



**ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
SCHOOL OF CHEMICAL AND BIO- ENGINEERING
(LEATHER TECHNOLOGY STREAM)**

**STRUCTURAL INVESTIGATION OF ETHIOPIAN CAMEL HIDES (CAMELUS
DROMEDARIUS) AND It's SUITABILITY FOR LEATHER MANUFACTURE**

**BY
BELAY MELES**

Advisors

Dr. R. Aravindhan

Dr. R. Karthikeyan

A Thesis

**Submitted to the School of Graduate Studies of Addis Ababa University
In partial fulfilment of the Degree of Master of Science in Chemical Engineering
(In Leather Technology Stream)**

**By
Belay Meles**

SEPTEMBER, 2014

STRUCTURAL INVESTIGATION OF ETHIOPIAN CAMEL HIDES (*CAMELUS DROMEDARIUS*) AND it's SUITABILITY FOR LEATHER MANUFACTURE



A Thesis

**Submitted to the School of Graduate Studies of Addis Ababa University
In partial fulfillment of the Degree of Master of Science in Chemical Engineering
(In Leather Technology Stream)**

**By
Belay Meles**

Advisors

Dr. R. Aravindhan

Dr. R. Karthikeyan

**ADDIS ABABA UNIVERSITY INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO- ENGINEERING
(LEATHER TECHNOLOGY STREAM)**

SEPTEMBER, 2014

DECLARATION

I, the undersigned, declare that this thesis is my original work and that all sources of materials used for the thesis have been dully acknowledged.

Signature

Date

Approved by examining Board

Dr. –Ing Birhanu Assefa _____
School of Chemical and Bio-Engineering, Signature Date
Department Head

Dr. R. Aravindhnan _____
Advisor Signature Date

Dr. R. Karthikeyan _____
Advisor Signature Date

Dr. Abubekar _____
Internal Examiner Signature Date

Dr. P. Thanikevelan _____
External Examiner Signature Date

DEDICATION

This work is dedicated to all of my family

1. Worknesh Mirach (My mother)
2. Meles Gebre (My father)
3. Brothers and sisters

ACKNOWLEDGMENTS

- First of all, I would like to pay tribute to almighty God. He always stands by my side in all of my life.
- My heartfelt thanks also go to Ato wondu Legesse, Director General, LIDI, Ethiopia, for granting me to pursue my Masters degree under Twinning program, Dr. B. Chandrasekaran and Mr. P. Saravanan Coordinators, Twinning Project for their efforts to carry out my M.Sc. program successfully.
- I would like to express my sincere gratitude to my advisor Dr. R. Aravindhnan and Co-Advisor Dr. R. Karthikeyan, for their valuable support, coaching approach, encouragement, supervision and useful suggestions throughout my research work. In the absence of my Advisor, who most of the time be in India, moral support and continuous guidance and the great effort of my Co-Advisor made my research work be completed successfully.
- I would also like to thank Dr. Gnanamani for her continuous guidance and support in conducting my tasks during my stay in CLRI, India. In addition, my thanks also go to Dr. Punitha Velmurugan for her great effort and constructive suggestions during my stay in CLRI, India. Similarly, my gratefulness goes to Dr. Usha and Mr. Mutukrishnan, Kavitha, and Raja for their support in guiding and supporting while doing my experimental works during my stay in CLRI, India.

My special thanks also go to Dr. Swarna V. Kanth for her great effort to adapt life and make everything easy during our stay in CLRI, Chennai, India. She was not only instructor but also mother as she did what every mothers do.

Table of Contents

Acknowledgement	iv
Table of content.....	v
List of Tables.....	viii
List of figures.....	ix
Abbreviations and Acronyms.....	xi
Abstract	xii
List of Abbreviations and Acronyms.....	xi
1. Introduction	1
1.1 Back ground.....	1
1.2 Statement of the Problem.....	3
1.3 General and specific objectives	3
1.3.1 General objective.....	3
1.3.2 Specific objectives.....	3
1.4 Significance of the research.....	4
1.5 Scope of the study.....	4
2. Literature Review	5
2.1 Skins and hides	5
2.2 Composition of hides and skins	6
2.2.1 Fat distribution in Camels.....	6
2.2.2 Collagen Content	6
2.2.3 Nitrogen content	6
2.3 Hydrothermal stability of collagen	6
2.4 Physiological adaptation	6
2.5 General breed information	7
2.6 World live stock status.....	7
2.7 Live Stock Status and annual growth in Ethiopia.....	8

2.9 Off-take rate and selling price.....	11
2.10 Live animal exports in Ethiopia.....	12
2.11 Production of hides and skins in Ethiopia.....	13
2.12 Supplies of raw hides and skins	14
2.13 Alternative raw materials for the Ethiopian tanning industries	15
2.14 Camel population and present distribution	17
2.15 Herd diversification in Low lands of Ethiopia.....	18
2.16 Economic Evaluation of Camels.....	18
2.17 Utilization of camel hides for leather manufacture.....	19
2.18 Biological and Compositional Analysis.....	20
2.19 Physical and chemical Analysis.....	21
3. Materials and Methods.....	22
3.1 Raw materials, Chemicals and Reagents	22
3.1.1 Raw materials	22
3.1.2 Leather chemicals	22
3.1.3 Reagents.....	22
3.2 Laboratory equipment, instruments and Apparatus	22
3.2.1 Laboratory instruments and Apparatus used for biological and chemical analysis	22
3.2.2 Laboratory instruments and Apparatus used for physical analysis	23
3.2.3 Leather processing equipments and apparatus	23
3.3 Methods.....	24
3.3.1 Biological and chemical Analysis	24
3.3.1.8 Chromic oxide content of leather	33
3.3.2 Physical Testing of Leather	34
3.3.3 Evaluating the suitability of the raw material for leather products	39
4. Results and Discusson.....	43
4.1 Biological and chemical Analysis.....	43
4.1.1 Histological features of camel hides.....	43
4.1.2 Scanning Electron Microscope (SEM) Analysis	46
4.1.4 Fat content	49

4.1.5 Collagen Content Estimation.....	50
4.1.6 SDS-PAGE analysis	51
4.1.7 Circular Dichroism Analysis	52
4.1.8 Hydrothermal stability	53
4.1.9 Chromic oxide content of wet blue leather.....	54
4.2 Physical Testing.....	55
4.2.1 Tensile strength.....	55
4.2.2 % Elongation at break.....	55
4.2.3 Tear strength.....	56
4.2.4 Grain distension at grain burst.....	57
4.2.5 Total Ash Content Estimation	57
4.2.6 Water vapour permeability	58
4.2.8 Statistical Analysis on Proximate composition and performance properties of Camel.....	59
5. Conclusion and Recommendations.....	60
5.1 Conclusion	60
5.2 Recommendations.....	61
6. Reference.....	62
Annex 1	64
Annex 2.....	68
Annex 3.....	80
Annex 4.....	83

LIST OF TABLES

Table No.	Title	Page No.
2.1	Annual livestock production growth (percent per annum)	8
2.2	Livestock resources of Ethiopia (10,000 heads)	9
2.3	Production capacity of Ethiopian tanning industries	10
2.4	Ethiopia's Live Animals export by species	13
2.5	Production of hides and skins (Year 2014 figure in million pieces)	14
2.6	Non-conventional animal population size in Ethiopia	15
4.1	Absorbance Reading for standard Hydroxyproline	50
4.2	Tensile strength results of Camel shoe upper	56
4.3	Elongation results at break (%)	57
4.4	Tear strength results of Camel shoe upper	57
4.5	Lastometer test result for camel upper leather	58
4.6	Statistical analysis on proximate composition and performance properties of camel hide and leather	60

LIST OF FIGURES

Figure No	Title	Page No.
2.1	The anatomy of hides and skins	5
2.2	Camelus dromedaries	7
2.3	Camelus bactrianus	7
2.4	Prevalent use (%) of Ethiopian camels by sex	19
3.1	Experimental design flow chart	23
3.2	Ultra Microtome	24
3.3	Optical Microscope	24
3.4	Gold plating machine	25
3.5	Plates for mounting samples	25
3.6	Scanning Electron Microscope	25
3.7	Elemental analyser	27
3.8	Centrifuge Machine	28
3.9	Uv-vis spectrophotometer	28
3.10	Micro pipette	28
3.11	SDS-PAGE setup	29
3.12	Circular Dichroism spectropolarimeter	30
3.13	Hot air oven	31
3.14	Soxhlet apparatus	31
3.15	Acid digestion of wet blue leathers	32
3.16	Shape of Test specimen for Tensile Strength	35
3.17	Thickness gauge	35
3.18	Universal Tensile Meter (UTM)	35

3.19	Steam absorption set up	36
3.20	Steam absorption Tester	36
3.21	Lastometer	37
4.1	%Moisture content of wet salted camel hides	43
4.2	Cross sections of camel hide at raw stage	44
4.3	Cross sections of camel hide at wet blue stage	45
4.4	SEM images of wet blue camel leathers	46
4.5	% Nitrogen Content of raw and limed pelt	48
4.6	% Fat Content	49
4.7	HiMark™ Pre-Stained Protein Standard and Camel	52
4.8	CD- spectrum of Camel collagen solution	53
4.9	Shrinkage temperature of camel wet blue leather	54
4.10	Chromic oxide content of camel wet blue leather	55

LIST OF ABBREVIATIONS AND ACRONYMS

AA	Acetic Acid
CD	Circular Dichroic
d ₁	First dilution
d ₂	Second dilution
d ₃	Third dilution
FAO	Food and agriculture organization
ILRI	International Livestock Research Institute
EIAR	Ethiopian Institute of Agricultural Research
HCl	Hydro chloric acid
Hrs	hours
BCS	Basic Chromium Sulphate
HWB	Hide Wet Blue
L-HP	L-Hydroxy Proline
Nm	nano meter
PDAB	Para di-methyl Amino Benzaldehyde
Tris	tris (hydroxymethyl) amino methane
RH	Relative Humidity
Rpm	revolution per minute
SEM	Scanning Electron Microscope
T _s	Shrinkage Temperature
Uv-vis spec	Ultra violet- visible spectrophotometer
v ₁	volume at first dilution
v ₂	volume at second dilution
v ₃	volume at third dilution
WS	Wet salted
SNNP	Southern Nations Nationalities and people

Abstract

Ethiopia has the largest livestock population in the African countries, providing a strong raw material base for the growing leather and leather products sector. The main source of raw material for the Ethiopian tanning industry comes from sheep, goat and cattle. Since the Ethiopian leather industry is booming, the industry is now looking to exploit the alternative raw materials available in the country. Camel (*Camelus dromedarius*) is one of the most important livestock in the East African countries. Due to lack of awareness and technology, most of the hides are not utilized fully by the tanners. Wet salted camel hides were used for this study. In the present study an attempt has been made to develop shoe upper leathers from camel hides. Owing to the excellent strength properties and the attractive grain pattern, attempts were also made to develop leather goods and belting leathers. The raw material was characterised for fat and collagen content and converted into finished leather by using suitable tanning methodology and the leathers were utilized for the preparation of different types of leathers. Histological analysis of the camel hides were carried out. Based on the histological understanding, the strategies for making different types of leathers were established. Three different types of finished leathers were developed and the physical and chemical properties were also evaluated. The results obtained from the chemical and physical tests revealed that the raw material was suitable for the manufacture of upper leather, leather goods and belting leather.

Keywords: Camel hides, leather goods, belting leather, leather products

CHAPTER ONE

1. INTRODUCTION

1.1 Back ground

Leather making is a complex process, which undergoes various physical and chemical changes during soaking to finishing. There are lots of “do’s and undo’s” in these unit operations of which liming-deliming, pickling-de-pickling-re-pickling and degreasing-fat liquoring are the major ones. During this leather making, the properties such as fibre opening, fibre splitting, thermal resistance, and utility properties such as softness, fullness, colour and water resistance are incorporated in to the leathers for different applications.

Ethiopia is one of the countries with higher livestock population standing first in Africa and fourth in the world. The total livestock population of the country is estimated at 35 millions of cattle, 25.5 millions of sheep, 22.8 millions of goats and 1.1 millions of camels ¹

The development of tanning industry in Ethiopia

Modern tanning industry in Ethiopia goes back in to the mid of 1920s ². Recently, there are about 30 tanning industries in Ethiopia. Because of its high quality, the Ethiopian leather, particularly sheepskin and goatskin leather can easily be marketed in the major leather importing countries. Moreover, there is also a high domestic market potential of finished leather for the growing local leather products manufacturing industries.

The Ethiopian industry bases itself on the country’s livestock population. This enormous population of livestock provides ample opportunity for the development of the leather industry in the country. The main source of raw materials for the Ethiopian tanning industries come from cow, sheep and goat. In addition to these conventional raw materials, Ethiopia also possesses potential livestock populations such as donkeys, horses, mules and camels. Regardless of its potential livestock populations, Ethiopia didn’t get much benefit out of its `raw material sources due to many reasons of which the insufficient availability of quality raw materials, less off-take rate of the country, poor

value chains of hides and skins, and the lack of efficient technologies are believed to be the major ones.

This research work enables us in finding a new source of raw material for the tanning industries. Camel hides are being considered as an additional source of raw material for the tanning industries. In this research work, wet salted camel hides were analyzed for various compositions, structural changes at various stages and evaluated for the suitability of the raw material for leather making.

Production Capacity of Ethiopian tanning industries

Currently, there are 22 tanneries operating in Ethiopia with installed daily capacity of producing 5,760 square feet of hides and 101,600 square feet of skins. The actual daily capacity utilizations, however, are 81% and 44.97% for hides and skins, respectively. Out of 22 tanneries, 9 are 100% export oriented in semi-processed skins mainly pickle and wet blue. The other tanneries managed to produce finished leather products by introducing new technologies and thus, are selling almost 20% of their products in the local market.

The Ethiopian leather industry comprises of key sub sectors such as footwear industries, leather garments and leather goods.

Global production of leathers

According to FAO, in 2007 the global production of leather was close to 8 billion pieces of hides and skins and the share of developing country was about 39%. The top three major leather producers are the Peoples Republic of China, Italy and India ³.

Impact of the Ethiopian leather sector in the national economy

The industrial policies in the leather sector have been largely effective driving strong growth. This growth, however, has not been in par with its potentials. Market problems along the supply chain, limited processing and marketing capacity, inefficient regulations and enforcement capacity and coordination problem have resulted in to below-potential levels of production and hence export earnings ⁴

1.2 Statement of the Problem

The tanning industry is among the manufacturing industries that play role in boosting the national economy of a country. Tanning industries use the by-products of the meat industry (Hides and Skins). The skins (from sheep and goats) and hides (commonly from cattle) are the main inputs to the tanning industries. Now days, the tanning industries in the world are suffering from the scarcity and poor quality of skins and hides. Ethiopia is also one among these countries facing the problem, regardless of its high livestock population. Tanning industries in India use raw materials from buffalo in addition to the skins and hides from sheep, goats and cattle. But Ethiopian tanning industries rely only on sheep, goats and cattle for the manufacture of different leather products. Such dependence brings the scarcity of the raw materials for leather manufacture. This research work focuses in finding an additional raw material resource for leather manufacturing. Camel hides are being considered as an additional source to the leather industries.

In the low lands of Ethiopia (Afar, Somali regions and Oromia region, particularly Ogaden) the camel hides are used for the preparation of traditional materials like ‘Akimada’, which is one of the problems that leads to this research. Another point which leads to this research work is the export share of Ethiopia in the world market being very limited and its import share being very high at about 9.1% in 2010 ⁵

1.3 General and specific objectives

1.3.1 General objective

The general objective of this research work is to characterize the nature and composition of Ethiopian camel hides and use these raw materials as an additional resource for leather manufacturing.

1.3.2 Specific objectives

- Biological and chemical analysis of Ethiopian camel hides
- Understanding how the histological features of an animal affect the physical properties of the final leather
- Identifying the best type of leather from this raw material
- Designing the process recipe for the manufacture of the identified end use leather

1.4 Significance of the research

This research work will add the knowledge of how the histological features of an animal affect the final properties of the leather. In addition to this, the research work will enable us how to approach the manufacture of leather products from a new resource material that didn't get much application in the leather manufacturing.

1.5 Scope of the study

The research work focuses on the scientific study to determine nature and composition of Ethiopian camel hides, finding the suitability of the chosen raw material for the manufacture of leather, development of different types of finished leathers and evaluation of the developed leathers.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Skins and hides

The main composition of hides and skins are moisture (65%), proteins (33%), minerals (0.5%) and fats (2-6%)⁶. The composition of hides and skins vary from region to region, species to species and within the hide/skin. For example highland sheep skins contain more fat compared to low land sheep skins. This is the beauty of nature. These changes in composition are supposed to be because of feeding system, breed and age of the animals. The use of leather goes back to the pre-historic times. The principal raw material is the hide or skin of animals from the meat industry. The following figure enables us to have the understanding of the anatomy of hides and skins:

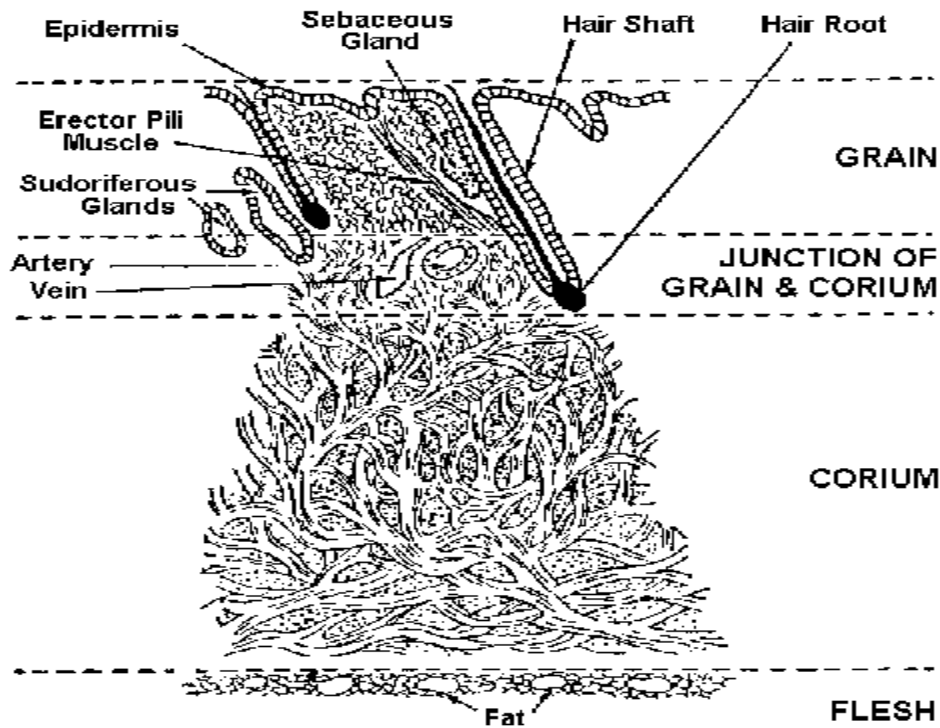


Fig 2.1:- The anatomy of hides and skins

2.2 Composition of hides and skins

2.2.1 Fat distribution in Camels

In most mammals fat is spread over the body surface just under the skin. However, in the camel, the fat is accumulated in the hump which enables sweat to be evaporated easily over the rest of the body surface and this is adaptation to heat transmission [Dorman, 1984]. The camels in Ethiopia are adapted to arid and semi arid regions of the country. Accordingly, nature is supposed to provide them long legs to keep them away from the hot ground, less fat content, less hair per square inch, more sweat glands compared to cow, sheep and goat

2.2.2 Collagen Content

Collagen is one of the more important structural proteins in the body being of particular importance in connective tissues by providing their durability. As such, knowledge of at least the amount of collagen in a particular tissue is essential for the complete understanding of the structural and mechanical properties of that tissue ⁷

Collagen is an abundant structural protein in all animals. So far, there are about 29 types of collagens in animal tissues. The most common types of collagens are type-I (Abundant and widespread: dermis, bone, tendon, ligament), type-II (Cartilage, vitreous) and type-III (Skin, blood vessels, intestine) ⁸

2.2.3 Nitrogen content

Nitrogen determination has a long history in the area of analytical chemistry. Johan Kjeldahl first introduced the Kjeldahl nitrogen method in 1883 at a meeting of the Danish Chemical Society ⁹

2.3 Hydrothermal stability of collagen

Hydrothermal stability is one property that is routinely used to characterize collagen whether native, structurally modified or chemically modified ¹⁰

2.4 Physiological adaptation

The camel is an important livestock species uniquely adapted to hot arid environments. Camels can stay without water for as much as 3weeks on average.

During exceptionally hot seasons, depending on vegetation available for browsing, they are watered every 6-7 days.

2.5 General breed information

There are two varieties of camels, namely *Camalidae* dromedaries, the single-humped found in the tropics, and *C.bactrianus*, living in the cold regions. It is most numerous in the arid areas of Africa, particularly in the arid lowlands of Eastern Africa namely Ethiopia, Somalia, Sudan, Kenya and Djibouti. Approximately 11.5 million animals in this region represent over 80% of the African and two thirds of the world's camel population [Schwartz 1992]. The global population of domestic camels is relatively stable, at around 22 million, with only 5% of them being Bactrian camels. The largest herds existed in the African nations of Somalia, Sudan, Ethiopia, Mauritania, Kenya, Chad, Mali, and Niger and the subcontinent countries of Pakistan and India ¹¹. The Afar and Somali regions of Ethiopia are known for the large population of camel hides.



Fig 2.2:- Camelus dromedarius



Fig 2.3:- Camelus bactrianus

2.6 World live stock status

Like crop production, growth in livestock production, mirrors growth in total agricultural production, although the observed deceleration in growth is slightly less than for crop production as the consumption of livestock products continues to increase its share in total food consumption. Sub-Saharan Africa is the only region where livestock production growth will to be fairly strong, while only slow growth is foreseen for the regions.

Worldwide the camel is used extensively for its meat, milk and hide products as well as for transportation. Production and consumption are centred in Northern Africa, the Middle East and the former Soviet Union ¹². In Australia the camel was used extensively as a form of transport until trucks replaced them in the middle of the twentieth century when they were slaughtered or released to the wild.

Table 2.1: - Annual livestock production growth (percent per annum)

	1961-2007	1987-2007	1997-2007	2005/2007-2030	2030-2050
World	2.2	2	2	1.4	0.9
Developing countries	4.3	4.5	3.4	2.0	1.3
Idem, excl. China and India	3.4	3.6	3.5	2.1	1.5
Sub-Saharan Africa	2.5	2.8	3.3	2.7	2.6
Latin America and the Caribbean	3.2	3.8	3.8	1.6	0.9
Near East/North Africa	3.3	3.3	3.0	2.2	1.7
South Asia	3.7	3.6	3.2	2.7	2.2
East Asia	6.5	5.9	3.4	1.8	0.8
Developed countries	1.0	0.1	0.6	0.6	0.2

Source: - WORLD AGRICULTURE TOWARDS 2030/2050, the 2012 Revision

2.7 Live Stock Status and annual growth in Ethiopia

Ethiopia has one of the largest livestock populations in the world providing a strong raw material base for the leather industry. This livestock sector has been contributing considerable portion to the economy of the country, and still promising to meet round the economic development of the country ¹³. According to the CSA of Ethiopia, the total population of Ethiopia is estimated at about 53.4 million cattle, 25.5 million of sheep, 22.78 million of goats, about 2 million horses, 6.2 million donkeys, 1.1 million camels and about 0.38 million mules. In Ethiopia, the pastoralist and agro-pastoralist areas such

as Borena, Afar and Somali are considered the traditional source of livestock, supplying 95% of livestock destined for export market ¹⁴

The livestock population of Ethiopia is not exactly known and hence the total livestock population is having different figure in many literatures. According to the report of Ministry of Agriculture And Rural Development on A Comprehensive Plan for supporting the meat Export Industry of 2008, the livestock population in species is tabulated as follows:-

Table 2.2: - Livestock resources of Ethiopia (10,000 heads)

Regions	Cattle	Sheep	Goats	Camel	Poultry	Pack Animals
Tigrai	262.23	81.35	239.98	3.28	313.12	39.72
Afar*	237.67	254.19	439.86	88.43	6.96	19.36
Amhara	1,007.73	753.05	485.65	1.48	940.09	190.64
Oromia	1,824.80	808.46	538.36	12.20	1,222.68	304.72
Somali*	124.67	707.85	622.48	126.31	17.52	14.07
Beinshangul	35.039	6.89	31.43	-	63.56	4.14
SNNP	804.32	340.31	205.41	-	639.11	67.10
Gambela**	12.62	4.37	4.91	-	23.79	0.06
Harari	3.74	0.45	3.28	-	3.33	0.70
Addis Ababa*	6.73	1.65	1.02	-	6.24	1.74
Diredawa	3.84	5.42	12.41	0.64	4.92	1.01
Total	4,323.36	2,964.01	2,584.78	232.32	3,241.32	643.26

Source: - * for Afar, Somali and Addis Ababa CSA of 2003/04; ** for Gambela, CSA of 2004; Others, CSA of 2005/06

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, 0.5% for goats and 1.14% for camels while annual off take is estimated at 10% for cattle, 35% for sheep, 38% for goats and 6.5% for camels.

2.8 Production capacity of Ethiopian tanning industries

The production capacity of Ethiopian tanning industries differ from tannery to tannery. The installed production capacity of the Ethiopian tanning industries and respective performance is tabulated as shown below:-

Table 2.3:- Production capacity of Ethiopian tanning industries (x1000)

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
Debre Birhan	-	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		Soaking 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

Source: - Leather Industry Development Institute, 2014

2.9 Off-take rate and selling price

Hides and skins are the by-products of meat industry and consequently, the volume of hides and skins is determined by meat production. Most of the hides and skins are sourced from rural slaughter slabs and homestead slaughter [Wayua and Kagunyu, 2008]. The average selling price of live Ethiopian camel was estimated to be 1784 ETB and 2011 ETB for kebribeyah and Babilie woredas of the Jijiga Zone, Somali Region in 2007 [Yohannes Mehari, et al., 2007]. Ethiopia is generously endowed with livestock resources. Its cattle population of more than 53 million, along with sheep and goat populations of 25.5 and 24.1 million, respectively, put the country first in Africa ¹⁵ with

annual off-take rate of nearly 10% for cattle, 33% for sheep and 38% for goats, the country is endowed with enormous potential for cheap supply of skins and hides.

In addition to the selling of live camels, camel meat is also available in the market in these two woredas. The gross off take rate was found to be 7.09 and 8.22% for Babilie and Kebribeyah woredas, respectively ¹⁶. On average meat production potential of a camel is found to be (230 – 240 kg) for male and (187 – 195 kg) for female in Babilie, respectively, whereas in Kebribeyah it was found to be (214 – 225 kg) for male and (199 – 207 kg) for female respectively. According to the information obtained from Addis Ababa abattoirs enterprise, on average 10 camels are slaughtered per day and 300 camels/month and 3,600 camels/year and the selling price of camel hides is very cheap compared to the conventional raw hides and skins. According to the same source, the average selling price of camel hides is 2Birr/kg, which is very less compared to 6.5Birr/kg and 75Birr/piece of cow and sheep skins respectively.

2.10 Live animal exports in Ethiopia

During the period (July 2007 to June 2008), the total number of live animals exported was about 297,644. The three major import markets in the same year were the Kingdom of Saudi Arabia (KSA), Djibouti, and Yemen, accounting for 48 percent, 17 percent, and 15 percent, respectively, of the total live animal exports from Ethiopia¹⁷. According to the same source, Yemen alone accounted for 47 percent of cattle export from Ethiopia while Djibouti accounted for 50 percent of total Ethiopian camels' exports.

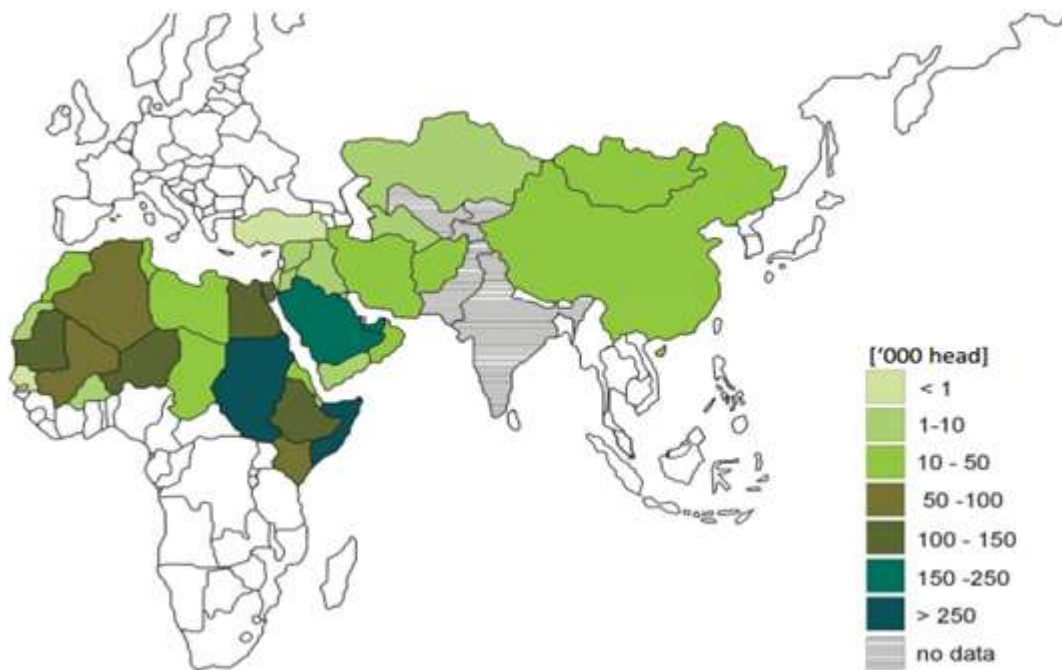
In addition to this, other source also indicates that Ethiopia earned US\$ 105 million during July __December 2010 from export of 8,013 tonnes of meat and 244, 862 head of live animals, a 93% percent boost for same months in 2009. Export of live animals contributed 73% of the earnings and the balance from meat export. Export of camel and cattle has showed a remarkable increment over the last three years ¹⁸

Table 2.4: - Ethiopia's Live Animals export by species

Species	July-Dec. 2010		July-Dec. 2009		July-Dec. 2008	
	No	Value (000 USD)	No	Value (000 USD)	No	Value (000 USD)
Camels	54,347	24,315	29,543	13,909	15,824	7,131
Cattle	105,685	48,196	45,405	20,885	51,582	21,319
Shoats	84,721	3,992	123,450	5,058	82,256	3,614
Others	109	1	660	2	886	518
Total	244,862	76,504	199,058	39,854	150,548	32,583

Source: - Focus on Ethiopia's Meat and Live Animal Export: Trade Bulletin 4, April, 2011

Slaughter of camels for internal consumption in 2011



Source: FAOSTAT 2013

2.11 Production of hides and skins in Ethiopia

The hides and skins are supplied to the Ethiopian tanning industries from different parts of our country. The most regions where hides and skins are collected include Oromia,

Amhara, Tigray, SNNP and the two city administrations of Addis Ababa and Diredawa. The average supplies of hides and skins for the last six months for these regions is shown as follows:

Table 2.5: - Production of hides and skins (Year 2014 figure in million pieces)

S/No	Region	Plan			Accomplishment			Total		%
		Hide	Sheep skins	Goat skins	hide	Sheep skins	Goat skins	Plan	Accomplishment	
1	Oromia	7.22	25.85	17.92	2.02	6.7	2.07	50.98	10.80	21.2
2	Amhara	12	60	39.1	2.26	17.8	11.75	111.1	31.81	28.6
3	SNNP	4.55	7.24	2.75	3.28	6.40	2.83	14.53	12.51	86.1
4	Tigray	0.54	2.7	4.37	0.39	2.41	3.72	7.60	6.52	85.8
5	Addis Ababa	1.25	3.7	0.65	1.68	2.63	0.70	5.6	5.02	89.1
6.	Diredawa	0.14	0.24	0.36	0.13	0.21	0.36	0.74	0.70	96.4
		25.7	99.72	55.12	9.76	36.2	21.43	190.54	67.36	35.3

Source: Ethiopian Leather Industry development institute, 2014

2.12 Supplies of raw hides and skins

Around 8.5 million pieces of sheep skins, 7 million pieces of goat skins and 1.2 million pieces of hides are supplied to the tanneries per annum. Almost 100% of sheep skin is supplied in wet salted. About 75% of goats' skin supplied in wet salted and the 25% as air

dried. With regard to the cattle hide 10% are processed as fresh, 60% are in wet salted and 30% air dried.

The main feed stock of the leather supply chain, hides and skins are a by-product of the meat and dairy market chains. Therefore the production of hides and skins is almost inelastic to changes in their price, but is influenced by factors that drive the meat and dairy markets. On the other hand the consumption of footwear with leather uppers and other leather products is positively related to changes in the purchasing power of consumers, as reflected by the fact that high income countries import proportionately more footwear than poor countries ¹⁹

2.13 Alternative raw materials for the Ethiopian tanning industries

The conventional raw material resources to the Ethiopian tanning industries comprise of cattle hides, sheep and goat skins. However, the country possesses other livestock populations such as camels, donkeys, horses and mules. Because of the religious and ethics existing in the country, the people in Ethiopia do not consume the meat of donkeys, horses and mules. But, camel meat is consumed as part of food and hence the hides from camels can be considered as alternative and additional raw material source to the existing raw hides and skins. The equine population of the world is 98.3 million (40 million donkeys, 15 million mules, 43.3 million horses). In the distribution pattern, 98% of all donkeys, 97% of all mules, and 60% of all horses are found in developing countries ²⁰

Table 2.6:- Non-conventional animal population size in Ethiopia

S/NO	Category	Population (millions)
1	Mule	0.385
2	Camel	1.1
3	Horse	2.03
4	Donkey	6.21

Source: CSA of Ethiopia, 2010

Tanning industry is a raw material and labour intensive industry. Raw materials account for 50-70% of production cost, labour 7-15%, chemicals about 10%, energy 3% ²¹. To maintain a good market share in the world, a better approach is needed in the selection of cheaper and quality raw materials. Currently, the price of camel hides is the cheapest among the existing raw materials. This is due to the lack of awareness and less off-take rate and hence is utilized for poultry feed, glue manufacture and for the production of low value traditional materials.

Ethiopia possesses the highest livestock population. However, the extent to which the available resource is exploited depends on the off-take rate, which is in turn a result of the level of economic development of a Country ²².

Facts about camels

- Females reach sexual maturity at around 3 years of age and mate around age 4 or 5
- Males begin to mate at around 3 years of age too, but still are not sexually matured until six years of age
- Mating occurs in winters but is peak in the rainy season
- A female camel carries a single young, called a calf, inside her body for about 13 months before giving birth.
- A camel usually bears a single calf, and occasionally twins.

- The normal life span of a camel is 40 years, although a working camel retires from active duty at 25

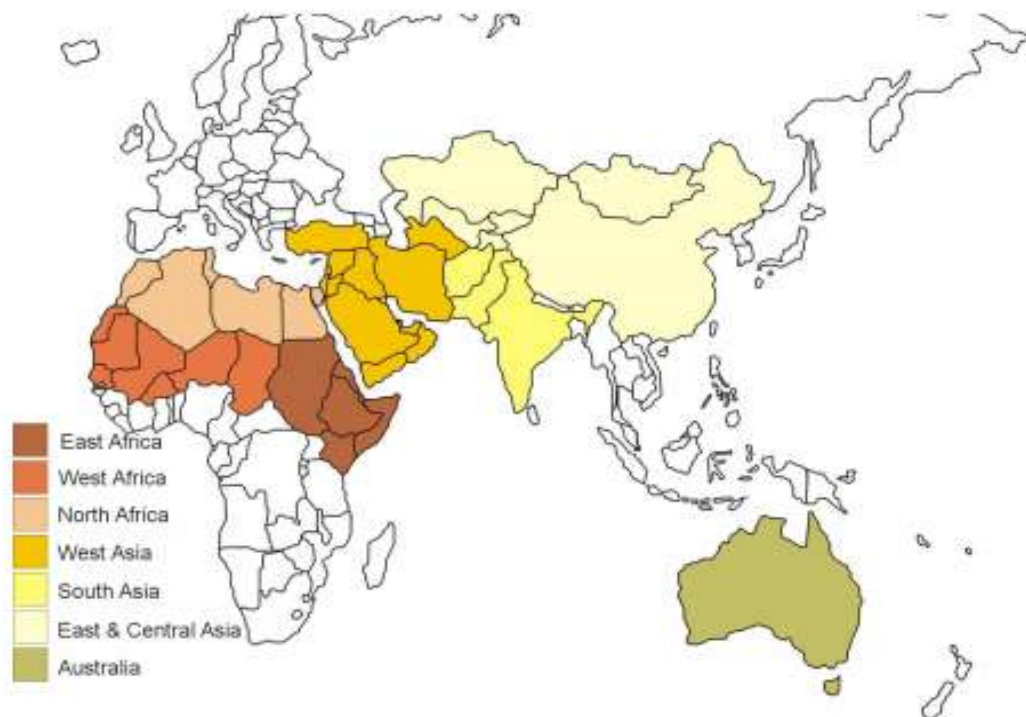
2.14 Camel population and present distribution

The camel (*Camelus dromedaries*) is an important livestock species uniquely adapted to hot arid environments. It is most numerous in the arid areas of Africa, particularly in the arid lowlands of Eastern Africa namely, Somalia, Sudan, Ethiopia, Kenya and Djibouti. Approximately 11.5 million animals in this region represent over 80% of the African and two thirds of the world's camel population [Schwartz 1992].

East Africa (Djibouti, Ethiopia, Kenya, Somalia, Sudan) covering 2,669,500 km² of arid zone has the largest camel population in Africa, of about 10 million ²³.

World Camel population is estimated to be around 25.89 million spread across 47 countries. About 85% of the camel population inhabits mainly eastern and northern Africa and rest in Indian subcontinent and Middle East countries. Somalia has the highest population of 7 million followed by Sudan 4.25 million, Ethiopia 2.40 million ²⁴.

Regions where camels are found in larger numbers (FAOSTAT for production)



2.15 Herd diversification in Low lands of Ethiopia

Overview of livestock production in Ethiopia

The diverse agro-climatic conditions of Ethiopia make it very suitable for the production of different kinds of livestock. Most of the livestock are produced by pastoralists, agro-pastoralists, and smallholder mixed crop–livestock farmers and sold to private entrepreneurs operating in a marketing chain involving collection, fattening and transportation up to terminal markets. National livestock statistics data collected at different times are not always directly comparable primarily because the entire country has never been covered in any survey or census ²⁵

Herd diversification reduces risk and insures against natural as well as human-made shocks. Nowadays many pastoralists are changing their livestock species composition from grazers that feed on grass (cattle and sheep) to browsers that eat bushes (camels and goats) ²⁶.

2.16 Economic Evaluation of Camels

The contribution of camels to the human welfare of developing countries is generally obscured by several factors, of which the estimates of camel populations being inaccurate and their products seldom enter a formal marketing system are the major ones. As a consequence, less attention has been given to camel improvements for many years in the national development plans ²⁷.

Iqbal (1999) and Raziq (2009), while working on socio-economic importance of camel, described the camel as an animal of great importance in large tracts of the industrializing world, where it serves as a cheap source of power for drawing water from wells, ploughing, levelling of land, working mini mills for oil extraction (from oil seeds), grinding wheat, corn and other grains crushing sugarcane and pulling carts for the transportation of goods as well as people. Camels are also engaged in the transport of salt, fuel wood, agricultural produce and household goods.

Sale of live camels, usually males and unproductive females for slaughter, is very common in East Africa and there are now increasing numbers of camel butchereries in many urban centres. There is also a growing export trade of slaughter camels to the

Arabian Peninsula. The camel is also a means for transportation and for domestic use as drawing water from wells, rivers and dams.

From a global perspective, the economic significance of camel production is minimal in comparison with that of other domestic animals. Nevertheless, in Africa, especially in East Africa and Sahel countries (Senegal, Mauritania, Mali, Burkina Faso, Algeria, Chad, Sudan, Somalia, Ethiopia and Eritrea), the camel population makes a significant contribution to national economies. However, it is difficult to evaluate this economic contribution as most of the camel products are traded in the informal sector.

Ethiopia has been exporting both meat and live animals to Egypt since 2005. Pan Africa Trade has been a major buyer of Ethiopian live animals ²⁸.

The eastern part of Ethiopia is considered as the heartland of the camel population, because it is home to two-thirds of the nation's camels [CSA 1988]. Although the contribution of camels to the national economy is not fully quantified, [Schwartz, 1992] estimated that 20,000 tonnes of camel meat and 174,000 metric tons of camel milk were produced annually in the country.

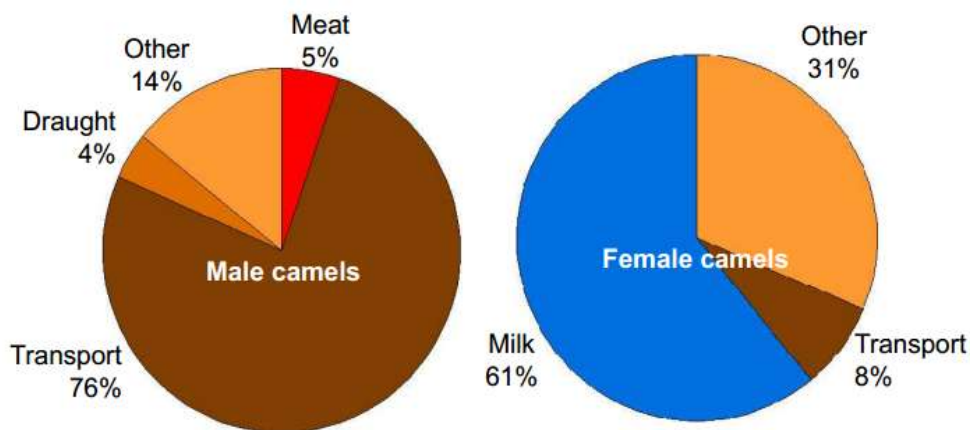


Fig 2.4:- Prevalent use (%) of Ethiopian camels by sex

Source: - Statistical Bulletin 570, Federal Republic of Ethiopia, Central Statistical Agency, Addis Ababa, 2013

2.17 Utilization of camel hides for leather manufacture

The commercial tanning of camel leather was pioneered in Australia. It is very versatile leather which has two unique properties. These are its exceptional tensile strength and the

attractive grain pattern on the tanned product. These features ensure its demand for the manufacture of a wide range of products.

Historically footwear manufacturing has been estimated to consume 60 to 65% of all the leather tanned in the world, its importance has shrunk over the years and was estimated at 48% in the 2004-7 period. Nevertheless it still remains the biggest single user of leather, thus it is used as a proxy of the level of demand at the end market of the chain. It is assumed that an increase in the consumption of footwear would increase demand of leather ²⁹.

Apart from its meat products the camel hides in the east African countries are consumed for the manufacture of less value materials such as mats, ‘AKIMADA’ and benches.

2.18 Biological and Compositional Analysis

The biological and chemical analysis of raw hides/skins and leathers at different stages reveal important information regarding the nature and composition of material under investigation and enables the leather technologists to design appropriate process recipe for the production of leathers for different applications. The bio-chemical analyses commonly investigated include fat content, collagen content, histological analysis, SEM analysis, chromic oxide content and so on.

There are clearly advantages in being able to understand how the characteristics of an animal’s raw hide/skin relate to the physical properties of the leather produced from it. Such knowledge assists in the selection of those breeds, which will yield the best leather for a given application ³⁰. Although there have been a number of studies relating animal and skin/hide characteristics to leather properties for bovine, sheep and goat, leather research on this topic appears less well developed for camel hides and its leather.

The SEM analysis of animal tissues is an important task that should be carried out in examining the surface and cross-sectional portions of the animal hide/skin at different stages of leather making.

2.19 Physical and chemical Analysis

Depending on the end-use and types of leather, a wide spectrum of tests based on visual, physical and chemical and instrumental techniques have to be carried out in testing laboratory. With leather being a non-homogeneous commodity, performance tests have an important role to play in assessing its quality.

The quality of leather is assessed by its properties or specific characteristics. The properties are dependent on the physical structure, chemical composition and mechanical finishing operations during the manufacture of leather. The physical structure (size) decides the properties of the finished products to a large extent ³¹. After the leathers were produced, they were tested to assess whether they will serve the ultimate purpose and if required to improve the properties of these leathers. The physical and chemical analysis at least involves the assessment of the final leathers for their fitness for use.

CHAPTER THREE

3. MATERIALS AND METHODS

3.1 Raw materials, Chemicals and Reagents

3.1.1 Raw materials

Wet salted camel hides were used as a raw material. Biological, chemical and physical analysis were carried out on camel hides after each treatment starting from soaking to finishing using standard procedures for testing, as these tests are crucial in determining the suitability of the material for leather manufacture.

3.1.2 Leather chemicals

The leather chemicals used were of commercial grade. These were the chemicals to be consumed during the leather making starting from soaking to finishing as in the conventional method of leather manufacture.

3.1.3 Reagents

The reagents used for the biological and chemical analysis were of analytical grade.

3.2 Laboratory equipment, instruments and Apparatus

3.2.1 Laboratory instruments and Apparatus used for biological and chemical analysis

- Surgical blades and its holder;
- Drums for leather processing;
- Sample holders (zip_lock cover);
- Elemental Analyser;
- Refrigerator;
- Common glass wares;
- Soxhlet apparatus;
- Hot air Oven;
- Burettes;
- Micropipettes
- Heating mantle;
- SEM;

- Shrinkage temperature tester;
- Thermometer;
- UV-Vis Spectrophotometer;
- Circular Dichroic Spectropolarimeter;
- SDS-PAGE set up;
- Magnetic stirrer and paddle retriever;
- Analytical weighing balance;
- Butter papers and filter papers

3.2.2 Laboratory instruments and Apparatus used for physical analysis

- Shrinkage temperature tester;
- Universal Tensile Meter (UTM);
- Lasto-meter;
- Flexo-meter and
- Rub fastness tester

3.2.3 Leather processing equipments and apparatus

- Testing drums;
- Fleshing machine;
- Shaving machine;
- Sammying machine;
- Vacuum dryer;
- Spraying machine;
- Roller cotter machine and embossing machine

3.2.4 Experimental Design

Fresh camel hides were washed and preserved as usual by applying sodium chloride and processed conventionally and examined for biological, chemical and physical properties in the laboratory to assess the suitability of the raw material for the production of finished leather products for various applications. Here under fig 3.1 illustrates the flow chart of the design:-

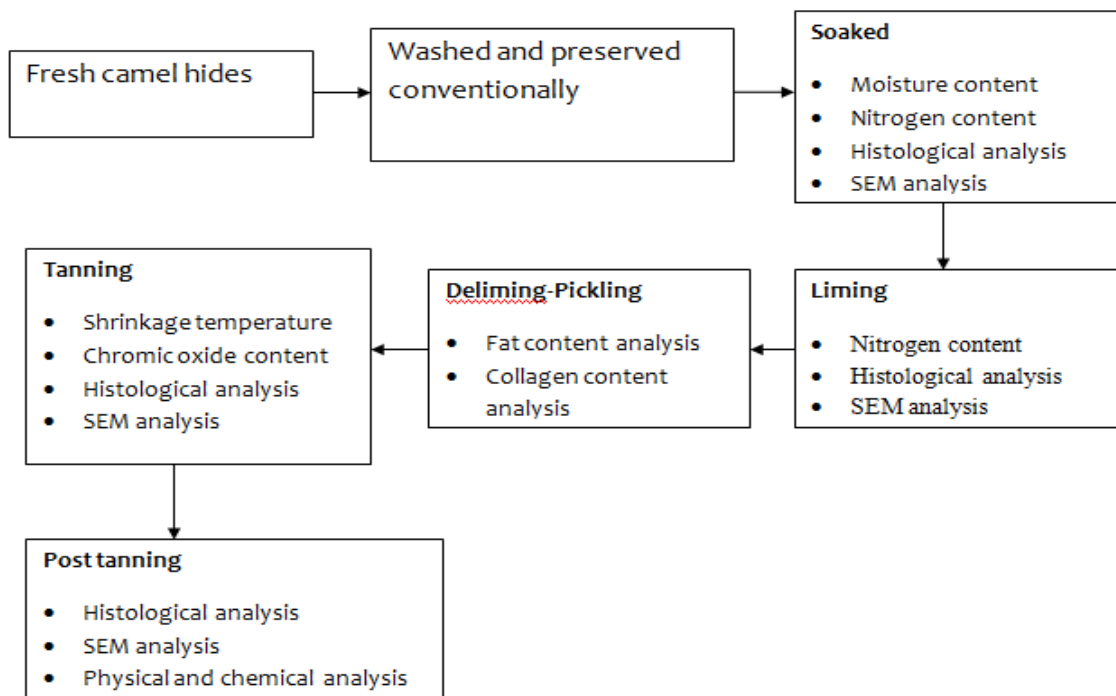


Fig 3.1:- Experimental design flow chart

3.3 Methods

3.3.1 Biological and chemical Analysis

All regions of wet salted camel hide sides were cut using official method of sampling (IUC/2). All regions of the hides were processed in a conventional beam house, tanning, and post tanning unit operations. At the end of each unit operation, samples were collected and stored in refrigerator prior to analysis. The samples were analyzed for the histological features, surface and cross-sectional examination (SEM analysis) and compositional analysis.

3.3.1.1 Histological Analysis

Reagents used

The reagents used during the preparation of the samples for histological analysis include formaldehyde solution (AR), sodium phosphate monobasic anhydrous (AR) and sodium phosphate dibasic dehydrate (AR). In addition to these reagents, Hematoxyline-Eosin were used as a staining agents

Apparatus and instrument used

The apparatus used while conducting the study were surgical blades, beaker, measuring cylinder, ultra microtome and Optical microscope



Fig 3.2: - Ultra Microtome



Figure 3.3:- Optical Microscope

Methods

- Samples were taken along the backbone and across the backbone;
- The sample specimens at raw stage, limed pelt stage and wet blue stage were fixed with formalin buffer to prevent tissue autolysis
- The samples were then embedded with paraffin wax based histological waxes and sectioned with microtome to 15 microns
- The sample specimens were then stained with Hematoxylin and Eosin and finally, the specimens were visualized under optical microscope at a magnification of 40x.

3.3.1.2 Scanning Electron Microscope (SEM) Analysis

Apparatus and instrument

The apparatus and instrument used while conducting this study were surgical blades, beakers, measuring cylinder, desiccators, Edwards sputter coater and Scanning Electron Microscope



Fig 3.4: - Gold plating machine

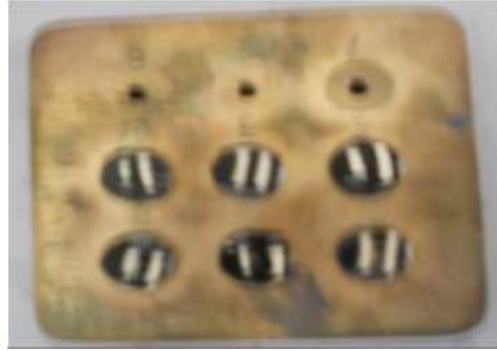


Fig 3.5: - Plates for mounting samples



Fig 3.6: - Scanning Electron Microscope

Reagents

The reagents used while conducting this study were acetone (AR), Ethanol (AR), glutaraldehyde (AR) and formaldehyde (AR)

Methods

- The samples from all stages were cut in to a convenient size for mounting
- The specimens were then immersed in a fixative solutions of 5% glutaraldehyde and 5% formaldehyde (formalin buffer) to prevent tissue autolysis
- The specimens were then dehydrated gradually with solutions of ethanol and acetone
- After complete dehydration, the specimens were kept in desiccators to avoid the absorption of moisture and attached to a mounting stub with double face cello tape
- The specimens were then coated with gold using an Edwards E306 sputter coater to impart conductivity to these biological samples and mounted on to the chamber

- Finally the SEM micrographs were taken for both the cross-section as well as the grain surface at high vacuum with an accelerating voltage of 15kv at different magnifications.

Sampling for chemical testing

Sampling was made according to the standard procedure (SLC 1) for sampling of chemical testing

3.3.1.3 Nitrogen Content Estimation

Apparatus and instruments

The apparatus and instruments used during the determination of this study were scissors, weighing balance, crucible, hot air oven and Elemental analyzer

Methods

- The samples were cut in to pieces at the stages of raw and limed pelt
- The pieces were then allowed to dry to make them free of moisture in an oven at a temperature of $102 \pm 2^{\circ}\text{C}$ until constant weight was obtained
- A pinch of the sample at each stage was feed to the Elemental analyzer for CHNS analysis
- The combustion products were measured quantitatively by a means of a non-dispersive IR absorption detection system, except for the N_2 which is determined via a thermal conductivity detector (TCD)



Fig 3.7: - Elemental analyser

3.3.1.4 Collagen Content Determination

Reagents and chemicals

The reagents and chemicals used during the determination of collagen content were n-butanol, Hydrochloric acid (6N), Chloramine-T (Sodium p-toluene sulfox chloramide), perchloric acid, PDAB

Apparatus and instrument

The apparatus and instruments used for this study were analytical weighing balance, beakers, measuring cylinders, micro pipettes, centrifuge, magnetic stirrer, Refrigerator, Uv-vis spectrophotometer



Fig 3.8:- Centrifuge Machine



Fig 3.9:- Uv-vis spectrophotometer



Fig 3.10:- Micro pipette

Hydroxy Proline Estimation

Methods

Sample from the pickled pelt was taken and were cut in to pieces. The determination of hydroxyproline in the pickled pelt involved hydrolysis of the sample solutions (collagen) to liberate the amino acids from the peptide linkages, oxidation with Chloramine-T followed perchloric acid acidification and reaction of this product with p-dimethylaminobenzaldehyde (pDAB) to give a pink chromophore [Neumann and Logan, 1950]. Camel pickled pelt (50mg) containing moisture content of 70%) was hydrolyzed using 6N HCL in an oven at 110 °C for 12hrs in a sealed hydrolysis tube. After the completion of the acid hydrolysis, the tubes were de sealed and poured in to a porcelain dish for evaporation of the HCL. Rinsed well with double distilled water and then, the contents (1.5ml) was kept in a 50ml standard flask and made up to the mark with distilled water. Finally, 500µL of the collagen solution was taken for chloramines-T oxidation and the absorbance was recorded at 557nm. At the end the collagen content was calculated using the following formula:

$$\text{Collagen concentration (mg)} = \text{HP concentration (mg)} * 7.4$$

$$\% \text{ Collagen content} = \text{HP concentration (mg)} * 7.4 / 100$$

Standard preparation

A stock solution was prepared by dissolving 10mg of L-HP in 100ml of 0.001N HCL. Standards were then prepared by diluting the stock solution with DD H₂O to obtain concentrations of 1-10 µg/ml.

3.3.1.5 SDS-PAGE Analysis

Materials used

- Polyacrylamide gel
- Electrophoresis apparatus for protein analysis

Apparatus Used

The SDS-PAGE setup was used for the determination of the molecular weight distribution of the collagen solution extracted from camel.



Fig 3.11:- SDS-PAGE setup

Methods

- Thaw the standard at room temperature and vortex gently to ensure the solution is homogeneous,
- Load the standard on the gel (10 μ l volume) to get a thickness of 1mm,
- The electrophoretic analysis was performed by using 30% acrylamide, 1.6M Tris buffer, 10% SDS, 10% APS, TEMED in both resolving gel (6%) and stacking gel (4%). The sample was dissolved in 0.5M AA and then mixed with 60mM Tris-HCl buffer containing 10% glycerol, 2% SDS, 5% β -mercaptoethanol and 0.04% Bromophenol at pH 6.80,
- The treated sample was injected into 6% gel wells and run for 120 minutes. The gel was stained with 0.1% (w/v) Coomassie Brilliant Blue R-250 in 10% methanol (v/v) and 7% AA (v/v) and was de-stained with 40% methanol (v/v), 10% AA (v/v) after the given period of time. High molecular weight markers (30-460 KDa) were used to estimate the molecular weight distribution of the camel collagen solution

3.3.1.6 Circular dichroism (CD) analysis

Apparatus and instruments

Circular dichroism spectrometry was the instrument used during the conformational analysis of the purified camel collagen

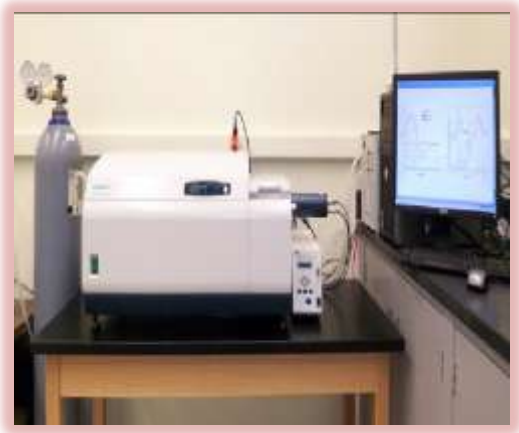


Fig 3.12:- Circular Dichroism spectropolarimeter

Methods

The pepsin soluble collagen conformation was studied using dichroic spectroscopy measurements conducted on a JASCO J-815 CD spectrophotometer equipped with a Peltier temperature control-423S/15 (JASCO Inc.) using acetate buffer (pH 4.2) under the nitrogen atmosphere. For CD data collection, 350 μL of protein was used in a 0.1cm path length quartz cell. CD spectra were recorded in the far UV region (190-260 nm) under constant purging of nitrogen gas at 25°C employing 1.0 nm bandwidth, 0.1nm step size, for an average time of one second. A scan speed of 20nm/minute was used. A reference spectrum was recorded for collagen types I-III and the raw data in millidegree unit was recorded in molar ellipticity $[\theta]$ in the CD apparatus.

3.3.1.7 Fat Content Estimation

Reagents and chemicals

The reagents used while conducting this study was the extracting solvent petroleum ether (60-80⁰C)

Apparatus and instruments

The apparatus used while carrying out this experiment were analytical weighing balance, crucibles, Soxhlet apparatus and hot air oven



3.13:- Hot air oven



Fig

Fig 3.14: -Soxhlet apparatus

Methods

- The sample was cut in to pieces and placed in a crucible of known weight,
- The sample was then dried in an oven at a temperature of $102 \pm 2^{\circ}\text{C}$ to constant weight,
- The cut pieces were then kept in a thimble, already kept in a bottle and run for about 3hrs using petroleum ether as an extracting solvent
- After extraction, the bottles were kept in a hot air oven at a temperature of $102 \pm 2^{\circ}\text{C}$ to constant weight and the weight was taken
- The fat content was then calculated as weight difference as given below:

$$\% \text{Fat content} = \frac{\text{weight of bottle after extraction and drying} - \text{weight of bottle} \times 100}{\text{weight of bottle}}$$

3.3.1.8 Chromic oxide content of leather

Reagents and chemicals

The reagents used during this experiment were sulphuric acid, Nitric acid and perchloric acid

Apparatus and instrument

The apparatus and instruments used during this experiment were scissors, weighing balance, hot air oven, Erlenmeyer flask, heating mantle, Standard Measuring Flasks, pipettes, pH meter and Uv-vis spectrophotometer



Fig 3.15: - Acid digestion of wet blue leathers

Methods

- Wet blue leathers were cut in to pieces and allowed to dry to a constant weight in a hot air oven at a temperature of $102 \pm 2^{\circ}\text{C}$,
- 0.5g of the dried pieces was taken and placed in an Erlenmeyer flask to which acid mixture of 3.5ml Sulphuric acid, 5ml Nitric acid and 11.5ml perchloric acid were added for digestion,
- The solution was then placed in 100ml Standard Measuring Flask and made up to the mark with distilled water to prepare a stock solution,

- 10ml was taken from the stock solution and kept in 50ml Standard Measuring Flask and made up to the mark with distilled water and the pH was then adjusted beyond 10 using sodium hydroxide pellets and absorbance was taken at 372nm,
- Finally, the chromic oxide content was calculated and expressed as %Cr₂O₃ using the formula: $\%Cr_2O_3 = \frac{A}{\epsilon} \cdot \frac{152 \cdot 52}{104} \cdot \frac{1}{1000} \cdot \frac{d_1}{v_1} \cdot \frac{d_2}{v_2} \cdot \frac{d_3}{v_3} \cdot 100$

Where: A is absorbance, ϵ is molar extinction coefficient (4820 L mol⁻¹cm⁻¹ at 372nm)

3.3.1.9 Hydrothermal stability of the leather

Reagents and chemicals

The reagent used while conducting the experiment was glycerol and water mixture

Apparatus and instrument

The apparatus used during this experiment was a Thiess shrinkage tester with a thermometer aligned together and Bunsen burner

Methods

- A rectangular piece of wet blue leather of 50±2mm x 3±0.2mm was cut according to the official method of sampling,
- The test piece was then pierced and fixed on the test piece holder,
- The test piece was then immersed in to the apparatus for measuring shrinkage temperature, already filled with distilled water and then heated at a rate of 2±0.2⁰C with Bunsen burner until the leather specimen starts to shrink
- Finally the temperature was read from the thermometer and reported as T_S= T⁰C.

3.3.2 Physical Testing of Leather

Sample Preparation

The samples were cut using the standard procedure for sample preparation (SLP 2). As the properties of the leather are affected by atmospheric temperature and varying humidity and as in the same place in different seasons of the year and with the hours of the day, it is essential to condition the leathers prior to testing in a room under controlled conditions of 20±2 ⁰C and 65±2% % RH for 48 hours prior to testing.

3.3.2.1 Moisture content determination

The moisture content of the leather samples at different stages prior to different tests was conducted as per the test method SLC 3.

3.3.2.2 Tensile strength

Apparatus and instruments

The apparatus and instrument used while conducting the experiment include hydraulic cutting machine, a steel die of standard dimension, thickness measuring device and universal tensile meter (UTM)

Methods

- A dumb-bell shaped sample was punched out using a steel die of standard dimension (10mm x 50mm),
- The samples were then taken for measurement of thickness (mm),
- The prepared samples were then conditioned using chemicals at a temperature of 20 ± 2 °C and 65 ± 2 % RH for 48 hours
- The specimens were then mounted in to the jaws in a universal tensile measuring machine (UTM)
- The load was applied so that the jaws move apart at a constant rate of 100mm/min

Tensile strength= Breaking load (N)/Thickness (mm)*width (mm)

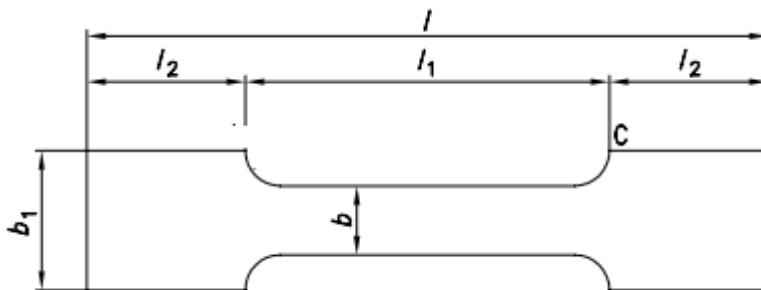


Fig 3.16: - Shape of Test specimen

Where L is 110mm, L_1 is 50mm, L_2 is 30mm, b is 10mm and b_1 is 25mm



Fig 3.17: - Thickness gauge



Fig3.18: - Universal Tensile Meter (UTM)

3.3.2.3 Percentage elongation at break

This was simultaneously measured with the measurement of tensile strength and it is also a useful index of the stretching quality of the leather under investigation.

- Two reference marks were made in the narrow portion of the specimen before testing,
- The distance between these points was measured,
- The machine was then allowed to run for some time and then stopped
- Both the distance between the two reference and the corresponding load were noted
- The extension was then expressed as the percentage elongation at that load

3.3.2.4 Tearing strength

Tearing strength is the load required to continue a tear in a leather sample, once it is started. There are different ways of doing this. The most commonly used method (double edge tear) was followed.

- The samples were punched out using a steel die of standard dimension,
- The prepared samples were taken for thickness measurement,
- The samples were then conditioned at conditions similar to those samples of tensile test pieces,
- The prepared samples were then mounted in the UTM,
- The load was applied at a constant rate of 100mm/min,
- The load was then recorded in Newton (N)

3.3.2.5 Water vapour permeability

- Samples were cut in the form of disc using standard steel dies
- The samples were then kept in a bottle filled with silica gel and closed tightly with a cap
- The whole assembly was then weighed
- The weight was noted at known intervals (2hrs, 24hrs)
- The increase in weight was then taken as a measure of the water vapour that had been permeated through the leather sample and was expressed in mg of water vapour per unit cross-section per unit time



Fig 3.19: - Steam absorption set up



Fig 3.20: - Steam absorption Tester

3.3.2.6 Grain distension at grain burst Apparatus and instruments

The apparatus and instruments used while conducting this experiment were hydraulic cutting machine and lasto-meter



Fig 3.21: - Lastometer

Methods

- The samples in triplicate were cut in a circular form,
- The prepared specimens were then conditioned as usual at a temperature of 20 ± 2 °C and $65\pm 2\%$ RH for 48 hours,
- The samples were then clamped in the Lasto-meter (bursting strength tester) with the grain side up
- The hydraulic pressure was then applied at a constant rate of 0.2mm/s continuously until the occurrence of grain burst
- The load (N) and the distension (mm) was then noted

3.3.2.7 Resistance to perspiration

Principle

The surface of a test piece is wetted with artificial perspiration solution and placed in contact under load with a white reference fabric wetted with the same solution at specified temperature and for specified period of time. Subsequently the test piece is reconditioned and change in colour of the leather and staining of the fabric are assessed using the gray scale.

Reagents and chemicals

The chemicals and reagents used during this analysis were sodium chloride, sodium hydroxide, tris (hydroxymethyl) amino methane, urea, nitrilo tri acetic acid $[N(CH_2COOH)_3]$, distilled water and hydrochloric acid (HCL)

Apparatus and instruments

The apparatus and instrument used while conducting this test include hot air oven, steel die and hydraulic press machine

Methods

- Set the oven to 37 ± 2 °C
- Preheat a 4.5kg weight for at least 1 hour
- Cut a test piece of dimension 100mm x 36mm

- Cut 1 or 2 pieces of multi-fibre fabric which is 100mm x 36mm in dimension
- Immerse the test piece and the fabric in two different vessels containing the artificial perspiration solution
- The specimens were then laid down over the white fabric on both sides of the leather specimens and another glass plate was then placed on to the specimens
- The whole set up was then kept in an oven at 37⁰C for three hours
- Remove the whole set up and let the specimens dry in an open air
- Finally, the specimens were evaluated for colour migration using grey scale

3.3.2.8 Total ash content determination

Reagents and chemicals

The reagent used during this test was sulphuric acid

Apparatus and instrument

The apparatus used while conducting this test was muffle furnace

Methods

- Silica crucibles were weighed accurately,
- Leather sample was cut into pieces,
- Approx. 5g of the leather pieces were placed in the crucible and weighed,
- The sample was incinerated in a burner and kept in a muffle furnace at a temperature of about 500⁰C until all the carbon was consumed and the leather was fully ashed,
- The sample was removed and kept in desiccators with granular silica gels to cool,
- The sample together with the crucible was then weighed and the weight of ash was calculated in grams (x g)
- Finally, the percent total ash was calculated as:

$$\% \text{ Total ash} = (x/5) * 100$$

3.3.3 Evaluating the suitability of the raw material for leather products

Wet salted camel hides were taken and allowed to pass through different treatments to incorporate the desired requirements in to the final leathers. From this raw material, shoe

upper leather, bag leather and belting leather were produced and evaluated for the requirements by physical and chemical means in the laboratory.

3.3.3.1 Process description

Temporarily preserved raw camel hides were first rehydrated in a process known as soaking, and the soaked hides were then green fleshed to enhance the penetration of the chemicals used in the subsequent operations. After green fleshing, the raw hides were subjected to liming in order to remove keratinous and other non-collagenous materials present in the raw hides and open up the fibres. At this stage the hides are known as pelts. The pelts were then subjected to various pre-tanning operations such as deliming, bating, and pickling depending on the requirements to condition the same for the subsequent tanning systems. At this stage, the tanned materials are known as leathers. The raw, pelts and leathers were then analyzed for bio-chemical analysis and physico-chemical analysis and shaved to the desired thickness prior to conducting the post tanning operations where the leathers are incorporated with utility properties like softness, fullness, colour, and water resistance. The understanding of the histological features, physical and chemical properties of the raw material of interest enabled to establish various designs for the manufacture of different leathers for different applications.

3.3.3.2 Beam house operations

Beamhouse processes are known to contribute 60-70% of the total pollution load in leather processing. Beam house operations include the process steps such as soaking, liming, deliming, bating and pickling.

Soaking

This is the first chemical based leather making process stage where, the skins and hides are immersed in water containing soaking auxiliaries, bactericide and sodium carbonate (soda ash) in order to rehydrate the raw hides and skins and aid these raw materials regain the physiological state that had been lost during preservation. During soaking unwanted materials such as blood, dung and preserving salts are also removed. The completion of soaking can be determined from experience by just touching the raw hides/skins.

Liming

Liming is the process stage where the soaked hides and skins are treated with lime powder, sharpening agents (sodium sulphide, sodium hydrogen sulphide), and liming auxiliary aiming to remove hair and open up the fibres.

Deliming

Deliming is the process stage where fleshed limed pelts are treated with acidic salts such as ammonium sulphate or ammonium chloride, to remove the lime used in the preceding unit operation (liming) depending on the application of final leather.

Bating

This process step is usually used for the removal of short hair to achieve further fibre opening and fibre splitting. This process stage is mostly applied to skin products for the manufacture of leathers of the likes of dress glove and garment requiring more softness. The use of enzymes in the beam house was the sign of new era of biochemistry based processing, which characterizes the leather industry of the twenty-first century ³². During this, operation, the limed pelts from camel were treated with alkaline bating enzyme.

I. Pickling

Pickling is the process step conducted primarily to prepare the hides' and skins' collagen for chrome tanning. During pickling, the delimed pelts were treated with solution of acids usually formic and sulphuric acids.

3.3.3.3 Tanning

Tanning is the process step where the putrescible organic raw materials are converted in to a stable material that resists thermal, chemical and bacterial action and be used for the production of wide range of products. Among solo tannages, the effect of chromium (III) appears unique in conferring high hydrothermal stability ³³. During tanning, the pickled pelts are treated with acidic salts most commonly basic chromium salts to incorporate colour change, handle, smell, rise in denaturation temperature and degree of performance to the changes. Mineral tanning agents, especially those of transition/pseudo transition metal ions have the ability to form effective complexes with the collagen matrix, which leads to the stabilization of the same against heat and the enzyme, collagenase ³⁴. During tanning, the pickled pelts from camel were treated with Basic

Chromium Sulphate (BCS) and vegetable extracts to incorporate the desired properties to the final leather.

3.3.3.4 Post tanning

As its name indicates, post tanning is an operation that is carried out after tanning. This operation is primarily done to incorporate properties such as fullness, softness, colour and handle to the final leather. During this unit operation, retanning materials, dyes and fat liquors to achieve the properties mentioned.

3.3.3.5 Finishing

Finishing is a process which finally completes the leather manufacturing process. Finishing of leather involves application technology based on certain scientific principles, and stimulation of personal creativity aided with sensitive appreciation of art. During finishing, film-forming agents are applied either manually or mechanically on the leather surface aiming to improve appearance, feel, grain character and surface protection in relation to the end use.

3.3.3.6 Organoleptic properties

Physical and chemical tests are the most crucial ones to judge the suitability of leathers for different applications. But, in addition to this, there are some properties that are not able to be tested with instruments and apparatus and hence evaluated by visual examination of the leathers produced. Organoleptic properties enable us to evaluate the leathers produced for various applications for their requirements by experienced industrial personnel and senior scientists. Accordingly the leathers were evaluated and were given scores 1-10 (See Annex-3).

3.3.3.7 Statistical analysis

All analytical determinations were conducted in triplicate and the values were averaged. The data were analyzed by one way analysis of variance (ANOVA) and independent t-test to investigate if there was any significant difference between the mean values along the backbone and across the backbone for the leathers produced using Design-Expert 7.0.0 software version and homogeneity of variance was checked. The analysis was also supported with F-value and P-value.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1 Biological and chemical Analysis

Moisture content

The moisture content of wet salted camel hide was taken at the soaking stage and found to be $57.33 \pm 2.52\%$. Determination of the moisture content has an advantage in deciding whether proper soaking is conducted or not. This indirectly tells us the readiness of the raw material for the subsequent operations. In addition to this, the moisture content determination is also important to report the test results in dry weight basis. The results in triplicate are shown below in figure 1:-

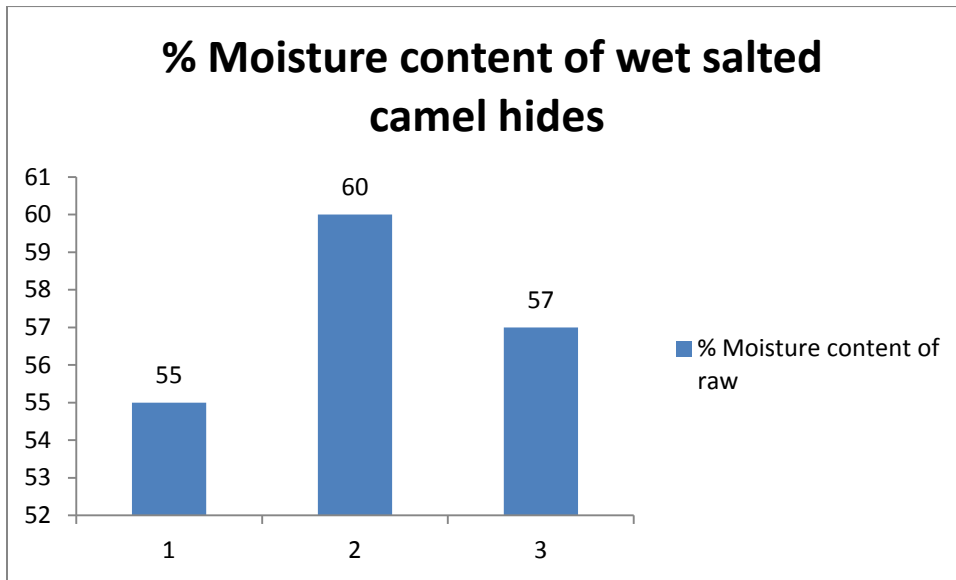


Fig 4.1:- %Moisture content of wet salted camel hides

4.1.1 Histological features of camel hides

While studying the histological features of the camel hide at different stages of leather making units, the fibre compactness, the grain to corium ratio were examined using the Hematoxyline-Eosin staining. The histological examination of the camel hide revealed important information on how to approach the manufacture of suitable leathers out of the resource raw material under investigation.

Be it sheep, goat, cow or other sources, every hides/skins has its own structure and different end uses. The basic histological features surely have some influence on the end properties of the leather.

Cross section of camel hides from belly and but region after main soaking, were observed under microscope. 12.5 X objective lens were used. The real magnification was found to be 40X. Figure show images of the cross sections after main soaking.

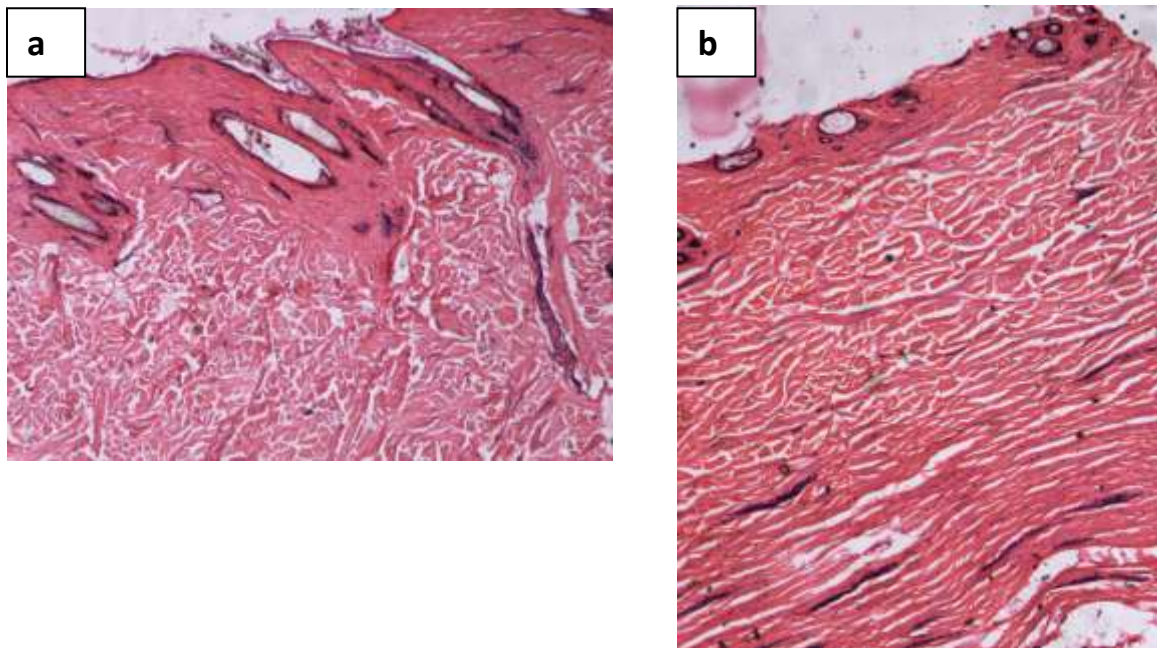


Fig. 4.2 Cross sections of camel hide at raw stage (after main soaking): a) belly and b) butt region

It could be seen from the figure that the collagen fibres in the grain region are compact and the fibres in the corium region are relatively loosely woven. It could also be observed that the camel hides have less grain to corium ratio indicating that it has less grain layer and more corium layer. From the figure it is also clear that both belly and butt region have loose and spongy corium structure. The angle of weave is found to be lower in both butt and belly region. Possessing low angle of weave tells us the raw material is expected to have higher tear and tensile strength³⁵. The flesh layer in the butt region has very loosely arranged flesh layer. The hair follicles are found to be present in the grain layer

and it is not seen in the corium layer. The diameter of the hair follicle is also seen to be little higher, indicating the camel has a thicker hair.

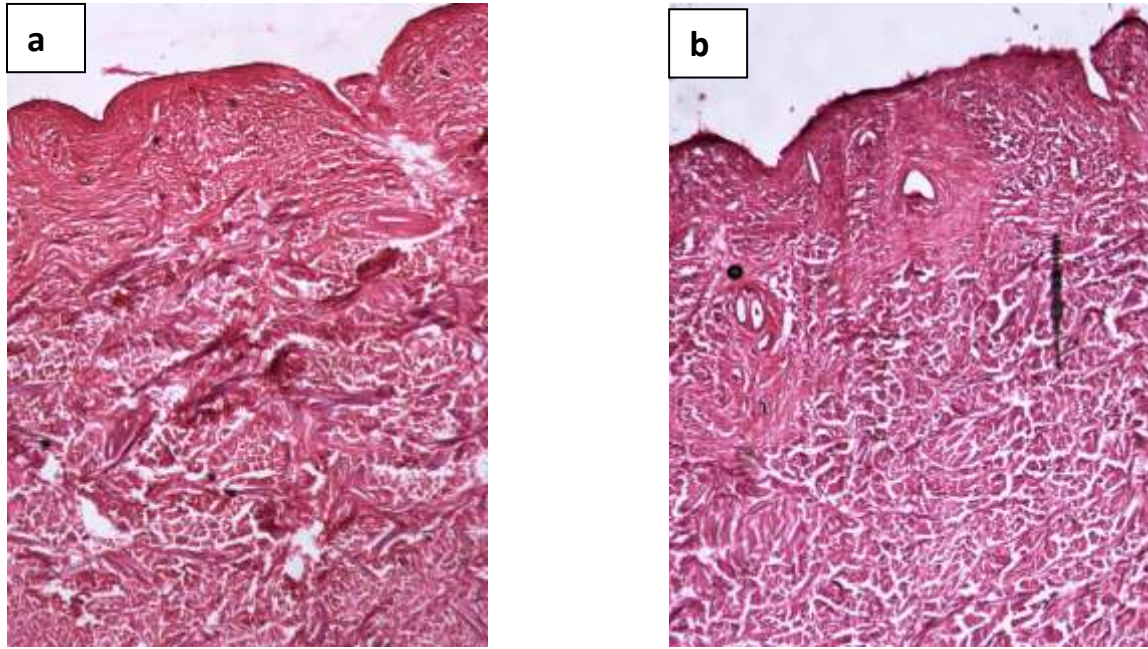


Fig 4.3 Cross sections of camel hide at wet blue stage a) belly and b) butt region

The cross sections of wet blue leather from both belly and butt regions are shown in Figure 4.3. There seems to be clear demarcation between grain and the corium layers, with the compactness of the fibre bundles. It is observed that compactness of fibre weave is more in the grain region than in the butt region in both belly and butt region.

When we see the fibre compactness of the camel at different stages, it is clear that it possesses more compact fibres compared to the conventional raw materials in use. This information enables us to use longer liming and may also require using some alkalis in addition to the lime powder in the liming stage to get the optimum opening of fibres. Having the information on the fibre compaction (fibre density) of the raw material, the tanner/ leather technologist will be able to make decision on the amount and nature of fat liquors used to get the desired level of softness.

4.1.2 Scanning Electron Microscope (SEM) Analysis

The scanning electron microscope analysis provides us with information regarding the fibre compactness and the grain surface patterns of the leather and helps decide for what products the raw material will be suitable. In addition, the SEM micrographs also aid us how to approach the manufacture of different leather products from the raw material resource of interest in the course of leather making unit operations

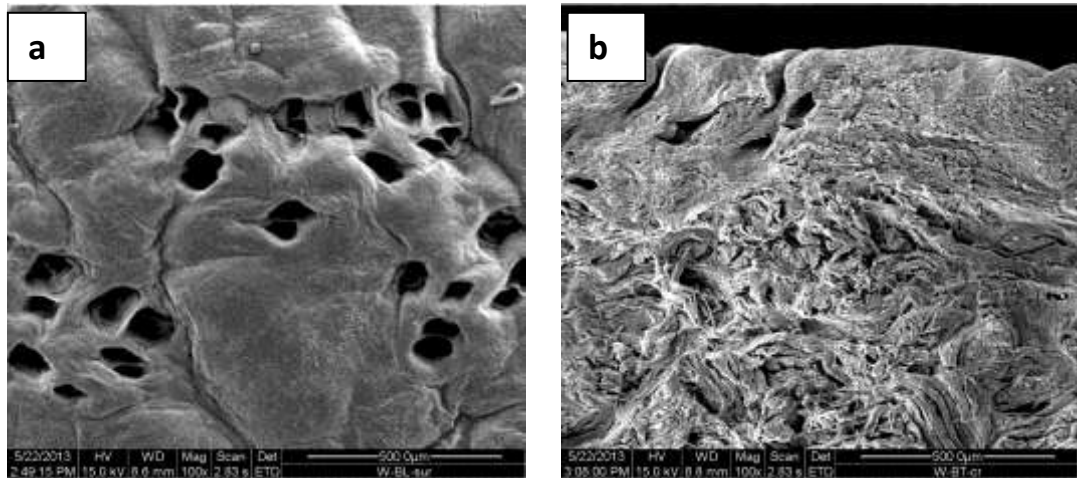


Fig 4.4 SEM images of wet blue camel leathers a) grain surface and b) cross section

The SEM images of surface and the cross section of the wet blue camel leathers are shown in Figure 4.4. It could be observed from the figures that the grain of the camel hides does not have a uniform surface. It has lot of indentations on the surface, which might be the reason for rough feel of the final leathers. Also, it could be observed that the distribution of hair is also not uniform, and does not follow any pattern as in the case of sheep, or goat skins. The hair follicles also seem to be slightly bigger indicating that the camel hairs are thicker. From the cross section of the wet blue leathers, it could be seen that the hairs are not deeply rooted.

The fibre compactness seems more in the grain layer than in the corium layer. This structure resembles to that of Indian buffalo hides. This feature of the camel leather enables us to produce various products with tighter grain and makes the water vapour permeability of the leather produced higher than those leathers made from the

conventional raw materials and this also supports the suitability of the raw material for the manufacture of shoe upper.

The SEM micrographs at different magnifications revealed that the fibre structure of the camel hides were compact at the raw stage and fibre opening and fibre splitting after treatment in the liming stage, and cross linking was observed after tanning. The same is true in the post tanning process where the fibre splitting was further being developed as a result of the fat liquors getting in to the fibres to reduce the friction between fibres and enhance the splitting of the fibres. The SEM micrographs also aid us how to approach the manufacture of different leather products from the raw material resource of interest in the course of leather making unit operations.

As we can see from the SEM micrographs of the leather, the grain to corium ratio is about 1:3. The ratio can reveal us the raw material is suitable for the manufacture of shoe upper leathers. Another important feature of the raw material under investigation is the grain tightness of the leathers produced, meaning the grain tightness seems to be uniform going from belly portion to the butt portion except small looseness in the neck portion, which is part of its body used to browse branches from tall trees, which indicates that the looseness in this portion could be the result of more mechanical action during its life.

4.1.3 Nitrogen content

The test result for the nitrogen content at different stages was obtained and presented as in the bar graph shown below:-

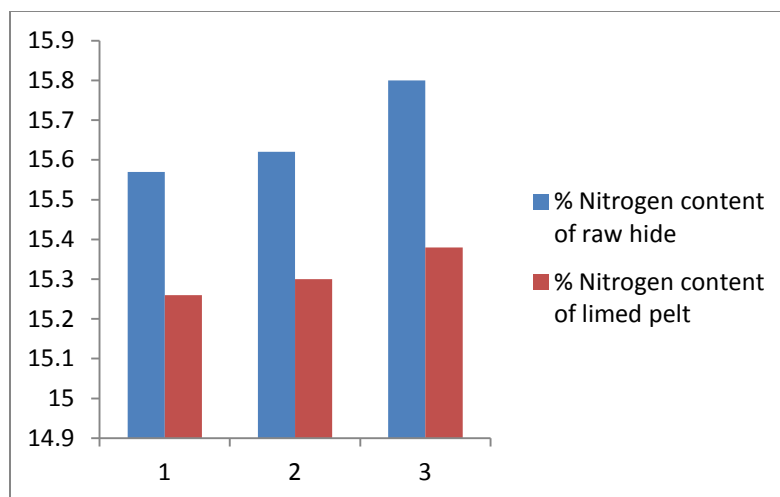


Fig 4.5:- % Nitrogen Content of raw and limed pelt

As it can be seen from the bar graph, the nitrogen content of the camel hide was obtained to be 15.66 ± 0.12 and 15.31 ± 0.06 at the raw and limed pelt stages respectively. Different literatures reveal that the determination of nitrogen content at the raw and limed pelt stages is very important in designing the process recipe for liming. From this, one can understand that the number of hair per square inch is very small in camel hides but deep rooted and this could also indicate that the noncollagenous components of camel hides was very less.

Analyzing the nitrogen content of the camel hide at the raw stage and the limed stage provides information on how the hair is being removed and also the proper removal of unwanted non fibrous proteins from the hide and design your approach to achieve these purposes. The technique involves combustion of test sample in an oxygen rich environment. The products of combustion in a CHNS analysis (CO_2 , H_2O , N_2 and SO_2) were carried through the system by helium as a carrier gas.

The nitrogen content is the result of the proteins that exist in the raw hides and skins. The nitrogen content analysis was made in the raw stage and limed stage using the CHNS elemental analyzer to estimate the percent composition of nitrogen. The nitrogen content in the limed pelt was lesser compared to the raw camel hide. This could be due to the removal of non-fibrous proteins and keratin in the liming stage.

4.1.4 Fat content

Determination of the fat content plays its role in designing the process recipe for the manufacture of the final product. Here petroleum ether was used for extraction of fat from the camel hide at the pickled stage. This was expressed based on the dry weight basis. The weight difference was taken after complete moisture removal in an oven at $102\pm 2^{\circ}\text{C}$ and keeping the sample in desiccators until the weight was constant. The fat content examined in triplicate was obtained to be as follows:

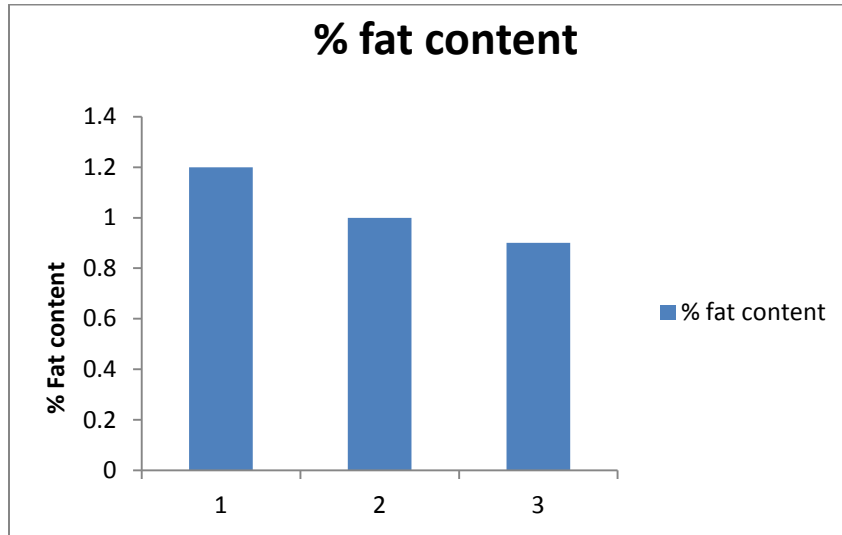


Fig 4.6:- % Fat Content

The fat content of the camel hide at the pickled pelt stage was found to be 1.03 ± 0.15

The amount of natural fat in the skins and hides varies depending on various factors such as sex, breeding, feeding system and so on. It is approximately 2-4% in cattle, 12-15% in goat and 30% in sheep skin ³⁶. The percent fat content results for the camel at the pickled pelt stage shows that the raw material contains lesser natural fat compared to the conventional raw materials (sheep, goat and cow).

From this, we can understand that the huge amount of fat in camel is stored in its hump and not throughout its body unlike the others. Therefore, it is not necessary to degrease the raw material while processing it for the manufacture of leather products for various applications. This in turn shows that it might be required for you to use more fat liquors

to get the desired level of softness of the leathers made out of the raw material under investigation compared to the other raw material sources.

4.1.5 Collagen Content Estimation

Collagen is the major structural protein found in tissues. As such, knowledge of at least the amount of collagen in a particular tissue is essential for the complete understanding of the structural and mechanical properties of that tissue ³⁷.

Hydroxyproline content is to be determined via the procedure detailed by Lollar. Collagen content is to be calculated on the basis that the hydroxyproline is 14% by weight of the collagen. This value has its own role in evaluating the suitability of this raw material in the manufacture of specific leather products.

The collagen content of mammals is expressed as % Hydroxy proline content. Different literatures reveal that the hydroxy proline content of collagen is approx. 14%. The collagen content of the camel hide was determined at the pickled stage after degreasing the cut pieces in 10% n-butanol and the collagen content was found to be 0.708mg/mg of pickled pelt on dry weight basis or alternatively 70.80% based on dry weight basis. Accordingly, the HP content (%) was found to be 9.57. This less result could be due to systematic as well as personal error or simply due to problems occurring during measurement, series of dilutions and so on.

Table 4.1: - Absorbance Reading for standard Hydroxyproline

HP Concentration (µg/ml)	Absorbance
1	0.1232
2	0.151
6	0.2415
8	0.2789
10	0.3236
12	0.3236

The Standard graph of Hydroxy Proline is presented in Annex 3.

Different literatures say that the collagen content of hides and skins should be in the range of 80-85%. The lesser result obtained could be as a result of incomplete hydrolysis, systematic error (errors which occurs due to instrumentation problem, including weighing balance, spectrophotometer and possibly personal error. Another reason could be the testing method might not be sufficient to carry out collagen content estimation of non-conventional raw hides and skins especially for hides and skins like camel possessing hard and compact fibre structure. One more reason could be the presence of fats and hair roots which could lead to the observation of less absorbance value and hence concentration as well.

4.1.6 SDS-PAGE analysis

The method of Laemmli (1970)³⁸ was used during the analysis where HiMark™ Pre-Stained Protein Standard previously stored in buffer containing Tris-HCl, Formamide, SDS and Phenol Red were used in order to accurately determine molecular weight of high molecular weight proteins. This standard consists of 9 pre-stained protein bands ranging in molecular weight from 30–460kDa.

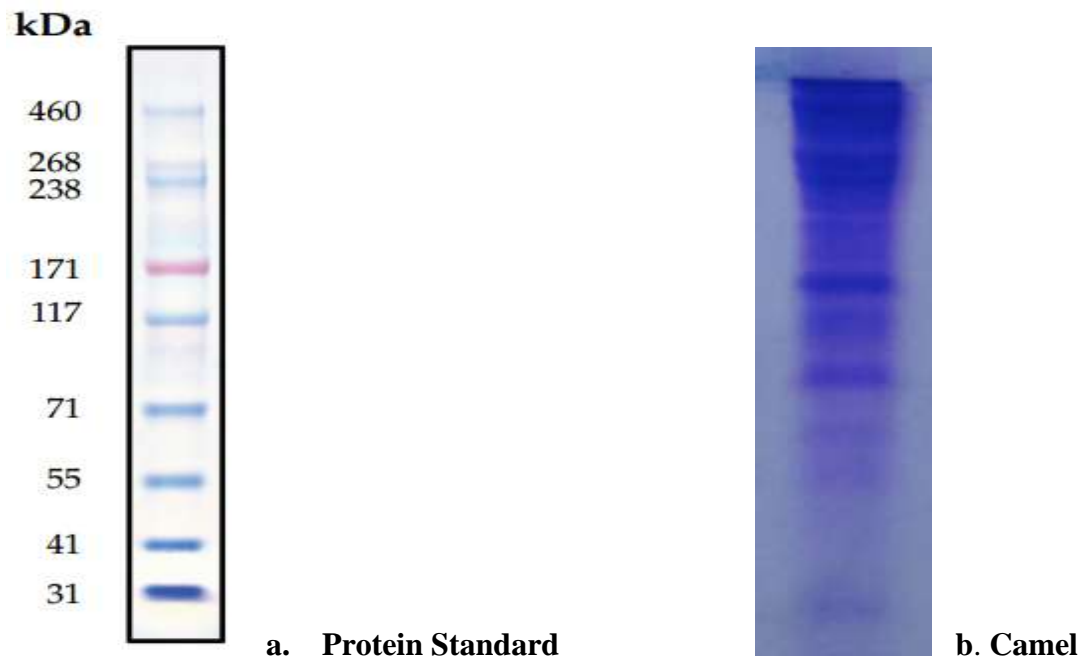


Fig 4.7: - a) HiMark™ Pre-Stained Protein Standard and b) Camel collagen solution

Collagen displayed one β -band (200 kDa) and two α -bands (100 kDa for α_1 and α_2), which were the unfolding polypeptide chains of the triple helix ($[\alpha_1(I)]_2[\alpha_2(I)]$). The molecular weight of type I collagen was found to be about 300 kDa

4.1.7 Circular Dichroism Analysis

Circular dichroism (CD) spectroscopy has been a valuable method for the analysis of protein secondary structures for many years³⁹. It is the most widespread technique used for estimating the secondary structures of proteins and polypeptides in solution⁴⁰. Circular dichroism (CD) spectra revealed that there were two peaks, a positive peak around 221nm and a negative peak around 197nm for the collagen extracted from camel, which are the characteristics of collagen triple helix⁴¹ and the CD spectra revealed that the collagen extracted from camel was type-I collagen.

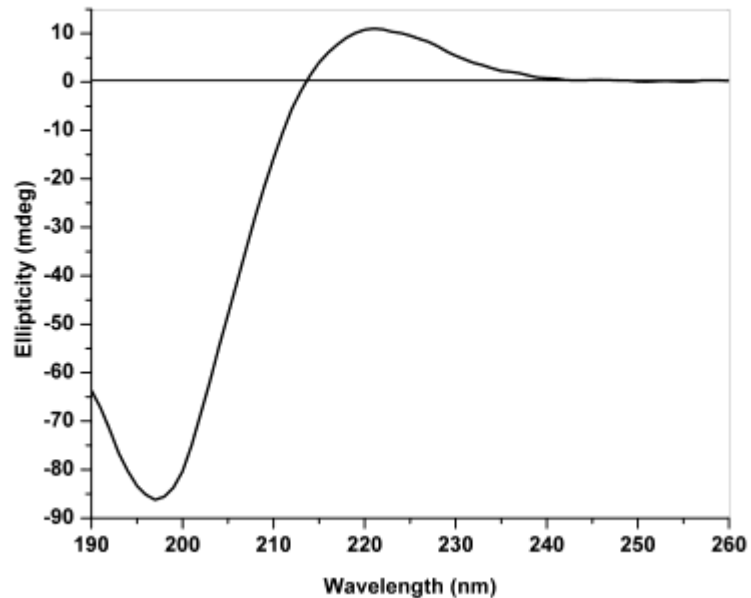


Fig 4.8:- CD- spectrum of Camel collagen solution

The CD method can thus be used to prove the suitability of the collagen solution extracted from the animal under investigation for the manufacture of different leathers for various applications.

4.1.8 Hydrothermal stability

This test was conducted using a Theis shrinkage tester ⁴² and the hydrothermal stability of the wet blue leather was conducted in a triplicate and was found to be as shown below:-

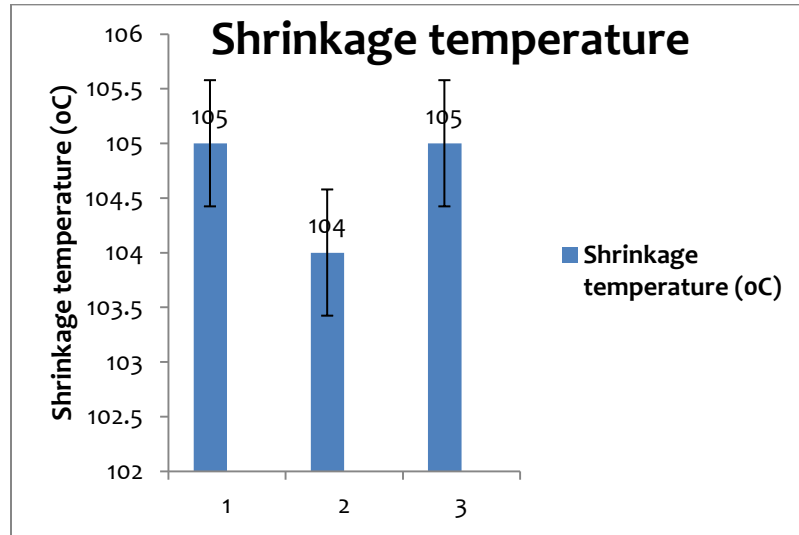


Fig 4.9:- Shrinkage temperature of camel wet blue leather

As a means of measuring collagen or leather stability and tannage in practice, shrinkage temperature is used by leather manufacturers and researchers ⁴³.

Collagen fibre shrinks to one third its original length at a characteristic temperature called the shrinkage temperature when thermal energy is provided. Hydrothermal stability or shrinkage temperature of the collagen fibres is a measure of the stability of the matrix as a whole, which arises due to the long range ordering of the matrix. The shrinkage temperature for native collagen is 60°C which then increase up on cross linking ⁴⁴.

The hydrothermal stability of leather is the measure of the leather to resist against hot water and chemicals. The hydrothermal stability is an indication of the suitability of the wet blue leather for the manufacture of different leather products for different applications. As we can see from the results, the wet blue leather was capable of standing a temperature of 104.7 ± 0.58 °C, which is fit for use according to the ASTM for wet blue leather requiring a minimum of 95°C.

4.1.9 Chromic oxide content of wet blue leather

The analysis was done by the oxidation of the wet blue leather using acidic mixtures and involves the use of sulphuric acid, nitric acid and perchloric acid. The chromic oxide content results of the wet blue leather and spent liquor in triplicate were found to be as shown below:-

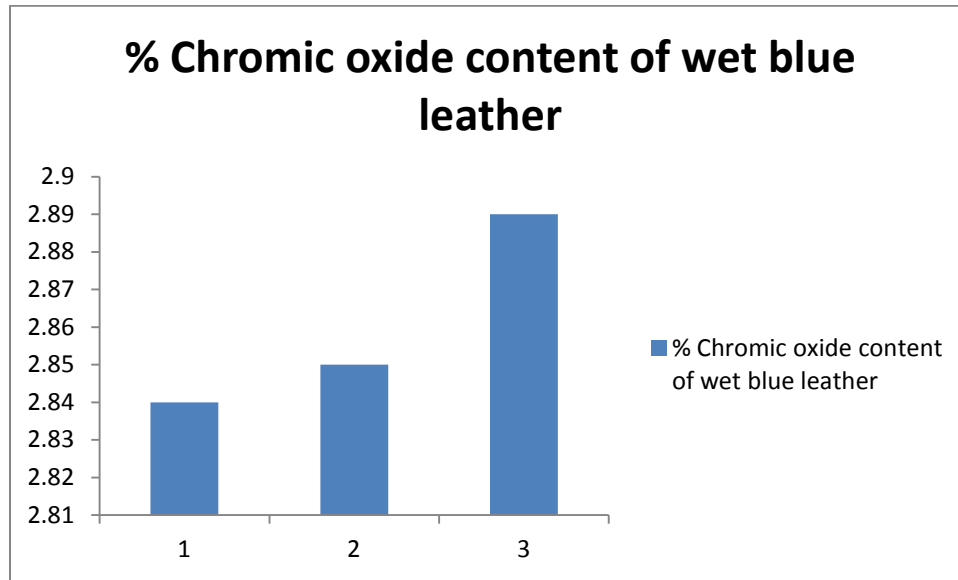


Fig 4.10:- Chromic oxide content of camel wet blue leather

The chromic oxide content result was reported by taking the average and standard deviation. As we can see from the results, the wet blue leather produced using chrome tanning was found to contain $2.86 \pm 0.03\%$ chromic oxide expressed as % Cr_2O_3 . ASTM standards reveal that the minimum required percent of chromic oxide content for wet blue leather ranges from 1 to 5%. The result shows that the wet blue leather fulfils the % Cr_2O_3 content of standard wet blue leather that is suitable for the production of different leather for various applications.

4.2 Physical Testing

4.2.1 Tensile strength

The tensile strength was measured in a universal tensile meter (UTM) for both along and across the backbone of the leather samples, in triplicate and reported in N/mm^2 as shown below:-

Table 4.2: - Tensile strength results of Camel shoe upper

Colour: Black	Tensile strength (N/mm^2)	
	Along the backbone	Across the backbone
Average	24.6	29.10
Standard deviation	1.26	1.77
Standard*	Minimum of 15 N/mm^2	

*** indicates that this is not the standard value for camel leathers**

The tensile strength of the camel shoe upper was found to be 26.85 N/mm^2 . A good tensile strength is an attribute in general for all types of leathers. It is a valuable guide for judging the quality of leathers. It is the strength property of leathers that predicts the performance of the leather for different end use. As we can see from the results, the tensile strength is higher for the test specimen taken across the backbone. But this does not mean always true, meaning the specimen taken along the back bone might possess higher tensile strength compared to that of specimen taken across the back bone. In addition to this, the tensile strength for both directions shows that the leather is suitable for the manufacture of shoe upper leather.

4.2.2 % Elongation at break

Apparatus and instruments used

The apparatus and instrument used during this analysis include thickness gauge and Universal Tensile Meter (UTM)

Methods

- The jaws were separated 50mm apart,
- The distance between the two jaws was recorded in millimetre (x) after break of the test specimen,
- The percentage elongation was calculated as:

$$\% \text{ Elongation at break} = (x/50) * 100$$

Table 4.3: - Elongation results at break (%)

Colour: Black	Elongation at break (%)	
	Along the backbone	Across the backbone
Average	49.27	46.13
Standard deviation	3.64	0.9

4.2.3 Tear strength

The tear strength of the produced shoe upper leather samples was determined using the standard procedure stated above in the test method. The double-edge tear test was done in triplicate for both along the back bone and across the back bone. The tear strength was reported in N/mm and was found to be as shown below: -

Table 4.4: - Tear strength results of Camel shoe upper

Colour: Black	Tear strength (N/mm)	
	Along the backbone	Across the backbone
Average	106	99.34
Grand average	102.67 N/mm	
Standard deviation	1.92	3.31
Standard*	Minimum of 70 N/mm	

NB: - * indicates that this is not the standard value for camel leather products

As we can see from the table, the tear strength result of the camel shoe upper specimens was found to be 102.67 ± 4.71 N/mm. As per the ASTM standards, the tear strength of shoe upper leather made from cattle hides should possess at least tear strength of 70N/mm. Therefore, the produced camel shoe upper leathers met the requirement kept in the standard. To sum up the performance properties (tear strength and tensile strength) of were able to reflect the exceptional strength properties of the camel leathers.

4.2.4 Distension and strength of grain at grain burst

This test is a test which is able to indicate the performance of the produced leather for the manufacture of the intended end use. This test method is used especially to evaluate the final leather whether it can stand loads that tears the leather without any damage to the grain. The test results were obtained and tabulated as in the following:-

Table 4.5: - Lastometer test result for camel upper leather

Colour: Black	Load at grain burst (N)	Distension at grain burst (mm)	Strength of grain (Kg)
Average	486.67	8.55	48.67
Standard*	-	Minimum of 7.0mm	Minimum of 20Kg

The standard from ASTM reveals the required value for grain distension of upper leather must be a minimum of 7 mm. Similarly, the Strength of the grain must be a minimum of 20kg. As we can see from the table, the grain distension of the upper leather was found to be 8.55 ± 0.1 . From the test results, we can see that the produced leather is fit for use in the production of shoe upper leather and others which require higher strength such as belting leather.

4.2.5 Total Ash Content Estimation

The total ash content of finished leather is an important parameter used to evaluate the suitability of the leather for use. The produced upper leather was tested for the percent total ash content (expressed as percent sulphated total ash) as per the standard test method (SLC-6) and was obtained to be 5.7 ± 0.45 . Dry ashing procedures use a high temperature

muffle furnace capable of maintaining temperatures of between 500 and 600°C. Water and other volatile materials are vaporized and organic substances are burned in the presence of the oxygen in air to CO₂, H₂O and N₂. Most minerals are converted to oxides, sulphates, phosphates, chlorides or silicates.

Ash content is usually determined to find out the inorganic present in the final finished leather. If the inorganic is very high, then the resulting leathers would show salt spew. As we can see from the test result, the sulphated total ash content of the upper leather was found to be within the standard.

4.2.6 Water vapour permeability

There are many properties that differentiate leather from synthetic materials. Among this, the most important one is the breathability of the leather. Leather products allow air and water vapour to pass through, even though it is up to the finishing techniques that bring the difference in breathability of different leathers. The Air and water vapour permeability of the produced leather was conducted in triplicate and was found to be 12.95 mg/cm²hr.

4.2.7 Evaluating the suitability of the raw material for leather products

During liming, the soaked hides were fleshed and treated with a sharpening agent, liming auxiliary (1% based on fleshed weight), and 0.5-1 g/L of caustic soda based on the article being produced. In addition to the addition of the alkali, the duration (drumming time) was also prolonged for up to three days. After the completion of liming, the pelts were fleshed and delimed and taken for bating (1.5% based on the fleshed weight), after which the pickled pelt was then tanned with both chrome tanning and vegetable tanning. The wet blue leathers were then shaved at desired thickness and treated with different chemicals to incorporate utility properties for the produced upper and bag leathers. The produced leathers were then finished with different pigments, binders and auxiliaries. The vegetable tanned leathers were also made in to belting leathers of different colours. Finally, the leathers were tested in the laboratory to assess the requirements. In addition to the laboratory test, organoleptic properties were also evaluated by experienced senior people.

4.2.8 Statistical Analysis on Proximate composition and performance properties of Camel

Table 4.6 Statistical Analysis on proximate composition and performance properties of camel hide and leather

	Tear strength	Tensile strength	Nitrogen Content	Elongation at break (%)
Along the backbone	106±1.92 ^a	24.6±1.26 ^b	-	49.27±3.64
Across the backbone	99.34±3.31 ^a	29.10±1.77 ^b	-	46.13±0.9
Raw stage	-	-	15.66±0.12 ^c	
Limed pelt stage	-	-	15.31± 0.06 ^c	

Different superscripts within a column represent statistically significant difference (P<0.05)

As we can see from table 4.6, the sampling position has significant effect on the strength properties and the percent elongation at break. From the same table one can understand the treatment of the raw hides with alkalis in the liming operation reduces the nitrogen content of the material (limed pelt).

4.2.9 Limitations of the study

This study has great importance to both the pastoralists and the tanners. But, there are some limitations as well. The off-take rate being very less, the mode of camels' raising and management being traditional; very limited information on camel husbandry, the multiple changes in the dry land environmental and lack of veterinary services coupled with low reproductive performance make camel raising difficult [Alemayehu Mengistu, 2003]; and slower rate of production (usually calve once per year) are among the major problems associated to the less recovery of camel hides. In addition to these problems, the surface quality of the raw material being inferior is another limitation to the study. But these problems could be managed if both the government and nongovernmental organizations, ILRI, LIDI and other institutions work hard together to enhance the recovery of quality raw hides from the camel.

CHAPTER FIVE

5. Conclusion and recommendations

5.1 Conclusion

Globally, the scarcity of raw hides and skins highly affects the tanning industries not to operate on their full processing capacity. The scenario is similar in the Ethiopian tanning industries. Despite its high potentials of livestock population, Ethiopia didn't exploit its source for the tanning industries and hence its foreign exchange is very less than the expected. The dependence of the Ethiopian tanning industries only on the conventional raw materials such as sheep, goat and cattle is one among the reasons that bring the scarcity of raw hides and skins. In Ethiopia we have many alternative animals where the hides and skins obtained from them could be processed in to leather, out of which camel was considered as best alternative due to its higher off take rate compared to the rest of the others. The biological, chemical and physical analysis of the developed products revealed that the raw material chosen was suitable for the manufacture of shoe upper leathers, leather goods and belting leathers.

5.2 Recommendations

The Ethiopian government should provide a system where any legal people can farm camels for the purpose of meat and milk products. In addition to this, the government should also facilitate the opportunity in the marketing of the camel products. By doing so, we will be benefited by processing the camel hides for different applications. Another important thing is, the tanners can utilize the raw hides and skins that did not get much application for leather making by making good relationship to the Ethiopian Leather Industry Development Institute (LIDI), meaning the industry can get the opportunity to get new technologies for developed leather products, new findings relevant to the industry and so on. In addition to LIDI, the Ethiopian Leather Industries Association (ELIA) and International Development Partners (UNDP, UNIDO, USAID, Italian Cooperation), ECF-World Bank, COMESA-LLPI, etc.) Should work together in order the Ethiopian leather industry to come out as a vibrant, attractive and internationally competitive sector. For this to occur the Ethiopian government should also set facilities for good husbandry practices for camels like the other animals and should protect the sales of live animals through borders of neighbouring countries illegally. Apart from its application point of view, the test method (Chloramine-T) oxidation method should be revised while conducting the compositional characterization of new resource raw materials.

6. Reference

1. Central Statistical Agency of Ethiopia, 2010
2. Investment Opportunity Profile for Tanning of Hides and Skins up to Finished Level In Ethiopia, 2008
3. SOLOMON LEGESE HAILU, CARBON NEUTRAL DEVELOPMENT IN THE TANNING INDUSTRY, APRIL, 2011
4. Girum Abebe et al. Experimenting with Industrial Polices in the Leather Industry in Ethiopia, 2013
5. AFRICA'S TRADE POTENTIAL: EXPORT OPPORTUNITIES IN GROWTH MARKETS, 2012
6. K Vijayalakshmi, et al. Novel plant based formulations for short term preservation of animal skins, CLRI, May 2009
7. C.A. EDWARDS et al. Clinica Chimica Acta, 104 (1980) 161-167
8. Matthew D.Shoulders et al. National Center for Biotechnology Information, university of Wisconsin, Madison, Wisconsin, Collagen structure and stability, March, 2010
9. Jones, J. Benton. Kjeldahl Method for Nitrogen Determination, Athens, GA, 1991
10. Anthony D Covington, tanning chemistry, 2009, 23
11. B Zeng and M McGregor, Review of commercial options for management of feral camels, 2008
12. Assessing the potential for a Commercial Camel Industry in Western Australia, August 2000
13. Federal democratic republic of Ethiopia Central Statistical Agency, agricultural sample survey, report on livestock and livestock characteristics, 2010/11
14. Getachew Legese et al. EIAR and ILRI, Live animal and meat export value chains for selected areas in Ethiopia: Constraints and opportunities for enhancing meat exports, 2008
15. Girum Abebe et al Experimenting with Industrial Polices in the Leather Industry in Ethiopia, Dec. 2013
16. Yohannes Mehari, et al. Camel and camel product marketing in Babilie and Kebribeyah woredas of the Jijiga Zone, April, 2007

17. Asfaw Negassa, et al., Livestock Production and Marketing August 2011
18. Ethiopia Sanitary & Phytosanitary Standards and Livestock & Meat Marketing Focus on Ethiopia's Meat and Live Animal Export: Trade Bulletin 4, April, 2011
19. Global Hides and Skins Market: Review of 2004-2007 and Prospects for 2008
20. Bewketu Takele, et al. Ethiopian Vet.J.,2013,17(1),13-30
21. European Commission, Integrated pollution prevention and control, Reference document on Best Available techniques for the tanning of hides and skins, Feb. 2003
22. Investment Opportunity Profile for Tanning of Hides and Skins up to Finished Level in Ethiopia, May, 2008
23. D. BOURZAT, et al. Rev. sci. tech. Off. int. Epiz., 1987, 6 (2), 383-389
24. Dr. N. V. Patil, National Research Centre on Camel, Indian Council of Agricultural Research, July 2011
25. Getachew Legese et al., 2008, Live animal and meat export value chains for selected areas in Ethiopia, ILRI
26. Pastoralist Forum Ethiopia, International Institute of Rural Reconstruction and Development Fund, Pastoralism and Land: Land tenure, administration and use in pastoral areas of Ethiopia, 2010
27. S. Ahmad, et al, 2010, Pakistan veterinary journal, 30(4): 191-197, Economic Importance of Camel: A Unique Alternative under Crisis
28. Investment Opportunity Profile for Tanning of Hides and Skins up to Finished Level in Ethiopia, May, 2008
29. Global Hides and Skins Market: Review of 2004-2007 and Prospects for 2008
30. Y. L. WANG, et al., JSLTC, 1993, vol.78, p.55, Strength of Brazilian Goat skin leathers in relation to skin and animal characteristics
31. Dr. V S SUNDARA RAO, Vegetable tanning materials, Central Leather Research Institute, Jan, 2001
32. Anthony D Covington, Tanning Chemistry, The Science of Leather, The University of Northampton, Northampton, UK, 2009
33. A.E Musa et al. Journal of Applied and Industrial Sciences, April, 2013, 1 (1): 43-48
34. A. SUNDARRAJAN et al. JALCA, VOL 98, March 2003, 101-106
35. B.M. HAINES, et al., Journal of Materials Sciences 10 (1975) 525-538

36. Altan Afsar, et al. Indian Journal of chemical Technology, (15), Sep. 2008, p.507-510
37. C.A. EDWARDS et al. modified assay for determination of hydroxyproline in a tissue hydrolyzate, Sept. 1979
38. Eyre, et al. 1984, 53.717-748 crosslinking in collagen and elastin. Annu.Rev.Biochem
39. Lee Whitmore, et al. Wiley Inter Science, Protein Secondary Structure Analyses from Circular Dichroism Spectroscopy: Methods and Reference Databases September 2007
40. Ramamourthy Gopal, et al. Int. J. Mol. Sci. 2012, 13, 3229-3244; 8 March 2012
41. Zhongkai Zhang, et al., Journal of the Society of Leather Technologists and Chemists, September 2005, Vol. 90 p.23
42. McLaughlin, G.D.; Theis, E. R. The Chemistry of Leather Manufacture, Reinhold publishing corp. 1945
43. Nuray Olcay IŞIK, et al. 2012, Ege University, Department of Leather Engineering, İzmir, Turkey
44. N NISHAD FATHIMA, et al. J. Chem. Sci., Vol. 121, No. 4, July 2009, pp. 509–514

Annex 1

Reagent Preparation

I. Solvent preparation for dehydration of specimens for SEM analysis

Ethanol and acetone solutions were prepared for the dehydration of the samples prior to SEM analysis. The solutions were prepared at different concentrations for gradual dehydration.

10% ethanol solution: This was made by taking 10ml of ethanol (99% purity) and 90ml of water. Similarly 20%, 30%, 50%, 70% and 100% of ethanol solutions were prepared for gradual dehydration. In addition to these concentrations of ethanol, 100% acetone was also used for final dehydration of these sample specimens prior to analysis.

II. Collagen Content Estimation

Preparation of Acetic Acid

0.5M acetic acid (M.wt=60g) was prepared by taking 15ml of acetic acid and then made up to a final volume of 500ml in a standard flask and mixed very well and then kept in a refrigerator at 4⁰C before use.

Preparation of Buffer

50g of citric acid monohydrate, 12ml of glacial acetic acid, 120g of sodium acetate trihydrate and 34g of sodium hydroxide were made up to a total volume of 1L in DD-H₂O. The pH was carefully adjusted to 6 and the buffer was then stored in refrigerator.

Preparation of chloramine-T (Sodium p-toluene sulfox chloramide)

0.05M solution of chloramines-T was prepared by dissolving 1.41g of chloramines-T in 20ml of DD-H₂O, 30ml of ethylene glycol and 50ml of buffer.

Preparation of Perchloric acid

3.15M solution of perchloric acid was prepared by taking 27ml from a stock solution (70%) and diluting with DD-H₂O in 100ml SMF up to the mark.

Preparation of PDAB

20% solution was prepared shortly before use by adding ethylene glycol to 20g of PDAB to give a final volume of 100ml. This was warmed to 60⁰C to facilitate solubilisation

Preparation of 6N HCL

50ml of 6N HCL was prepared by taking 26ml of a stock solution (11.6N) HCL and made up to the mark in a 50ml SMF. The preparation was done according to the dilution law ($N_1V_1=N_2V_2$).

III. SDS-PAGE ANALYSIS

Solution A: Aryl amide stock: 30% acryl amide, 0.8% N,N, Methylene bis acrylamide.

- Take 30g of Acrylamide
- Add 0.8g N,N, Methylene bis acrylamide
- Dissolve the contents in 70ml of distilled water and leave overnight
- Next day, fill the SMF (100ml) with DD-H₂O

Solution B: Separating gel buffer: 1.5 M Tris, pH-8.8

- Take 18.17g of Tris
- Dissolve in 70ml of distilled water
- Adjust the pH to 8.8 with 4N HCL and made up to 100ml in SMF

Solution C: Stacking gel buffer: 1M Tris,pH-6.8

- Take 12.11 g of Tris
- Dissolve in 70ml distilled water
- Adjust the pH to 6.8 with 4N HCL and made up to 100ml in SMF

Solution D: Running buffer: (5X) 0.25M Tris, 0.5%SDS, 1.92M glycine

- Take 30.3 g of Tris and 144.1 g of Glycine
- Dissolve in 700ml of distilled water
- Adjust the pH to 8.3 with 4N HCL
- Add 5g of SDS and made up to 1000ml in SMF

Solution E: Sample buffer:

- 5ml of Stacking buffer, 4g sucrose, 800mg SDS
- Filter the contents and made up to 10ml with stacking buffer in SMF

Solution F: 0.45% ammonium per sulphate

Solution G: 0.15% (V/V) N N N – TEMED

Solution H: water saturated iso butanol

Solution I: staining and fixing solution:

Fixing solution: The fixing solution is prepared by mixing 50% methanol, 10% acetic acid and 40ml of distilled water

Staining solution: The staining solution was prepared by mixing 50% methanol, 10ml acetic acid, 40ml of distilled water and 0.25 mg of CBB and then filtered and stored in 100ml bottle

Solution J: destaining solution: The destaining solution was prepared by mixing 100ml methanol, 100ml Acetic acid and 800ml of distilled water

Sample preparation: take 10 μ g of sample then add 10 μ L of distilled water and 40ml of sample buffer

Preparation of sealing gel: (15%): This should be freshly prepared and immediately transferred

- Take 500 μ L of acrylamide stock
- Add 500 μ L of distilled water
- Add 15 μ L of TEMED and then add 1 pinch of ammonium per sulphate

Preparation of separating gel (8%)(10ml): This should be freshly prepared and immediately transferred

- Take 2.6 ml of acryl amide stock
- Add 4.7 ml of distilled water
- Add 2.5ml of separating buffer
- Add 0.1ml of 10% SDS
- Add 15 μ L of TEMED and 1 pinch of ammonium per sulphate
- Overlay of iso-butanol for producing uniform layer

Preparation of stacking gel (5ml)

- Take 3.4 ml of distilled water
- Add 0.83 ml of acryl amide stock
- Add 0.63 ml of separating buffer
- Add 0.05 ml of 10% SDS
- Add 15 μ L of TEMED and 1 pinch of ammonium per sulphate

IV. Perspiration resistance Test

Preparation of artificial perspiration solution

1L of artificial perspiration solution was prepared by taking

- 5g of sodium chloride,
- 5g of tris(hydroxyl methyl) amino methane,
- 0.5g of urea,
- 0.5g of nitrilo tri acetic acid $[N(CH_2COOH)_3]$ and make up to the mark of 1L SMF with distilled water and the pH was adjusted to 8.0 ± 0.1 using HCL

Annex 2

Preparation of camel shoe upper

A. Soaking

Raw material used: Wet salted Camel hides **Quantity:** sides **Drum No:** _____

Operations	%	Chemicals used	Amount (kg/ g)	Time	Remark
Soaking	500	+ Water		30'	Drain
	500	+Water			
	0.5	+sodium silico-fluoride			
	0.5	+Boron DN		Run 10'/hr and Keep O/N stationery	Check Soaking completion
	0.5	+Soda ash			Check PH (8-9) (20 hrs), Green fleshing

NB: - The soaking process recipe is the same for all product type

B. Liming

Raw material used: Soaked Camel hides **Weight:** kg **Drum No:** _____

Operations	%	Chemicals used	Amount (kg/ g)	Time	Remark
Liming					
Unhairing	200	+ Water			
	3	+Sodium sulphide			
	10	+Lime powder			
	0.5	+Sintorene AR		2 days	Drain
Opening up	250	+ Water			
	10	+Lime powder			
	0.5	+Sintorene AR			

	0.5	+Soda ash		2 days	Check plumping
	0.5	+Soda ash			
	0.5	+Sintorene AR			Check plumping
Add 1g/L of sodium hydroxide pellets and run 10' each hour for one day and handle once each hour					
D/W/D and flesh properly					

C. Deliming-Tanning

Raw material: Limed pelt **Weight:** - based on fleshed weight

Operations	%	Chemicals used	Amount (kg/ g)	Time	Remark
Washing	200	+ Water		10'	Drain
	200	+ Water		10'	Drain
	100	+ Water			
Deliming	1.5	Ammonium sulfate		40'	Check PH (8-8.5)___
	0.5	Basozyme CM		45'	Check the completion of bating
Washing	200	+ Water		10'	Drain
	200	+ Water		10'	Drain
Pickling	100	+ Water			
	10	+Common salt		10'	Check ⁰ Be (7-8)
	0.5	+Formic acid (1;10 with cold water)		15'	
	1.5	+sulphuric acid(1;10 with cold water)		3x10'+45'	Check PH (2.8-3)___ Drain 50% of the float
Tanning	4	+BCS (33%)		30'	
	4	+BCS (33%)		2hrs	Check-complete

					penetration
Basification	1.5	+Sodium formate		10'	
	1	+Sodium bicarbonate		2x15+4 hrs	Check PH (3.8-4)____ check exhaustion
	0.15	+Preventol WB		20'	Drain and Pile
Sum setting and Shaving (Ready for post- tanning operations)					

D. Retanning and Dyeing **Product:** Camel shoe upper **Drum No:** ____

Material used: Wet blue leather **Date:** _____ **Quantity:** _____

Operations	%	Chemicals used	Amount (kg/ g)	Time	Remarks
Wetting back	300	+ Water			
	0.3	+Wetting agent		2hrs	L/O/N
	0.3	+ formic acid		20'	
	200	+ Water		10'	Drain
Rechroming	150	+ Water			
	2	+ Novaltán PF		10'	Check PH (2.8-3.0)
	6	+BCS (33%)		60'	
	3	+Sintal tan 40 SC		20'	Chrome syntan
	2	+fish oil			
Basification	1.5	+Sodium Formate		30	
	1	+Sodium bicarbonate		30	Check pH (3.8-4)____ check exhaustion, Drain, wash
Neutralization					
	150	+Water			
	2	+Sodium formate			
	1	+Neutralizing syntan		20'	

	1	+Sodium bicarbonate		3*10+ 30'	pH (5.4– 5.6)____, D/W/D
Retanning and dyeing	100	+Water			
	1.5	+Novaltán MAP		20'	Acrylic polymer, Drain
Washing	150	+water		10'	Drain
	2	+Fosfol LP		20'	Lecithin based fatliquor
	4	+Retanal MD-80			Melamin syntan
	3	+Retanal LSF-100			Phenolic syntan
	2	+Mimosa			
	2	+Quebracho			
	4	+Dye		60'	Check Ø
Fatliquoring					
	8	+Fosfol 54			Synthetic fatliquor
	2	+Fosfol LP			Lecithin based fatliquor
	1	+Fish oil			
	2	Tafigal HK		60'	
Fixation	3	+Formicacid (1:10 cold water)		3*10+ 30'	Check PH (3.8-4.0) Check exhaustion, Drain
	100	+Water@50 ⁰ C			
Cationic toping	1	+Cationic fatliquor (dilute 1:5@50 ⁰ C)		20'	
W/D, pile flat, set-out, wet vacuum , hang to dry, stacking , dry vacuum, ready for finishing					

E. Retanning and Dyeing Product: Burnish Shoe Upper

Material used: Wet blue leather **Date:** 24,07,2014 **Quantity:** 1side **weight:** 1.25kg

Operations	%	Chemicals used	Amount (kg/ g)	Time	Remarks
Wetting back	300	+ Water	7.5L		
	0.75	+Wetting agent	9.5g	2hrs	L/O/N
	300	+ Water	7.5L	10'	D/W/D
	0.75	+Incoflore black GTN	9.5g		
	0.25	+Navy blue	3g	20'	
Neutralization					
	150	+Water	19L		
	2	+Sodium formate	25g		
	2	+Neutralizing syntan	25g	20'	
	2	+Sodium bicarbonate	25g	3*10+30 '	pH (5.8- 6)____, D/W/D
Washing	300	+Water	7.5L	10'	W/D/W
Retanning	200	+water	2.5L		
	2	+Fosfol LP	25g	30'	Lecitin based fatliquor
	10	+Mimosa	125g		Vegetable extract
	10	+Quebracho	125g		“
Dyeing	5	+Incoflore black GTN	63g		
	1	+Navy blue	12.5g	60'	Check Ø
Fatliquoring					
	4	+Genosoft SE	63g		Synthetic fatliquor
	4	+ Genosoft FC	50g		“
	1.5	+Softenol-100	38g		Neats foot oil
	1.5	+Nexopol NT	19g	60'	Fish oil

Fixation	5	+Formic acid (1:10 cold water)	63g	3*10+30'	Check PH (3.8-4.0) Check exhaustion, D/W/D
	2	Mimosa	12.5g	30'	
	0.5	Softenol-100	6.5g	30'	To give burnish effect
	1	Formic Acid	12.5g	2*5'+20'	
W/D, pile flat, set-out, vacuum drying, hang to dry, stacking, conditioning, milling, Toggling, ready for finishing					

Preparation of Belt Leather

A. Liming - Tanning **Product:** Camel belt leather **Drum No:** 03

Material used: Wet salted camel hides **Date:** 13, 08, 2014

Quantity: 8 sides

Operations	%	Chemicals used	Amount (kg/ g)	Time	Remarks
Liming	100	+Water			
	3	+Sodium sulphide		20'	
	10	+Lime powder		2days	Run 10' each hour
	200	+Water			
Add 1g/L of sodium hydroxide pellets and run 10' each hour for one day and handle once each hour					
Deliming	100	+Water			
	1	+Ammonium sulphate			
	0.5	+Sodium bisulphite		1hr	Check pH (8-9)
Bating	1	Basozyme CM		45'	Check bating completion, D/W/D
Pickling	100	+Water			
	8	+Common salt		15'	

	0.5	+Formic Acid (1:10 @cold water)		3*10'	Check pH (4.5-5)
Tanning	15	Mimosa powder			
	10	Quebrach powder		2hrs	Check penetration
	6	Mimosa powder			
	4	Quebrach powder		2hrs	Check complete penetration, Check Ph (4-4.2)
D/W/D, pile flat, Sam-setting, Shave to remove flesh only, ready for post tanning					

B. Retanning and Dyeing Product: Belt Leather

Material used: Vegetable tanned leather **Date:** 22, 08, 2014 **Weight:** ----kg

Operations	%	Chemicals used	Amount (kg/ g)	Time	Remarks
Wetting back	300	+ Water			
	0.5	+Wetting agent		2hrs	D/W/D
Rechroming	150	+Water			
	0.3	+Formic Acid		30'	Check pH (3-3.5)
	1	+Nexopol NT			Fish oil
	0.75	Incoflore black GTN			
	0.25	Navy Blue		20'	
	5	+BCS			
	5	+Chrome syntan		60'	
Basification	1	+Sodium formate		10'	
	1.5	+Sodium bicarbonate		3*10+30	Check pH (3.8-4), D/W/D
Neutralization	150	+Water			
	1	+Sodium formate			
	1	+Neutralizing syntan		20	
	1	+Sodium bicarbonate		3*10+30'	pH (5.2-5.6)____, D/W/D

Retanning and dyeing	150	+Water			
	4	+Retanal MD-80			
	4	+Retanal LSF-100			
	3	+Mimosa			
	3	+Quebracho			
	4.5	Incoflore black GTN			
	1.5	Navy Blue		90'	Check Ø
Fatliquoring					
	3	+Genosoft SE			Synthetic fatliquor
	3	+ Genosoft FC			Lecithin based fatliquor
	2	+Nexopol NT			Fish Oil
	2	+Fosfol 41			
	2	+Fosfol AR-75			
Fixation	6	+Formic acid (1:10 cold water)		3*10+30'	Check PH (3.8-4.0) Check exhaustion, D/W/D

Preparation of Bag Leather

A. Liming

Raw material used: Soaked Camel hides **Quantity:** sides **Drum No:** _____

Operations	%	Chemicals used	Amount (kg/ g)	Time	Remark
Liming					
Unhairing	200	+ Water			
	3	+Sodium sulphide			
	10	+Lime powder			
	0.5	+Sintorene AR		2 days	Drain
Opening up	250	+ Water			
	10	+Lime powder			
	0.5	+Sintorene AR			
	0.5	+Soda ash		2 days	Check plumping
	0.5	+Soda ash			
	0.5	+Sintorene AR		1 day	Check plumping
Wash, Drain and flesh properly					

B. Deliming-Tanning

Raw material: Limed pelt **Weight:** - based on fleshed weight **Product:** Bag Leather

Operations	%	Chemicals used	Amount (kg/ g)	Time	Remark
Washing	200	+ Water		10'	Drain
	200	+ Water		10'	Drain
	100	+ Water			
Deliming	1.5	Ammonium sulfate		40'	Check PH (8-8.5)_
	0.5	Basozyme CM		45'	Check the completion of bating
Washing	200	+ Water		10'	Drain
	200	+ Water		10'	Drain
Pickling	100	+ Water			
	10	+Common salt		10'	Check ⁰ Be (7-8)

	0.5	+Formic acid (1;10 with cold water)		15'	
	1.5	+sulphuric acid(1;10 with cold water)		3x10'+45'	Check PH (2.8-3)____ Drain 50% of the float
Tanning	4	+BCS (33%)		30'	
	4	+BCS (33%)		2hrs	Check-complete penetration
Basification	1.5	+Sodium formate		10'	
	1	+Sodium bicarbonate		2x15+4 hrs	Check PH (3.8-4)____ check exhaustion
	0.15	+Preventol WB		20'	Drain and Pile
Sum setting and Shaving (Ready for post- tanning operations)					

C. Retanning and Dyeing Product: Bag Leather

Material used: Wet blue leather **Date:** _____ **Quantity:** _____

Operations	%	Chemicals used	Amount (kg/ g)	Time	Remarks
Wetting back	300	+ Water			
	0.3	+Wetting agent		2hrs	L/O/N
	0.3	+ formic acid		20'	
	200	+ Water		10'	Drain
Rechroming	150	+ Water			
	4	+BCS (33%)		40'	
	2	+Sintal tan 40 SC		20'	Chrome syntan
	2	+fish oil			
Basification	1.5	+Sodium Formate		30'	
	1	+Sodium bicarbonate		30'	Check pH (3.8-4)____ check exhaustion, D/W/D

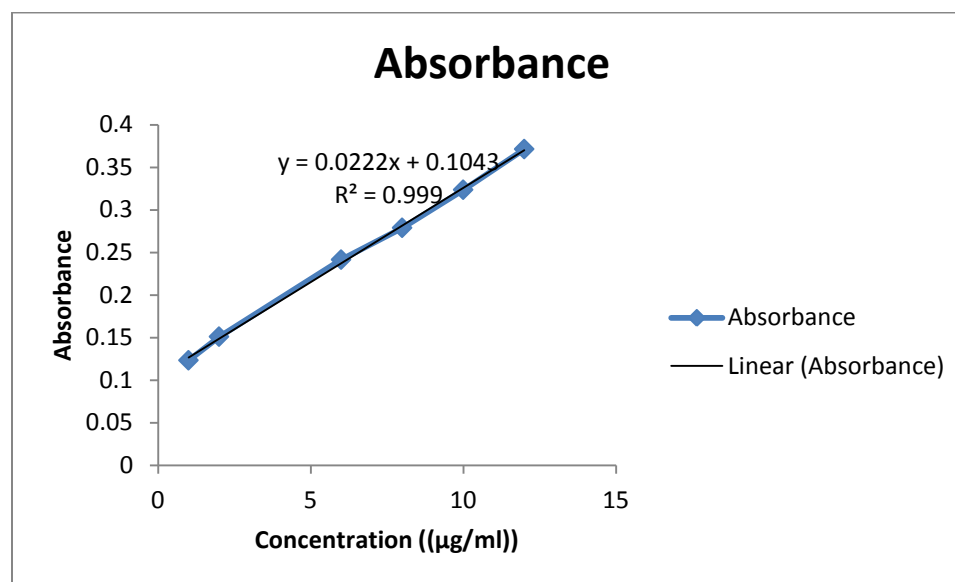
	0.25	+Coriastel Dark brown N			
	0.75	+Criastel Havana J		30'	
Neutralization	100	+Water			
	2	+Sodium formate			
	1.5	+Neutralizing syntan		20'	
	1	+Sodium bicarbonate		3*10+ 30'	pH:(5.8-6)____, D/W/D
Retanning and dyeing	100	+Water			
	2	+Novaltan-MAP		30'	
	2	+Fosfol LP		20'	
	3	+Retanal MD-80			
	2	+Retanal LSF-100			
	1.5	+Mimosa			
	1	+Quebracho			
	1	+Coriastel Dark brown N			
	3	+Criastel Havana J		60'	Check Ø
Fatliquoring					
	4	+Genosoft SE			
	3	+ Genosoft FC			
	2	+Fosfol AR-75			
	2	+Fosfol 41			
	2	+Fosfol LP			
	1	+Fish oil		90'	
Fixation	4	+Formicacid (1:10 cold water)		3*10+ 30'	Check PH (3.8-4.0) Check exhaustion, Drain
	100	+Water@50 ⁰ C			
Cationic topping	1	+Cationic fatliquor		20'	

		(dilute 1:5@50 ⁰ C)			
W/D, pile flat, set-out, wet vacuum , hang to dry, stacking , dry vacuum, ready for finishing					

Annex 3

Absorbance Reading for standard Hydroxyproline

HP Concentration (µg/ml)	Absorbance
1	0.1232
2	0.151
6	0.2415
8	0.2789
10	0.3236
12	0.3236



Standard graph for Hydroxy Proline

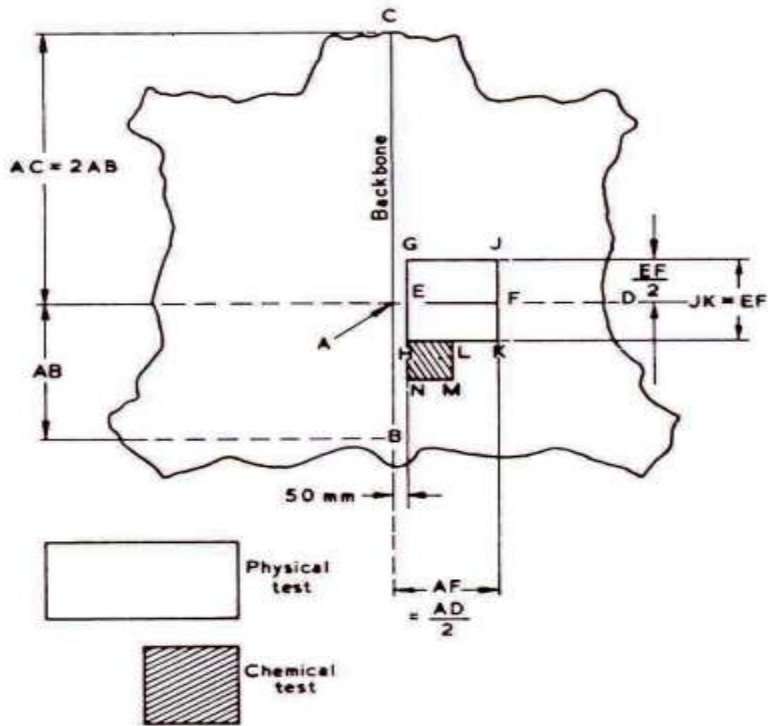


Sample collection site (Addis Ababa Abattoirs)

Ethiopian Livestock Information

Species	Quantity
Cattle	52 million
Sheep	27 million
Goat	22 million
Camel	2.3 million
Others	NA
Cattle Off take Rates:	7%
Sheep Off rake Rates:	30%
Goat Off take Rates:	31.5%
Camel Off take Rates:	2%

Source: - COMESA, June, 2014



Sampling location for whole skins, sides and hides

Organoleptic Properties Evaluation result

1. Shoe upper leather

S/No	Color	Grain tightness	Fullness	Roundness	Softness	Color uniformity
1	Black	8	9	8	8	8
2		7.5	7	7	6.5	6.5
Average		7.75	8	7.5	7.25	7.25
1	Brown	8.5	9	8	7	7
2		8	7.5	8.5	7	6.5
Average		8.25	8.25	8.25	7	6.75

2. Belt Leather

S/No	Color	Grain tightness	Stretch	Fullness
1	Black	8	8.5	9
2		8.5	9	8
Average		8.25	8.75	8.5
	L/Brown	8	8.5	9
		8	8	8.5
Average		8	8.25	8.75

3. Leather Goods

S/No	Color	Grain tightness	Softness	Color uniformity
1	Beige	8	8	7
2		7.5	8.5	6.5
Average		7.75	8.25	6.75

Annex 4

1. NITROGEN CONTENT

Response: Nitrogen Content

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.18	1	0.18	20.01	0.0110	significant
A-A0.18		1	0.18	20.01	0.0110	
Pure Error	0.037	4	9.183E-003			
Cor Total	0.22	5				

The Model F-value of 20.01 implies the model is significant. There is only a 1.10% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this case A are significant model terms.

Treatment Means (Adjusted, If Necessary)

Estimated Mean	Standard Error
1-Raw stage	15.66
2-Limed pelt stage	15.31

Mean Treatment	Difference	Standard dfError	t for H0 Coeff=0	Prob > t
1 vs 2	0.35	10.078	4.47	0.0110

Values of "Prob > |t|" less than 0.0500 indicate the difference in the two treatment means is significant.

2. TENSILE STRENGTH

Design Summary

Study Type	Factorial	Runs	6
Initial Design	Full Factorial	Blocks	No Blocks
Center Points	0		
Design Model	Main effects		

Factor	Name	Units	Type	Low Actual	High Actual
A	SAMPLING POSITION	NA	Categorical		Along Backbone
	Across Backbone	Levels:	2		

Response	Name	Units	Obs	Analysis Minimum	Maximum	Mean
Y1	TENSILE STRENGTH	N/mm ²	6	Factorial	23.70	30.71

Response: TENSILE STRENGTH

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	29.75	1	29.75	12.62	0.0237	
<i>A-SAMPLING POSITION</i>	29.75	1	29.75	12.62	0.0237	
Pure Error	9.43	4	2.36			
Cor Total	39.18	5				

The Model F-value of 12.62 implies the model is significant. There is only a 2.37% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case sampling position are significant model terms.

Treatment Means (Adjusted, If Necessary)

Estimated Mean	Standard Error				
1-ALONG BACK BONE	24.62	0.89			
2-ACROSS BACK BONE	29.08	0.89			

Treatment	Mean Difference	Standard Error	t for H0	Coeff=0	Prob > t
1 vs 2	-4.45	1	1.25	-3.55	0.0237

Values of "Prob > |t|" less than 0.0500 indicate the difference in the two treatment means is significant.

3. Elongation at break

Response: Elongation at break

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Sum of	Mean	F	p-value		
Source	Squares	df	Square	Value	Prob > F
Model	14.73	1	14.73	2.10	0.2209
<i>A-Sampling position</i>	<i>14.73</i>	<i>1</i>	<i>14.73</i>	<i>2.10</i>	<i>0.2209</i>
Pure Error	28.05	4	7.01		
Cor Total	42.78	5			

The "Model F-value" of 2.10 implies the model is not significant relative to the noise. There is a 22.09 % chance that a "Model F-value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this e there are no significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

Treatment Means (Adjusted, If Necessary)

	Estimated	Standard
	Mean	Error
1-Along the backbone	49.27	1.53
2-Across the backbone	46.13	1.53

Treatment	Mean	Standard	t for H0	Prob > t
	Difference	dfError	Coeff=0	
1 vs 2	3.13	12.16	1.45	0.2209

Values of "Prob > |t|" less than 0.0500 indicate the difference in the two treatment means is significant.

4. TEAR STRENGTH

Response: TEAR STRENGTH

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	61.50	1	61.50	8.400.0442	significant
<i>A-Sampling position</i>	<i>61.50</i>	<i>1</i>	<i>61.50</i>	<i>8.40</i>	<i>0.0442</i>
Pure Error	29.27	4	7.32		
Cor Total	90.78	5			

The Model F-value of 8.40 implies the model is significant. There is only a 4.42% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case sampling position are significant model terms.

Treatment Means (Adjusted, If Necessary)

Estimated Mean	Standard Error
1-Along the back bone 105.79	1.56
2-Across the back bone 99.39	1.56

Mean Treatment	Difference	Standard Error	t for H0	Coeff=0	Prob > t
1 vs 2	6.40	2.21	2.90	2.90	0.0442

Values of "Prob > |t|" less than 0.0500 indicate the difference in the two treatment means is significant.