather is tanned in this way.

Basic chromium sulphate [Cr2 (SO4)3] (7-10%) containing 25% Cr2O3 and sodium sulphate(25-30%) is used in chrome tanning. Part of the pickle bath is used for chrome tanninoperation. The pH is increased to 3.8-4.0 at the end of chrome tanning process which iscalled basification. The semi-finished leather after chrome tanning is called wet blue. [11, 12]

- **Vegetable Tanning**

Vegetable tannins are extracted from plant materials that contain commercially viable concentrations: this may be done with water or with organic solvents. The extracts typically contain Non-tans, tans and gums. Vegetable tanning technologies use drums to facilitate rapid penetration. The reaction is typically conducted at about pH 3.5 and up to 38°C, but in zero float. [10]

- **Combination tannage**

Strictly, the term combination just refers to the use of more than one tanning agent.

The retanning of chrome tanned leather could be viewed as a combination tannage. [10]

j) Post Tanning

The term 'post tanning' refers to the wet processing steps that follow the primary tanning reaction. Post tanning can be separated into three generic processes:

1. **Re-tanning: -** The purpose is to modify the properties and performance of the leather. These changes include the handle, the chemical and hydrothermal stability or the appearance of the leather. Re-tanning chemicals include: minerals, Aldehydic reagents, polymers or resins and syntans.
2. **Dyeing: -** This is the colouring step. Almost any colour can be struck on any type of leather.
3. **Fat-liquoring: -** This step is primarily applied to prevent sticking when the leather is dried after completion of the wet processes. A secondary effect is to control the degree of softness conferred to the leather. One of the consequences of lubrication is an effect on the strength of the leather. Fat-liquoring is usually conducted with self-emulsifying, partially sulphated or sulfonated (sulfited) oils, which might be animal, vegetable, mineral or synthetic. This step might also include processing to confer the leather a required degree of water resistance. [10]

k) Finishing

Leather finishing process in general is nothing but applying a coat on the surface of the leather. This exercise is done for the following reasons. To attain uniform appearance throughout the leather, To camouflage some surface defects, to have the colour of customer choice, to achieve aesthetic appeal for fashion purposes, and to offer durable coat which in turn improves water resistance and easy cleaning and maintenance.[11,12]

2.3 Overview livestock population of the world

From table 1.1 the total livestock population of world was estimated approximately 1.62 billion for bovine animals, 1.08 billion for sheep and lambs, and 0.91 billion for goat and kids (FAO 2011). Share of global herd 80.7% for bovine, 70.4% for sheep and lambs and 95.3% for goat and kids are found in developing countries. From developing country Africa shared 13.6% for bovine, 19.7%sheep and lambs and 28.2% for goat and kids. Out of this 3.23% for bovine, 2.35% for sheep and lambs and 2.44% for goat and kids are found in Ethiopia. [1]

The contribution of developed country is small compare to developing country, which is 19.3% for bovine, 29.6% for sheep and kids and 4.7% for goats and kids.

Table 2.1 Livestock population of the world: Average 2009-2011

livestock population	Bovine animals Million head	Sheep and lamb Million head	Goat and kids Million head
World	1616.6	1083.5	909.4
Developed countries	311.3	321.0	42.5
Developing countries	1303.3	762.5	866.9
Africa	220.6	213.8	256.6
Ethiopia	52.2	25.5	22.2

Source: FAO World Statistical Compendium for Raw Hides and Skins, Leather and Leather Footwear 2011

2.4 Productions of raw hide and skin

Production of bovine hide for the world is approximately 353.4 million pieces out of this 243.9million pieces found in developing countries which is contribute approximately 69%, world production of sheep and lambs 531.6 million pieces from this 356.2 million pieces found in developing countries which is approximately 67% and for goat and kids world production is 473.9million pieces and developing countries production is 455.1 million pieces, approximately 96%.

From 69% of bovine hide Africa contribute 7.8% and out of this Ethiopia contribute 1.05%, from sheep and lambs for Africa approximately 14.58% and Ethiopia 1.6% and from goats and kids for Africa 18.2% and Ethiopia contribute 1.65% (FAO 2011). [1]

Table 2.2 Raw hide and skin: Average 2009-2011

Raw hide and skin	**Bovine-hide million pieces**	**Sheep and lamb skin million pieces**	**Goat and kids million pieces**
World	353.4	531.6	473.9
Developed countries	109.4	175.5	18.87
Developing countries	243.9	356.2	455.1

Africa	27.57	77.5	86.1
Ethiopia	3.7	8.53	7.83

Source: FAO World Statistical Compendium for Raw Hides and Skins, Leather and Leather Footwear 2011

2.5 production of leather

The total world production of leather is around19.99 billion sq. ft. Out of this only 0.55 billion sq.ft is heavy leather, the remaining 19.45 billion sq. ft is light leather. Around 72.7% and 71.5%of heavy and light leather production of the world leather is produce from developing countries. (FAO 2011)

Table 2.3 production of heavy and light leather: Average 2009-2010

Hide and skins	Heavy Leather Thousandtonnes	LightLeather Millionsq.ft
Bovine hidesandskins		
World	**545.9**	**14, 203.15**
DevelopingCountries	396.6	9,104.7
DevelopedCountries	149.3	5,098.45
Africa	4.4	267.05
Ethiopia	0.3	20.4
Sheep and goat skins		
World		**5 245.55**
DevelopingCountries		4 136.45
DevelopedCountries		1109.15
Africa		285.25
Ethiopia		61.3

Source: FAO World Statistical Compendium for Raw Hides and Skins, Leather and LeatherFootwear2011

2.6 Leather Market

2.6.1 Quality and market acceptance of skin

Having a standard system by which the value of a skin can be determined is vital. This is directly related to leather-making characteristics, mainly yield and quality. This standard system is essential both for the seller and buyer in the skin trade. The system is based on various quality grades taking into account all possible defects. The

price of a skin depends on its grade and weight range. The principle of grading skins is similar in many countries. The following shows some of the Ethiopian standards related to skins.

Market acceptance of skins is directly related to quality as determined by the criteria previously discussed. In developed countries, descriptive trade standards have evolved and have been codified in many cases and are often supported by national or international specifications. These are sufficiently respected in trade practice, to facilitate matching sellers' offers and buyers' needs. A similar situation exists in some developing countries. But when heterogeneity prevails, as in many developing countries, values are diminished and lower prices are realized. Therefore, as far as marketing is concerned, there is a need for both improvements of quality and of sorting/ grading to achieve consistency in the lots offered to local tanners or for export. [13, 14]

2.6.2 Local Market of upper and glove

Ethiopia is a country with a population sizes of more that 80 million. Assume that 20 million people wear shoe made of leather. And let's assume also that one pair of shoe per person is the annual footwear consumption. A pair of shoe on an average would consume 3 sq. ft finished leather on an average. So the demand for finished leather can be roughly estimated to be 60 million square feet per annum.

The country`s requirement upper leather has been met both from domestic manufacturing and imports. The present (2012) demand for upper leather is estimated at 3, 967,293 $m^2$for the domestic market. The demand for upper leather for domestic is projected to reach 5,163,400 $m^2$by the year 2017. [15]

The country`s requirement of leather hand gloves is met through local production and import. The present (2012) unsatisfied local demand and export demand for leather hand gloves is estimated at 597,153 pairs. The unsatisfied local demand for the product is projected to reach 829,603 pairs by the years 2017. [16]

2.6.3 International Market

About 19.5 billion square feet of light leather is produced in the world by the leather industry, which comes to a total estimated value of about US$17.08 billion.Over72.1% of the world's leather production, is from the developing countries

(FAO2011). [1] 65% of the world leather production is produced from bovine hides, 15% from sheep, 11% from pig and 9% from goat. All other types of leather from other animals comprise less than 0.2% (ICT2007). From the world's annual leather production, approximately 52% of it goes in to leather footwear production alone (ITC2007).The global footwear production with leather upper amounts to around 4.5 billion pairs, which comes to been approximated worth of US $43.8 billion Only 4.4% goes to leather glove production (FAO2011). [1]

Table 2.4.world leather use by end products–ICT estimates 2007

	million	%oftotal
Footwear	11,925	52
Garments	2,290	10
Auto	2340	10.2
Furniture	3,210	14
Gloves	1010	4.4
Other leather products	2155	9.4
Total	22930	100

For Ethiopia, the demand for upper leather, export market is projected to reach 6,663,400 m^2 by the year 2022. The unsatisfied export demand for the product is projected to reach 1.26 million pairs by the years 2025. [15]

The Ethiopian government supports an export sector of high-value, finished leather products, not semi-processed leather For example, highland hair sheep skin, Cabretta leather, prized for golf gloves, because of its strength and elasticity, brings the Ethiopian herder $2 for the skin needed for one glove, $5 to the exporter of the leather, and $25 to the retailer of a glove manufactured outside of Ethiopia. [17]

About sixty percent of the world's finest quality leather used for making gloves originates from Ethiopia (Teshome, 2008). All these factors suggest that Ethiopia could benefit from a comparative advantage in this sector. However, despite this wealth of raw material, Ethiopia has long been a major importer of finished leather products, such as footwear. Exports are mainly in the form of low value added, semi-processed leather, in 2006 such exports composed less than 0.2% share of the global leather market (ecbp, 2008). Hides and skins account for 97%of all leather related exports, of this, about 87

percent is constituted by semi-processed hide and skins. Export in the form of finished leather and leather products remain insignificant (Teshome, 2008)

Table 2.5 Foreign investment increment in Ethiopia

year	2004	2005	2006	2007	2008	2009	2010
percent	0.43	4.93	23.95	13.28	9.71	74.29	58.53

Source: Ministry of Commerce, "Statistical Bulletin on China's Outward FDI 2010."

From the above table the number of foreign investor increased year to year specially in 2009 and 2010 drastically increased compare to 2008 this is due to Ethiopian government was planned five year GTP and highly promote foreign investor.

The world export of heavy and light leather from bovine hide 56.1% and 56%respectively for developing countries, sheep and goats 73.5% of light leather is for the developing countries. Africa contributes 0.7% of light leather from bovine and Ethiopia 0.04%. From sheep and goats approximately 14.58% for Africa and 2.35% is for Ethiopia.

Table 2.6 Export of heavy and light leather from bovine animals, sheep's and goats: Average 2009-2010

Hide and skins	**Heavy Leather Thousand tonnes**	**Light Leather Million sq.ft**
Bovine hides and skins		
World	57.65	**8291.45**
Developing Countries	32.35	4646.2
Developed Countries	25.3	3645.25
Africa	0.0	58.25
Ethiopia	0.0	3.5
Sheep and goat skins		
World		**1749.45**
Developing Countries		1285.85
Developed Countries		463.65
Africa		255.1
Ethiopia		41.05

Source: FAO World Statistical Compendium for Raw Hides and Skins, Leather and Leather Footwear2011

2.7 Raw material and off-take rate in Ethiopia

Ethiopia stands eighth for cattle, twelfth for sheep and eighth for goat livestock populations (FAO2011). 52.2 million cattle, 25.5 million sheep and 22.2 million goat livestock population are found in Ethiopia ,which is the share of Ethiopia is 4.3% of the world livestock population. [1, 18]

The overall cattle off-take rate in Africa is estimated at approximately 12%, compared to 40% in the USA, and 35% in Australia. Off-take rates range of Africa is vary from 8% to 30% for cattle, from 9% to 45% for sheep, and from 7% to 37% for goats. Ethiopia has Africa's largest raw material supply, and off-take/kill rates there are lower for cattle, but higher for sheep and goats: 8% for cattle, 33% for sheep, and 37% for goats. [19]

However, according to the report of ILRI, 2008 on Live animal and meat export value chains the annual growth of livestock is estimated at 1.2% for cattle, 1% for sheep and 0.5% for goats while annual off take is estimated at 10% for cattle, 35% for sheep and 38% for goats. .

2.8 Ethiopian Sheep Breeds

There are about 14 traditionally recognized sheep populations in Ethiopia. These populations are called sheep types in some literatures. The sheep types are named after their geographic location and/or the ethnic communities keeping them. [20]

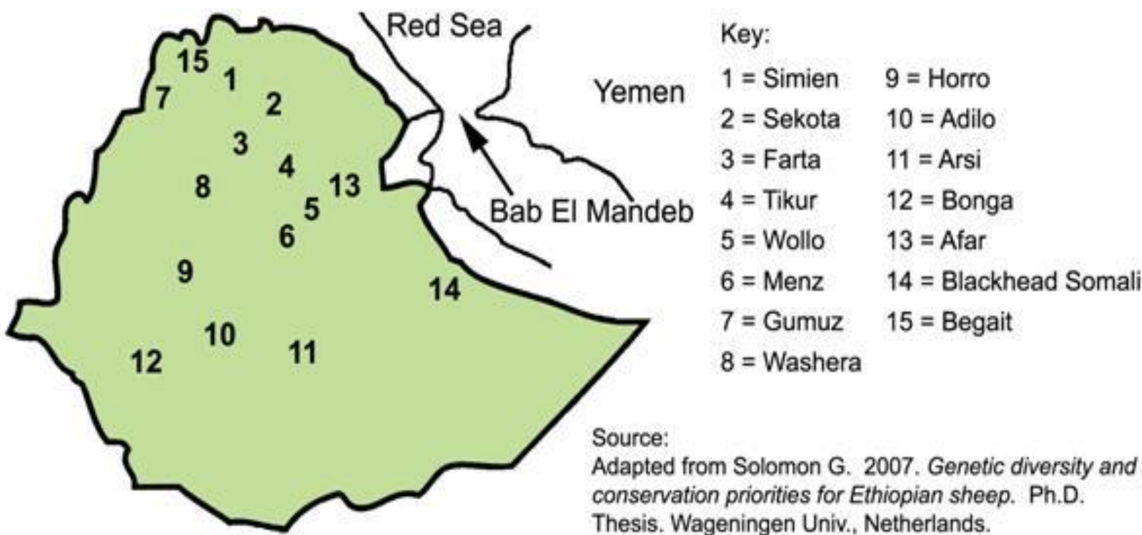


Figure 2.1 Geographic distribution of some of the major Ethiopian sheep breeds

Geographical distribution of sheep breeds of Ethiopia is shown in Figure 2.1. This location map of the breeds can also be used to identify the breed of a population of sheep in Ethiopia. Generally about fourteen sheep type or breeds are recognized in Ethiopia. These are Simen, Sekota, Farta, Tikur, Wollo, Menz, Washera, Horro, Arsi-Bale, Adilo, Bonga, Afar, Black head Somali and Gumuz. The sheeps are classified in to four major groups and nine genetically distinct breeds as shown below (Solomon, 2008). [20, 21]

2.8.1 Some breeds of highland hair sheep [20, 21, 22]

2.8.1.1 Menz sheep (shoa highland sheep)

Short, fat tail turned-up at end; small body size; short-legged; commonly black with white patches, white, brown, white with brown patches; straight-faced; horned males; short semi-pendulous ears with 12% rudimentary ears in the population.

Fig. 2.2 Menz sheep breed

2.8.1.2 Sekota sheep (Tigray highland sheep)

Short, fat tail turned-up at end and fused with main part; hair coat (white animals have fine hair or wooly udder-coat); medium-sized; predominantly plain brown or white coat, few blacks with brown belly; semi-pendulous or rudimentary ears in Wag Himra and Tigray, predominantly rudimentary in Tekeze valley.

Fig. 2.3 Sekota sheep breed

2.8.1.3 Semien sheep

Short, fat tail; well developed wooly undercoat; largest of the highland wooled sheep; plain brown, plain white, brown/white with white/brown patches, plain black and black with brown belly; unique long laterally spiral horn in males and short horns in most females; Reared by Amhara communities.

Fig. 2.4 Semien sheep breed

2.8.1.4 Tikur sheep

Short fat tail, wooly undercoat, small body size, predominantly (60%) black coat; majority short semi pendulous ears.

Fig.2.5 Tikur sheep breed

2.8.1.5 Wollo sheep

Short, fat tail with short twisted/coiled end, occasionally turned up at end; well developed wooly undercoat; small size; predominantly black, white or brown, either plain or with patches of white, black or brown; long hair with wooly undercoat; horned males.

Fig.2.6 Wollo sheep breed

2.8.1.6 Farta sheep

Short, fat tail; wooly under coat; medium size; commonly white (37.5%), brown (27.5%) and black with brown belly (15%), white/brown with brown/white patches; males are horned.

Fig.2.7 Farta sheep breeds

2.8.1.7 Washera (Agew, Dangilla)

Short, fat tail; short-haired; large body size; predominantly brown; both males and females are polled.

Fig. 2.8Washera sheep breeds

2.9 Histology and Chemical composition of skins

Mammalian skin has many physiological functions such as regulation of body temperature, storage of body a requirements, protection, elimination of waste products, sensory detection and communication. The most important for leather making is the protein. Approximate composition of a freshly-flayed hide: Water 64 %, Protein 33 % (**structural proteins** and **non-structural proteins**) **and** others 3% (fat, pigments, mineral salts).

Structural proteins contains: Elastin 0.3 %, Collagen & Reticulum 29 %**and** Keratin 2 %. **Non-Structural proteins:** Albumins and Globulins 1 %, Mucins and Mucoids 0.7 %. **Albumins** are soluble in water and dilute salt solutions, acids and alkali and Coagulates by heat. **Globulins** are insoluble in water but dissolve in salt solutions of moderate concentrations. They are insoluble in strong salt solutions and

coagulate by heat.**Others are:** Fats 2 %**,** Mineral salts 0.5 % and other substances 0.5 % (pigments, etc.) [10]

2.9.1 Histology

Histology is the study of the cellular organization of body tissues and organs. The term is derived from the Greek "histos" meaning web or tissue, and refers to the "science of tissues". The light microscope is the tool used most widely for clinical applications of histology. However, the advent of the electron microscope greatly extended the detail at which sub-cellular structure can be studied. Thus, histology now embraces the study of the structures of both tissue and cells, and the relationship between these structures and physiological function.

The structure of cells and tissues can be distinguished at two levels. The **fine structure** is that which can be distinguished at the level of light microscopy (a magnification of 1000 x or less).Electron microscopes are generally employed to study **ultrastructure** B the detailed structure of the cell cytoplasm, organelles and membranes that is not discernable with a light microscope. [23, 24]

2.9.2 Structural composition of skin

There are three layers to the skin, of which two, the epidermis or outer layer and dermis or middle layer, are important in leather making. The third layer is the flesh layer and is composed of meat, fat, etc., and is removed in the tanning process. The most important layer for leather production is the dermis that is composed of a network of finely interwoven bundles of tissue. The dermis is composed of the grain layer, the corium layer, and the junction or layer where the grain and corium meet. The skin also contains structures and components such as hair, pores, sebaceous glands, hair erector muscles, white collagen, yellow fibers (elastin), blood vessels, sweat glands, hair root capillaries, hair follicles and underlying muscle sheath. [22]

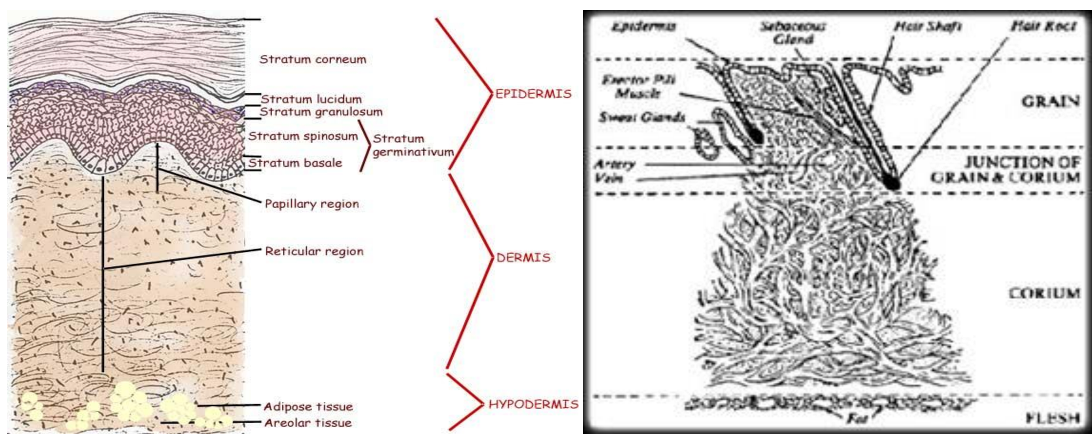


Figure.2.9 cross-section of the skin

a) Epidermis

This is the outermost layer of the raw skin, the barrier between the animal and the environment: it is composed of so-called 'soft keratin' Characterized by a relatively low content of cystine composed to cysteine, i.e. less oxidation of the thiol groups to the cross linking disulfide group.[12] Generally it characterized by

- About 1 to 2% of the total thickness
- In two layers of cells - the outer or horny layer and the inner or soft layer.
- Reproduction of the epithelial cells gives rise to structures such as hair, fat glands, sweat glands, hoofs, horns, nails, scales etc.
- The top most layer - formed by dried up, dead and flat cells which is commonly called the horny layer or Stratum corneum ,
- The lower most layer of the epidermis consisting of the soft cells is called Malpighian layer or stratum germinatum, rests on the corium layer consists of living new created cells which are slightly elongated. Being nourished from corium, they multiply by division. The upper cells gradually get flattened and dehydrated for want of nourishment. When they reach near the top they become more or less dried up and finally turn scaly. This process is continuous.
- The other layers above the malpighian layer are called stratum granulosum, stratum lucidum and stratum corneum. In the early stages of processing, when hair or wool is removed from the skin, particularly by chemical dissolving techniques, the epidermis is also removed. [10]

b) Grain

The uppermost layer in un-haired or de-wooled pelt, the corium minor, is also referred to in the jargon as the grain layer. The structure is fibrous, but the fibres are so fine the appearance is more like solid. The lack of fibber interaction, in comparison with lower layer of the skin, makes the grain weak. There is a layer of collagen on the grain surface, known in the jargon as the grain enamel, it concentrates in the grain.

The surface of the grain is the most valuable part of the skin, because it provides the appearance of the grain: in particular, the enamel confers the appearance to the naked eye of a continuous, reflective surface.

Chemically, the grain is the same as the more obviously fibrous corium, so the impact of chemical modification is the same. However, because the grain has a more solid structure, filling it with stabilising chemicals can be brittle it, allowing it crack when stressed, especially if it is not adequately lubricated. [10]

c) Junction

The grain corium junction is the transition zone between the very fine fibres of grain and the much larger fibres of the corium.

It is an open structure. Consisting of relatively small fibres and carrying other structural components of the skin: these include the veinous system and, in the case of sheepskins, lipocytes, which are the cells that contain triglyceride fat.

The junction is vulnerable to breaking by flexing through mechanical action in the process vessel. The consequent defect is called looseness, in which the detachment of the layer becomes visible when the pelt or the leather is flexed. The effect can occur in any skin or leather, but is facilitated by the presence, and particularly the removal, of the fat cells from sheepskin. The fault affects the ‘break’ of the leather: this is the rippling in the grain surface observed when the leather is bent with the grain uppermost. Coarse rippling, coarse break, is a sign of inferior quality: fine break is desirable and is a feature of high quality leather. [10]

d) Reticular layer (corium major)

The main part of the skin is the obviously fibrous structure called the corium or the corium or the corium major. Found below the grain or thermostat layer, it constituting about 75-90% of the total thickness. Net like woven structure. Fibers are thicker and longer than thermostat layer. The fiber structure varies through the cross section of hide or skin: the fibers increase in size, reaching a maximum fiber diameter in the center of the corium and then decreasing a little as they approach the next lower layer.

The network of fibers, often referred to as wave, consists of fibers dividing and recombining with other fibers. This makes the corium strong, able to resist stresses placed on it: the distribution of a stress imposed on the fibers structure from the point of stress, observed as strength.

An important feature of the corium structure is the angle of weave: experienced observers of corium structure can estimate the average angle- the magnitude of the can provide useful information regarding the process history of the pelt. The average angle of weave in raw skin is about 45°; a lower value indicates greater depletion or relaxation of the corium and a higher value indicates a degree of swelling.

Generally corium is:

- Network of collagen fibers.
- Strongest part of the skin. Towards the center, fibers are coarser and stronger. Predominant angle at which they are woven can indicate properties of leather.
- If fibers are more upright and tightly woven, firm hard leather with little stretch is expected. If they are horizontal and loosely woven, soft stretcher leather is expected.
- Excessive growth of fat cells weakens the corium fiber structure.
- Corium fibers are composed of rope-like bundles of smaller fibrils which consist of bundles of sub-microscopic micelles. These in turn are made of very long, thread like molecules of collagen twisted together. This gives a very strong, tough, flexible structure. [10]

e) Flesh layer

The so-called flesh layer is the layer of the skin closest to the flesh of the animal: although it has a distinct fiber structure, it is still part of the corium. Its structure is characterized by the low angle of weave, always lower than the corium angle of weave. Consequences of the lower angle and finer nature of the fibers are as follows:

1. There is a lesser ability for the flesh structure to relax, to spread out to create greater area, than in the corium: hence, the flesh layer has a controlling effect on the area of the skin or leather.
2. The flesh layer is stronger than the corium.
3. The smaller fibers can be abraded to fine nap for making suede leather, unlike the coarse fibers of the center of the corium. [10]

f) Flesh

A thin layer appended to the corium is called flesh or adipose layer. It is the loose connective tissue lying between the hide or the skin and the actual body of the animal. The flesh consists of adipose (store fat) tissue, elastic fibers, blood vessels, nerves and voluntary muscles. The flesh is removed in the fleshing and shaving operations. [10]

CHAPTER THREE

3. Material and Methods

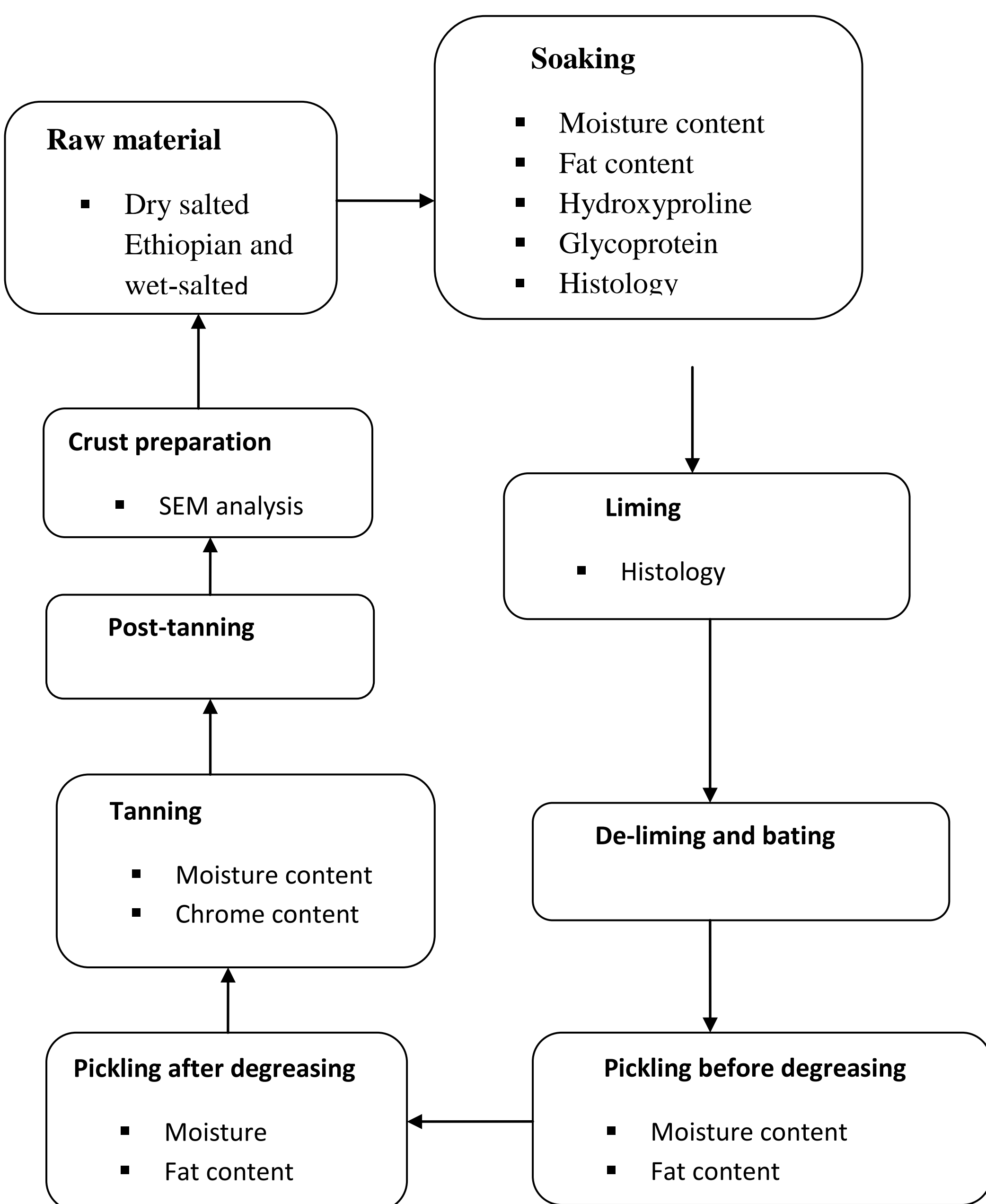


Fig. 3.10 Experimental design of the process

3.1 Materials

3.1.1 Raw materials

Raw materials used for this research were dry salted Ethiopian highland hair sheep skin and wet-salted Indian hair sheep skins.

3.1.2 Leather processing equipment

The equipment that used for the process were: Weighing balance, Drums, fleshing machine, scudding machine or manual scudding operation, summing machine, set-out machine, Vacuum dryer, shaving machine, stacking machine, Gage for thickness measurement, milling drum and finishing operation machine etc.

3.1.3 Laboratory Equipments

Laboratory equipments for conducting histological analysis, chemical and physical testing were: Analytical Weighing balance, sample preserving refrigerator, thermometer, titration standing, Beakers, water bath shaker, desiccators, measuring cylinder, burettes, micro pipettes, filter paper Sohxelet apparatus for fat content estimation, Hot air heating oven, glass blowing section for hydroxyproline and hexosamine estimation, Kel-plus apparatus for nitrogen determination, Different sized standard measuring flasks, Fume hood, UV spectrophotometer, light microscope, scanning electron microscope (SEM), Physical testing equipment (Universal Tensile Meter, lasto-meter, flexo-meter).

3.1.4 Chemicals for laboratories analysis

Chemical and reagents used for histological analysis and chemical testing were potassium sulphate, copper sulphate, sodium hydroxide , boric acid, sulphuric acid hydrochloric acid, Ethanol, di-ethylether, PDAB (p-dimethyl amino benzaldehydes), perchloric acid, hydroxyproline, chloroamineT, methylcellsolve, Buffer (citric acid, glacia acetic acid, sodium acetate trihydrate), Glucoseamine or hexosamine, redistilled acetyl acetone, acetone, formaldehyde, distilled water, sodium hydrogen phosphate anhydrous and sodium dihydrogen phosphate monohydrate and Hematoxylene-Eosine (H & E).

3.2 Methods

3.2.1 Histological analysis [24]

Materials

- **Sample**

The samples of both Ethiopia highland hair sheep skin and as a control Indian hair sheep skin were taken from different part and stages means from neck, belly and butt regions at raw, liming.

- **Reagents for fixation**

Fixation of the sample used for prevent the sample from autolysis. For this purpose we use reagents: formaldehyde, distilled water, sodium hydrogen phosphate anhydrous and sodium dihydrogen phosphate monohydrate. And for the staining we use the reagent Hematoxylene-Eosine (H & E)

Method (paraffin method)

All histological procedures can be divided into a similar series of steps. For the Paraffin method these steps are as follows:

I. fixation

The fixation process must be started as quickly as possible after removal of the sample. The primary function of a **fixative** is to preserve the cellular structure of the tissue. Fixation is necessary to protect and harden the tissue against the deleterious effects of later procedures which otherwise would disrupt cellular structure beyond recognition. Furthermore, fixation minimizes a process called autolysis. Autolysis is the degradation of cellular structure which results from the release of degradative enzymes from the excised tissue itself.

1. Label the plastic sample jar with the names of the sample
2. Fill the labelled jar 2/3 of fixative.
4. Place the sample inside fixative
5. Store the sample with the fixative on the bench top of work area.

III. Dehydration.

After fixation, the water must be removed from the tissue block, a process called **dehydration. Isopropyl alcohol** (IPA) is a favoured reagent because it is miscible in paraffin. The tissue must not be dehydrated rapidly because this will cause distortion of the tissue. The tissue passing through a series of solutions by increasing IPA concentration. In this way the water is fully leached out and replaced with IPA.

Supplies of IPA needed in increasing order:-

70%, 85%, 95% and 100% IPA solutions that was prepare

Steps for dehydration of the sample

1. sample tissue removed from formalin solution
2. washed using water for 1 hr
3. placed the sample in 70% IPA solution for 1 hr
4. placed the sample in 70% IPA solution for 1 hr
5. placed the sample in 85% IPA solution for 1 hr
6. placed the sample in 95% IPA solution for 1 hr
7. placed the sample in 100% IPA solution for 1 hr
8. placed the sample in 100% IPA solution for 1 hr

IV. Infiltration and embedding.

Prior to sectioning, the tissue block must be **infiltrated** with a material that acts as a support during the sectioning process. For the method described here, **paraffin** serves this purpose. We will be using **Paraplast Plus (Fisher Scientific).** During infiltration, the paraffin was equilibrating within the tissue block, eventually occupying all of the space in the tissue that originally held by IPA. After infiltration, the tissue is allowed to solidify in a mold, **embedded** within a small cube of paraffin.

Supplies needed:

- Melted paraffin in metal pitchers
- 4 base molds

Infiltration

1. Discard the 100% IPA from the last dehydration step, and fill with melted paraffin.
2. Allow tissue to equilibrate for 1 hour in an **incubator set at 58°C**.
3. Pour the paraffin into the container labelled for paraffin disposal.

4. Repeat step 1 using fresh melted paraffin.

- **Embedding**

1. Place base-pieces for two embedding molds in a plastic Petri plate – label the plate along the edge with sample name.
2. Decant the paraffin from the second infiltration step into the waste container.
3. Working quickly but carefully, use forceps to transfer the tissue blocks to the well of separate base mold, snap the base of tissue cassette into the base mold and then fill the mold with paraffin.
4. Allow the paraffin to solidify at room temperature. If the paraffin begins to solidify homogeneously around the tissue block, allow the paraffin in the base mold to melt in the incubator, and then allow it to solidify.

V. Sectioning.

Sectioning is accomplished by using a cutting apparatus called a **microtome**.

The microtome was driving a knife across the surface of the paraffin cube and produces a series of thin sections of very precise thickness. The objective is to produce a continuous "ribbon" of sections adhering to one another by their leading and trailing edges. The thickness of the sections can be preset, and a thickness between 5 - 10 µm is optimal for viewing with a light microscope. The sections can then be mounted on individual microscope slides.

Preparation and mounting of the embedded tissue block on the microtome is very important to successful sectioning. The paraffin surrounding the tissue block must be first trimmed, and then secured to a holder which is then mounted on the microtome.

- **Trimming**

Trimming used to correct section. It was trimmed in such a way that the material lies in the centre of the perfect rectangle.

VI. Mounting of sections on microscope slides.

The sections are permanently attached to microscope slides.

<u>Supplies needed</u>

- Microscope slides.
- Slide storage box
- **Hematoxylin (Surgipath/Leica)**

- **Eosin (Surgipath/Leica)**

Preparing the microscope slides

1. Label the microscope slides at one end with the tissue type
2. Wash the microscope slides with soap and water, and rinse free of soap with tap water.
3. Place the slides in a coplin jar and rinse several times with roH2O.
4. Handling the slides only by their edges, place the slides in slide storage box, and allow them to dry.

Mounting sections on microscope slides

During sectioning that the sections are not perfectly flat, but rather slightly crinkled. Then sections become flattened by floating them on water heldat 45°C. The solution also contains an adhesive, **StayOn (Surgipath/Leica),** which causes the tissue section to bind to the slide.

1. Carefully transfer the sections to a solution held in a 45OC water bath. Within a few seconds we can see the sections flatten and the wrinkles disappear.
2. Dip a clean microscope slide into the adhesive solution, and slowly pull it upward, out of the solution, allowing sections to adhere to the surface. Make sure that the slide is oriented with the label facing upward.
3. Dry the bottom of the slide and carefully blot excess adhesive from around the sections (be careful not to touch the sections themselves).
4. Allow the slides to dry overnight in the storage box.

VII. Clearing and staining.

Before a section can be stained the paraffin must be removed, a process called **clearing**. After clearing, only the tissue remains adhering to the slide. Clearing is accomplished by passing the mounted sections through the solvent **Clearene (Surgipath/Leica) or zylene** that dissolves the paraffin.

The two stains most widely used for routine work are **hematoxylin and eosin Y** (commonly abbreviated as **H & E**. (Hematoxylin stains negatively charged structures, such as DNA, a blue color. Eosin imparts a red color to most of the other cell components. To produce permanent staining with hematoxylin, the dye must be

oxidized to "hematein", which is achieved by treating the tissue sections with **Scott's solution**.

Supplies needed (per group of two):

5. coplin jars IPA solutions
6. Hematoxylin Eosin
7. **Clearene (Surgipath/Leica)** – clearing agent

Clearing and staining of slides was done with the following steps

- **Clearing and Rehydration**

1. Clearing agent #1 3 minutes
2. Clearing agent #2- 2 minutes
3. Clearing agent #3 1 minute
4. 100% IPA 30 seconds
5. 85% IPA 30 seconds
6. 70% IPA 30 seconds
7. Tap water 30 seconds

- **Staining**

8. Hematoxylin 2 minutes
9. Tap water 30 seconds
10. Scott's solution 1 minute
11. Tap water 30 seconds
12. Buffer 1 minute
13. Tap water 30 seconds
14. 70% IPA 1 minute
15. 95% IPA 1 minute
16. Eosin Y 1 minute

- **Rinsing, Rehydration & Mounting Prep**

17. 95% IPA 3 minutes
18. 100% IPA 3 minutes
19. Clearing Agent 1 minute
20. Clearing Agent 1 minute
21. Clearing Agent 1 minute

VIII. preparing permanently mounted sections.

The final step in this procedure is to permanently mount the sections under a cover slip. This is accomplished by covering the section in a medium that will harden and produce a clear binder between the slide and cover slip. The ideal mounting medium should not distort the stain colour, or yellow and become brittle with age. We will use a mounting resin called **Permount (Fisher Scientific).** .

1. Place 2-3 drops of resin over the section.
2. To avoid entrapping air bubbles, lower the cover slip slowly from one side of the droplet.
3. Place the slide on the slide warmer and carefully place a lead weight on top of the cover slip. There should be enough mounting medium to completely cover the bottom of the cover slide, and budge slightly around the edges.
4. Leave slides on the warmer for at least 24 hours; excess medium can then be cut from edges of cover slip with a blade.

3.2.2 SEM analysis

Materials

Raw Materials used in this experiment are both Ethiopian and Indian hair sheep skin at crust stage from butt region

- **Apparatuses: -**

  For this analysis are: - Surgical blade, desiccators, measuring cylinder, beaker, Edwards sputter coater and SEM.

Lyophylzer

Samples mounted on plates

Gold Sputtering Equipment　　　Scanning Electron Microscope

Fig.3.11 SEM Equipments

- **Reagents:** acetone and ethanol are the main reagents while the specimen is at crust stage. Formaldehyde and glutaraldehyde are used when the spacemen is raw to protect it from putrefaction.

Methods

- **Fixation**

  Is the first step, in the case of crust sampling no need of fixation because the sample was in crust stage means already stabilized.

- **Dehydration**

After complete fixation the sample were dehydrated gradually with the solution of acetone with the increasing concentration (50%, 70%, 90%, 90% and 100%) each for 1hr.

After dehydration with acetone the sample were treated with different percent of hexamethyldisilazane (HMS), to get the original shape of the sample. Which is the sample tissue was placed in HMS with increasing concentration (30%, 60%, 80%, 100% and 100%) 1 hr each

Then the sample was freezed in deep freezer at -40 ^{o}C for overnight. And the sample was dried in lyophilizer at -40°C for 1 day to avoid the absorption of moisture. After this the samples were single cut in parallel and perpendicular position in small size and attached to a mounting stub with double face cello tape. Before mounting the

samples, the plates was cleaned with acetone and then both side adhesive tape was placed on the plates, trimmed and peeled the outer cover of the tape. Then on single plate both the parallel and perpendicular samples were mounted. After this the two side edges of the samples were coated with carbon so as to make them conductive. Then the samples were coated with gold in gold coating machine. And then the samples were taken for SEM and the tissues were observed at different magnification power.

3.2.3 Chemical characterization

3.2.3.1 Moisture content [25]

Moisture content of the skin is different at different stage (raw, pickle and wet-blue)

Materials

- **Sample:** The sample were taken at raw, pickle and wet-blue stage from butt area
- **Apparatus:** The apparatus used for this analysis were china dish, scissor, weighing balance and hot air oven.

Methods (SLC 3 (IUC5)

The method used for this test was SLC (IUC5) and the testing procedures are:-

The samples were taken and weighing from raw, pickle and wet-blue stage. Then it cut in to pieces , allowed to dry to make them free from moisture in an oven at a temperature of 100°c for 3-5hr or until constant weight was obtained. Then, allowed to cool inside the desiccators to prevent moisture absorption. The dried samples were taken the final weight.

Finally, the moisture content was estimated by using the following formula

$$\%\mathrm{moisturecontent} = \frac{\mathrm{massofsamplebefordrying} - \mathrm{Massofsampleafterdrying}}{\mathrm{massofsamplebeforedrying}} \times 100$$

3.2.3.2 Fat content estimation [26]

Fat content of raw skin, pickle before and after degreasing are different.

Materials

- **Sample:** The sampling position were taken from butt area of Ethiopian and Indian hair sheep skin at raw, pickle before and after degreasing stages.
- **Apparatus:-**The apparatus used for this analysis were thimble, scissor, weighing balance, filter paper, soxhlet apparatus, round bottom flask, stove, hot air oven, desiccators, crucibles and hood chamber.

Fig 3.12 Soxhlet apparatus

- **Reagent /chemical:** The main reagent to conduct this analysis was petroleum ether

Method

The method for this test was SLC319. Using the following procedure

5gm of samples were weighed and cut into small pieces and prepare a thimble. Then the small pieces of samples were rolled with filter paper and staple using stapler. Then put it in soxhlet estimation apparatus using petroleum ether as an extractor by Filling it three fourth (3/4) of the round bottom flask with petroleum ether. After this it was left it for 5 hr on the stove at a temperature of 70°c. After 5 hr petroleum ether was

evaporated inside the chamber hood until it remains small amount. Then put round bottom flask inside the hot air oven until all the remaining amount of Petroleum ether evaporated. After totally evaporating petroleum ether the round bottom flask was put inside desiccators to cool it and prevent absorption of moisture. Finally the round bottom flask was weighed

The amount of fat content was estimated using the following formula

$$\%\ \text{fat content} = \frac{\text{finalwt} - \text{initialwtx100}}{\text{dry base wt of ample}}$$

3.2.3.3 Nitrogen and Hide substance estimation using KEL plus system [27]

Materials

- **Sample:** The samples were taken at raw and wet-blue stage from butt, neck and belly area for this analysis.
- **Apparatus:** The equipments used to conduct this study were, weighing balance, scissor, blade, KEL plus system, conical flask, funnel, titration stand and burette. The main apparatus for this is

Fig: 3.13 Kjeldahl apparatus

- **Reagents:** chemicals used in this study were, Potassium Sulphate, Copper Sulphate, and Conc. H_2SO_4, boric acid, alkali (NaOH), mixed indicator and Hydrochloric acid.

Method

For this test ASTM standard test method was used. It contain three main steps

Digestion

- System switched on and the unit was initially pre-heated to 200 ^oC then gradually increase up to 350^oC.
- Sample was taken in 250 ml Macro DTL tube
- Convenient mass of catalyst mixture [5:1 (Potassium Sulphate: Copper Sulphate)] was added to the digestion tubes.
- Known volume (20ml) of Conc. H_2SO_4 added
- Samples loaded in the digestion unit with manifold.
- The KelVac system was switched on and tap water was connected with maximum pressure for KelFlow system.
- The temperature was then increased to 400 ^oC
- After 2 hours, a clear green colour was observed indicating that the digestion of the sample was over.
- Then allow to cool

Distillation

- After the digested sample cooled the system was switched on.
- Before starting the sample testing, the tap water was opened for cooling purpose (INLET and OUTLET were checked).
- A solution of boric acid , alkali (NaOH) and Hydrochloric acid was prepared (4% , 40%, 0.1 N respectively)
- The water level, Tap and cap must be opened so it must be checked
- The alkali, Boric acid solution was loaded to the system through silicon hoses provided at the back of the equipment while you wait for the READY signal.
- A known volume (25ml) of Boric acid with mixed indicator (2-3 drop) was taken in 250ml conical flask and place at the receiver end.
- The sample tube was loaded in sample side.

TITRATION

1. Taken 0.1N HCl in burette. (10 ml burette were used)
2. First find out the Blank value (BV)
3. Titrate the sample and note down the Burette value (TV)

Finally the amount nitrogen in raw skin and wet-blue leather were calculated as follow

$$\% \text{ ofNitrogen} = \frac{14.01 \times 0.1\text{N} \times (\text{TV} - \text{BV})}{\text{W} \times 1000} \text{x } 100.$$

Hide substance can estimate by multiplying the value of nitrogen content by a factor of **5.62**.

3.2.3.4 Chrome content estimation [28]

Materials

- **Sample :** The sample were taken from butt area at wet blue stage
- **Reagents:** Chemicals used in this analysis were, DH_2O, Nitric acid, sulphuric acid, perchloric acid and sodium hydroxide pellets.
- **Apparatuses:** The equipments used to conduct this study were, weighing balance, funnel, conical flask, parcela flask, UV- Vis spectrophotometer, stove (hot plate), alkali PH paper, chamber hood, pipette and50 or 100 ml standard flask.

Method

The method for this test was acid digestion (perchloric acid oxidation) method

- 0.5gm of solid samples or 3 ml of liquid sample were weigh.
- Acid digestion was taken using – 5ml of nitric acid, 3.5ml of sulphuric acid and 11.5 ml of perchloric acid.
- The funnel was placed over the mouth of conical flask + parcela flask and kept it on hot plate until the solution turns to orange.
- Then cooled it and add 10 ml of distilled water and boiled for 5 min, so that the chrome gets completely digested.

- The digested solution was made up to 100ml means stock solution using standard flask pipette out 10 ml from stock and make up to 50 ml or 100ml to dilute the solution.
- Then sodium hydroxide pellets was added in to diluted solution so that the acid PH turns to alkaline above 12PH.
- OD of the solution was read at 372nm.
- Finally the % of chromium were calculated as follow

$$\% \text{ of chromium } (Cr2O3) = \frac{\text{ODvalue}}{4820} \times \frac{152x52}{104} \times \frac{100}{\text{wtofsample}} \times \frac{100}{10} \times \frac{100}{1000}$$

Remark:-

- 4820 :- molar extinction coefficient (ε)
- 152:- Molecular wt. of chromium oxide
- 52:- atomic wt of chromium
- 100 volume of stock solution
- 104 : atomic wt of molecular chromium
- 100:10 dilution factor

3.2.3.5 Determination of Hydroxyproline [29]

Materials

- **Sample: -**The samples were taken at raw and pickle stage from different area (neck, butt and belly) of both Ethiopian and Indian sheep.
- **Apparatus:-**The apparatus used for this analysis were: weighing balance, scissor, blade, hydrolysis tube, glass blowing, test tube stand, hot air oven, china dish, water bath, PH paper 5 or 10ml of standard flask and UV Vis spectrophotometer.
- **Reagents:-** The chemicals used for this analysis were: - HCL, DH_2O, Chloramine T, Perchloric acid, PDAB, citric acid monohydrate, glacia acetic acid, sodium acetate trihydrate, NaOH, methyl cellosolve, methoxyl ethanol and standard hydroxyproline solution.

Method

The method used for this analysis is Woessner JF (1993) ‘’the determination of hydroxyproline in tissue and protein samples’’.

This method contains preparation of standards and reagents.

- **Procedure for preparation of standards**
  - Different standard hydroxyproline solution was prepared from a known concentration (i.e. 1mg/1ml).
  - A stock solution was prepared by dissolving 10 mg of liquid hydroxyproline in 100ml of 0.001NHCL standards were prepared by adding the stock with water to obtain concentration of 2-10µg/2ml
  - From this known hydroxyproline solution take 20, 40, 60, 80, 100 and 120µl were taken and placed in test tubes. Each test was made up to 2000 µl by adding distilled water.
- **Preparation of Reagents**
  - **Chloramine T: -** 1.41 g chloramine T in 20 ml water, add 30 ml methyl cellosolve and 50 ml hyprobuffer.
  - **PDAB: -** prepared for 20ml volume (5:1 ratio of methylcellosolve to PDAB) means 4gm of PDAB dissolve in 20ml methoxyl ethanol.
  - **Perchloric acid: -** 30ml prepare for that 8.1ml perchloric acid plus 21.9ml
  - **Buffer:-** 5gm citric acid monohydrate, 12ml of glacia acetic acid, 12gm of sodium acetate trihydrate and 3-4gm of NaOH were made up to a final volume of 100 in distilled water, the PH was carefully adjusted to 6.0 and the buffer was stored in refrigerator
- **Procedure for conducting this analysis**
  - 0.015gm of sample was weighed.
  - Then it was placed in hydrolysis tube.
  - To this 1 ml of 6N HCl was added.
  - After this the tubes were sealed in glass blowing section.
  - Then the tube was incubated at 100 ^{o}C in hot air oven for 20 hours or until completely hydrolysed.
  - After cooled down the hydrolysis tubes were de-sealed.

- The hydrolysed samples were taken and placed in china dish and were allowed to evaporate in water bath.
- The evaporation of HCL was continued by adding distilled water to the china dish until the pH reaches 7 or the smell of HCL is removing.
- The final solution was made to 5 (pickle stage) or 10 ml (raw stage) by adding distilled water. From this solution 60µl was taken. Means
    - 60µl from belly sample then add 1940µl of D.H_2O
    - 60µl from butt sample then add 1940µl of D.H_2O
    - 60µl from neck sample then add 1940µl of D.H_2O
- Then add 1 ml of chloroamine.T to all test tubes (blank, std. and sample) then kept for 20min at room temp.
- 1 ml of percholoric acid was added after 20 min incubation and then incubated for 3-5 min at room temperature.
- PDAB solution was incubated for certain min. at 60^0c in water bath to solubilize it.
- After this 1 ml PDAB was added and incubated at room temperature for 5 min. This followed by 20 min incubation at 60 ^oC by keeping in water bath. Then taken out from water bath allow to cool at room temp.
- After finished incubation time both standard and sample solution was taken for measurement of absorbance at 557 nm in UV Vis spectrophotometer. At the same time blank solution without standard hydroxyproline was also prepared and its absorbance was measure similar to others.

Finally, hydroxyproline content was calculated based on dry basis moisture content and from standard curve using the following formula.

First find the concentration from standard curve

y= mx + b

Where, y = OD value of the sample, m = slope, x = unknown concentration of the sample that calculated from std. Graph and b = intercept we can use or not use in calculation because the value of this is almost approach to zero

$$\text{Concentration} = x = \frac{\text{OD}}{\text{slope}}$$

Hyp = $X/(\text{mg of sample (tissue)})$

To convert HYP to collagen, we can multiply the result by factor of 7.54

Collagen content = $(X * 7.54)/(\text{ mg of sample})$

3.2.3.6 Determination of Glycoprotein (hexosamine) content [30]

The hexosamine condenses readily with acetyl acetone to give pyrroles. The pyrroles give colour reaction with P-dimethyl amine benzaldehyde.

Materials

- **Sample: -**The samples were taken at raw stage after main soaking from butt, neck and belly area of both Ethiopia and Indian sheep skin.
- **Apparatuses :-** Equipments used for this analysis were: hydrolysis tube, balancing weight, scissor, blade, hot air oven, and glass blower, test tubes with its stand, alkali PH paper and UV-ViS Spectrophotometer
- **Reagents: -**Chemicals used for this study were: redistilled acetyl acetone, 0.5M Sodium carbonate, 4-N, N' dimethylamino benzaldehyde, absolute ethanol, conc. HCl, NaOH, DH_2O and standard hexosamine.

Method

Glycoprotein content of the sample tissues was estimated by Elson-Morgan Assay

Preparation of reagents

Reagent 1:- 1ml of redistilled acetyl acetone was added to 50ml of 0.5M Sodium carbonate

Reagent 2:-0.8gm of 4-N, N' dimethylaminobenzaldehyde was added to 30 ml of absolute ethanol mixed with 30ml of conc. HCl.

Procedure for this analysis

- 0.5g of raw Ethiopia and India Sheep skin was taken from (Butt, Belly and Neck) for determination.
- Then it was placed in hydrolysis tube. To this 3.75ml of 6N HCl was added.
- After this the tubes were sealed in glass blowing section. Then the tubes were incubated at 100 ^{o}C in hot air oven for 20 hours.
- Hydrolysis tubes were de-sealed after completely hydrolysed.
- Acid hydrolysed samples were neutralized to pH 10 and made up to a known volume by adding of 4M NaOH and distilled water respectively.
- Hydrolysate (or standard) solution (250µl containing, 80µl hexosamine) was mixed with 250µl of reagent 1 and the final volume of the solution was adjusted to 600µl with distilled water.
- The tube was stoppered and heated at110^{O}C for 20 min. The solutions were allowed to cool to room temperature.
- 1ml of absolute ethanol was added, taking care to wash down all droplets of condensation into the bottom of the tube.
- 250µl of reagent 2 was added and diluted to a final volume of 2.4ml with absolute ethanol.
- The tubes were heated at 65°C for 10 min and the colour was slightly pink/ red, then cooled at room temperature and absorbance was measured at 530 nm in Shimadzu 2100 S UV-VS Spectrophotometer. The unknown values calculated from standard curve by using the same formula to estimation of HYP.

$$\mathbf{y = mx + b}$$

$$\text{Concentration} = x = \frac{\text{OD}}{\text{slope}}$$

$$\text{GP} = \frac{x}{\text{mg of sample (tissue)}}$$

3.2.4 Physical characterization

For every physical testing, before starting any test the sample was conditioned for 48hr in a specified temperature and humidity. For this purpose we use the standard test method [31]

3.2.4.1 Tensile strength and Elongation at break [32]

Tensile strength is the ultimate strength of the leather that includes grain, corium and flesh layers. In this test elongation property of the leather can also be measured. Permanent elongation that is responsible for permanent set (plastic character) of the leather also can be tested. Both are a type of bulk properties. Tensile strength is defined as strength of material in terms of force per unit area of cross section while applying force in linear direction.

Materials

- **Sample:-**The sample were taken from butt area of both cabretta and glove
- **Apparatus and equipment:-**Apparatuses used for this test were: hydraulic cutting machine, steel die of standard dimension, steel ruler, and thickness gauge, Tensile strength testing Machine (Dynamometer) or universal tensile meter (UTM) and PC system.

Method

For this testing ISO3376:2002 standard testing method was used

Procedures:-

- Dumbbell shaped of test pieces was cut with a required shape and size (10mmx50mm).
- The sample cutting positions were from parallel to back bone direction of leather (along direction) and three samples right angle to back bone direction (across direction),
- Then conditioned them in a controlled atmospheric condition (20±2°C & 65±5 % R.H or 23±2°C &50±5 % RH) for 48 hours
- The thickness of each test pieces were measured using thickness gauge at three places on grain side of the leather test specimen and record the average thickness.
- The width of the leather was measured using a steel rule.
- The area of cross-section was calculated on the test specimen by multiplying its width and thickness.
- The distance between the grips of the tensile tester was set as 50 mm for standard test specimen.

- The test specimen was inserted between the grips, then tighten the grips with sufficient pressure.
- The tensile testing machine was operated at a speed of 100±2 mm/minute until the leather sample breaks.
- The machine was stopped immediately, and then the distance between the two grips was measured and recorded the maximum force found at leather break.

Finally both Tensile strength and percentage elongation at break were calculated as follow

$$tensile\ strength\ = \frac{breaking\ load\ (N)}{width\ (mm) * thickness\ (mm)}$$

$$\%\ Elongation = \frac{(b - a)x100}{a}$$

Where, a = Initial distance between the jaws in mm and b = final distance between the jaws in mm.

3.2.4.2 Double edge Tear strength- [33]

Tear strength is also another important bulk property test. This test is the most preferable test for leather than tensile strength by many of the customers including BS EN ISO 20345 Safety shoe standards.

Materials

- **Sample: -** The samples were taken from butt area of cabretta and glove**.**
- **Apparatus and equipments:-** The apparatuses used for this test were: hydraulic cutting machine, cutting knife 50 mm x 25 mm size having a central slot, L shape sample holder, thickness gauge, universal tensile meter (UTM) and PC s

Method

The method for this test is ISO3377/IUP 8:2002 test method was used.

- Cut six test specimen (three test specimen from along direction and three test specimen from across directions) using a cutting knife 50 mm x 25 mm size having a central slot.

- Condition the test specimen for 48 hours and measure the thickness.
- Insert one of the test specimens through the slit into the sample holding "L" clamps that are fixed to the tensile tester.
- Conduct the test by operating the tensile tester at the rate of 100 ± 10 mm/ minute speed until the test piece is torn apart.
- Record the maximum force and continue the test for remaining test specimen.Finally it was calculated as follow:

$$Tear\ resistance\ (N/mm) = \frac{Average\ force}{Thickness}$$

3.2.4.3 Stitch Tear Strength, Double Hole [34]

This test method is designed to measure the load required to tear leather through two holes in the test specimen. It gives an indication of the resistance of leather to tearing. It is particular value in estimating the durability of leather to withstand tearing stresses encountered in the manufacture of Glove, garments, and upholstered products. The thickness of the specimen and direction of tear relative to the backbone will affect the uniformity of the test results.

Materials

- **Sample:-** The samples were taken from butt area of cabretta and glove
- **Apparatus:-**Thickness Gage, a dead weight type of thickness gage, steel Dieto cut test specimens, Paper Clip with wire diameter, universal tensile meter (UTM) and PC.

Method

ISO 5914:2002 standard test method was used

- Determine the thickness of the specimen on the long axis near one end.
- Bend the wire into a "U" shape, preferably by bending over a 1⁄4 in. (6.35 mm) rod, and pass the ends through the holes in the specimen so that both ends project from the flesh side of the specimen. Clamp both ends of the wire in the testing machine grip, the jaws of which have been covered. Clamp the free end of the specimen in the other grip of the testing machine.
- Operate the machine at 10 ± 2 in. (254 ± 50.8 mm) per min until the specimen tears. At the instant that the specimen begins to tear, note and record the load

registered by the machine. Finally the stitch tears strength of the specimen was calculated same as double edge tear strength.

$$Stich\ Tear\ resistance\ (N/mm) = \frac{Average\ force}{Thickness}$$

3.2.4.4 Lastometer test [35]

This test method is intended to determine the grain crack force and distension of leather when used for shoe upper. Shoe upper leather often shows slight crack in the toe area at the time of lasting operation in-spite of the leather has good tensile and tear strength properties. This is due to weak grain surface characteristics of leather by more filling and loading of tanning and re-tanning materials in the grain side.

Materials

- **Sample: -** The sample was taken from butt area of cabretta.
- **Apparatus and equipments: -** Equipments used were: - lastometer it consists of a6.25 mm spherical steel ball headed rod to press from flesh side the leather to produce distension, circular cutting knife and hydraulic cutting machine.

Fig 3.14 Lastometer equipment

Method

For this test ISO 3379/2005 test method was used. Using the following procedures

- Three test specimens were cut with 44.5 mm diameter using a circular cutting knife.
- The test specimens were conditioned at $20^oC \pm 2^oC$ and $65 \pm 2\%$ RH for 48 hours.
- Then one test specimen was tightly clamped between the circular rings facing grain side upwards in the machine.

- The machine was started by forcing the plunger at the rate of 0.2 ± 0.05mm/s.
- Continuously observed the surface of the specimen at the centre for initial crack on the grain.
- The maximum distance and force at this point was recorded.
- This test was repeated for the remaining two specimens.

Finally the mean values of the test results were calculated as follow.

a. Grain crack load in Kgs or N

b. Distension at grain crack, mm

3.2.4.5 Flexing Endurance (flexing resistance) of finished leathers [36]

Flexing endurance is one of the wear properties of leather. If leather surface coating (finish) is not properly applied with correct proportions and following all technical procedures, the finish surface upon bending repeatedly develops cracks, flaking, brittle and delamination.

Materials

- **Sample: -**The samples were taken from butt area of cabretta.

- **Apparatus and equipment: -**

Apparatuses used for this test were: - hydraulic cutting machine, rectangular cutting knife, and vamp flexor equipment.

Fig 3.15 vamp flexor

Method

For this test vamp method was used. It is primarily intended to determine the tendency for materials to crack or otherwise fail at flexing creases. In particular this test simulates conditions in the vamp part of footwear during walking. The test can be conducted with either wet or dry specimens at room temperature. The test procedures are as follow:

- 64±1 x 64±1mm square of four test specimens were cut, two from along direction and two from across direction.
- Then conditioned it for 48hours at 20°C and 65 % RH.
- The test specimens were folded evenly over the pair of V-shaped clamps and hold in place by fitting the upper V-shaped part of each clamp.
- Half of the test specimens were mounted with their along direction running between the clamps, and the other half at 90° to this so that the across direction runs between the clamps.
- At the end the clamp was fully tighten, ensured the test specimen was not loose and then tighten the clamp at the other end.
- Then slowly moved the clamps together and the specimen were watched to ensure that the centre section of each specimen folds downwards. If this was not the case, apply gently pressure to the centre of the ridge as the clamps move together to see the downward fold.
- For wet test, flesh side of the specimen was wetted with 1ml. of distilled water using a pipette; it was spread uniformly with a glass rod to within 5mm from the edge of the test specimen.
- Then the wet specimen was loaded on to this machine.
- The machine was run and the test specimen was assessed at 10,000, 50,000, 60,000, 70,000, 80,000, 90,000, 1,000,000, 2,500,000, 3,000,000 and 5,000,000 flexes.
- After completion the above no of cycles the machine was stop and removed the test specimen and the specimens are visually examined for sign of damage.

For all the test specimen of the flexing damage, the following descriptions was used

1. No effect or slight creasing or piping

2. Marked to severe creasing or piping
3. Slight cracking
4. Marked cracking
5. Severe cracking
6. Complete failure

3.2.5 Processes description for cabretta and glove

The process follows for these products were convectional process. 5 pc for cabretta and 3 pc for gloves of dry salted Ethiopian sheep skin and wet salted Indian sheep skins were taken. Then soaked 2 days for Ethiopia sheep due to it was dry salted however Indian sheep was for 5--7 hr only. After completing soaking the sample were taken from butt, neck and belly area for conducting of histological analysis, moisture content, fat content, and hydroxyproline and glycoprotein estimation of two species. The convectional processing for liming was continued, for cabretta one and half day drum liming was done however for glove leather 2-3 days drum liming (long liming) were done to give the softness for glove. Then fleshing operation was done using fleshing machine, after this the sample were taken for Histological analysis to see opening up of the fibre. Then de-liming and bating operations were continuing using conventional process. For glove, the percentage of bating enzyme was more than cabretta to get more fibre opening.

Pickling process also conducting with conventional process, for glove leather the pelt was aged for 3 days in side pickle liquor and degreasing was conducting 2-3 times, however for cabretta simply done degreasing then proceeds to tanning process because we don’t want softening for cabretta. After completing degreasing, samples were taken for determining the fat content.

Tanning process was same for both product and then sample were taken for determination of chromium oxide. Post tanning also conducted using conventional process of glove and cabretta.

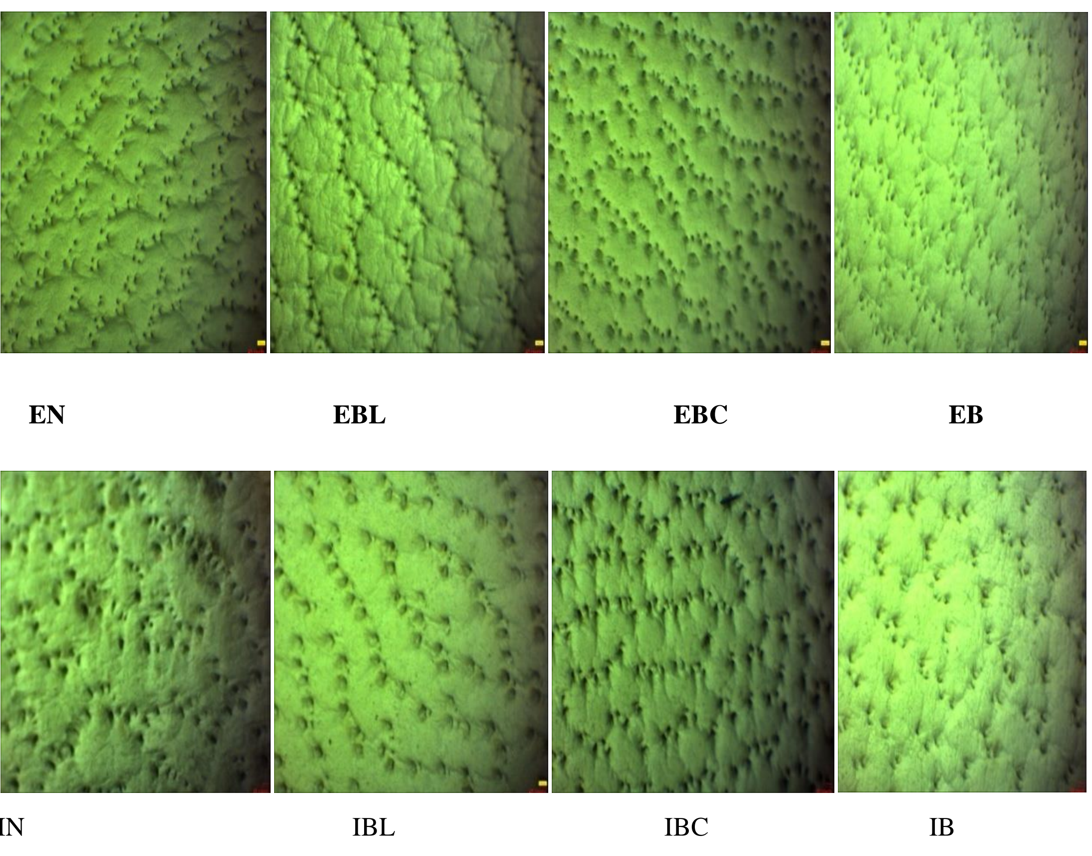
CHAPTER FOUR

4. Result and Discussion

4.1 Surface pattern and hair pore count

The samples taken from different region (neck, belly, backbone and butt) of crust leather first analysed using Stereo Microscope.

Fig. 4.15 shows the grain surface pattern and the hair pores of Ethiopian and Indian hair sheep skin. The hair of both sheep can be divided in to two kinds, coarse and fine. This can easily see from surface pattern. The hairs and their distribution of this two species are different at different region, in neck region we see more hair pores grouping than the other three regions and less hair pore grouping is found in belly region.



E-Ethiopian, **I**- India, **BL**- belly, **BC**- back bone, **B**- butt

Fig. 4.16 The distributions of hair in neck, belly, backbone and butt area of Ethiopian and Indian sheep crust leather

Table 4.7, shows the average number of hair pores per inch square of the four regions. From this table we can easily examine that the neck region of both sheep skin have more hairs per inch square and less in belly region. More hair pores in neck and backbone region shows that during un-haring process the hair cannot easily removed this is due to the depth and density of the hairs have much more in this regions and also we can easily see the mark of the pores on the grain patterns of the crust as well as finished leather. Whereas, in belly region the number of pores are small this is due to it is the loser or the thinner area in the skin than the other three region and the hairs also doesn't have depth and density also more are a type of fine hair. Number of hair per inch square in butt region is found in the medium these three regions.

Table 4.7 hair pore count

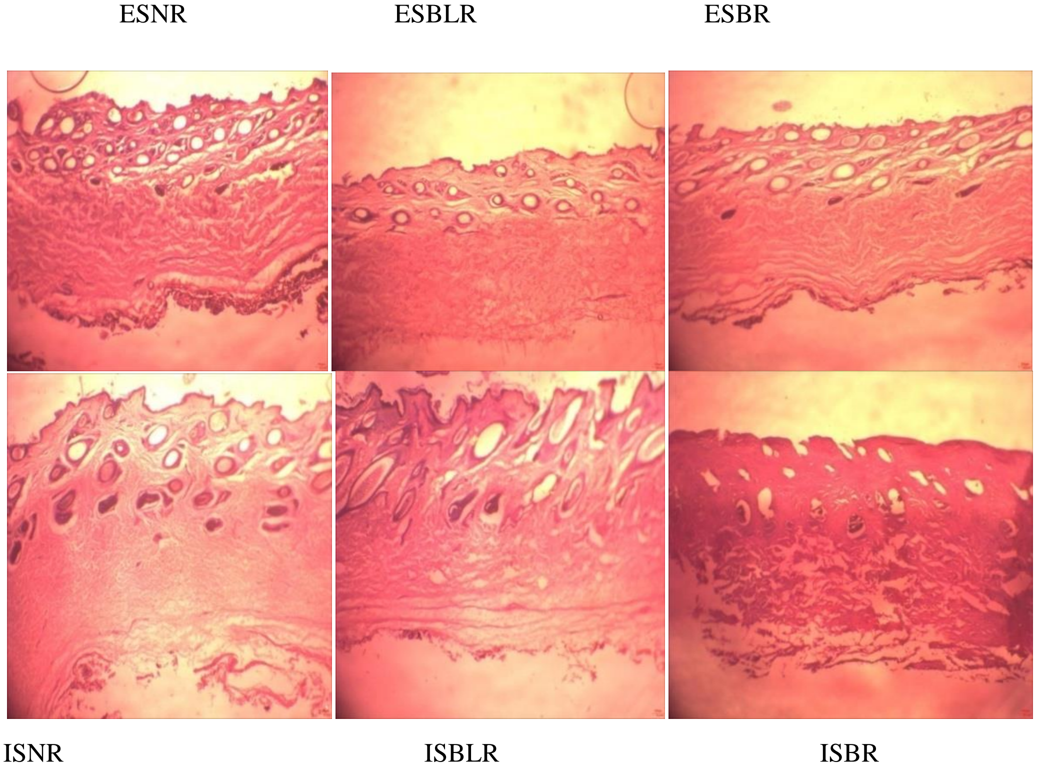
Type of skin	**Average number of hairs per inch square**			
	Neck region	Backbone region	Butt region	Belly region
Ethiopia sheep	15140±5	13729±5	12799±5	10465±5
India sheep	8,988±5	6302±5	5167±5	4167±5

When we compare to Ethiopian and Indian sheep skin, Ethiopian highland sheep skin have more hair pores than Indian sheep skin, this makes Ethiopian highland sheep skin has fine and smooth grain surface, which gets more acceptance in the world for making of good quality glove.

4.2 Histological analyses

Histological analyses of Ethiopian and Indian sheep skin were done by taking the sample from neck, belly and butt region at raw and liming stage. To see the cross section of these regions (25 micron thickness) the microscope of 4 X objective lens was used. Fig. 4.16 shows main structure of the skin from epidermis to flesh at raw stage after main soaking; we can easily see the layer the skin. As we seen previously from grain surface pattern neck region have more hair pores than the other here also see the same things, neck region on the grain layer has more hair in both Ethiopia and India hair sheep skin. The grain layer of Ethiopian sheep skin is thinner than the grain layer of Indian sheep skin whereas the corium layer of Ethiopia sheep skin thicker and

compact. When we compare the main leather making part (butt) region Indian is loser and less compact structure than Ethiopia.



E-Ethiopia, I-India, NR-neck raw, BLR-belly raw, BR- butt raw

Fig. 4.17 Histological structure of Ethiopia and India sheep skin at raw stage

The thickness of the cross section was measured with Adobe Photoshop and is given in Table 4.8shows the thickness of grain, corium, flesh, total thickness of skin, and total thickness of leather making part and grain to corium ratio at all regions, which are neck, belly and butt. From Table 4.8, in neck and butt region of Indian sheep skin have a little bit more grain to corium ratio than Ethiopian highland hair sheep skin this indicate that Indian sheep has more grain layer and less corium layer whereas Ethiopian sheep has less grain layer and more corium layer. In belly region both species comparatively have equal grain and corium layer.

Table 4.8 grain to corium ratio at raw stage

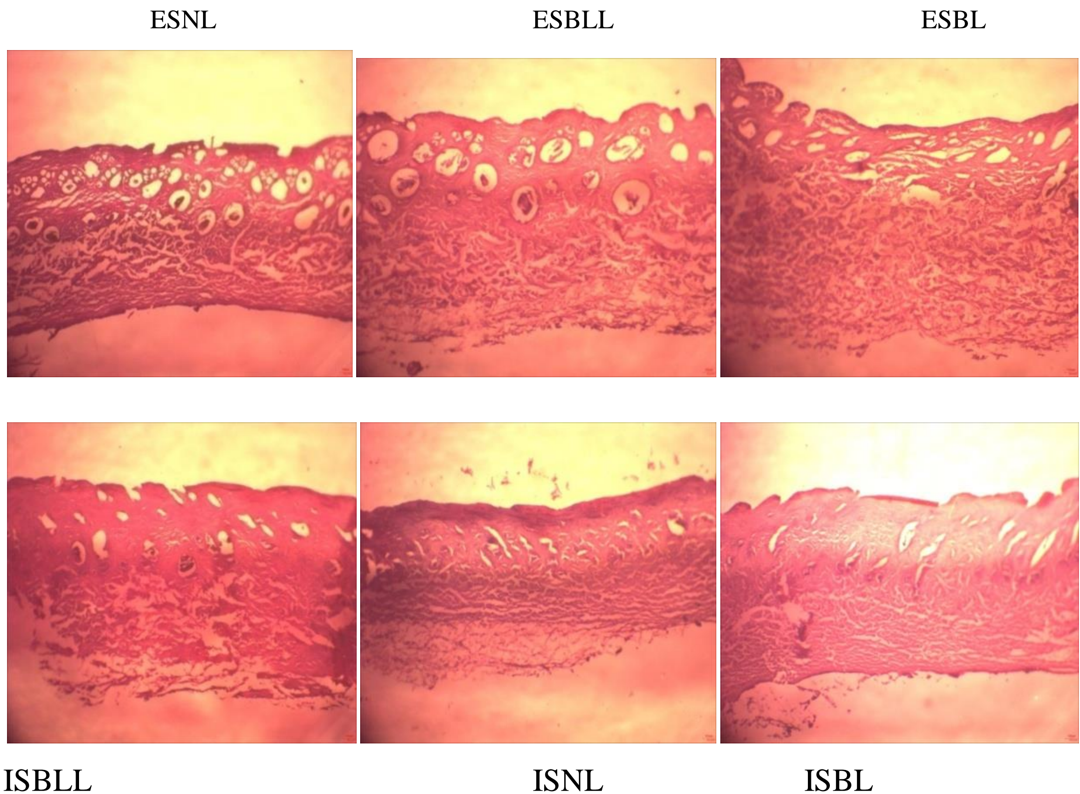
Typeof skin	Grain thickness, mm	Corium thickness, mm	Flesh thickness , mm	Total thickness of skin, mm	Total thickness of leather making part, mm	Grain to corium ratio
	Neck					
Ethiopia	0.47±0.08	0.69±0.06	0.19±0.07	1.35±05	1.16±0.03	0.68±0.02
India	0.53±0.03	0.45±0.02	0.28±0.04	1.26±0.02	0.98±0.01	1.17±0.01
	Belly					
Ethiopia	0.39±0.05	0.45±0.08	0.13±0.07	0.97±0.03	0.84±0.04	0.86±0.07
India	0.40±0.04	0.48±0.02	0.10±0.01	0.98±0.02	0.88±0.01	0.83±0.01
	Butt					
Ethiopia	0.43±0.07	0.71±0.06	0.14±0.08	1.28±05	1.14±0.05	0.6±0.7
India	0.45±0.04	0.55±0.02	0.18±0.01	1.18±0.04	1.0±0.03	0.81±07

Table 4.9 grain to corium ratio at liming stage after fleshing

Type of skin	Grain thickness, mm	Corium thickness, mm	Total thickness of skin, mm	Grain to corium ratio
Neck				
Ethiopia	0.51±0.01	0.96±0.03	1.47±0.01	0.53±0.01
India	0.64±0.03	0.77±0.07	1.41±0.04	0.83±0.03
Belly				
Ethiopia	0.45±0.02	0.75±0.01	1.2±0.03	0.68±0.03
India	0.5±0.01	0.79±0.04	1.29±0.02	0.63±0.04
Butt				
Ethiopia	0.47±0.07	1.14±0.01	1.59±0.04	0.4±0.01
India	0.51±0.01	0.89±0.04	1.4±0.02	0.57±0.03

The thickness of grain, corium, total thickness of leather making part and grain to corium ratio at all regions, like neck, belly and butt as well as the cross section of lime pelt, respectively are shown in Table 4.9 and Fig. 4.17.

All region thickness almost becomes double especially in butt and neck region this is due to the opening up of compact fibre bundles and absorbing of water. Grain thickness also increases but when we compare it from the two it is lesser. Grain to corium ratio decrease compare to raw stage due to corium layers increase in size. The structure is fibrous, but the fibres are so fine the appearance is more like solid. It has the lack of fibber interaction, in comparison with lower layer of the skin (corium). Chemically, the grain is the same as the more obviously fibrous corium, so the impact of chemical modification is the same.



E-Ethiopia, I-India, NL-neck lime, BLL-belly Lime, BL- butt lime

Fig 4.18 Histological structure of both Ethiopia and India sheep skin at liming stage after fleshing

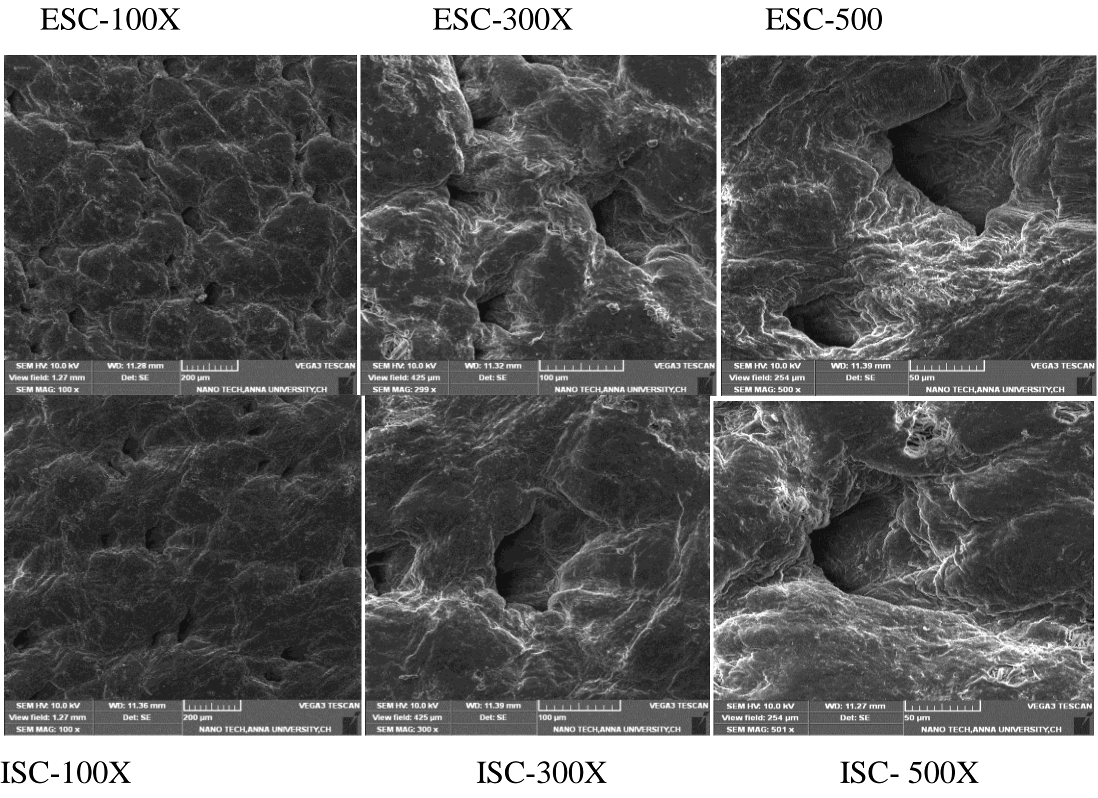
From the literature the average angle of weave in corium layer of raw skin is about 45°; hence a lower value indicates greater depletion or relaxation of the corium and a

higher value indicates a degree of swelling that is why the thickness of corium become doubled. Across the process stages, compactness decreases during liming.

4.3 SEM Analysis

4.3.1 Surface pattern and cross section of Ethiopian and Indian sheep cabretta

The surface pattern and cross section structure cabretta leather of the two species at crust stage from butt area is shown in figure 4.18. These SEM images were taken at 100, 300 and 500x magnifications. When the magnification is increased hair pores can be easily seen. At 300 and 500x magnification Ethiopian highland hair sheep skin has more hair pores, this is already seen from the result of hair pore count that was captured using stereo microscope.



ESC-Ethiopia sheep cabretta, ISC- Indian sheep cabretta

Fig. 4.19 surface pattern of sheep cabretta using SEM

Cross section of the butt portions of two species at increasing magnification is shown in figure 4.18. In each magnification we can see the opening up extent of the fibres. The fibres of Indian hair sheep more opened up than Ethiopian sheep skin, this shows Ethiopian highland sheep skin has compact fibres than Indian. When we compare to

the cross section to glove leather of both species crust has compact structure this is due to the chemicals that used in post tanning process and mechanical actions give tightness, fullness and firmness of the fibre in addition to the nature of the raw material, which is expected and essential properties for cabretta leather.

ESC-100X ESC-300X ESC-500X

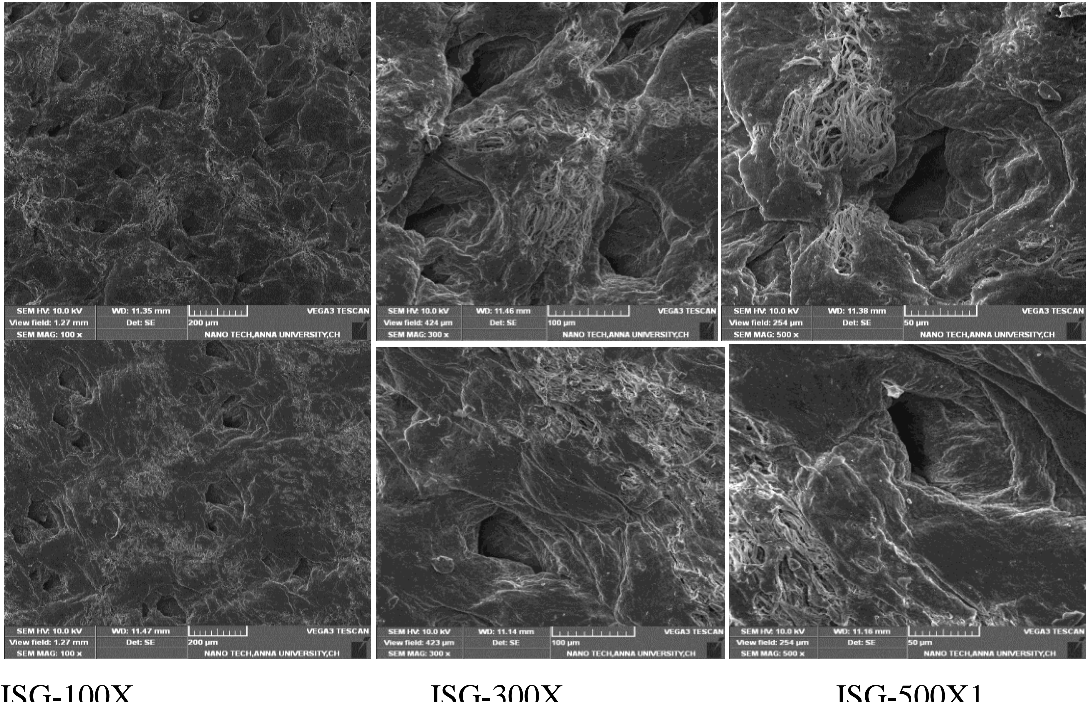
ISC-100X ISC-300X ISC-500X

Fig 4.20 Cross-section of Ethiopia and India sheep cabretta.

4.3.2 Surface pattern and cross section of Ethiopian and Indian sheep glove

The surface pattern and cross section structure of glove crust leather of the two species from butt portions is shown in figure 4.20. These SEM images were taken at 100, 300 and 500x magnifications same as cabretta. As the magnification is increased hair pores can easily be seen and Ethiopian highland hair sheep skin has more hair pores than Indian, this is already seen from the result of hair pore count that was captured using stereo microscope, the surface of Glove in both species seems softer than cabretta.

ESG-100X ESG-300X ESG-500X



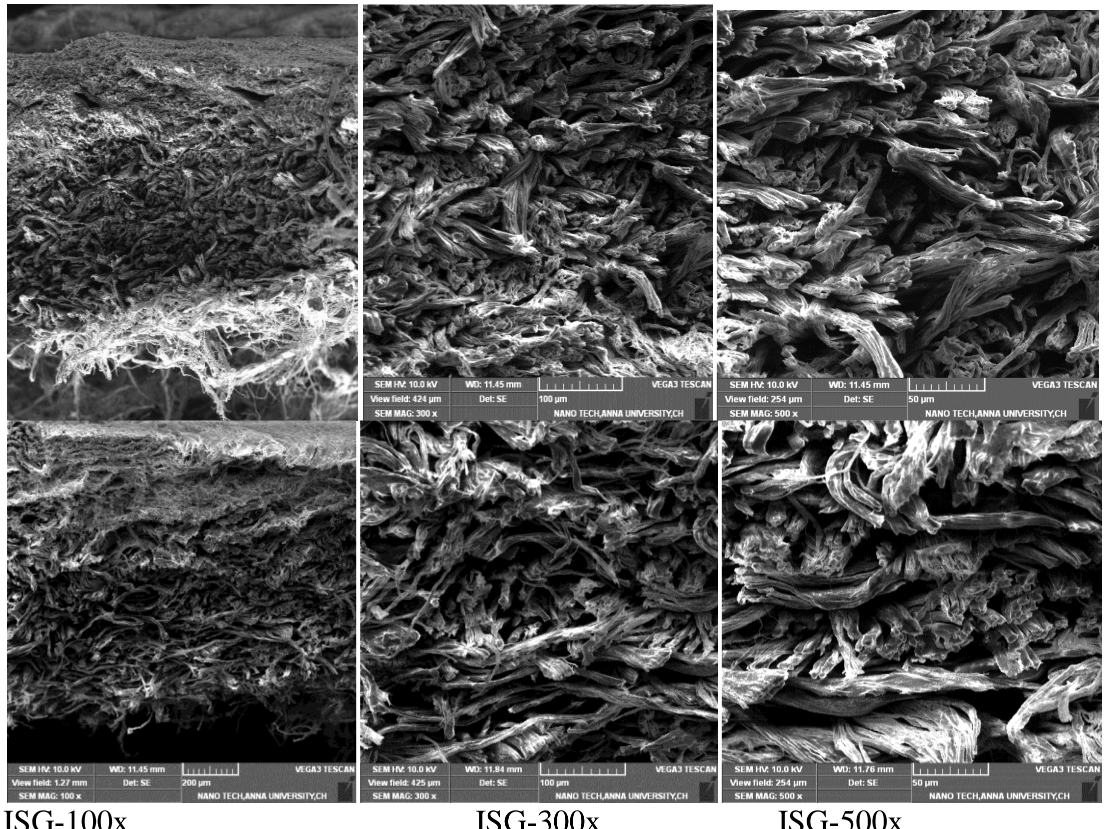
ISG-100X ISG-300X ISG-500X1

ESG- Ethiopian sheep glove, ISG-Indian sheep glove

Fig 4.21 surface pattern of sheep glove

From figure 4.21shows the opening up extent of the fibres of the two species. The fibres of Ethiopian highland sheep skin more opened up than India sheep skin, this due to the hair pores of Ethiopia is more than India as well as the process strategy of glove gives fibres break down and opening up as well as softness, which is essential properties for glove.

ISG-100x ISG-300x ISG-500x



ISG-100x ISG-300x ISG-500x

Fig 4.22 cross section of Ethiopian and Indian sheep glove

4.4 Chemical characterization

4.4.1 Moisture content

Moisture content of both Ethiopian and Indian is taken at raw stage after main soaking, pickling and wet blue stage. Estimation of moisture content is important to know whether proper soaking is done or not to conduct the next processes and in addition the result of moisture content used for the estimation of other chemical characterization like Nitrogen, HYP, Hide substance, Fat contents etc. on dry weight basis.

Figure 4.23 dried samples of both Ethiopian and Indian sheep skin

$$\% \, moisture\ content = \frac{Mass\ of\ Sample\ before\ drying - Mass\ of\ sample\ after\ drying}{Mass\ of\ sample\ before\ drying}$$

Table 4.10moisture content at raw, pickle and wet blue stage

Raw material	% moisture content	% of dry basis
E. raw	69.148	30.852
I. raw	71.629	28.37
E pickle	81.773	18.227
I. pickle	82.246	17.754
E. wet blue	73.234	26.766
I. wet blue	74.524	25.476

E-Ethiopia, I-India

From the table, moisture content is increase in pickle stage this shows that the fibres can uptake more water. The moisture content of Ethiopia sheep skin at raw stage is smaller than Indian, this is due to the raw material was soaked on dry salted whereas Indian was wet salted.

4.4.2 Fat content determination

The fat content estimation is important to decide where degreasing is necessary or not based on final product.

The fat content of two species is done at raw, pickling before and after degreasing stage by taking 5.05gm of sample for both species. Especially for glove leather it is important things to prevent the fat spew from the surface of final glove leather.

Fat content can be determined by taking the difference of initial and final wt of sample and divide with dry base of sample that gets previously from moisture content at raw stage and pickling stage:

$$\% \, fat \ content = \frac{final \ wt - initial \ wt \ x100}{dry \ base \ wt \ of \ ample}$$

Table 4.11 fat content at raw and pickle stage of before and after degreasing

Raw material	Wt. of sample in gm	%fat content
Ethiopia At raw stage	5.05	4.44
India at raw stage	5.05	1.67
Ethiopia at pickle stage before degreasing	5.0018	1.36
India at pickle stage before degreasing	5.0070	1.019
Ethiopia at pickle stage after degreasing	5.0086	0.649
India at pickle stage after degreasing	5.0030	0.557

From the above table we can predict that Ethiopian highland hair sheep skin has more fat content than Indian sheep skin. This indicated that Ethiopian sheep skin needs more degreasing than Indians. Two third of fat present in Ethiopian sheep skin gets removed in other processes before degreasing. An Indian sheep skin doesn’t need an

extensive degreasing. However, in order to compare similar extent of degreasing was performed for both the Ethiopian and Indian skins. The final fat content of the two species are almost similar.

4.4.3 Nitrogen content

Determination of nitrogen content of both species at raw and wet blue stage gives an idea about proteins as the main component of leather, therefore we can know about the effect of leather process on protein.

Table 4.12 % of nitrogen content at raw and wet-blue stage

S. No.	Type of Sample	Wt. of Sample	Titrant volume (TV) in ml	Normality of HCl (N)	Blank volume (BV) in ml	% Nitrogen content	Average % N
1	Ethiopia butt raw	0.5018	18.1	0.1	1.5	15.02	15.67
2	Ethiopia neck raw	0.5009	17.6	0.1	1.5	15.6	
3	Ethiopia belly area raw	0.5022	16.3	0.1	1.5	13.4	
4	India butt area raw	0.5044	16.1	0.1	1.5	14.3	13.61
5	India neck area raw	0.5046	15.8	0.1	1.5	13.9	
6	India belly area raw	0.5004	14.3	0.1	1.5	12.63	
7	Ethiopia butt wet-blue	0.505	19.6	0.1	1.3	13.684	13.86
8	Ethiopia neck wet-blue	0.511	19	0.1	1.3	14.81	
9	Ethiopia					13.08	

	belly wet-blue	0.515	21.5	0.1	1.3		
10	India butt area wet-blue	0.5046	13.1	0.1	1.3	11.14	11.80
11	India neck area	0.5102	14.5	0.1	1.3	12.32	
12	India belly area wet-blue	0.5004	19.7	0.1	1.3	11.95	

The results obtained from nitrogen determination analysis conducted with the Kjeldahl method in Ethiopia sheep raw samples is 15.67% and in wet blue 13.86% where us in India sheep raw 13.61% and in wet blue stage 11.80%.

% Nitrogen for Ethiopia highland hair sheep skin is higher than Indian in both stage, this implies that Ethiopia sheep has more protein content than Indian sheep.

Amount of nitrogen content is decreased in wet-blue stage in both species this is due to in raw stage there is interfere of other material like hair root (keratin) this have nitrogen hence it increased the amount of nitrogen in raw stage whereas in wet blue stage the amount of nitrogen is decreas while in this stage we have only leather making protein that is collagen.

- **HIDE SUBSTANCE**

To find the hide substance we can multiply %Nitrogen by a factor of5.62

Hide substance for Ethiopia sheep:-

- at raw stage = 5.62 * 20.48% = **88.07%**
- At wet-blue stage = 5.62 * 13.86% = **77.89%**

For India: -

- Raw stage:- 5.62 * 13.61% = **76.49%**
- Wet-blue stage:- 5.62 * 11.80 % = **66.32%**

If nitrogen content of skin is determine indirectly we can determine hide substance of the skin using the above calculation. From the result Ethiopian sheep skin has higher amount of hide substance than Indian sheep.

4.4.4 Chrome content estimation

The chrome oxide content analysis is important to give the information for us regarding hydrothermal and chemical resistance of the final leather to be produced.

This analysis is done by acid digestion of wet blue leather. The result is expressed as $\%Cr_2O_3$.

$\% \, of \, chromium \, (Cr2O3) = \frac{OD \, value}{4820} \, x \, \frac{152x52}{104} \, x \, \frac{100}{wt \, of \, sample} \, x \, \frac{100}{10} \, x \, \frac{100}{1000}$, The dilution factor would be 100ml for this test.

Table 4.13 % of chromium oxide

Type of sample	Wt. of sample in gm	Dilution factor in ml	OD value	$\%Cr_2O_3$
Ethiopia wet-blue leather	0.5030	100	0.698	2.2
India wet-blue leather	0.5004	100	0.620	1.96

Ethiopian sheep wet blue has slightly more chrome content than Indian sheep. Based on the standard test method the final chrome content value of wet-blue leather is lies between 1-5%. Therefore the result of the two species wet blue leather lies on this value.

4.4.5 Hydroxyproline content result

Hydroxyproline Content of both species is done on raw and pickle stage. The sampling area of is from neck, belly and butt.

The colour change of both standard and sample solution is started when the reagent Chloroamine.T added, it becomes yellowish.

After adding of the remaining two reagents (PDAB and percloric acid) and incubated them for certain minutes the colour becomes pink this indicate that hydroxyproline is

present in the solution. Hydroxyproline concentration is determined by the reaction of oxidized hydroxyproline with PDAB.. Hydroxyproline is largely restricted to collagen, the measurement of hydroxylproline levels can be used as an indicator of collagen content.

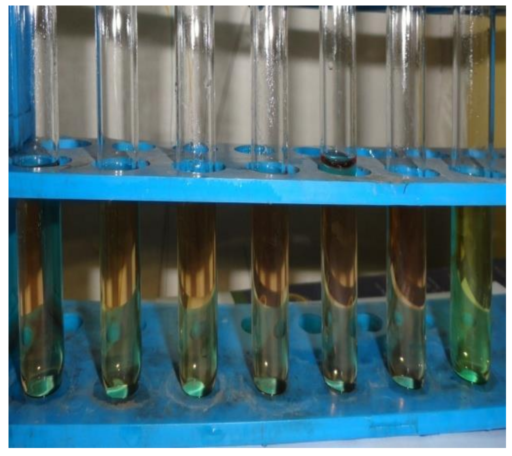


Figure 4.24 standard solution

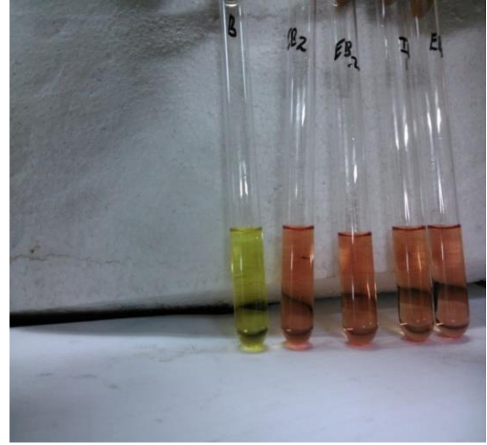


Figure 4.25 blank (yellow) and sample solution

Table 4.14 OD value for std. Solution of Hydroxyproline

standard	Conc. in µg/µl	µg/1000µl	OD. Value
S1	20	2	0.114
S2	40	4	0.241
S3	60	6	0.462
S4	80	8	0.576
S5	100	10	0.695
S6	120	12	0.856

Table 4.15 the OD result of both Ethiopian and Indian species

Sample Ethiopian hair sheep skin	**OD Value**
Butt	0.205
Belly	0.187
Neck	0.215
Average	**0.202**
Indian hair sheep skin	**OD value**
butt	0.174
belly	0.140
Neck	0.143
Average	**0.152**

Unknown concentration of the samples is found from the following standard graph.

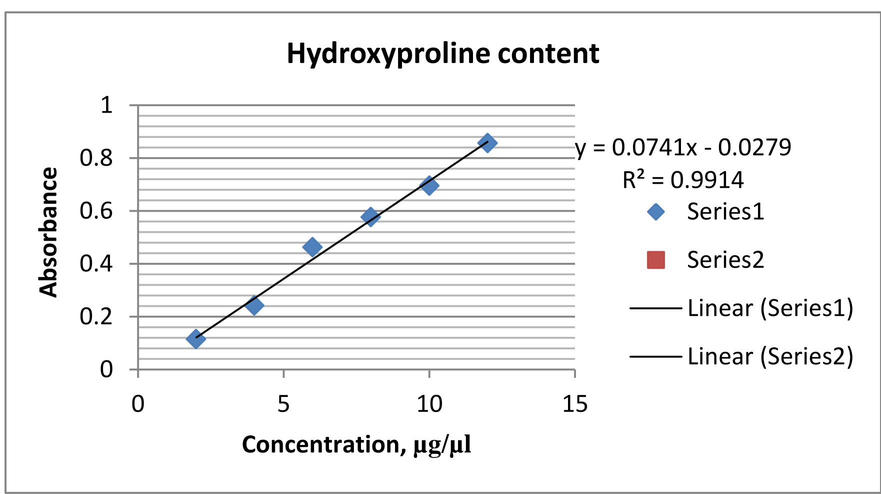


Fig. 4.26 Standard graph for hydroxyproline

For this calculation we use Butt = 15.3mg, belly = 15.3mg, neck = 15.4mg and for India butt= 15.7mg, belly= 15.5mg and 15.1mg. After hydrolysis made up to 10 ml (10000 µl) and from this was take 60µl for preparation of sample solution for OD

$y = mx + b = 0.074x - 0.027$, concentration $= x = \frac{OD}{slope} = \frac{y+0.027}{0.074}$

Table 4.16 Hydroxyprorline and collagen content in Ethiopian and Indian raw sheep skin.

Area of sampling	Amount of hydroxyproline in **mg**	Amount of collagen in **mg**	Percentage of collagen
Ethiopia neck	0.642	4.833	94
Ethiopia belly	0.482	3.63428	76.99
Ethiopia butt	0.516	3.8944	82.35
Average value	**0.547**	**4.121**	**84.45**
Indian neck	0.383	2.89	62.02
Indian belly	0.376	2.84	59.39
Indian butt	0.453	3.416	70.53
Average value	**0.404**	**2.851**	**63.98**

The amount of hydroxyproline of Ethiopia is higher than Indian sheep skin. The average amount of collagen and % of collagen are:-4.12mg, 84.45% for Ethiopia and 2.85mg, 63.98%for India. This indicates that Ethiopian highland hair sheep skin has more collagen content than Indian hair sheep skin

4.4.6. Glycoprotein estimation

The sample is taken from the three sampling areas at raw stage. The sample solution that taken for OD is slight pink colour is the same as the standard solution. The colour change comes due to the Glycoprotein that found inside standard and sampling solution respectively. This glycoprotein condensed readily with acetyl acetone to give pyrroles. The pyrroles give colour reaction with PDAB.

Figure 4.27 blank and standard solutions for glycoprotein.

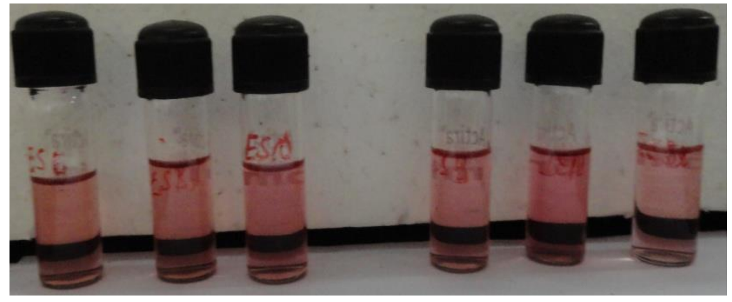


Figure 4.28 sample solution for glycoprotein

After measuring OD value of these two solutions the result is as follow

Table 4.17 OD value of std. Solution for glycoprotein estimation

standard	Conc. µg/µl	Conc. µg/1000µl	OD. Value
S1	20	10	0.132
S2	40	20	0.259
S3	60	30	0.380
S4	80	40	0.458
S5	100	50	0.624
S6	120	60	0.741
S7	140	70	0.804

Table 4.18 OD value of sample solution for glycoprotein

Sample Ethiopian hair sheep skin	**OD Value**
butt	0.135
belly	0.211
neck	0.279
Average	**0.208**
Indian hair sheep skin	**OD value**
butt	0.114
belly	0.201
Neck	0.263
Average	**0.193**

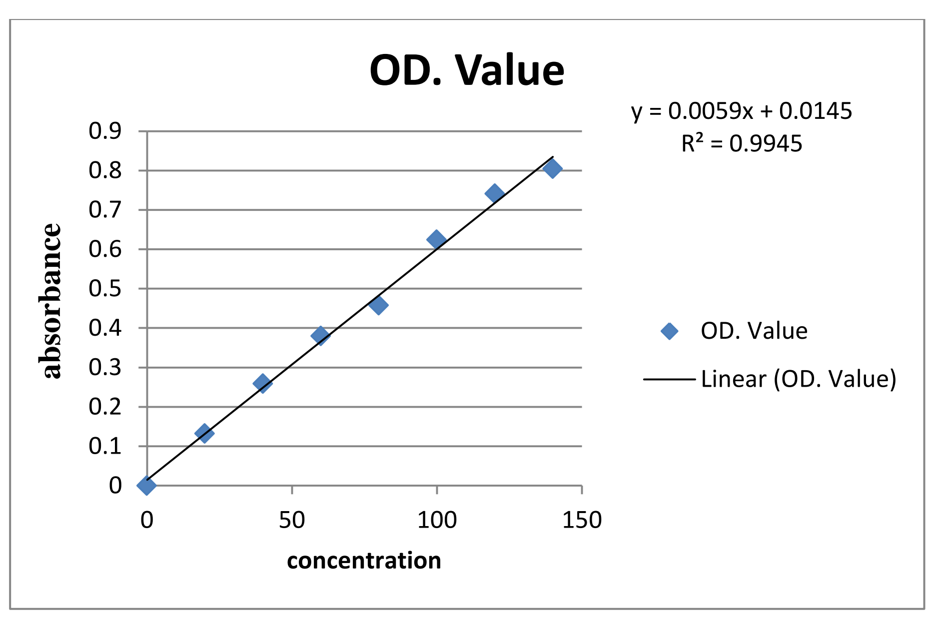


Figure 4.29 Standard graphs for glycoprotein estimation

The way to calculate amount of glycoprotein is same as Hydroxyproline estimation. $y = mx + b = 0.005x + 0.014,$

$$\text{concentration} = x = \frac{\text{OD}}{\text{slope}} = \frac{y - 0.014}{0.005}$$

Based on the std. graph calculation was done same fashion to Hydroxyproline. The result summarized as follow.

Table 4.19 Amount and percentage of Glycoprotein in Ethiopian and Indian raw sheep skin.

Sampling area	**Amount of glycoprotein in mg**	**Percentage of glycoprotein**
Ethiopian neck	0.12	3.9
Ethiopian belly	0.093	2.9
Ethiopian belly	0.056	1.8
Average value	**0.09**	**2.9**
Indian neck	0.119	3.6
Indian belly	0.091	2.71
Indian but	0.047	1.64
Average value	**0.086**	**2.65**

From the result of glycoprotein both species has almost similar glycoprotein amounts, and from the literature the total amount of glycol protein of raw skin is 1.7% but this value is a little bit greater, this is may be sheep skin by nature it has more amount of non structural protein. These proteins can remove early stage of the process and the skin become open up and gives the leather softer property especially for glove leather; hence after liming and bating operation the skin become pure collagen.

4.5. Physical properties

4.5.1 Organoleptic properties

Evaluation of the properties such as softness, Run, grain smoothness, looseness, fluffiness, colour uniformity, General appearance and looseness, fullness, softness, Grain tightness, Grain smoothness, Roundness, colour uniformity and General appearance for Glove and Cabretta respectively. The results are expressed on 1 to 10 scale in which the higher the value, the better the property.

The results of the evaluation are presented in Table 4.20. From these properties we observed that an Ethiopian highland hair sheep skin is slightly higher than Indian sheep skin in all organoleptic properties. This indicates that Ethiopian sheep skin has suitable and essential properties for these two articles.

Table 4.20 Organoleptic properties

Parameters	Sheep glove	
	Ethiopia	**India**
Softness	9.5	9.0
Run	9.25	9.25
Grain smoothness	9.5	9.0
Looseness	8.5	8.5
Fluffiness	9.5	9.0
Color uniformity	9.25	9.0
General appearance	9.25	8.9
Parameters	**Sheep cabretta**	
	Ethiopia	**India**
Looseness	9.25	8.25
Fullness	8.75	8.5

Softness	8.75	9.0
Grain tightness	9.0	8.25
Grain smoothness	8.75	9.0
Roundness	9.25	8.5
color uniformity	9.0	8.5
General appearance	9.25	8.5

4.5.2 Tensile strength of leather

Tensile strength of both Glove and Cabretta was measured in a universal tensile meter (UTM) for both along and across the back bone of the leather sample and reported in N/mm^2 as shown below in Table 4.21

Table 4.21 tensile strength of both Ethiopian and Indian sheep glove and cabretta

Type of test	**Direction**	**Glove**		**Cabretta**	
		Ethiopia	**India**	**Ethiopia**	**India**
Tensile Strength (N/mm^2)	Parallel/ along	22.37	15.07	28.68	17.733
	Perpendicular/ across	15.94	7.77	20.42	13.08
Elongation At break (%)	Parallel/ along	84.84	57	53.78	54.11
	Perpendicular/ across	91	86.17	67.89	60.33
Thickness (mm) ave.		0.69	0.67	1.01	0.96
Standard req.	Tensile strength Min. $15N/mm^2$ and elongation at break 40-80%				

Tensile strength of leather is the ultimate strength of the leather that includes grain, corium and flesh layers. In this test elongation property of the leather can also be measured. The tensile strength helps the leather to withstand the various mechanical operations like staking, shaving and buffing.

From tensile strength of the two species we conclude that Ethiopian highland hair sheep skin has higher tensile strength than Indian hair sheep skin in both product (glove and cabretta). It was seen from SEM structure, Ethiopian highland hair sheep skin has better fibre orientation (fibre network) than Indian hair sheep skin this may be give better tensile strength for Ethiopian sheep leather. From the above table Ethiopian sheep glove (22.37N/mm^2 and 15.94N/mm^2) and cabretta(28.68N/mm^2 and 20.42N/mm^2) has more tensile strength in both directions, it is above the minimum standard requirement than India sheep glove (15.07N/mm^2 and 7.77N/mm^2) and cabretta (17.733N/mm^2 and 13.08N/mm^2) specially in across/perpendicular direction Indian sheep glove and cabretta has small value that is below minimum requirement of standard value.

In both species product tensile strength of along/ parallel direction is higher than across/perpendicular direction this is due to the fibres more oriented to the backbone and give high strength, where us the fibres that found across the backbone are not oriented to it and less compact or far apart each other than along direction. Where us in the case of percentage elongation this result is in opposite manner, means that the fibres that are not more oriented to the back bone has better elongation than the more oriented (parallel/ along) this is due to the fibres are far apart and they have free space for elongation to a maximum percentage. Here also Ethiopia sheep skin has better elongation than Indian sheep.

4.5.3 Tear strength of leather

Tear strength test is most preferable test for leather than tensile strength by many customers. This is essential to estimating the durability of the leather to withstand tearing stresses encountered in manufacturer of shoes, garment, glove and upholstered products. The tear strength of both Cabretta and Glove leather samples were determined using standard procedure. Double- edge tear test was done for both products (cabretta and glove) shows on table 4.22, whereas special type of tear strength was done for glove called double hole stitch tear strength. Apart from the

extreme thinness of glove leather (thickness 0.5-0.6mm), the situation is further complicated with use of very fine stitching, both in construction and decoration of the gloves, the leather being practically cut out of existence along the stitching. Without sufficient stitch-tear strength, good leathers often tear along the seams after making up. Hence this test is very essential for glove.

Table 4.22 Tear strength of Glove and cabretta

Type of test	**Direction**	**Glove**		**Cabretta**	
		Ethiopia	**India**	**Ethiopia**	**India**
Double edge Tear Strength (N/mm)	Parallel/ along	45.31	42.045	33.34	30.07
	Perpendicular/ across	44.16	41.39	40.097	39.34
Thickness (mm) ave.		0.65	0.62	0.95	0.90
Double hole stitch tear strength (N/mm)	Parallel/ along	93.07	92.35	**Not necessary**	**Not necessary**
	Perpendicular/ Across	90.88	82.75	**Not necessary**	**Not necessary**
Thickness (mm)		0.65	0.61	**Not necessary**	**Not necessary**
Min. Stad requirement	Double edge tear for glove leather 15N/mm and for cabretta min 20N/mm, stitch tear min.80N/mm				

From the above table the tear strength (double edge and double hole stitch tear) of the two species are above the minimum requirement this shows both species have good tear strength and the difference of parallel and perpendicular direction is small almost they have approach value. But along direction is little bit larger than across direction

this is due to the fibres are entangled together and can't easily separate. Ethiopia highland hair sheep skin has better value than Indian hair sheep skin in all tear strength property.

4.5.4 Lastometer Test

The grain of the leather is subjected to more stain in shoe making process. Therefore the grain is liable to exhibit grain cracks on the shoe surface especially at toe area. This may be due to filling of more re-tanning materials into the leather matrix to give sufficient substance. Therefore selection of leather for shoe making has to be made after testing the leather for grain crack load and distension properties using standard test equipment called lastometer.

Determination of the grain crack force and distension of Ethiopia and India sheep cabretta was done by this test method. The result shown table 4.23

Table 4.23 lastometer test for cabretta

At grain burst for crust cabretta				
Trial	**Ethiopia sheep cabretta**			
	Distension at grain burst (mm)	Load at burst (N)	A.d.b (mm)	A.L.b (N)
1	12.1	318	12.133	286.333
2	12.1	252		
3	12.2	289		
	Indian sheep cabretta			
	Distension at burst (mm)	Load at burst (N)	A.d.b (mm)	A.L.b (N)
1	10	193	9.57	146.333
2	9	93		
3	9.7	153		
At grain crack for finished cabretta				
Trial	**Ethiopia sheep cabretta**			
	Distension at grain crack	Load at crack (kg)	A.d.c (mm)	A.L.c (kg)

	(mm)			
1	8.10	36	7.943	35.67
2	8.09	36		
3	7.64	35		
	Indian sheep cabretta			
	Distension at grain crack (mm)	Load at crack (kg)	A.d.c (mm)	A.L.c (kg)
1	7.65	33.5	7.75	30.17
2	7.41	22		
3	8.2	35		
Standard req.			Min. 7	Min. 20

A.d.b (average distension at burst), **A.d.c** (average distension at grain crack), **A.L.b** (average load at burst) and **A.L.c** (average load at crack)

From the table we conclude that both Ethiopia and India sheep cabretta have the value of above the minimum requirement. This shows that they are not more filled by re-tanning materials to give sufficient substance because naturally they have good substance this is important property for cabretta. When we compare to two species Ethiopia sheep skin have better substance and the fibres are more compact, hence it has not more void space between the fibre that filled by re-tanning material this gives better resistance to load at crack than Indian sheep cabretta.

4.5.5 Flexing resistance

Determination of the material to crack or fail at flexing creases is done by flexing resistance test methods**.** For this vamp flexing method is used than belly flexing method because vamp flexing used to estimate flexing creases in the vamp part of shoes during walking. The test was done between 10,000-500,000 number of cycle for 8 -12 hr for both Dry and Wet condition of Ethiopia and India finished sheep cabretta. This number of cycle is show that the maximum number walking of a person.

Table 4.24 flexing resistance of cabretta

Ethiopia sheep cabretta				
No. of cycle	**Along-dry**	**Across- dry**	**Along-wet**	**Across-wet**
10,000	**A**	**A**	**A**	**A**
60,000	**A**	**A**	**A**	
70,000			**A**	
80,000			**A**	**A**
90,000			**B**	**B**
100,000			**B**	**B**
300,000	**A**	**A**		
500,000	**B**	**B**		
India sheep cabretta				
No. of cycle	**Along-dry**	**Across- dry**	**Along-wet**	**Across-wet**
10,000	**A**	**A**	**A**	**A**
50,000	**A**	**A**		
80,000				**A**
90,000			**A**	**B**
100,000			**B**	**B**
250,000		**A**		
300,000	**A**	**B**		
500,000	**B**	**B**		

A: no effect, **B:** Slight creasing, **C:** slight pipiness, **D:** marked creasing, **E:** severe creasing, **F:** severe pipiness, **G**: slight crack, **H:** marked crack**, I:** sever crack, **J:** complete failure

From the result of this test both species product has good flexing resistance, they don't have severe problem. When the number of cycle is increased slight creasing is happen. When we compare to the two species product, for Ethiopia sheep cabretta slight creasing is happen at large number of cycle (500,000) for dry test where as India sheep cabretta slight creasing start at 300,000 number of cycle. In wet test both species slight creasing starts at 90,000 number of cycle. This result shows that on dry

condition Ethiopia sheep cabretta has good flexing resistance than India. This test is done for finished cabretta; the creasiness is happen if the finished is more loaded on grain of the leather, but in this case the result shows that no effect and at large no of cycle only slight creasing hence it is not loaded by finishing materials.

CHAPTER FIVE

5. Conclusion and recommendation

5.1 Conclusion

The highlands are a major source of sheep for slaughter in the cities. Ethiopian high land sheep skins, estimated to comprise about 70% of national sheep skin production. They have an international reputation for their unique characteristics such as fine quality, thickness, cleanness, flexibility and strength and compact texture. Owing to these properties Ethiopian highland sheep skin are excellent raw materials for making high quality leathers for dresses gloves, sport gloves, garments and high quality shoes upper leathers (cabretta).

Histological characterization shows that Ethiopian highland hair sheep skin has good compactness and fullness than Indian hair sheep skin hence giving good tensile and tear strength. This has been confirmed from the physical testing results. Chemical testing results, especially nitrogen and hydroxyproline analysis showed that Ethiopian sheep skins have high hide substance and collagen content than Indian sheep skins.

It was also observed that fibre compactness of the Ethiopian sheep skins is better and because of this, it is more suitable for making cabretta leathers. Also, from the hair pore count, it was observed that, owing to more hair pore in Ethiopian sheep skin, the grain seems to be smoother, finer and the softness and suppleness feel of the leather make it suitable for making glove leathers.

5.2 Recommendation

- The use of this Ethiopia sheep skin is very high in Ethiopian leather industries. However, owing to poor animal husbandry and diseases the quality of the skin gets affected. Hence, Ethiopian government including all respected bodies must work on this area to get profit from the sector.
- Ethiopian government should have to promote and increase the number of local and foreign investors to set up factories making glove leathers and gloves. This project work gives scientific information in support of the superior quality of the Ethiopian sheep skins, which would be of help to the investors to understand the uniqueness of the Ethiopian sheep skins.
- In this project work, highland sheep skins that collected from different parts of highland area like Menze, Washera, Tikur, Sekota, Semen etc have been studied. In future, it is recommended the **Selale sheep skins**, the indigenous sheep variety of Ethiopia could be could be characterized in similar lines and the suitability of these skins to produce high quality leather be ascertained.

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Annexure

Annexure1: production and soaking capacity of Ethiopian tanneries

Name of Tannery	Daily installed Production Capacity		Daily Soaking capacity Plan for 2014		Soaking capacity Plan for 2014 (280 working days)		Actual Production Performance		Performance against plan (%)	
	Hides	Skins	Hides	skins	Hides	Skins	Hides	skins	Hides	Skins
Addis Ababa	0.90	2.50	0.90	2.30	252	644	141.3	116	56	18
Bahirdar	0.30	2.0	0.20	0.20	56	560	3.43	81.66	6	15
Batu	1.00	2.50	1.00	2.30	280	644	332	266	119	41
China Africa	0.40	12	-	12	-	3,360	10	2,247	---	67
Colba	0.60	6	0.60	6	168	1,680	113.80	1,954.7	68	116
DebreBirhan	-	5.00	-	2.00	-	560	-	76	---	14
Dire	0.60	6	0.60	6	168	1,680	132.34	1,680.3	79	100
East Africa	-	7	-	6	-	1,680	-	769	---	46
ELICO	1.00	13	1.00	10.50	280	2,940	213.75	1,099.8	76	37
Ethiopia	1.20	12	1.20	12	336	3,360	272.48	1,535.23	81	46
Farida	-	7	-	5	-	1,400	0.133	308.8	---	22
Friendship	1.00	10	1.00	10	280	2,800	31.5	1,583	11	57
Gelan	-	3	-	2	-	560	-	246.86	---	44
Habesha	-	3	-	2	-	560	-	227.80	---	41

Name of Tannery	Daily installed Production Capacity		Daily Soaking capacity Plan for 2014		capacity Plan for 2014 (280 working days)		Actual Production Performance		Performance against plan (%)	
	Hides	Skins	Hides	skins	Hides	Skins	Hides	skins	Hides	Skins
Hafde	0.25	6	0.25	4	70	1,120	6.57	393.30	9	35
Hora	-	3	-	2	-	560	-	152.40	---	27
Kombolcha	-	6.0	-	3.0	-	840	-	570.75	---	68
Mersa	0.30	6	0. 30	3	84	840	50.50	299.4	60	36
Mesaco	-	2.50	-	2	-	560	0.45	7.70	---	1
Modjo	0.50	7	0.50	6	140	1,680	36	1,788.60	26	106
New Wing	-	-	-	-	-	-	2.50	50	---	---
Sheba	0.60	6	0.60	6	168	1,680	104.58	1,208	62	72
United Vasan	-	3	-	3	-	840	-	229	---	27
Wallia	0.50	5	0.50	3	140	840	32	151	23	18
Total	9.5	141.5	885	114	247.80	31,948	1,487.	17,0428	60	53

Annexure 2: Process recipes for cabretta

Table 1: pre-tanning-tanning

Process	**%**	**Chemicals**	**Time**	**Comment**
Soaking	200	water		
	0.3	Preservative		
	0.1	Wetting agent		Over night
Panting	10	Water		
	2.5	Sodium sulphide		
	7	Lime		
Apply the paste on the flesh side and pile over night or 3-4 hr next day do unhairing				
Drum re-liming	100	water		
	2	lime		
Drum liming by rotating the drum for 5min and stop 55min for 1 day then do fleshing				
Washing	200	water	10’	Drain
De-liming	100	water		
	1.5	Ammonium sulphate	30-45min	PH 8-8.2
Bating	1	Bating agent	60’	Check. Using phenolphthalin Drain/wash /drain
Pickling	80	water		
	8	salt	20’	Check B^{O} 6-7
	0.5	formic	20’	
	0.8-1	Sulphuric acid	4x10’ + 60’	PH 2.8-3.0
One day ageing				
De-pickling	150	water		
	10	salt	10’	

	2	Sodium formate	20’	
	0.7	Sodium bicarbonate	20’	
	0.7	Sodium bicarbonate	20’	
	0.7	Sodium bicarbonate	20’	PH 5-5.5, Drain completely
Degreasing	1.5	ND 01(Degreasing agent)	60’	
washing	300	water		
	6	salt	20’	Drain
Re-pickling	70	water		
	7	salt	10’	
	0.5	Formic acid	10’	
	0.8	Sulphuric acid	10’x3 + 30’	PH 2.8-3.0, drain 1/3 float
Tanning	4	Basic chromium sulphate (BCS)		
	0.5	Sodium formate	60’	
	4	BCS		
	0.5	Sodium formate	60’	Check penetration
	80	water	30’	
	1.5	Sodium bicarbonate	5’x4 + 60’	PH 3.8-4, pile O/N

Table 2 Post-tanning recipe

Article	**Sheep cabretta**		**Color**			**Black and dark brawn**	
Input raw material	Sheep wet blue extra large (Ethiopia & Indian)		Thickness			0.8-1.0mm	
weight	4.5	kgs	Process type			Retanning, dyeing and fatliqouring	
quantity	5	pcs					
All percentage are based on wet blue shaved weight							
We have 0.9mm							
process	%	kgs	chemicals	°C	Min	PH	Comment
Wet back	200	9	water	35			
	0.5	0.0225	Relugan GTW/GT50		15	4.2	
	0.5	0.0225	Formic acid		30	3.0	Drain
washing	200	9	water	35	15		Drain
Re-chroming	100	4.5	water	35			
	1.0	0.045	RicacidBlack NBS/ dark brawn		10		
	3.0	0.135	Acrylic syntan ACR 40/Novaltan MAP		30	4.2	
	0.2	0.009	Formic acid		5		
	0.5	0.02	Sulphited oil				

		25	EA1/ Fosfol AUTC-6				
	2.0	0.09	BCS				
	3.0	0.135	Syntan CR 505/CD		30		
	100	4.5	water				
	1.0	0.045	Sodium formate				
	1.0	0.045	Tanigan PAK/Basyntan DI		2x10 +45	3.8	Check drain/wash/drain pile O/N
Neutralization	150	6.75	water	35			
	1.0	0.045	RickacidBlack NBS/ dark brawn		10		
	4.0	0.18	Novaltan MAP/MR70				
	0.5	0.0225	Sodium formate				
	0.5	0.0225	Tanigan PAK/Basyntan DI		2x5+30	4.8	Drain /Wash /Drain
Retan, Dye &Fatliqour	75	3.375	Water	35			
	1.0	0.045	Gensoft FC/ EXP				
	5.0	0.225	Retanal LSF100/PF80& SX20				
	5.0	0.225	Retingan R7 (dye levelling)				
	3.0	0.13	Mimosa / GS				

		5	powder				
	3.0	0.13 5	Quebracho				
	2.0	0.09	RickacidBlack NBS/ dark brawn		60		
	100	4.5	water	60			
	3.0	0.13 5	Syntan FB6/ Nerfil powder				
	2.0	0.09	Syntan DI/Filler R		20		
	2.0	0.09	DensodrinEN/S X25				
	3.0	0.13 5	Genosoft FC/EXP				
	1.0	0.04 5	Synthetic natural raw oil(BL2 or 2FB or BSF)/Fosfol 54		10		
	0.1	0.00 45	Preventol WB		30		
	2.0	0.09	Acrylic syntan ACR 40/Novaltan MAP		30		
	3.0	0.13 5	Formic acid		3x5+ 45		Check. Drain / wash/ Drain
Top dyeing	150	6.75	Water	60			
	0.5	0.02 25	RickacidBlack NBS/Dark brawn		10		

	0.4	0.018	Formic acid		15		
	0.5	0.0225	RickacidBlack NBS/Dark brawn		10		
	0.6	0.027	Formic acid		3x5+15		
	0.5	0.0225	Synthetic natural raw oil(BL2 or 2FB or BSF)/Fosfol 54				
	0.5	0.0225	Catalics GS		20		Check. Drain/wash/ Drain
							Sam, set out and vacuum dry @60°C

Annexure3. Process recipe for glove

Table 1 pre-tanning-tanning

Process	%	Chemicals	Time	Comment
Soaking	200	water		
	0.3	Preservative		
	0.1	Wetting agent		Over night
Panting	10	Water		
	2.5	Sodium sulphide		
	7	Lime		
Apply the paste on the flesh side and pile over night next day do unhairing				
Drum re-liming	100	water		
	2	lime	48hr	Check plumpness
Drum liming by rotating the drum for 5min and stop 55min for 2 day then do fleshing and scudding				
Washing	300	water	20'	Drain
De-liming	100	water		
	5	Ammonium chloride	30-45min	PH $\leq$ 8
Bating	1.5	Bating agent	60'	Check. By squeezing and thump pressing Drain/wash /drain
Pickling	80	water		
	8	salt	20'	Check B^{O} 6-7
	0.5	formic	20'	
	0.8-1	Sulphuric acid	4x10' + 60'	PH 2.0-2.5
3 day ageing				
De-pickling	150	water		

	10	salt	10’	
	2	Sodium formate	20’	
	0.7	Sodium bicarbonate	20’	
	0.7	Sodium bicarbonate	20’	
	0.7	Sodium bicarbonate	20’	PH 4.5-5 Drain completely
Degreasing I	1.5	ND 01(Degreasing agent)	60’	
washing	300	water		
	6	salt	20’	Drain
Degreasing II	1	ND 01(Degreasing agent)	60’	
washing	300	water		
	6	salt	10’	Drain
Degreasing III	1	ND 01(Degreasing agent)	60’	
Washing	300	water		
	6	salt	10’	Drain
Re-pickling	70	water		
	7	salt	10’	
	0.5	Formic acid	10’	
	0.8	Sulphuric acid	10’x3 + 30’	PH 2.8-3.0, drain 1/3 float
Tanning	4	Basic chromium sulphate (BCS)		
	0.5	Sodium formate	60’	
	4	BCS		
	0.5	Sodium formate	60’	Check penetration
	80	water	30’	

	1.5	Sodium bicarbonate	5'x4 + 60'	PH 3.8-4
	0.5	Preservative(busan)	30'	pile O/N

Table 2 Natural crust recipe (post-tanning)

Article: sheep wet-blue		Date:	Pcs:				
Colour : white	Thickness: 0.5mm	Size: medium					
Stage	**Chemical list**	**Temp.(°c)**	**%**	**kg**	**Time**	**PH**	**Comment**
Washing	Water	35	300		15'		Drain
Wetback	Water	35	300				
	Wetting agent		0.1		15'		
	Acetic acid		0.25		15'		
	Oxalic acid		0.25		15'	3.5	D/W/D
Acid bating	Water	35	50				
	Sodium bicarbonate				15'	4.5	
	Defat ACP(cid bating agent)		0.6		60'		Check bating , D/W/D
Re-chroming	Water		50				
	Formic		0.25		15'	3.5	
	Novaltan MAP		4		60'		
	BCS		4		45'		
	Water	35	200				
	Sodium Formate		0.5		30'		D/W/D, pile L/O/N
Neutralization	Water	40	80				
	Neutralizing syntan		2		20'		

	Sodium formate		2				
	Sodium bicarbonate		1.8		3x5' + 30'	6-6.5	
	water		70		15		D/W/D
Fat-liquoring	Water	50-60	150		10'		
	Phosphol LP		6				
	Fish oil		2				
	Genosoft FC		10		60'		
	Formic acid		2		20'		Check penetration
D/W/D/Pile O/N							

Next day setting out, hang dryer, stacking, toggling

Table 3 Natural crust dyeing recipe

Article: sheep natural crust		Date:		Pcs:			
Colour : pink/ Havana orange	Thickness: 0.5mm	Size: medium					
Stage	Chemical list	Temp.(^{o}c)	%	kg	Time	PH	Comment
Wetback	Water	40	300				
	Wetting agent		0.2				
	Ammonia		0.5		60'	6.5-7	D/W/D
Dyeing	Water	40	50				
	Ammonia		1			4.5	
	Havana J (dye)		4		20'		Check. Pen.
	Ammonia		1				

	Havana J (dye)		4		20’		Check. Pen.
Re- fatliqour	Water	60	200				
	Fosphol LP		2				
	Fish oil		1				
	Genosoft FC		3				
	Catalics GS (cationic fatliqour)		1		45’		
Fixation	Formic acid		3		3x10’ +20’		D/W/D pile O/N
Next day: over head drier, toggle and shaved							

Annexure 4: dynamometer (Tensile testing machine)