ADDIS ABABA UNIVERSITY

ADDIS ABABA INSITUTE OF TECHNOLOGY (AAiT)

SCHOOL OF CHEMICAL AND BIO ENGINEERING

HIGH PERFORMANCE GLOVE LEATHER FROM GOAT SKIN: ROLE OF PHYSICO-CHEMICAL PROPERTIES

By

Tarekegn Jida Bekele

September, 2014

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A Thesis submitted to Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in Partial Fulfilment of the Requirements the Attainment of the Degree of Master of Science in Chemical Engineering Under Leather Technology stream.

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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:-……

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List of Abbreviations and acronyms

SEM – Scanning Electron Microscope

Hypo – Hydroxyproline

FAO – Food and Agricultural Organization

GTP - Growth and Transformation Plan

LIDI – Leather Industry Development Institute

CLRI – Central Leather Research Institute

ISO – International Standard Organization

SLC – Standard for Leather Chemicals

SLP - Standard for Leather Physical

TV – Titrant Volume

BV – Blank Volume

JALCA – Journal of American Leather Chemist Association

ASTM – American Standard Test Method

ESGPIP - Ethiopian Sheep and Goat productivity improvement program

GAGs - Glycosaminoglycan

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Abstract

The chemical and physical characteristics of the goat skins are essential to make glove leathers. The characteristic of skin can be analyzed by using Scanning Electron Microscope (SEM), light microscope and studying histological structure of the skin as well as through various chemical characteristics. The fiber opening operation as well as the post tanning auxiliaries like syntans and fatliquors are known to significantly influence the properties of glove leathers. The right choice of lyotropic agents, fatliquors and syntans are critical to obtain the leathers with good gloving property. Hence, in this thesis an attempt has been made to study the physico-chemical properties of the skin and to study systematically the influence of various lyotropic agents, fatliqours and syntans on the gloving properties of leather made from goat skins. Care was taken to ensure that the properties of gloving leathers *viz.*run, softness, strength properties and other subjective properties like smoothness and stretch based on the physico-chemical properties of the skin were obtained.

1 Introduction

1.1 Leather Industry

The leather industry is a world-wide leading market concerning the processing of skin or hide of animals, which by tanning are transformed into a durable material preventing its decay and making it persistent and flexible. Since the Prehistoric Age, primitive people have preserved pelts with smoke from wood combustion, ash and animal fat to craft garments, shoes, sheds, etc.

It is important to remember that the leather Industry market is strictly connected to the meat market. In fact, this industry is able to convert a by-product of the food industry into a noble material which otherwise should be disposed into waste. [1]

As a matter of fact, the outcome of the tanning process is highly dependent on the quality of the original raw hides, with special regard to the conservation status. Autolysis of collagen, in fact, starts just following the death of the animal due to the activity of spoilage bacteria producing proteolytic enzymes.

Since any impairment of the collagenous network leads to severe losses in terms of final leather quality, a proper conservation of the hides represents one of the major issues in the leather making industry.

Mammalian skin is an organ fulfilling many physiological functions such as regulation of body temperature, protection, elimination of waste products, sensory detection, etc. The aim of the tanning process is to enhance some of its natural properties, remove any unwanted matter, to stabilize its structure and at the same time to prevent putrefaction. The most important component of hide in the leather making view is collagen. [2]

The modern tanning industry in Ethiopia was started in mid of 1920s. Presently, Ethiopia's leather industry is in the forefront of the leather sector development within the Eastern and Southern Africa region.

1.2 Leather production and its value

Totally, about 19.3 billion square feet of light leather is produced worldwide by the leather industry a year, which comes to a total estimated value of about US$ 16.9 billion. Over 60% of the world's leather production is from the developing countries [3]. 65% of the world leather production is produced from bovine hides, 15% form sheep, 11% from pig and 9% from goat. All other types of leather from other animals comprise less than

0.2% of world's annual leather production; an estimated 52% of it goes into leather footwear production alone. The global footwear production with leather upper amounts to around 4.5 billion pairs, which comes to be an approximated worth of US$ 43.8 billion [3].

Table 1.1Leather and Leather Footwear: Production, Average 2008-2010

Input	**Heavy Leather Thousand tonnes**	**Light Leather Million sq.ft.**	**Footwear with leather upper (Million pairs)**
Bovine hides and skins			
World	542.9	14139.6	4534.0
Developing Countries	394.3	8 995.3	3 540.6
Developed Countries	148.6	5 144.3	993.4
Sheep skins and goat Skins			
World		5 237.5	
Developing Countries		4 127.2	
Developed Countries		1 110.3	

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

Table 1.2 World leather use by end products

Leather use	million square feet	% of total production
Footwear	11,925	52
Garments	2,290	10
Auto	2340	10.2
Furniture	3,210	14
Gloves	1010	4.4
Other leather products	2155	9.4
Total	22930	100

Table 1.3 Leather and Footwear: Value of Exports Average 2008-2010

	Rough-tanned and finished leathers all types		Footwear with leather uppers	
		Share in the world total	Million USD	Share in the world total
WORLD	16 914.6	100	43 834.8	100
Developing countries	8 249.3	48.8	20 823.5	47.5
Developed countries	8 665.3	51.2	23 011.3	52.5

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

1.3 Overview of Ethiopian Leather Sector

Leather sector industry is one of the priority sectors (textile and garment, sugar and sugar related, cement, metal and engineering, chemical, pharmaceutical and agro processing industries) in which has been given a particular emphasis and which has been identified as a potentially competitive in the global market. The five-year growth and transformation plan [10] attaches due importance on increasing leather export earnings by way of developing new leather units and expansion of the existing units. The plan aims at raising the earnings from the sector from US$ 76 million end of 2009/10 to US$ 497 million in 2014/15. Furthermore the plan aims upgrading the production of the tanneries

to 90% full capacity by importing raw hides and skins, pickle, wet blue, and crust so as to solve the supply of raw materials. [4]

1.4 Raw material Availability

Ethiopia is one of the countries in the world that possess large livestock population. Ethiopia stands eighth for cattle, twelfth for sheep and eight for goat livestock populations [5]. 53.4 million cattle, 25.5 million sheep and 22.78 million goat livestock population are found in Ethiopia, which is the share of Ethiopia is 2.5% of the world livestock population [6]. Even though the country is endowed with the high livestock population, the production is less.

Table 1.4The raw skin and hide production and the off take ration

Animals	**Population thousand heads**	**Raw skin & hide Production (Million pieces)**	Off-Take Ratio (%)
Cattle	52,000	3.7	7.12
Sheep	27,096	8.7	32.11
Goats	22,094	8.1	36.66

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

One of the aims of the leather industry is the development of glove leathers that require special attention. Gloves are used to protect the hand or part of the hand against impurities, infections, accidents and hazards.

A good glove should act as a defense against cold and water, maintain the body temperature and leave the hand movable enough to drive a vehicle, to grasp some heavy object lying underneath and to operate a machine etc.

1.5 Goat breeds of Ethiopia

Based on differences in physical characteristics and genetic differences at the DNA level, four families and 12 breeds of goats have been identified in Ethiopia [7].A family is a group of breeds that are genetically more related and physically more similar than breeds outside the group. The families and breeds are named after their geographical location,

the ethnic communities maintaining them, or based on some identifying physical features (Table 5).

It should be noted that some breeds are known by different local names in different localities. Breeds are also not bounded by political boundaries and the same breed can be present in different countries for example the Barka goat in Eritrea (known as Begayit in Ethiopia) and Nuer sheep in Sudan.

Table 1.5 Goat families and breeds of Ethiopia

Family name Other	Breed name	local names
Nubian family	Nubian	
Rift Valley family	Afar	Adal, Danakil
	Abergelle	
	Arsi-Bale	Gishe, Sidama
	Woito-Guji	Woyto, Guji, Konso
Somali family	Hararghe Highland	
	Short-eared Somali	Denghier or Deghiyer
	Long-eared Somali	Large white Somali, Degheir, Digodi, Melebo
Small East African family	Central Highland	Brown goat
	Western Highland	
	Western Lowland	Gumz
	Keffa	

1.6 History of glove leather

The symbolic sense of the middle ages early gave to the use of gloves a special significance. Their liturgical use by the church is dealt with below (pontifical gloves); this was imitated from the usage of civil life. Embroidered and jeweled gloves formed part of the insignia of the emperors, and also of the king of England. Thus Matthew of Paris, in recording the burial of Henry II. In 1989, mentions that he was buried in his coronation robes, with a golden crown on his head and gloves on his hands. Gloves were also found

on the hands of King John when his tomb was opened in 1797 and on those of King Edward I when his tomb was opened in 1774.

JOHN SHKESPEARE AND GLOVES

(Shakespeare's father)

John Shakespear, the father of William Shakespeare was a "whittaner"- a worker of kid, dog and deerskin. At the family home in Stratford on Avon, a room is dedicated to sowing the work he did in it to tan leather and make gloves. Nearby wood stock was a center of glove making, on account of the plentiful supply of deerskins. Shakespeare was himself born in 1564. His father who was a tanner and wool merchant was also sometimes money-leader.

1.6.1 Gloves in Religion, ceremonies and Fashion (1860)

Bishops began the tradition of wearing gloves for Holy Sacrament, which becomes a religious ritual. Traced back to 10th century, it is belied that popes, cardinals and bishops wore gloves to keep their hands clean for holy mysteries. Another historical theory suggests that gloves were adopted for pomp in the Fankish Kingdom. Wearing gloves then speared to Rome, where liturgical gloves were first used during the early half of the 11th century. Kings started to wear gloves for certain ceremonies and later as ornamental accessories that represented luxury. Matthew of Paris reported that Henry II of England was buried with gloves on his hands in 1189.

Glove: originally, gloves were functional. Primitive people wore them for protection against weather and injury from the growing things encountered in the forest and field. The glove is a covering for the hand made of textile, leather, wool, cotton; other recently developed manmade fibres and metal for protection and for the comfort. This article meant to protect the wearer from cold, heat, electrical shock, wetness, vibration and so on. Initially the mitten must have been made in a crude manner for the protection and the development took a shape and was made separate finger gloves.

Beginning as menswear, the glove was part of kingly attire for fighting, hunting and hawking, Sanctified by the church, it was used in Coronation ceremonies and increasingly become a symbol of pomp and circumstance. Bejeweled, embodied, fringed, scalloped and tasselled gloves captured the attention of ladies, who treasured them as articles of fashion and luxury.

Mittens ("Moufle") are the origin of the development of the gloves, which is worn by all classes in the early times. [8]

Then Rebekah took Esau's best cloths they were there in the house and instructed Jacob to put them on. And she made him a pair of gloves from the hair skin of the young goats and fastened a strip of the hide around his neck.

1.7 Statement of the problem

Tanneries in Ethiopia mostly use Goat skins for the manufacture of suede crust, upper and lining leathers. In the present work it is envisaged to use the goat skins for the manufacture of glove leathers. The outcome of this project would enable the Ethiopian tanners to look at the product diversification. All over the globe, the material preferred for making gloves is sheep skin, owing to its inherent histological characteristics. The properties, which make the sheep skins well suited material for glove leather making, are:

- The corium proper of sheep skin occupies approximately 25 to 45 % of the total thickness of the skin.
- The collagen fibre bundles are extremely thin and are not closely interwoven and tend to run parallel to the grain surface which accounts for the looseness of the structure.

Whereas, the goat skins have following characteristics;

1. The corium proper of the goat skin occupies approximately 45 to 70 % of the total thickness of the skin.
2. The collagen fibres present in this layer are firmer and fuller than the corresponding ones in the sheep skins. It is nearly equal to that of a cow calf skin. [9]
3. In goat skins a very low angle of weave is present.
4. A considerable amount of reticular tissue is present in goat skin [10]

Due to the firmer and fuller collagen fibre of goat skin and the above mentioned properties, it becomes difficult to produce softer leathers from goat skin. Also the cost of raw material is increasing day to day; quantity and quality (grade) of sheep skins are also getting decreased. Hence, this study is of great importance to the Ethiopian tanning industry, because the glove production from goat skin aims to overcome the scarcity of the raw material, to substitute sheep skin and also to satisfy the needs of global market.

1.8 OBJECTIVES

1.8.1 General objective

The main objective of this thesis work is to make high performance glove leather from goat skin by studying the role of physico-chemical characteristics.

1.8.2 Specific objectives

- To study the histological structure, chemical, and physical characteristics of Goat skin;
- To determine hydroxyproline (collagen) content of the skin;
- To study effect of chemicals on gloving character of goat skin;
- To devise a strategy for making high performance glove leather from goat skin;
- To overcome the raw material scarcity (in quality) of sheep skin by substituting goat skin;
- To achieve the properties of gloving leather;
- To satisfy the market demand on glove leather;

The rest of this thesis is organized as follows:

Chapter two presents an overview of relevant literature regarding the meaning of glove leather, its requirement and steps to be followed to produce the same.

Chapter three gives a description of the experimental design and the materials and methods applied in the present study.

Chapter four presents the major findings of the study, discusses it, and presents the limitations of the study.

Chapter five gives a summary of findings, conclusions and perspectives

2 Literature Review

2.1 What is Glove Leather?

Gloving leather is a class of its own with specific requirements of physical properties suited to its application. The wide classification of glove leathers based on its application makes obvious the need for certain degree of variance in physical properties for each kind of glove.

One of the important properties for glove leather is “Run” an elasto-plastic stretch, which is essential to fit snugly to the hand when pulled on and must not stretch on the wear. Run in the gloving leather is obtained mainly through good fiber splitting followed by fiber lubrication during leather processing. Longer liming, proper bating and ageing after pickling enhances the fiber splitting. The lubrication of fibers improves the gloving properties, which is achieved by proper fatliquoring. The selection of fatliquors plays a vital role in determining the extent of gloving properties. [11, 21]

The main requirements for Glove:

- Non elastic stretch (Run)
- Softness for comfortable wear
- Good grip
- Strength sufficient to carry fine swift movements

Most common type of glove leather manufactured in the past decades. Besides a high degree of softness the leather should have good elasticity with adequate tensile strength and stitch tear strength. It is produced in thickness of 0.6 – 1.2 mm depending on use requirements.

2.1.1 Run in Glove Leather

Run is important in glove leather; in order to fit the hand perfectly the glove must ease to the shape of the hand, but when removed and pulled length-wise should assume its original shape. The degree of extensibility and plasticity in both directions is, therefore, of importance. [12]

2.1.2 Requirements of production

Good opening up of skin in liming, good penetration of deliming, strong bating and intense penetrative neutralization. Dyeing is performed with metal complex dyes which are light fast and fast to bleeding. High-quality glove leathers are only sprinkled with talcum powder and subsequently plushed to make aniline glove leathers.

Very soft, elastic binder finishes with an emulsion lacquer coat are applied for tougher use requirements or for lower grade assortments. Glove should be free from harmful substances and should be washable without undergoing serious changes.[10]

2.2 Glove leather production

Soaking

Soaking is the first process applied to the raw stock. This and all subsequent chemical steps are most commonly conducted in drums. The purpose of soaking is to rehydrate the fiber structure with water, to remove the preservation salt, to remove non structural proteins, to remove dung, dirt and blood. The components of soaking solutions include: Water, detergents, biocides and alkalis. Soaking enzymes can also be used to speed up the rehydration process.

Liming and unhairing

Unhairing is a process of removing the hair from the pelt. The traditional method of dissolving the hair is to dissolve it, called 'hair burning'. Hair removal in alternative ways, 'hair saving', keeping the hair intact while removing it; each technology requires a different degree of process control. [2]

Enzyme-assisted chemical unhearing

Conventional hair burning can be accelerated by the presence of so-called 'alkali stable' proteolytic enzymes, obtained from bacterial fermentation. [2]

One of the most important pre-tanning operations is liming. Liming and reliming operation are the inevitable steps in leather processing. It removes all the interfibrous material especially proteoglycans.

The main objectives of liming are removal of hair, flesh and separation of the fiber bundles physico-chemically.[13]

Several lime and sulfide free liming methods have evolved during the past century. They include dehairing methods based on proteolitic enzymes, chlorine dioxcide, alkaline hydrogen peroxide, nickel carbonate and lactobacillus-based enzymatic application [14]. The interfibrillary proteins, which are mostly mucoids that contain carbohydrate as prosthetic groups, are removed during fiber opening. These non-collagenous proteins are known as proteoglycons. Enzyme, α-amylase can act on glycosidic conjugation of proteoglycans and hence can facilitate the removal of proteoglycans, resulting in the opening up of the fibrous collagen matrix.

Deliming Technologies

The functions of deliming are: - removing the lime, lowering the pH in preparation for bating, and reversing the swelling. It can be carried out by using: - Weak Acids, Acidic Salts, Ammonium salts (In industry it is common to use either ammonium sulfate or ammonium chloride) and Carbon dioxide [2]

Bating

Bating refers to the use of enzymes; its purpose is to break down specific skin components: usually the non-structural proteins are the target. [2]

Pickling

The pickling process is primarily conducted to adjust the collagen to the conditions required by the chrome tanning reaction. The traditional recipe for pickling based on limed pelt weight is 100% Float, 10% salt, 1% Sulfuric acid. [2]

Tanning

Tanning is the conversion of a putrescible organic material into a stable material that resists putrefaction by spoilage bacteria. [2]

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

The reasons for the popularity of chrome tanning when compared with vegetable tanning [2]

The process time for the chrome tanning reaction itself is typically less than 24 hours: the vegetable tanning reaction takes several weeks, even in modern process.

Chrome tanning confers high hydrothermal stability; a shrinkage temperature of 110^{o}C is easily attainable. This opens up new applications, compared with vegetable tanned leather, where the maximum achievable shrinkage temperature is 85^{o}C, depending on which vegetable tannin type used.

Chrome tanning alters the structure of the collagen in only a small way: the usual chrome content of fully tanned leather is 4% Cr_2O_3, whereas vegetable tanned leather may contain up to 30% tannin and hence the handle and physical properties are inevitably modified, restricting applications of the leather. Chromium (III) can act as a mordant (fixing agent for dyes) and its pale color allows bright deep and pastel shades (even though the base color of the leather is pale blue). Versatility is a key characteristic of the process. It is

theoretically possible to create any type of leather from any wet blue hide: men's weight or ladies' weight shoe upper, combat upper, soling, clothing, gloving, upholstery, etc. [2]

Post Tanning

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

Retanning: The purpose is to modify the properties and performance of the leather. These changes include the handle, the chemical and hydrothermal stability or the appearance of the leather. Retanning chemicals include: minerals, Aldehydic reagents, polymers or resins and syntans.

Dyeing: This is the coloring step. Almost any color can be struck on any type of leather.

Fatliquoring: This step is primarily applied to prevent sticking when the leather is dried after completion of the wet processes. A secondary effect is to control the degree of softness conferred to the leather. One of the consequences of lubrication is an effect on the strength of the leather. Fatliquoring is usually conducted with self-emulsifying, partially sulfated or sulfonated (sulfited) oils, which might be animal, vegetable, mineral or synthetic. This step might also include processing to confer the leather a required degree of water resistance. [2]

Fatliquoring of leathers are performed to impart softness, flexibility, feel, drape, run etc. The strength properties are also improved by fatliquoring. In effect, what is being aimed at in fatliquoring is to coat the individual fibres or fibre bundles (depending on the extent of fibre opening achieved in beam house operations for different types of leathers) with a thin layer of oil so that the internal friction is reduced and the fibres slide over one another to give the required softness and flexibility.

The choice of the oils for fatliquor preparation is done based on many parameters such as molecular size, viscosity, drying characteristics, degree of unsaturation measured in terms of iodine value (triglyceride types), free fatty acid content and pour point or solidification point (in the case of paraffinic oils). The smaller the size and lower the viscosity, the penetration will be very good. The higher the molecular size and corresponding bigger emulsion particle sizes better would be the body imparted but diffusion will be difficult. However, the smaller the size combined with linearity of the fibre structure (as in the case of paraffinic oils) will not result in good fibre separation resulting in dry feel of the resultant leathers. Hence, the molecular size and type of oils and the emulsifying groups will be important to build the necessary fatliquoring property in the product. The type of

emulsifying groups that can be introduced also will depend on the molecular structure of the oils.

2.3 Skin and its component

It is important to understand the nature of skin, in order to rationalize the structure-function, structure-property relation-ships.

Epidermis: The outermost layer of the skin, the barrier between the animal and its environment: it is composed of so called 'soft keratin', characterized by a relatively low content of cystine compared to cysteine, i.e. less oxidation of the thiol groups to the crosslinking disulfide group.

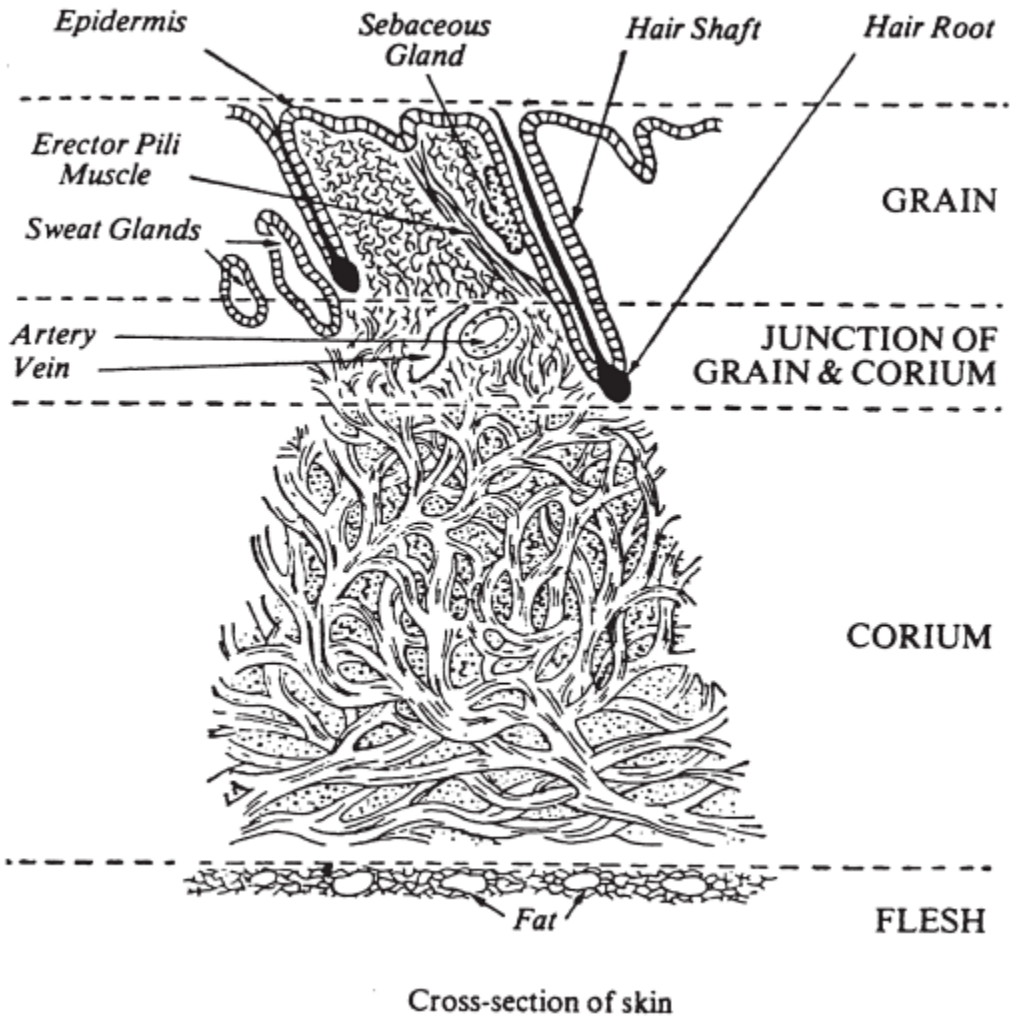


Fig 2.1 Illustration of the structure of skin cross section

Grain: The upper most layers in unhaired or de-wooled pelt, the corium minor, is also referred to in the jargon as the grain layer. The structure is fibrous, but the fibres are so fine the appearance is more like a solid. The lack of fiber interaction, in comparison with lower layer of the skin, makes the grain weak. The macro-structure is a convoluted sheet, because the grain layer is larger in area than the lower layers, so it has to be folded. This conformation is held in place by the presence of elastin.

Junction: The grain-corium junction is the transition zone between the very fine fibers of the grain and the much larger fibers of the corium. It is an open structure, consisting of relatively small fibres and carrying other structural components of the skin: these include the veinous system and, in the case of sheep skins, lipocytes, which are cells that contain triglyceride fat.

The junction is vulnerable to breaking by flexing through mechanical action in the process vessel. The consequent defect is called looseness, in which the detachment of the layer becomes visible when the pelt or leather is flexed. The effect can occur in any skin or leather, but is facilitated by the presence, and particularly the removal, of the fat cells from skin.

Corium: The main part of the skin is the obviously fibrous structure called the corium or the corium major. The fibres structure varies through the cross section of hide or skin: the fibres increase in size, reaching the maximum fiber diameter in the center of the corium and then decreasing a little they approach the next lower layer.

The network of fibres, often referred to as the weave, consists of fibres dividing and recombining with other fibers.

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

Flesh Layer: The so called flash layer is the layer of the skin closest to the flesh of the animal: although it has a distinct fiber structure, it is still part of the corium. Its structure is characterized by the low angle of weave, always lower than the corium angle of weave. [2, 12, 15]

2.4 Skin features and components

Collagen: collagens are proteins, i.e they are made up of amino acids. They can be separated into α-ammino acids and β-amino acids (figure 2.2). Each one features a terminal amino group and a terminal carboxyl group, which become involved in the peptide link, and a side chain attached to the methylene group in the center of the molecule.

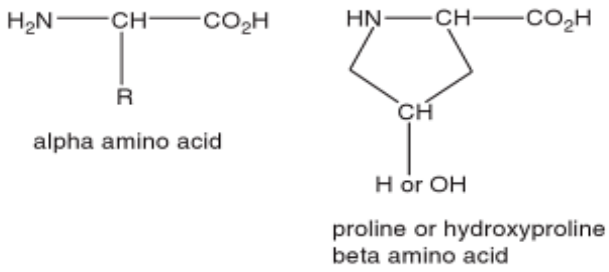


Figure 2.2 Amino acid structures

Elastin: The second most important protein in skin after collagen is elastin (Table2.1). It contributes greatly to the physical properties of the skin and leather, because it controls the elasticity of the grain layer. The material of the grain is weak, so it cannot stretch to accommodate stresses in the skin when, for example, a joint is flexed. Hence it adopts a convoluted, rippled form that can flatten as the corium stretches. The mechanism by which it returns to its convoluted state when a stress is removed is through the action of elastin fibres, which extend when the skin is stretched, then contract to the resting position when the stress is removed. The elastin fibres are centered on the follicles, with coarse fibres running parallel to the skin surface and finer fibres running at right angles to the skin surface.[12, 16]

Table 2.1Comparison of elastin and collagen

Amino acid type	Elastin	Collagen
Glycine	355	330
Apolar	431	170
Acidic	14	120
Basic	10	96
Hydroxy	20	57
Proline	125	126
Hydroxyproline	23	93

Several observations can be made concerning the numbers given in table2.1:

1. The proteins have similar glycine content by comparison with collagen, this indicates that structure of elastin could be helical, which it is.
2. Elastin has more polar amino acids therefore; the protein is more hydrophobic than collagen.
3. There are more acid and basic amino acids in collagen than in elastin making collagen relatively hydrophilic.
4. The proteins have similar proline contents, which supports the suggestion of helical structure in elastin.
5. There is less hydroxyproline in elastin so the structure is less reliant on hydrogen bonding than collagen.
6. The lack of basic residues in elastin means there is little lysine and very little histidine: covalent crosslinking of the type found in collagen is not possible. [2]

In addition, the following deductions can be made:

1. Although we know that collagen structure depends on covalent bonding, to hold the triple helix units together, there is not enough information within the amino acid composition alone to comment on the presence of covalent bonding in elastin.
2. Collagen structure depends on electrostatic salt links from the charged sidechains, but they are not important in elastin.
3. Collagen structure depends on hydrogen bonding based on the high HYPRO Content since the HYPRO Content is low in elastin, its structure relies less on H-bonding. This too supports the notion of the hydro-phobic character of elastin.
4. Bonding in elastin is dependent hydrophobic interactions, due to the high content of a polar sidechains. Such bonding is relatively unimportant in Collagen.
5. The differences in amino acid side chains affect the chemical reactivity of the proteins: reaction depends on the presence of charged sidechains will be less important in elastin than in collagen. Conversely, reactions dependent only on the back bone chemistry of the proteins will work the same in elastin and collagen. This difference can be exploited in the context of area yield.[2]

These deductions, based only on the amino acid composition, can be tabulated in terms of the relatively importance of the bonding types (Table 2.2). Elastin is an unusually stable protein, with a chain structure in the form of a single protein strand, twisted in to a double helix: it can resist boiling water, which offers a way of isolating it from collagen, because the less stable protein is denatured, degraded and solubilised by boiling water. The macro-structure of elastin is a cross linked network, which adopt a random, disordered conformation, creating regions of hydrophobically bonded groups, by excluding water, whether, in its native state or in leather, which still contains some water. [17] When elastin is extended, it has a more ordered structure, when the hydrophobic protein interacts with water. The protein acts like a familiar elastomers, such rubber, because the driving force to contract after stretching is entropic: the ordered nature of the fibers is

high energy and there is energy released when the random structure is regained. In addition, the high energy interaction of hydrophobic regions with water, in nature as well as in leather, will require the network to re-establish the energetically favoured hydrophobic bonding: this is an enthalpic driver, operating in the same direction as the entropic effect. [18, 22]

Table 2.2 Relative importance of bonding types in elastin and collagen: more stars means a greater role in protein structure.

Type of bonding	*Elastin*	*Collagen*
Covalent	**	***
Electrostatic	*	***
Hydrogen bonding	*	***
Hydrophobic bonding	***	*

Bonding in elastin is dependent on hydrophobic interactions, due to the high content of a polar side chains. Such bonding is relatively unimportant in collagen.

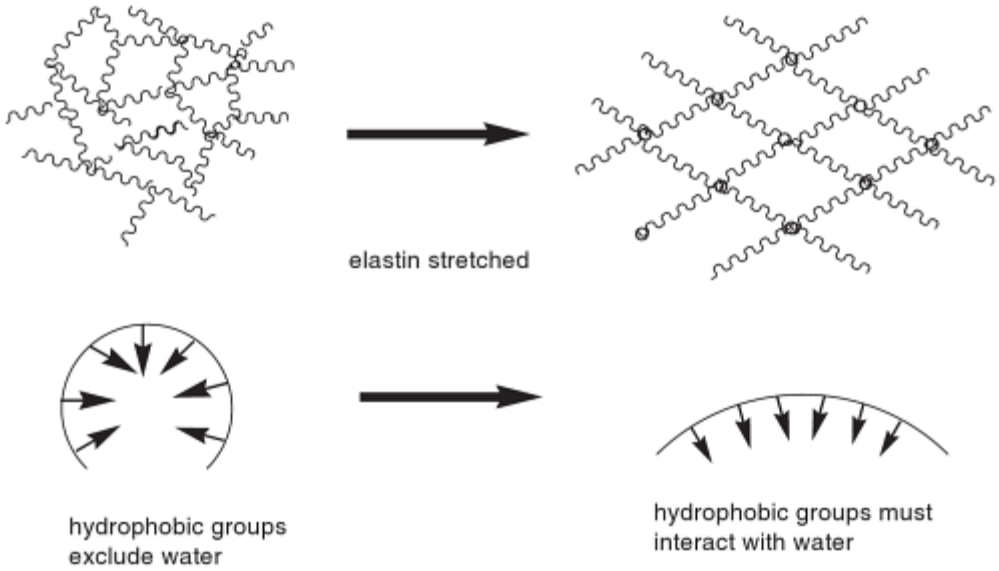


Fig 2.3Mechanism of elastin elasticity

In conventional processing, pancreatic enzymes may be employed in the so called bating step, intended to break down the non-structural proteins of skin: under these condition elastin is not degraded, nor does this occurs under the alkaline hydrolytic enzymes, which are often found in bacterial fermentation formulations also used for bating. These

enzymes can be used to break down the elastin structure, thereby allowing the grain to relax and flatten, so increasing the area of the skin.

The network is crosslinked by desmosine and iso-desmosine groups (Fig. 2.3).[19] In each case the aromatic crosslink is created from the condensation of three allysine side chains and one lysine side chain, apparent from the numbers of carbon atoms in the chains and in the ring. Isolation of these cross links provides the basis for assaying elastin content in a material.

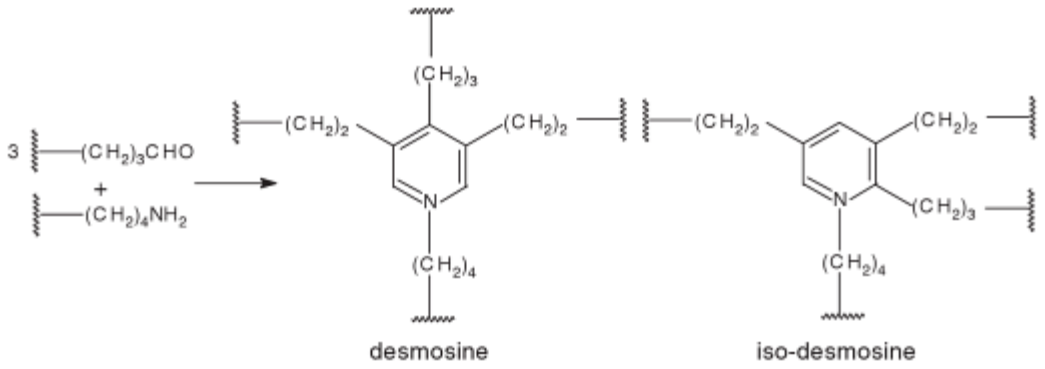


Fig. 2.4 structures of linking groups in elastin, desmosine and iso-desmosine

2.5 Non-structural Components of skin

Glycosaminoglycans (GAGs): Glycosaminoglycan is a generic term for a class of minor but significant components of skin, important in the leather making process. They can take the form of free polysaccharides, called glycosaminoglycans but may also have a protein component, when they are called proteoglycans.[12, 20]

Liming and reliming operations are the inevitable steps in leather making process. It removes all the interfibrous materials especially proteoglycans and produces a system of fibrous and fibrils of collagen matrix, which are clean. This has been achieved through the use of alkalies or enzymes. Proteoglycans are complex macromolecules containing several chains of strongly anionic linear polysaccharides that are covalently linked to a non-collagenous protein, constituting the core of the protein molecule. It is physically aggregated between the fibres to provide biophysical and biochemical functions to the skins.

Proteoglycans can be removed or cleaved during the fiber opening process. The extent of fiber opening primarily depends on the removal of proteoglycans. Hence, the elimination of proteoglycan from hides/skins can be used as a potential marker for the extent of fiber opening.

2.6 Structure of Goat skin

In many respects the skin of Goat may be regarded as having a structure intermediate between those of calf and sheep. The epidermis is thicker than in sheep skin and covers approximately 1.5to 1.8% of the total thickness of the skin. Unlike in Sheep, hair follicles in Goat are straight and less deeply rooted. The glands and fat cells, which are responsible for the sponginess of Sheep leather is very much less number in Goat skins and the glands are rather smaller in size. Hair muscle is well developed and longer in Goat skin than in Sheep skin.

The thermostat layer covers approximately 24-54% of the total thickness of the skin and is relatively thicker in the neck. A dense network of elastin is found in the Goat skin covering approximately two-third of its thermostat layer. As in Sheep skin, a relatively greater amount of elastin is present in the neck in Goat skin.

The corium proper in Goat skin covers approximately 45 to 75% of the total thickness of the skin, the percentage varying considerably over the entire area. The collagen fibers in this layer are fuller and firmer than those of the sheep but are hardly equal to those of the calf. Unlike sheep skin, fat cells and fat droplets are rarely found in this layer of Goat skin.

2.7 Chrome-Tanned Gloving Leather

This is commonly made from dry salted cape Sheep. These may be greasy and the hair may be of some value. The general requirement for gloving is that the leather should be very soft and flexible and should stretch easily, remain extended without springing back. This property is known as “run” and is essential for the production of a well fitted glove. The better qualities of gloving leather are straight-dyed and no pigment finish is used. The dyeing should be carried out accurately pattern, and carefully, so that the result is level and the skin is well penetrated; it should also be fast to perspiration and washing.[15]

2.8 Types of Glove Leather

There are different types of glove leather based on its application. The wide classification of glove leathers based on its application makes obvious the need for certain degree of variance in physical properties for each kind of glove. Some of them are mentioned as follows: [15]

- Sport glove, golf glove
- Dress glove
- Utility glove
- Industrial glove

Sport glove leather: is used for sport purpose like cricket, Hockey ball, Foot ball, volley ball.

Dress glove: as its name implies it is used for dressing purposes.

Utility glove: is used to protect hands from flame-resistance, to keep them protected in heavy-duty industrial environments or simply to stay hands-on in a general work environment.

Industrial glove: is made for industrial usage to hold and grip the materials i.e the leather to be non-greasy.

3 Materials and Methods

3.1 Materials

Skins

Fresh goat and sheep skins obtained from slaughter houses are used in this study. The time span between skinning off and laboratory study will be the same for both goat and sheep skins.

Chemicals

The chemicals used for chemical analysis are of laboratory grade and the leather processing chemicals starting from soaking to finishing are of commercial grade.

3.2 Laboratory Equipments

Electron Microscopes, Weighing balance both laboratory scale and industrial production scales, Thermometer and Baume meter, pH paper, Measuring cylinder, conical flask, Sample collecting bottles, Sample preserving refrigerator, Heating oven, Kjeldahl nitrogen distillation apparatus, Desiccators, Digestion rack, burettes, micro pipettes, heating mantle, Soxhlet apparatus, Hot air heating oven, different sized standard measuring flasks, fume hood, UV-spectrophotometer, light microscope, scanning electron microscope (SEM), softness measuring device, tensile strength measuring machine. Testing Drums, Cutting knives, Fleshing machine, Sammying machine, Shaving machine, Overhead drier, Wheel staking machine, Polishing machine etc

The description of the major equipment to be used:

- High resolution light microscope- for histological study of goat skin.
- Scanning electron microscope
- The heating ovens were used to determine the moisture content, fat and ash content.
- The Kjeldahl nitrogen distillation apparatus used to determine the nitrogen content of liquid samples prepared using an orbital shaker.
- Desiccators used to remove volatile components of samples used in the study

3.3 Grain Surface Pattern

The grain surface patterns of goat and sheep skin were studied using light Microscope. Samples from butt region of crust leather were examined. All the images were photographed at same magnification of 4X objective lens.

3.4 Hair Pore Count

The surface fineness or coarseness of goat and sheep skin was assessed by analysing the surface with respect to hair pore count. Samples at crust stage from neck, belly and butt area were taken. Magnification of 4X objective lens was used for all the samples. The generated images were photographed. Number of hair pore per in^2 were counted and recorded.

3.5 Histological Examination of Skin

3.5.1 Procedures for preparation of specimen for histological analysis

3.5.1.1 Fixation of samples with formalin

Neutral buffered formaldehyde (100 ml 40% formaldehyde + 900 ml distilled water + 4 gm sodium dihydrogen phosphate monohydrate + 6.5 gm disodium hydrogen phosphate anhydrous) was used to prevent autolysis of tissue samples .

3.5.1.2 Dehydration

After removing the tissue from formalin solution, it was washed with running water and gradually dehydrated with ethyl alcohol as follows:

a) Sample tissue was removed from formalin

b) Washed in running tap water for 3 hours

c) Placed in 30% alcohol for 3 hours

d) Placed in 50% alcohol for 3 hours

e) Placed in 70% alcohol and was left for overnight

f) Placed in 90% alcohol for 3 hours

g) Placed in 95% alcohol for 3 hours

h) Placed in 100% alcohol for 1 hours

i) Placed in 100% alcohol for 1 hours

j) Placed in 100% alcohol for 1 hours

3.5.1.3 Clearing

Process of dehydration leads to saturation of tissue with alcohol, which is immiscible with paraffin. Paraffin is used as embedding agent to give strength to the tissue sample during microtome sectioning. Thus the alcohol was removed from the tissue with a solvent so that the paraffin can infiltrate into the tissue. The clearing agent used was xylene, which brings about quick removal of alcohol from tissue and speed up the infiltration of paraffin into the tissue. The Samples were treated two times in xylene for 30 minutes.

3.5.1.4 Embedding

The aim of embedding is to standardize the tissue for microscopic examination by sectioning with microtome. Paraffin was used as they have a high degree of tissuration, hardness, plasticity and viscosity compared to other embedding substances. The samples were soaked in paraffin wax for 2 hours.

3.5.1.5 Block preparation

After the tissue was embedded with wax, it was casted into a block of paraffin. The mould was adjusted to accommodate the tissue and is filled with molten paraffin wax. Once the blocks become solid they were removed from the mould and stored until needed.

3.5.1.6 Trimming

The section to be cut was trimmed to correct section. It was trimmed in such a way that the material lies in the center of the perfect rectangle.

3.5.1.7 Mounting of block

The trimmed block was attached to a holder which can be inserted into the jaws of the microtome. The block holder was made of metal consist of a disc with rough surface attached to a cylindrical rod. The holder is heated and is pressed immediately with equal pressure on the block.

3.5.1.8 Section cutting

The rotary microtome was used in the preparation of the sections. It had central axis having an arrangement in its front to fix the block holder and two groves in which the razor holder can be moved. The knife is mounted on a pair of arms with the help of screws. The knife was placed at a desired angle.

1. Blocks were attached to a holder and inserted into the jaws of the microtome.

2. The knife was adjusted to the proper position (very close to the tip of the blocks)

3. The cutting mode (single or continuous), the cutting thickness, maximum number of cuts and speed of the microtome was set.

4. The block holder was adjusted and allowed to rotate continuously. During sectioning, the back surface of the knife was cleaned with small brush until unbroken ribbons of section were obtained.

3.5.1.9 Mounting and spreading of ribbons

The long ribbon is cut into pieces of small length which could be conveniently accommodated on a slide with sufficient space on the side of the slide for labeling. The slide is wiped clean and is smeared with an adhesive. The adhesive used was starch paste and Mayer's albumen. Mayer's albumen was prepared by thorough mixing of equal proportion of egg albumin and glycerol and adding a few crystals of thymol (preservative). The ribbons is put in hot water then taken on to a slide. The slide was then placed on hot plate so that the paraffin ribbon begins to stretch so also the section.

3.5.1.10 Staining

1. The slides were first deparaffinsed by keeping them in xylene for nearly 2-3minutes with two changes
2. Hydration: the deparaffinsed slides were allowed through a series of ethyl alcohol in descending order. i.e. 100, 90, 80, 70, 50 and 30% and water.
3. Staining alumhematoxylin of choice for nearly 2 to 5 minutes.
4. Wash well in running tap water. If over stained, destain by giving one or two dip in acid water (distilled water+ 1 drop HCl)

5. Immediately transfer slide to running tap water for 5 minutes or less when the section turn blue.
6. Differentiate with 1% acid alcohol (1% HCl in 70% alcohol for 5 to 10 sec)
7. Wash well in tap water until sections are again blue for 5 minutes or less
8. Counter stain in eosin for 1 to 3 minutes.
9. Allow the stain to remain in absolute alcohol for about 5 to 10 minutes, so that they are completely dehydrated.
10. Now transfer the slide to xylene for clearing whereby xylene penetrate the tissue and replace the alcohol. Give one or two change of xylene.
11. Mount with DPX mountant or Canada balsam.

3.6 Histological Analysis

The other methodological approach followed was aimed at studying the histological features of the experimental skin (goat skin) with the control skin (sheep skin) at different part and stage of the skin along the production line for making glove leather. For this, skin samples (from both goat and sheep) were taken from the neck, butt and belly region at different stages of the skin i.e. raw skin, limed pelt and pickled pelt. Histological studies were conducted following a standard procedure.

3.7 Grain to Corium Ratio

Cross section of raw goat and sheep skin from butt, neck and belly region after main soaking, were observed under light microscope. Cross section were prepared after passing a sequence of procedure for preparing specimen for histological analysis like dehydration, clearing, infiltration, embedding, block preparation, sectioning and staining. The cross sections were sectioned with a thickness of 15 microns and were stained with Haematoxylin and Eosin. Magnifications of 4 X objective lens were used for generating images of the cross sections. Measurements were made by using Adobe Photoshop software. The thickness of grain, corium, the total thickness and the grain to corium ratio were measured.

3.8 Verhoeff-Van Gieson (VVG) Staining Protocol for Elastic Fibers

NovaUltra Special Stain Kits

Description: This method is used for identifying elastic fibers in tissues such as skin, aorta, etc. on formalin-fixed, paraffin-embedded sections, and may be used for frozen sections as well. The elastic fibers will be stained blue-black and background will be stained yellow [23].

Fixation: 10% formalin.

Section: paraffin sections at 5 um.

Solutions and Reagents:

5% alcoholic hematoxylin:

Hematoxylin ---------- 5 g

100% alcohol ---------- 100 ml

Mix to dissolve with the aid of gentle heat. Filter.

10% aqueous ferric chloride (prepare fresh, not necessary):

Ferric chloride ---------- 10 g

Distilled water ---------- 100 ml

Weigert's iodine solution:

Potassium iodide ---------- 2 g

Iodine ---------- 1 g

Distilled water ---------- 100 ml

Use 4 ml of distilled water to dissolve potassium iodide. And then add iodine. Once iodine is dissolved, dilute this solution by adding 96 ml of distilled water. This solution may be prepared fresh as needed or made in larger quantities and stored in brown bottle in the dark at room temperature.

Verhoeff's Working Solution:

The working staining solution should be made up fresh for best results. It will not stain satisfactorily if it is kept more than one working day. Prepare the working solution by adding in order the following reagents:

5% alcoholic hematoxylin ---------- 20 ml

10% ferric chloride ---------- 8 ml

Weigert's iodine solution ---------- 8 ml

Mix the above amounts (or needed proportions thereof) well. Solution should be jet black. Use immediately and discard after use.

2% aqueous ferric chloride (prepare fresh, not necessary):

10% ferric chloride from above ---------- 10 ml

Distilled water ---------- 50 ml

5% aqueous sodium thiosulfate

Van Gieson's counterstain

1% aqueous acid fuchsin ---------- 5 ml

Saturated aqueous picric acid ---------- 100 ml

For nervous tissues may be prepared as follows

1% aqueous acid fuchsin ---------- 15 ml

Saturated aqueous picric acid ---------- 50 ml

Distilled water ---------- 50 ml

Procedure:

1. Deparaffinize and hydrate slides to distilled water.
2. Stain in Verhoeff's solution for 1 hour. Tissue should be completely black.
3. Rinse in tap water with 2-3 changes.

4. Differentiate in 2% ferric chloride for 1-2 minutes.
5. Stop differentiation with several changes of tap water and check microscopically for black elastic fiber staining and gray background. It is better to slightly under differentiate the tissue, since the subsequent Van Gieson's counterstain can extract the elastic stain somewhat.
6. Wash slides in tap water.
7. Treat with 5% sodium thiosulfate for 1 minute. Discard solution.
8. Wash in running tap water for 5 minutes.
9. Counter stain in Van Gieson's solution for 3-5 minutes.
10. Dehydrate quickly through 95% alcohol, 2 changes of 100% alcohol.
11. Clear in 2 changes of xylene for 3 minutes each.
12. Cover slip with resinous mounting medium.

Results:

Elastic fibers ----------can be identified with blue-black to blackcolouration by seeing it under the light microscope.

3.9 Scanning Electron Microscopic (SEM) Analysis

To analyze the effect of process on goat and sheep skins, different samples were taken from butt region at crust stage of the production line. For this purpose pieces of goat and one piece of sheep skins were soaked. Samples were taken after post tanning for SEM analysis. Sampling positions were from butt area. After this the following procedures of fixation and dehydration were carried out.

3.9.1 Procedure for preparation of specimen for SEM analysis

3.9.1.1 Fixation

The fixative used for the above samples was 5% formaldehyde and 5% of gluteraldehyde. Equal volume of this fixative were taken and mixed. The samples were immersed in the

above solutions for 1 hour. Then they were washed with distilled water for 10 minutes. Washing was repeated three times.

3.9.1.2 Dehydration

1. The tissue samples were placed in 25% acetone for 1 hour
2. Placed in 50% acetone for 1 hour
3. Placed in 70% acetone for 1 hour
4. Placed in 90% acetone for 1 hour
5. Placed in 95% acetone for 1 hour
6. Placed in 100% acetone for 1 hour
7. Placed in 100% acetone for 1 hour

After dehydration with acetone the tissues samples are further treated with different percent of Hexamethyldisilazane (HMS), which has a low surface tension, so that it can retain the original shape of the tissue.

1. The tissue sample was placed in 25% HMS for 1 hour
2. Placed in 50% HMS for 1 hour
3. Placed in 75% HMS for 1 hour
4. Placed in 100% HMS for 1 hour
5. Placed in 100% HMS for 1 hour

The sample was then freezed in deep freezer at -40 ^{o}C for overnight. And the sample was dried in lyophilizer at -40^{o}C for 24 hours. After this the samples were single cut in parallel and perpendicular position in small size and mounted along the cross section in circular plates. Before mounting the samples, the plates was cleaned with acetone and then both side adhesive tape was placed on the plates, trimmed and peeled the outer cover of the tape. Then on single plate both the parallel and perpendicular samples were mounted. After this the two side edges of the samples were coated with carbon so as to make them conductive. Then the samples were coated with gold in gold coating machine. And then the samples were taken for SEM and the tissues were observed at different magnification power.

(a) (b) (c)

Fig.3.1 (a) Samples mounted plates (b) Gold sputtering equipment (c) Scanning electron microscope

3.10 Chemical Characterization of the Skin

Apart from the Histological, Elastin stain and SEM studies, a strategy was followed to compare the result with the chemical characteristics of the skin at different stages i.e. raw, wet blue and crust. The main chemical characterization parameters used were the fat content, nitrogen content, glycoprotein content, hydroxyproline content and chrome content. They were used to compare the chemical characters of both Goat and sheep skins at different stages along the process following a standard procedure.

3.10.1 Fat content

The sample taken for fat determination was soaked skin of both goat and sheep. Standard procedure of [24] was followed.

- A known mass of sample is cut into small pieces and prepare a thimble.
- Put in Soxhlet estimation apparatus using petroleumether
- Leave it for 5 hrs
- Evaporate petroleumether and keep in the hot air oven for 1-3 hrs.
- Cool in desiccators and take the weight.

$$\% \text{ Fat content } = \frac{Final\ weight - Intial\ weight}{Weight\ of\ sample}$$

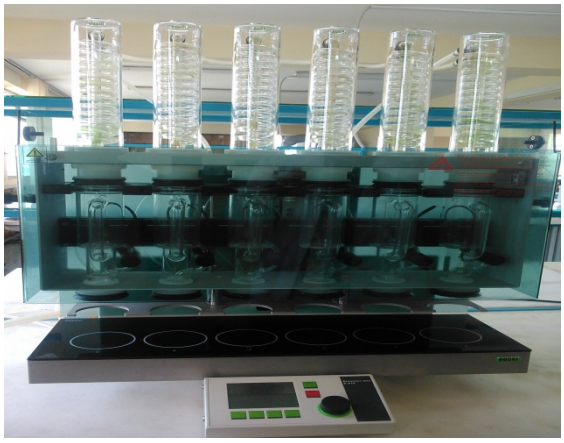


Fig.3.2 Soxhlet apparatus

3.10.2 Nitrogen content

3.10.2.3 Using Kelplus Apparatus

A known mass of both goat and sheep sheepskin were taken from the neck, belly and butt region, the hair was almost completely removed and the sample was ground and mixed. A representative sample was taken for nitrogen content determination using Kelplus apparatus. The procedure followed: [25]

Fig.3.3Kelplus system

3.10.2.4 Digestion

- System switched on and the unit was initially pre-heat to 350 ^{o}C
- Sample was taken in 250 ml Macro DTL tube
- Convenient mass of catalyst mixture. [5:1 (Potassium Sulphate: Copper Sulphate)] was added to the digestion tubes.

- Known volume of Conc. H_2SO_4 (98% H_2SO_4) added
- Samples loaded in the digestion unit with manifold.
- The Kelplussystem was switched on and tap water was connected with maximum pressure for KelFlow system
- The temperature was then increased to 420 ^oC
- After 2 hours, a clear green color was observed indicating that the digestion of the sample was over.
- The sample was kept in the cooling rack for cooling.
- Cooling took about half an hour

3.10.2.5 Distillation

- System was switched on.
- A solution of boric acid , alkali and Hydrochloric acid was prepared (4% Boric Acid, 40% Alkali, 0.1 NHCl)
- The water level, Tap and cap of the distilled water tank was checked
- The alkali, Boric acid and $KMnO_4$solution were loaded to the system through silicon hoses provided at the back of the equipment while you wait for the READY signal.
- A known volume of Boric acid with indicator was taken in 250ml conical flask and place at the receiver end.
- The solution was diluted with distilled water (dilution 10 ml to 20 ml)
- The sample tube was loaded in sample side.
- Before starting the sample testing, the tap water was opened for cooling purpose (INLET and OUTLET were checked).
- The sample testing was started after getting the READY signal.
- A known volume of the 40% alkali was added (until dark brown color appears)
- The process was then started. (Timing based on the sample's Nitrogen value)

- ❖ During the process, liquid ammonia was collected in the Boric Acid and the Boric acidcolor was change based on the indicator used.
- ❖ After completion of the process, the conical flask was removed from the receiver end and then titrate it.
- ❖ The DTL tube from the sample side was then removed.

3.10.2.6 Titration

1. 0.1N HCl was taken in burette. (10 ml burette was used)
2. The Blank value (BV) was first determined.
3. Titration was continued for the sample and the Burette value (TV) was noted down

The percentage Nitrogen content is determined using the relation:

$$NitrogenN\% = \frac{14.01 \times 0.1N \times (TV - BV) \times 100}{W \times 1000}$$

Where,

- BV- is the blank value
- TV -is the Burette value for the sample
- W -is the weight of the sample

3.10.3 Hydroxyproline Content [26]

A convenient weight of Goat and Sheep skin was taken for determination. Then it was placed in hydrolysis tube. To this 5 ml of 6N HCl was added. After this the tubes were sealed in glass blowing section. Then the tubeswere incubated at 110 ^{o}C in hot air oven for 20 hours. Then the hydrolysis tubes were desealed. The hydrolyzed samples were taken and placed in china dish and were allowed to evaporate in water bath. Evaporation of the acid was continued by adding distilled water to the china dish until the pH reaches 7. The final solution was made to a known volume by adding distilled water. From this solution a convenient volume was taken and equal volume of chloramine T was added, the mixture was incubated for 20 min at room temperature. In the same way, equal

volume of percholoric acid was added and was incubated for 5 min at room temperature. After this the same volume of PDAB (para dimethyl amino benzaldehyde) was added and incubated at room temperature for 5 min. This followed by 20 min incubation at 60 ^{o}C by keeping in water bath. This solution was taken for measurement of absorbance at 557 nm in UV Vis spectrophotometer.

Procedure for preparation of standards

Different standard hydroxyproline solution was prepared from a known concentration (i.e. 1mg/1ml). From this known hydroxyproline solution 10, 20, 30, 40, 50, 60, 70, 80 µl were taken and placed in test tubes. Each test was made up to 2ml by adding distilled water. Then 1ml chloramine T was added. Then it was incubated for 20 min at room temperature. 1 ml of percholoric acid was added and was incubated for 5 min at room temperature. After this 1 ml PDAB (para dimethyl amino bezaldehyde) was added and incubated at room temperature for 5 min. This followed by 20 min incubation at 60 ^{o}C by keeping in water bath. This standard solution was taken for measurement of absorbance at 557 nm in UV Vis spectrophotometer. At the same time blank solution without hydroxyproline was also prepared and its absorbance was measure similar to others.

Preparation of Reagents

Chloramine T (Sodium P-tolunesulfoxychloramide)**: -** 1.41 g chloramine T, 20 ml water, 30 ml methyl cellosolve and 50 ml buffer.

PDAB (P-dimethyl amino benzaldhyde)**: -** 4g PDAB dissolved in 20 ml of methoxyl ethanol (5:1 ratio) i.e 5 part methoxyl ethanol 1 part PDAB.

Perchloric acid: - 8.1ml of 70% percholoric acid and make up to 30 ml with distilled water.

Buffer:- 5g citric acid monohydrate, 1.2 ml of glacial acetic acid, 12g of sodium acetate trihydrate and 3.4 g of NaOH were made up to a final volume of 100 ml in distilled water, the pH was carfully adjusted to 6.0 and the buffer was stored in refrigerator.

3.10.4 Estimation of Glycoprotein content

The glycoprotein content of the pericardial tissues was estimated by Elson-Morgan assay. The glycoprotein condenses readily with acetyl acetone to give pyrroles. The pyrroles give colour reaction with P-dimethylaminebenzaldehyde.

Preparation of reagents

1) 1ml of redistilled acetyl acetone was added to 50ml of 0.5M Sodium carbonate.
2) 0.8gm of 4-N, N' dimethylaminobenzaldehyde was added to 30 ml of absolute ethanol mixed with 30ml of conc. HCl.

Procedure

10 mg of raw Goat skin and Sheep skin was taken from (Butt, Bely and Neck) for determination. Then it was placed in hydrolysis tube. To this 750µl of 6N HCl was added. After this the tubes were sealed in glass blowing section. Then the tubes were incubated at 100 ^{o}C in hot air oven for 20 hours. Then the hydrolysis tubes were desealed. The hydrolyzed samples were taken and placed in china dish and were allowed to evaporate in water bath. Evaporation of the acid was continued by adding distilled water to the china dish until the smell of HCl is disappeared.

Acid hydrolyzed samples were neutralized to pH 10 and made up to a known volume by adding of 4M NaOH and distilled water respectively.

Hydrolysate (or standard) solution (250µl containing, 80µl hexosamine) was mixed with 250µl of reagent 1 and the final volume of the solution was adjusted to 600µl with distilled water. The tube was stoppered and heated at110^{O}C for 20 min. The solutions were allowed to cool to room temperature. 1ml of absolute ethanol was added, taking care to wash down all droplets of condensation into the bottom of the tube. 250µl of reagent 2 was added and diluted to a final volume of 2.4ml with absolute ethanol. The tubes were heated at 65^{O}C for 10 min, cooled to room temperature and absorbance was measured at 530 nm in Shimadzu 2100 S UV-VS Spectrophotometer. The unknown values calculated standard curve.

3.10.5 Chrome content of leather

Samples of wet blue and crust leather were taken from both goat and sheep skin for all the trials to compare the chrome uptake of goat and sheep skins and at the same time to see the improvement in processing strategy followed. The samples were taken according to the standard sampling method for chromic oxide content. [27]

A known sample is taken and adds the following acids:

4ml Nitric acid

3.5ml Sulphuric acid

11.5ml Perchloric acid

- Place funnel over the mouth of conical flask add parcel in bits and add three (3) aids with sample in conical flask and keep it on hot plate until the solution turns orange colour.
- Then cool it and add 10ml of distilled water and boil for 5 min so that the chrome gets completely digested.
- The digest solutions are made up to 100ml i.e stock solution using standard flask. Pipette out 10ml from stock and make up to 50ml or 100ml to dilute the solution.
- To that add NaOH pellets. So that acid pH turns alkaline approximately 12 pH.
- Now read the solution @ 372nm

Result

$$\% \text{ of Cr as Cr2O3} = \frac{OD\ value\ X\ 152\ X\ 52\ X\ 100}{4820\ X\ 104\ X\ Weightofsample}$$

Where: 152 – is atomic weight of Cr_2O_3

52 – is atomic weight of Cr

100 – dilution factor of the stock solution

4820 – is value of epsilon (Ɛ)

104 – is atomic weight of Cr

3.11 Process Design and Standardisation

After understanding the characteristic of goat skins from the histology, SEM and chemical characterization, a method was devised to address the problem, and a number of trials were conducted to standardize the process for making high quality glove leather from goat skin.

Glove leather is required to be extremely soft, mainly for the purpose of comfort during wear. However, the degree of softness should not be to such an extent that the strength of the leather is affected.

The processes, which have been targeted for achieving softness, are bating, aging after pickling and fatliquoring. As far as bating and aging of pelts in the pickle liquor are concerned, consideration was given for the duration part of it and as far as fatliquoring was concerned, the composition part of it.

The strategy was mainly aimed at solving the following issues regarding goat skin.

- Removal of non-fibrous protein
- To open-up the fibres
- Increase the grip property of glove leather made from goat skin
- Improve the run (non-elastic stretch) property of goat glove leather
- Improve the softness of leather made out of goat skin
- Improve the strength properties of the leather

First strategy: To have an idea and to plan the project work in detail, one piece of goat and sheep skins each were taken for glove leather processing. The process recipe was designed based on the available information on goat skin for leather making. Particularly open-up of the fibre and increase the softness. In this strategy it is proposed to open up the fibre in liming stage and to remove all interfibrous materials, especially proteoglycans by using **enzymes** (α-amylase).The process recipe is described in ***Annex 1***.

Second Strategy:This strategy of processing of goat skin is the same as the first strategy up tounhairing stage.In reliming stage **calciumchloride** was used in the process, the process recipe is presented in ***Annex 2***.

Third strategy*:** This processing of goat gloving leather is similar to the conventional process, except that **urea treatment** was provided after deliming and before pickling process, for better opening-up of fibres; the process recipe is presented in ***Annex 3.

Fourth strategy: In this strategy, **hydrochloric acid** was used in pickling process recipe is presented in ***Annex 4***.

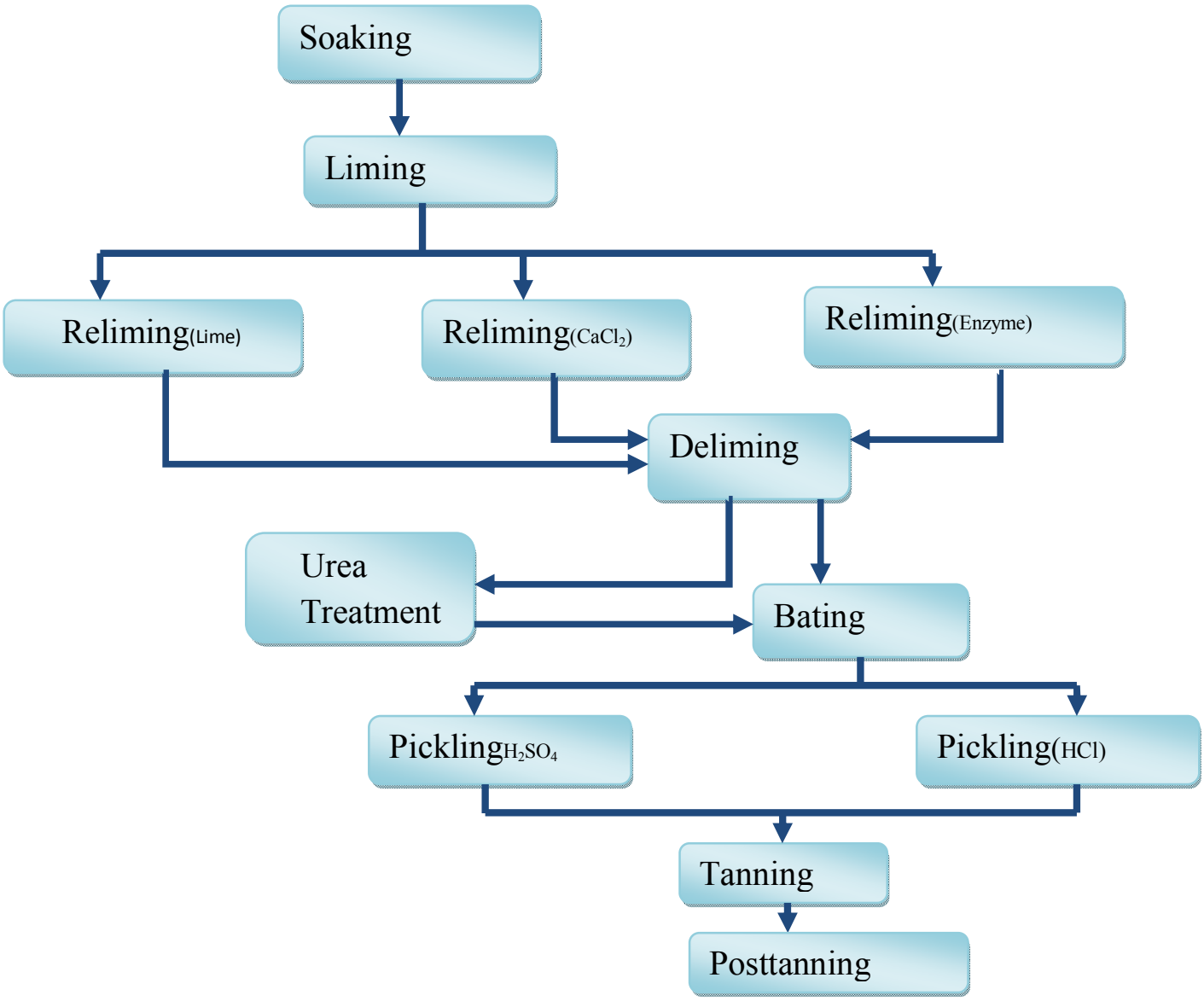


Fig.3.4 Process design of beamhouse to post-tanning process.

***Fifth strategy*:** In this strategy different chemical base of fatliqours, which find extensive usage in commercial practice, were screened for goat glove leather manufacture. The post-tanning experimental trials were carried out using select suitable fatliqours and retanning agents to obtain glove leather with improved softness, run and strength properties.

3.11.1 Influence of Fatliquors on Goat glove leather

Five fatliquors of different chemical bases, which find extensive usage in commercial practice, were screened for glove leather manufacture. The chosen fatliquors and their chemical base are shown in Table 3.1. An offer of 14% of fatliquor based on shaved weight was used for all the experimental trials. Six (6) experimental trials (E1 to E6) were

carried out varying the combination of fatliquors (F1 to F5) as shown in Table 3.2. Since synthetic fatliquors are known to impart better light weight and good fastness properties, the fatliquor based on synthetic fatliquor (F1) was kept constant for all the experiments.

Table 3.1 Selected fatliquors for post-tanning process

Fatliquors	Nature
F1	Synthetic based fatliquor
F2	Natural oil based fatliquor
F3	Lecithin based fatliquor
F4	Fishoil based fatliquor
F5	Alkanesulphonatesfatliquor

Table 3.2 Experimental trials using various fatliquors combination.

Experments	Fatliquor combination employed
E1	F1,F2 and F3
E2	F1, F2 and F4
E3	F1,F2, and F5
E4	F1, F3, and F4
E5	F1, F3 and F5
E6	F1, F4 and F5

The process recipe for retanning and fatliqouring process is presented in ***Annex 6 to 11***.

3.12 Physical Characterization of the Skin

3.12.1 Strength Characteristics

Both goat and sheep skins were converted to crust leathers following the process strategy designed. The resulting crust leathers were tested for physical strength properties. The samples from experimental and control leathers were cut from the official sampling position for physical testing and specimen were conditioned according to the standards [28].

The leather physical strength properties such as:

- Tensile strength determined with the standard [29]

- Elongation at break determined with the standard [29]
- Tear strength and Tear Load determined with the standard [30]

The softness properties of both the surface of goat and sheep were measured with standard procedure. These properties of the leather were used to compare the leathers produced from goat skin and those from sheep skin for the gloving leather properties.

3.13 Organoleptic properties

The organoleptic properties such as softness, run, fullness, roundness, smoothness of grain, uniformity of colour and overall appearance of the crust leather were evaluated. Table 3.3shows the organoleptic properties evaluation table, the values range from 1-10 the higher the value the better is the property.

Table 3.3: Goat and sheep organoleptic properties

S.No	Parameters	Goat	Sheep
1	Softness	1-10	1-10
2	Run	%	%
3	Smoothness of grain	1-10	1-10
4	Uniformity of colour	1-10	1-10
5	Overall appearance	1-10	1-10

3.13.1 Run measurement

The run in gloving leather was measured by stretching the leather lengthwise and measuring the breadth wise length of the leather under stretched condition. This length was taken as the initial length. Then the leather was stretched breadth wise and the stretched breadth wise length was found. The difference between the stretched length and the initial length is a measure of "Run". All run measurements were carried out by three experienced tanners and the average values are presented.

4. Results and Discussion

4.1 Grain Surface Pattern

Samples from neck, belly and butt region of crust leathers were examined using Stereo Microscope. The grain surface pattern of goat skin and sheep skin is shown in Figure 4.1. The presences of coarse and fine hairs are seen from the surface morphology figures of goat and sheep.

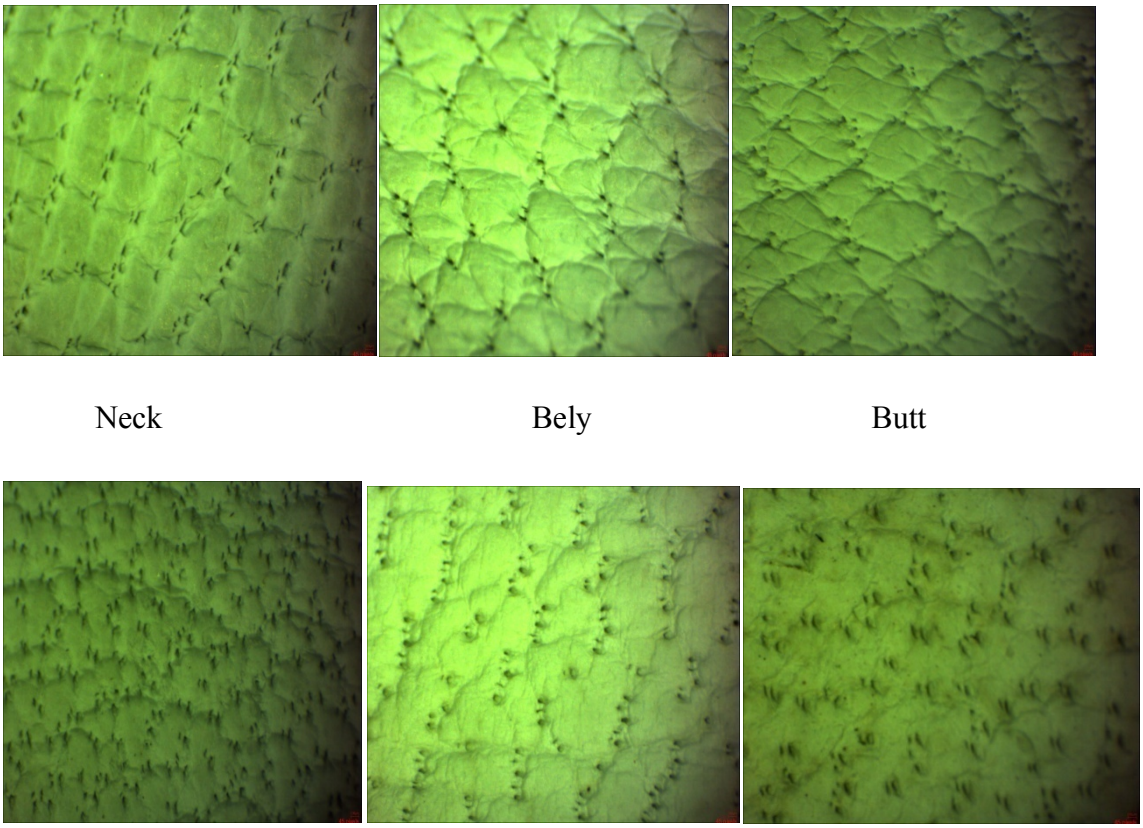


Fig. 4.1 Grain surface pattern of Goat skin and Sheep Skin at crust stage:above: Goat, below: Sheep

4.2 Hair Pore Count

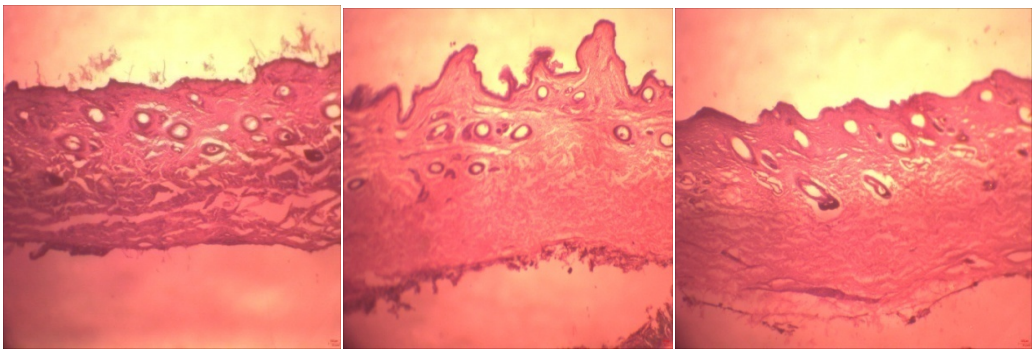
The average number of hairs per sq. inch of skins surface in neck, belly and butt location is given in Table 4.1. The table clearly shows that goat skin has less number of hairs per square inch than sheep skin. If the average number of hairs per unit area is higher, then it will produce better grain fineness. Therefore, the grain of sheep skin is finer than goat skin.

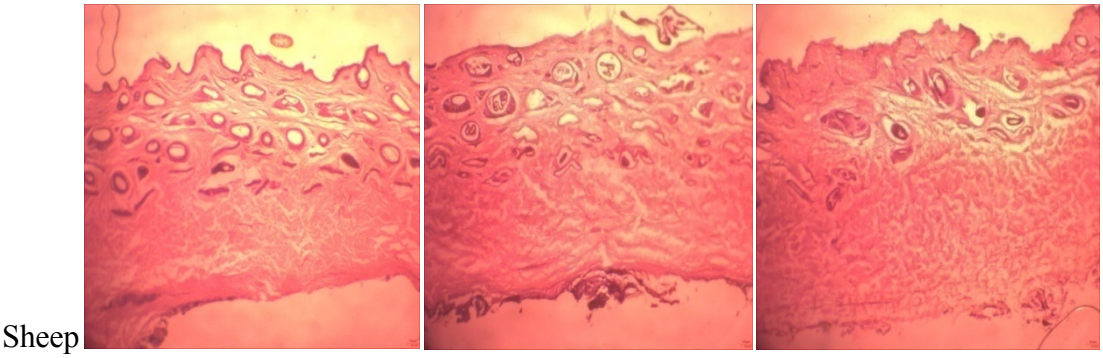
Table 4.1Hair pore count

Skin		Average number of hairs per sq.in
Goat	Neck	8751
	belly	7939
	butt	8810
	Avg.	8500
Sheep	Neck	10157
	belly	9839
	butt	12645
	Avg.	10880

4.3 Histological Analysis

Cross section of raw goat and sheep skin from butt, neck and belly region after main soaking were observed under microscope. 4.5X objective lens were used. Measurements were made by using Image focus software. The real magnification is found to be 100X. Figure 4.2 show images of the cross sections after main soaking stage. Table 4.2 demonstrates the thickness of grain, corium, the total thickness and the grain to corium ratio. The higher the grain to corium ratio indicates more grain layer and less corium layer and vice versa.

Goat 



Sheep

Neck Belly Butt

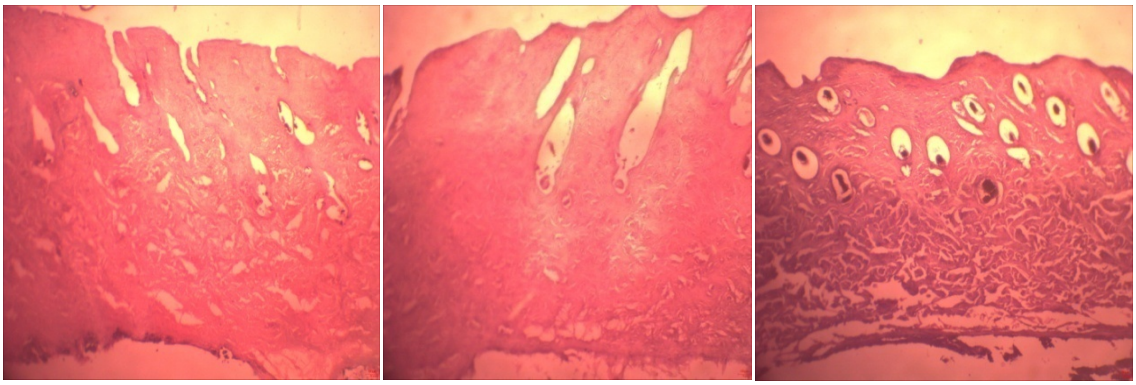
Fig.4.2 Cross section of Goat and Sheep at Raw stage (after main soaking), above: Goat, below: Sheep

Table 4.2 Grain to corium ratio

Breed	Grain Thickness, mm	Corium Thickness, mm	Total Thickness, mm	Grain to Corium ratio
		Neck		
Goat	0.62	0.59	1.21	1.05
Sheep	0.74	0.87	1.61	0.85
		Belly		
Goat	0.55	0.46	1.01	1.195
Sheep	0.66	0.65	1.31	1.015
		Butt		
Goat	0.59	0.54	1.13	1.09
Sheep	0.59	0.83	1.42	0.71

In butt region, goat skin has more value of grain to corium ratio indicating that it has more grain layer and less corium layer. In neck region, sheep has less grain layers and more corium layer, whereas goat skin has less corium and more grain layers. In belly region, sheepskin has almost equal proportions of grain and corium layer, whereas goat has more grain layer and less corium. From the Figure 4.2 and Table 4.2, it is clear that neck region has more thickness, loose and spongy structure. The insertion angle of hair follicles seems to be slightly higher in sheep skin than goat skin especially in the neck and butt region. The diameters of the fibre bundles are higher in goat skin. The angle of weave is low as expected of sheepskins.

The cross sections of goat pelts using different types of opening up are shown in Figure 4.3. It could be observed from the figure that the fibre opening is comparable, when calcium chloride, enzyme and lime where used for the process.



$CaCl_2$ fibre opening Enzyme fibre opening Lime fiber opening

Fig.4.3 Cross section of goat pelt after different types of fibre opening agents

Table 4.3 Comparison of conventional, Enzymatic and Calcium chloride liming

Process	Conventional liming	Enzymatic liming	Calcium chloride liming
Liming	• Fibres are open-up • The pelt is dirty	• Good opening-up • The pelt is clean	• Opening-up is better than convention one

4.4 Determination of removal of Elastin fibres

Elastin fibres contribute greatly to the physical properties of the skin as it controls the elasticity of the grain layer. The mechanism by which the skin returns to its normal state when a stress is removed through the action of elastin fibres, which extend when the skin is stretched, then contract to the resting position when the stress is removed. The elastin fibres are centered on the follicles, with coarse fibres running parallel to the skin surface and finer fibres running at right angles to the skin surface.The presence of elastin can be determined with the help of Verhoeff's stain. The elastin is stained in blue-black colouration. The Figure 4.4 depicts the Verhoeff's stained goat skin. The presence of blue-black colour inside the hair follicles ensures the presence of elastin fibres. From the figure it could be observed that the elastin is present in the raw goat skins.

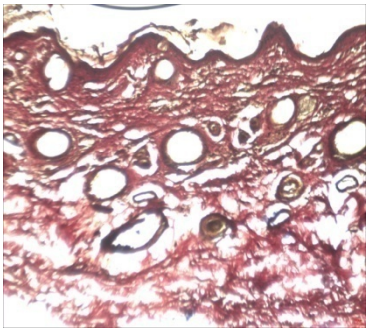
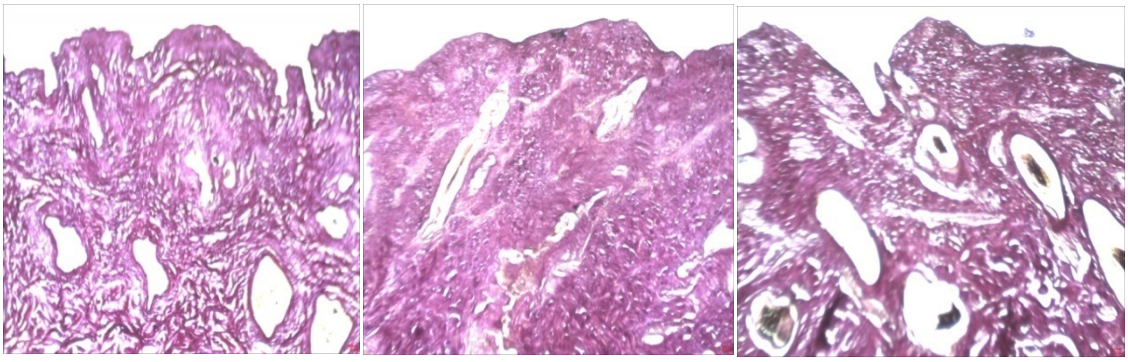


Fig. 4.4 Elastin content of raw goat skin

Further, effect of different fibre opening chemicals on the removal of elastin was studied and the pictures are provided in Figure 4.5



$Cacl_2$- fibre opening Enzyme - fibre opening Lime - fibre opening

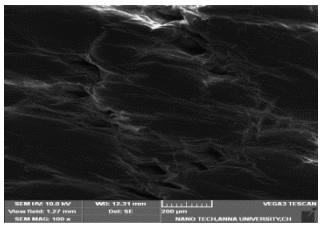
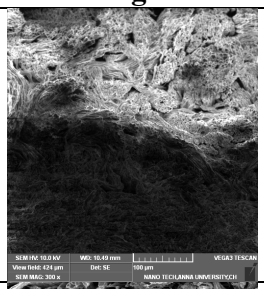
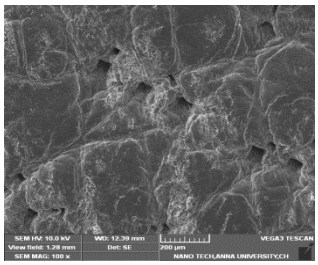
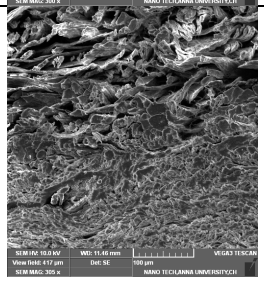
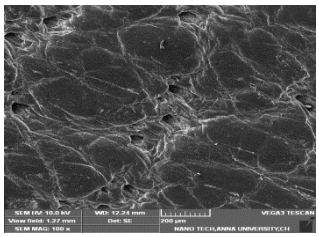
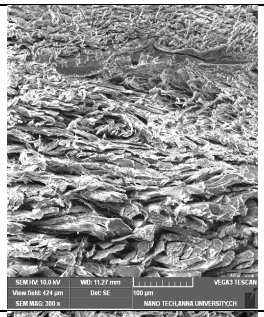
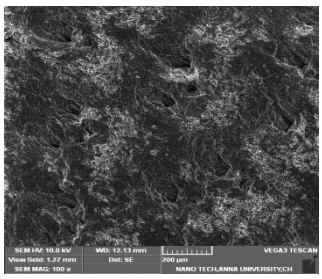
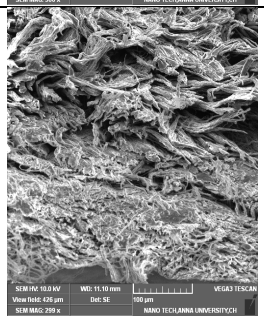
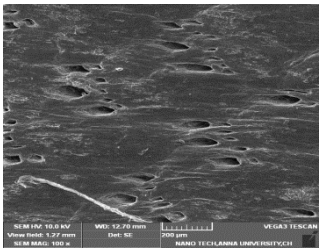
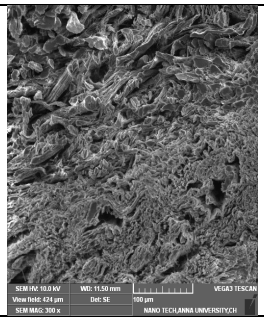
Fig. 4.5 Elastin content of Goat pelt after liming by different types of fibre opening chemicals

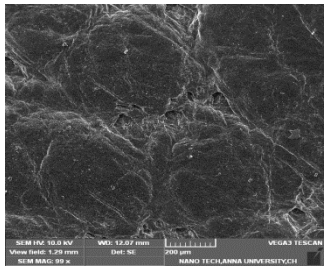
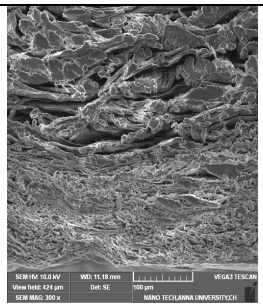
It could be observed that though calcium chloride, lime and enzyme based opening up process gave better results in terms of fibre opening, the enzyme based opening up provided better removal of the elastin fibres when compared to other two systems. The next best was the calcium chloride based fibre opening. Since, removal of the elastin fibres is essential for getting the run property, it is concluded that for making glove leather from goat skins, enzyme based fibre opening would be a better option.

4.5 SEM Analysis

The SEM images of grain and the cross section of goat glove leathers prepared by following various pre tanning processes are shown in Table 4.4

Table 4.4: SEM images of grain and cross section of goat skins after various pre tanning systems

S.No	Process	Grain at 100 X Magnification	Cross Section at 300 X magnification
1.	Control leather with conventional liming and pickling		
2.	$CaCl_2$ fiber opening and HCl pickling		
3.	$CaCl_2$ fiber opening and H_2SO_4		
4.	Enzyme fiber opening and HCl pickling		
5.	Enzyme fiber opening and H_2SO_4 pickling		

6.	Urea treatment after deliming		

It could be observed from the figures in the Table that the control leathers prepared using the conventional liming and pickling showed lesser opening up of fibers. The calcium chloride treated goat skins showed good fiber opening and the grain structure is also intact without any surface damage. Calcium chloride fiber opening and sulphuric acid pickling gave better results, when compared to hydrochloric acid based pickling. Some grain damage is observed when hydrochloric acid is used for pickling. Similarly, when enzyme and hydrochloric acid was used in pre tanning, the opening up was better, but the grain showed some damage, which might be due to the usage of enzyme or the lyotropic effect of hydrochloric acid. However, the opening up of fibers was better in this system. On the other hand, the enzyme based fiber opening and the use of sulphuric acid for pickling showed better results, having no grain damage. The urea treatment after deliming process gave improved opening up of the fibers owing to its lyotropic effect. Hence, for subsequent experiments, the enzyme based fiber opening, urea treatment and sulphuric acid based pickling were employed.

4.6 Chemical Characteristics

Fat content, chromic oxide content, % nitrogen, and hide substance, hydroxyproline and glycoprotein content were tested on goat and sheep skins at different stages of the process. The results are demonstrated in Table 4.9. From the table one can see that sheep has more fat content than goat. This may be one reason that when fat is removed by degreasing process, which cause the final leather less full. Nitrogen and hydroxyproline content is slightly higher in goat than in sheep skins. This indicates that goat has more collagen content than sheep skins. Chrome content at crust stage is higher for goat than sheepskins. The higher values of chrome at crust than wet blue is may be due to re-chorming. One can expect from the hide substance content that as the higher hide substance the higher the uptake of chrome. Moreover the calculated chrome to hide substance value indicates that, Goat have more reactive sites than Sheepskins.

Hydroxyproline Content Determination

The hypdroxyproline content can be determined based onthe standard graph shown in the fig.4.6. Hydroxyproline is a major component of collagen, where it serves to stabilize the helical structure. Because hydroxyproline is largely restricted to collagen, the measurement of hydroxyproline can be indicator of collagen content.

Table 4.5 Absorbance value of the standard hydroxyproline at 557 nm.

µg/µl	µg/1000µl	OD Value
0	0	0
20	2	0.114
40	4	0.241
60	6	0.462
80	8	0.576
100	10	0.695
120	12	0.856

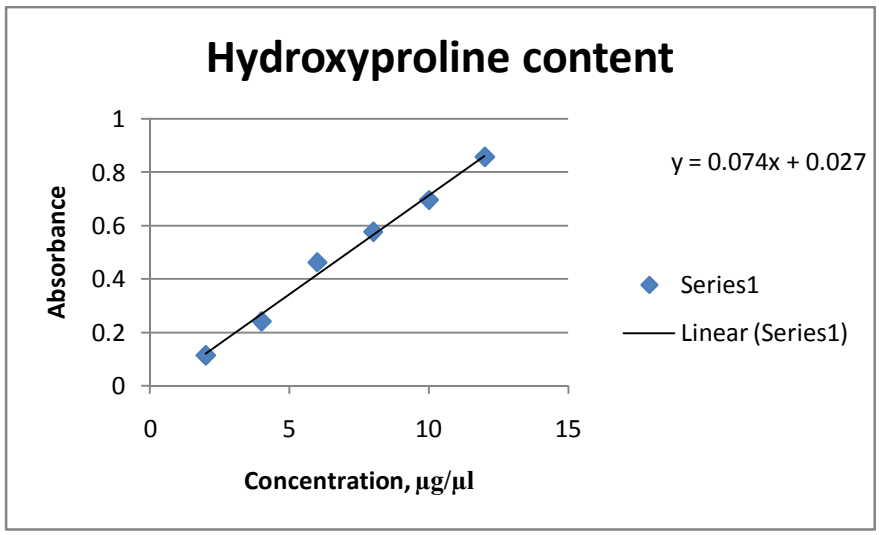


Fig. 4.6 Standard graph of hydroxyproline content

$$y = mx + b$$

$$Concentration = x = \frac{OD}{slope} = \frac{y - b}{0.074}$$

Table 4.6 absorbance value of samples at 557nm.

Sample	OD Value	
	Goat	Sheep
Neck	0.276	0.163
Butt	0.283	0.127
Belly	0.223	0.242
Average	**0.261**	**0.177**

The calculated hydroxyproline content of both goat skin and sheep skin are presented in table 4.9. It clearly shows the content of hydroxyproline is more in raw goat skin than in raw sheep skin. Thus, the collagen fibres in goat skin in fuller and firmer than those of sheep skin.

GlycoproteinDetermination

The glycoprotein content of the skin was estimated by Elson-Morgan assay. The amount of glycoprotein content of raw skin of goat and sheep are determined from the following standard graph of glycoprotein.

Skin matrix apart from collagen also contains other fibrillary and non-fibrillary proteins. The protein under non-fibrillary category viz., albumins, globulins etc are expected to remove during liming process as they are water and alkaline soluble.

Glycoprotein is determined by using the formula $y = mx + b$ from the standard graph and the calculated result is shown in table 4.9 below.

Table 4.7 Absorbance value of standard glycoprotein @ 530 nm.

µg/µl	µg/1000µl	OD value
0	0	0
20	10	0.132
40	20	0.259
60	30	0.38
80	40	0.458
100	50	0.624
120	60	0.741
140	70	0.804

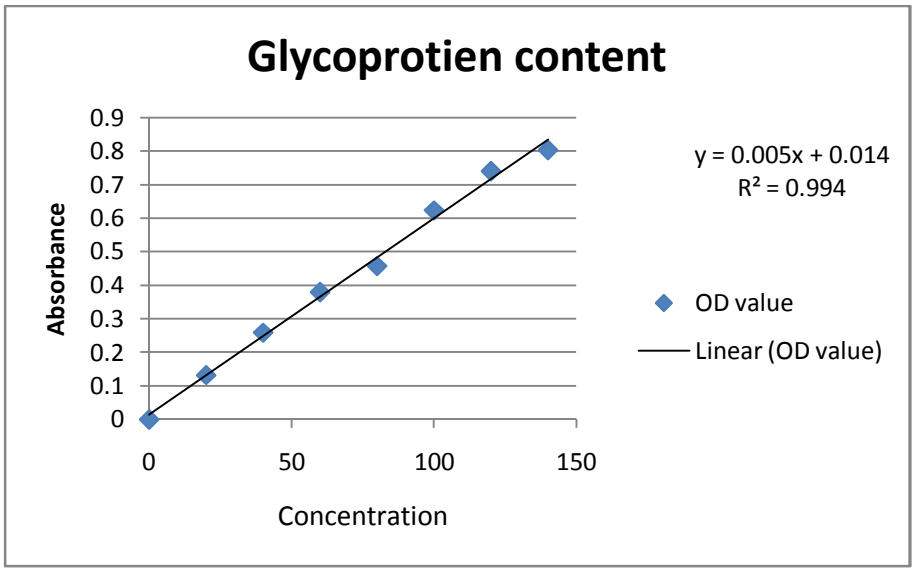


Fig. 4.7 Standard graph for the determination of glycoprotein content

Table 4.8 Absorbance value of samples at 530 nm

Sample	OD Value	
	Goat	Sheep
Neck	0.262	0.263
Butt	0.114	0.114
Belly	0.222	0.293
Average	**0.199**	**0.177**

Table 4.9 Chemical properties of Goat and Sheep at different stages

Chemical tests	**Sample**	**Goat**	**Sheep**
% Fat	Raw	2.29	3.2
% Free Fatty Acid	Raw	0.23	0.42
% N (Kjeldhal)	Raw	8.6	9.1
	Crust	12.87	13.21
% Glycoprotein	Raw	5.06	3.89
Hide Substance	Crust	72.33	74.24
% Cr_2O_3	Crust	2.23	2.16
% Cr_2O_3 per hide substance	Crust	0.03	0.029
% Hydroxyproline	Raw	9.00	6.01
% Collagen	Raw	67.95	45.29

Effect of Fatliqours on Gloving Properties

Different chemical base of fatliqours are screened to find their suitability for glove leather manufacture. Generally the combination of synthetic, natural and alkylanesulphonate are essential for glove leathers as they provide very good lubrication property, softness, run and good hand feel. Hence, in present work synthetic fatliqour (8%), Natural Fatiliqour (4%) and alkylanesulphonate (2%) based on shaved weight have been added for the last best experiment. Various experimental trials have been carried out by varying the combination of other four fatliquors as mentioned in Table 3.2. The leather generally exhibits significant variations from skin to skin due to structural differences in each skin.

Optimized process and Organoleptic Results

From the experimental trials discussed above, the following process conditions have been optimized:

- longer liming or enzyme based openingup
- longer bating
- sulphuric acid based pickling
- use of urea after deliming
- Optimized post tanning process as given in ***Annex 11***

Trials made with longer liming (72hrs) resulted in better opening of the fibres and gave softer leather. Similarly, leathers with enzyme based fibre opening resulted in softer leathers in shorter time. After fibre opening, the delimed goat skins were treated with urea and subsequently pickled with sulphuric acid. The optimized post tanning of full chrome goat leathers gave improved stretch, smoothness and softness suitable for glove leather. Evaluation of the properties such as softness, smoothness and stretch of the grain and general appearance were assessed by hand by three experienced tanners and the results of the evaluation are presented in Table 4.10. It is observed from the organoleptic properties that goat and sheep glove leathers exhibited similar bulk properties.

Table 4.10 Organoleptic prosperities of the best trial leathers

S.No	Parameters	Trial 1	Trial 2	Trial 3
1	Softness	9.0	8.5	8.0
2	% Run	80	80	75
3	Smoothness of grain	9.0	9.0	9.0
4	Uniformity of colour	9.0	9.0	9.0
5	Overall appearance	9.0	8.5	8.5

Physical Characteristics

The physical characteristics of the glove leathers prepared areusing different experimental trials are demonstrated in Table 4.11. From the table it is observed that experimental trial 1, which involved the enzymatic fibre opening and sulphuric acid based pickling, chrome tanning, followed by optimized fatliquors gave better results compared to other experimental trials.

Table 4.11Strength properties of other trial leathers

Physical test	Direction	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Tensile strength	Parallel	37.58	31.07	19.97	23.12	40.83
(N/mm^2)	Perpendicular	25.75	22.07	20.09	28.78	26.49
Elongation (%)	Parallel	50.11	51.00	64.77	40.66	47.89
	Perpendicular	79.00	71.11	58.00	80.56	108.11
Thickness (mm)		0.55	0.52	0.48	0.51	0.53
Tear strength	Parallel	75.26	107.30	163.72	149.5	158.84
(N/mm)	Perpendicular	102.16	117.36	133.98	180.32	176.31
Thickness (mm)		0.42	0.5	0.52	0.47	0.51

A comparison was made between Trial 1 goat glove leather and conventional sheep glove leather. The physical characteristics of the leathers are given in Table 4.12. It could be observed that the goat glove leathers showed improved tensile strength properties when

compared to sheep glove leathers. The values of tear strength properties are found to be lesser for sheep skins than goat crust leather. It is also seen that from softness value goat glove crust leathers and sheep glove leathers are almost equivalent.

Table 4.12 Strength prosperities of the best trial (Trial 1) leathers

Physical test	Direction	Goat	Sheep
Tensile strength (N/mm^2)	Parallel	37.58	29.52
	Perpendicular	25.75	20.29
Elongation (%)	Parallel	50.11	43.67
	Perpendicular	79.00	99.89
Thickness (mm)		0.55	0.47
Tear strength (N/mm)	Parallel	158.84	65.53
	Perpendicular	176.31	90.41
Thickness (mm)		0.51	0.42

5 Conclusion and Recommendation

5.1 Conclusion

Glove leathers from goat skins are developed in this study. Enzyme based fibre opening followed by sulphuric acid based pickling gave better results compared to other fibre opening systems involving calcium chloride or lime. In addition, the enzyme based fibre opening resulted in complete removal of elastin fibres, which is ascertained by Verhoeff's staining procedure. Various fatliquoring agents based on synthetic, lecithin and alkane sulphonates based fatiliqours at an offer of 8, 4 and 2%, respectively based on shaved weight along with glutaraldehyde syntan at an offer of 4% is suitable for making of glove leathers from goat skin. The semi quantitative correlation between run and other physical properties indicated significant correlation for softness. This study provides a systematic approach for the selection of suitable post tanning auxiliaries for the manufacture of glove leathers with required properties.

5.2 Recommendation

Based on the present findings, we recommend that:

- Further work has to be conducted in modifying the leather with appropriate fatliqours having special properties in order to produce leathers which have special effects like non-elastic stretch, inner softness and other required properties by understanding the principle of science and technology.
- There are different variety of goat breeds in Ethiopia, thus it could be characterized and study the suitability of these skins to produce high quality glove leather be ascertained.

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Annexs

Annexure 1

Second strategy: Liming by Enzyme (α-amylase)

Operation	%	Chemicals	Time	PH	Remark
Soaking	300	water	30’		Drain/wash
	200	Water	30’		
	0.5	Wetting agent			
Run 5’ stop 30’ overnight, next day drain float completely					
Unhairing	150	water			
	3	Sodium sulphide			
	5	Lime powder	Run 5’ stop 1 hr O/N		
Reliming	150	Water			
	1	Enzyme (α- amylase)	run 5’ stop 1 hr O/N		
	2	Lime powder		12	
Washing	200	Water	20’		
Drain					
Deliming	100	Water			
	5	Ammonium Chloride	45’	Check deliming by phenolphthaline indicator	
Bating	2	microbate	90’		Check porosity
Drain					
Washing	200	water	20’		
Drain					
Pickling	80	Water			
	8	Salt	20’		
Add	P.G.S		10’		
	0.5	Formic acid			
	5	Water	10’+10’		
	1.5	Sulphuric acid			
	15	Water	10’x4+20	2	
Leave over night, Next day pile, Ageing for one weak					

Annexure 2

First strategy: Liming by $CaCl_2$

Operation	%	Chemicals	Time	PH	Remark
Soaking	300	water	30’		Drain/wash
	200	Water	30’		
	0.5	Wetting agent			
Run 5’ stop 30’ over night, next day drain float completely					
Unhairing	150	water			
	3	Sodium sulphide			
	5	Lime powder	Run 5’ stop 1 hr O/N		
Reliming	150	Water			
	5	$CaCl_2$			
	2	Lime powder	run 5’ stop 1 hr O/N		12
Washing	200	Water	20’		
Drain					
Deliming	100	Water			
	5	Ammonium Chloride	45’	Check deliming by phenolphthaline indicator	
Bating	2	Microbate	90’		Check porosity
Drain					
Washing	200	water	20’		
Drain					
Pickling	80	Water			
	8	Salt	20’		
Add	P.G.S		10’		
	0.5	Formic acid			
	5	Water	10’+10’		
	1.5	Sulphuric acid			
	15	Water	4x10’+20	2	
Leave over night, Next day pile, Ageing for one weak					

Annexure 3

Third strategy: Urea Treatment

Operation	%	Chemicals	Time	PH	**Remark**
Soaking	300	water	30’		**Drain/wash**
	200	Water	30’		
	0.5	Wetting agent			
	100	Water			
Run 5’ stop 30’ over night, next day drain float completely					
Unhairing	150	water			
	3	Sodium sulphide			
	5	Lime powder	**Run 5’ stop 1 hr O/N**		
Reliming	150	Water			
	2	Lime powder	**Run 5’ stop 1 hr O/N**		12
Washing	200	Water	20’		
Drain					
Deliming	100	Water			
	5	Ammonium Chloride	45’		Check deliming by phenolphthaline indicator
Bating	2	microbate	90’		8.0 **Check porosity**
Drain completely					
	10	**8M Urea**	2 hrs		
Drain					
Washing	200	water	20’		
Pickling	80	Water			
	8	Salt	20’		
	P.G.S		10’		
	0.5	Formic acid			
	5	Water	10’+10’		
	1.5	Sulphuric acid			
	15	Water	10’x4+20	2	
L/O/N, Next day pile, Ageing for one weak					

Annexure 4

Fourth strategy: Pickling by HCl

From Each fibre opened pelts (enzyme, calcium chloride and urea treatment) one- one pelts are taken for HCl pickling.

Operation	%	Chemicals	Time	PH	Remark
Pickling	80	Water			
	8	Salt	20’		
	P.G.S		10’		
	0.5	Formic acid			
	5	Water	10’+10’		
	4.5	Hydrochloric acid			
	45	Water	10’x4+20	2	
L/O/N, Next day pile, Ageing for one weak					

Annexure 5

Tanning

Operation	%	Chemicals	Time	PH/^{o}Be	**Remark**
Depickling	100	Water			
	10	Salt	10’	6/7	
		P.G.S	20’		
	0.7	Sod. formate	20’		
	1.5	Sod.bicarbonate	30’	5.6-5.8	
	1.0	Degreasing agent	40’		
	100	Water	30’		
Drain					
Repickling	100	Water			
	10	Salt	10’		
	0.4	Formic acid	2X10’		
	0.6	Sulphuric acid	3X10’+30’	2.8-3.0	
	0.5	Sod.metabisulphite	60’		
Tanning	3.5	Chrome powder	40’		
	2	Corilene EFA			
	3.5	Chrome powder	40’		
	1	Sod.formate			
	2	Chrome syntan	30’		
Basification	100	Water	10’		
	2	Sod.bicarbonate	4X10’+60’	3.8/4.0	
Wash, Pile, Nextday, sum and shave(0.6mm)					

Annexure 6

Post Tanning Operation

Trial 1

Material: Goat wet blue **Article: Goat gloving** **Colour: Natural**			Weight: Size: M Thickness: 0.5/0.6 mm				
Operation	%	Chemicals	Time	Temp (^{O}C)	PH	Duration	Remark
Washing:	300	Water	15’	35			
Drain out							
Degresing:	300	Water		35			
	0.25	Wetting agent	15’				
	0.25	Formic acid	15’				
	0.25	Oxalic acid	15’		3.5		
Drain/wash							
Acid bating:	50	Water					
	1.50	Defat (Acid bate)	60’				
Drain/wash							
Rechrome	50	Water		45			
	0.25	Formic acid	15’		3.5		
	4	Novaltan PF (Aldhyde tanning agent)	60’				
	3	Chrome	30’				
	200	Water	30’				
Drain/wash							
Neutralisation:	80	Water		45			
	2	Sod.bi.carbonate	15’				
	2	Sod.formate	30’				
	70	Water		45	7.5		
Drain/wash							
Fat liquoring:	200	Water		50			
	8	Lipsol MSG (*Synthetic and natural softening agen*)					
	4	Proval BA (*natural phospholipids with synthetic softeners*)					
	2	Lipsol PES (*Alkanesulphonate)*	45’				
	0.25	Busan 30L					
	4	Formic acid	45’				
Drain, wash and pile. Next day, setout, hook dry and then wheel staking							

Annexure7

Trial 2

Raw material**: Goat wet blue**			Thickness**: 0.5mm**		
Article**: Glove crust**					
Operation	%	Chemicals	Time	PH/^{o}Be	**Remark**
	50	Water @35^{o}c			
	0.5	Sodiumbicarbonate	15’		
	0.5	Acid bate	60’		
Drain/Wash					
	50	Water @35^{o}c			
	0.25	Formic acid	15’		
	6	Derugan 3080 (mixture with glutaraldehyde)	60’		
	3	Chrome powder	30’		
	100	Water	15’		
Drain/Wash					
	100	Water @60^{o}c			
	2	Sodium Acetate	10’		
	2	Sodiumbicarbonate	15’		
Drain/Wash/ pile, Next day					
Neutralization	50	Water			
	2	Sodium acetate			
	1.5	Sodium formate	60’		
Fatliqouring	150	Water@ 50^{O}C	15’		
	6	Genosoft SE *(Synthetic fatliqour)*			
	6	Proval BA (*Natural based fatliquor)*			
	2	Nexopol NT *(Fish oil)*	60’		
	0.25	preservative	15’		
	2	Formic acid	45’		
Drain, wash and pile. Next day, setout, hook dry and then wheel staking					

Annexure 8

Trial 3

Raw material**: Goat wet blue** Thickness**: 0.5mm** Article**: Glove crust**					
Operation	%	Chemicals	Time	PH	**Remark**
	50	Water @35^{o}c			
	0.5	Sodiumbicarbonate	15’		
	0.5	Acid bate	60’		
Drain/Wash					
	50	Water @35^{o}c			
	0.25	Formic acid	15’		
	6	Derugan 3080 (mixture with glutaraldehyde)	60’		
	3	Chrome powder	30’		
	100	Water	15’		
Drain/Wash					
	100	Water @60^{o}c			
	2	Sodium Acetate	10’		
	2	Sodiumbicarbonate	15’		
Drain/Wash/ pile, Next day					
	50	Water			
	2	Sodium acetate			
	1.5	Sodium formate	60’		
	150	Water	15’		
	6	Genosoft SE *(Synthetic fatliqour)*			
	5	(Lipsol PES) Alkanesulphonatefatliqour			
	3	Nexopol NT *(Fish oil)*	3x30’+40’		
	0.25	preservative	15’		
	2	Formic acid	45’		
Drain, wash and pile. Next day, setout, hook dry and then wheel staking					

Annexure 9

Trial 4

Material: Goat wet blue **Article: Goat gloving** **Colour: Natural**			Weight: Size: M Thickness: 0.5/0.6 mm				
Operation	%	Chemicals	Time	Temp (^{O}C)	PH	Duration	Remark
Washing:	300	Water	15’	35			
Drain out							
Degresing:	300	Water		35			
	0.25	Wetting agent	15’				
	0.25	Formic acid	15’				
	0.25	Oxalic acid	15’		3.5		
Drain/wash							
Acid bating:	50	Water					
	1.50	Defat (Acid bate)	60’				
Drain/wash							
Rechrome	50	Water		45			
	0.25	Formic acid	15’		3.5		
	4	Novaltan PF (Aldhyde tanning agent)	60’				
	3	Chrome	30’				
	200	Water	30’				
Drain/wash							
Neutralisation:	80	Water		45			
	2	Sod.bi.carbonate	15’				
	2	Sod.formate	30’				
	70	Water		45	7.5		
Drain/wash							
Fat liquoring:	200	Water		50			
	6	Genosoft SE *(Synthetic fatliqour)*					
	5	*Fosfol LP (Lecithin based fatliqour)*					
	3	Nexopol NT *(Fish oil)*	60’				
	0.25	Busan 30L					
	4	Formic acid	45’				
Drain, wash and pile. Next day, setout, hook dry and then wheel staking							

Annexure 10

Trial 5

Material: Goat wet blue Article: Goat gloving Colour: Natural			Weight: Size: M Thickness: 0.5/0.6 mm				
Operation	%	Chemicals	Time	Temp (^{O}C)	PH	Duration	Remark
Washing:	300	Water	15’	35			
Drain out							
Degresing:	300	Water		35			
	0.25	Wetting agent	15’				
	0.25	Formic acid	15’				
	0.25	Oxalic acid	15’		3.5		
Drain/wash							
Acid bating:	50	Water					
	1.50	Defat (Acid bate)	60’				
Drain/wash							
Rechrome	50	Water		45			
	0.25	Formic acid	15’		3.5		
	4	Novaltan PF (Aldhyde tanning agent)	60’				
	3	Chrome	30’				
	200	Water	30’				
Drain/wash							
Neutralisation:	80	Water		45			
	2	Sod.bi.carbonate	15’				
	2	Sod.formate	30’				
	70	Water		45	7.5		
Drain/wash							
Fat liquoring:	200	Water		50			
	6	Lipsol MSG *(Synthetic fatliqour)*					
	5	Fosfol LP *(Lecitin based fatlior)*					
	3	Lipsol PES (*Alkanesulphonatefatliqour)*	3x30’+40’				
	0.25	Busan 30L					
	4	Formic acid	45’				
Drain, wash and pile. Next day, setout, hook dry and then wheel staking							

Annexure 11

Trial 6

Raw material**: Goat wet blue**				Thickness**: 0.5mm**	
Article**: Glove crust**					
Operation	%	Chemicals	Time	PH/^{o}Be	**Remark**
Wet back	300	Water	15’		
	0.25	Acetic acid	15’		
	0.25	Oxalic acid	15’	4.5	
Drain out the bath					
Acid bating	50	Water @35^{o}c			
	0.5	Sodiumbicarbonate	15’		
	0.5	Acid bate	60’		
Drain/Wash					
Rechrome	50	Water @35^{o}c			
	0.25	Formic acid	15’		
	3	Derugan 3080 (mixture with glutaraldehyde)	60’		
	3	Relugan GT-50			
	3	Chrome powder	30’		
	100	Water	15’		
Drain/Wash					
Neutralisation	100	Water @60^{o}c			
	2	Sodium Acetate	10’		
	2	Sodiumbicarbonate	15’		
Drain/Wash/ pile, Next day					
Fat liquoring	200	Water@60^{o}c	15’		
	8	Genosoft SE *(Synthetic fatliqour)*			
	4	Fosfol LP *(Lecitin based fatliqour)*			
	2	Proval BA (*Natural fatliqour)*	45’		

	0.25	preservative	15’	
	4	Formic acid	45’	
Drain, wash and pile O/N. Next day, setout, hook dry and then wheel staking				

Annexure 12

Dyeing

Operation	%	Chemicals	Time	PH	Duration	Remark
Wet back	80	Water@ 45°c				
	1	Ammonia	15’	6.8		
Drain						
	80	Water@50°c	30’			
	1	Ammonia				
	2	Lipsol MSG *(Synthetic fatliqour)*				
	6	Dyestuff	30’			Check penetration
	200	Water @50°c				
	3	Lipsol MSG *(Synthetic fatliqour)*				
	3	Natural based fatliqour				
	2	Lipsol PES (*Alkanesulphonate)*				
	2	Catipol GS *(Cationic fatliqour)*	45’			
	3	Formic Acid	3x5’+45’			
Drain /wash/pile						