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CHEMICAL AND BIO-ENGINEERING

STUDY ON VALUE ADDITION OF LEATHERS FROM ETHIOPIAN COW HIDES: STRATEGY TOWARD QUALITY IMPROVEMENT

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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 fully acknowledged.

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DEDICATION

This work is dedicated to all of my family

To: Taytu Ebrahim (My mother)
Yimer Amedie (My father)
Halima Endris (my wife)
Brothers and sisters

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List of Abbreviations and Acronyms

Hypo- Hydroxyproline

WB- Wet-blue

LIDI-Leather Industry Development Institute

CLRI-Central Leather Research Institute

RPM-Revolution per Minute

SATRA-Shoe and Allied Trades Research Association

ISO-International Standard Organization

ASTM-American Standard Test Method

IUP-International Union for physical test

DTL-Drift Tube Lianc

SLC-Standard for Leather Chemical

TV-Titrant Volume

BV-Blank Volume

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Abstract

Although the raw cow hide supplies for tanners are not small, producing quality leather is difficult, which can compete for international market. From the total export of finished leather in the year 2011/2012 only 10.7% is the share for finished cow leathers. Main types of problem that alter production of quality cow leather are both anti- mortem defects (scratches, rub mark, or horn rake pox, brand mark, wound etc) and post-mortem defects (fly cuts, fleshing cuts and putrification) that degrade the value. The study on this research reveals that surface defects mainly scratches and fly cuts largely and wound in certain extent are major drawbacks for not having quality product. To have an insight about our raw material, Ethiopian cow hide nature, and to standardize a process technology both chemical characterization such as hydroxyproline content, fat content, nitrogen content, moisture content and chromic oxide content and physical characterization such as tensile strength, tear strength, % elongation, grain crackiness and rub fastness were carried out, besides to these histology of the raw material, Scanning Electron Microscope (SEM) analysis at crust stage, hair pore count using stereo-microscope of the crust and organoleptic properties at crust stage and after finishing were carried out in comparison with Indian cow leather.

A newer approach of drum up-gradation using pigment and protein filler and modern type of finishing i.e. cationic compact finish were used to achieve the overall goal of producing quality leather. The results from the physical tests revels that grain crackiness of the experimental leathers is not affected by the use of pigment and filler in drum. The experimental leather showed better defect coverage and had better organoleptic properties. In the present study, promising results were found that can be used to add value to Ethiopian cow upper leathers to be salable in the world market.

Key Words: Hide, leather, Defect, Organoleptic properties, Histology, Scanning Electron Microscope

Chapter-one

1. Background

Ethiopia is one of the leading countries that have the largest livestock populations in the world providing a strong raw material base for the leather industry. Its livestock population is estimated at 50 million cattle, 25 million sheep and 23 million goats. About 80% of all hides and skins entering the formal market come from rural areas where they are collected by private traders. The remaining 20% are derived from slaughtering facilities found in major town and cities. About 15.5 million pieces of sheep and goat skins and 1.2 million pieces of cattle hides are supplied to the tanneries per annum [1].

Leather sector is among the one that deserves a particular emphasis in Ethiopia and identified as a potentially competitive in the global market. The five year growth and transformation plan {GTP} aims at raising the earnings from the sector US$ 76 million end of 2009/10 to US$ 497 million in 2014/15 [2].

Currently there are about 30 functional tanneries that create job opportunity for 8446 number of people and they process 67200 pieces of skin and 4353 pieces of hides per day, daily installed and actual soaking capacity of each tannery are listed {see annex 1}

Up to December, 2011, most tanneries were exporting semi-processed crust leather in huge quantity to different European and Asian countries with fewer prices. But due to the policy Change, tanneries were shifted to exporting only finished leather to the world market as well as supplying finished leather for local shoe manufacturing company, the table in the annex 2 figure out the quantity of exported finished leather in the year 2011/2012{see annex 2} [3].

In the case of cow hide finished leather many quality issues are bottle necks to sell in the world market. Due to quality problem (defects) most tanneries sell for local shoe manufacturing company in contrary with the aim of earning foreign currency from export.

1.1 Types of Defect and their description

1.1.1 Defects in the living animal

Brand marks - Produced by branding letters, numbers, figures by means of a red-hot stamping iron mainly in the butt, seldom in the forehead, neck or jaw. Several marks are often found. Visible, most severe scarrings on the finished leather, frequently going through the entire cross-section of the skin. These sections cannot be used as leather [4].

Scratches -when grazing animals chafe their bodies against thorn-bushes or barbed wire. Can be avoided by fencing the pasture with smooth electric fences [4].

Damage caused by smallpox - They result in spotty grain defects of the epidermis and formation of scarring [4] .

Flaying Damages

Gouges - Un-intentional cutting of flat pieces of skin out of the reticular layer when the skin is flayed. These sections result in a thinner quality of the finished leather.

Blood stains - If soiled and blood-stained skins are not washed adequately these incrustations may produce brownish stains on the raw hide. In the lime they lead to very dark iron stains and during vegetable tannage to blue-black stains [4].

Inadequate bleeding of the hide - Blood residues which remain in the veins encourage the development of microorganisms and thus increased putrefaction along the blood veins. This leads to a veiny appearance on the leather (grooves) [4] .

1.1.2 Preservation Damage

Lead stains - Lead compounds are contained as denaturing agents in curing salts, used mostly in overseas countries. They produce similar stains as iron [4].

Iron stains - Contact of the hides with iron parts or rusty iron compounds. They produce brownish stains which are further intensified by liming chemicals or tanning agents containing phenol [4].

In many cases it is possible to eliminate them by a treatment with complexing agents .

Rottenness - If curing is inadequate or is performed too late and if the hides are stored too long at excessive temperatures in the salt, an increased development of microorganisms occurs on the skin. It starts with slimy smears on the surface, followed by hair-slippiness and at an advanced stage a loosening of the grain layer in some sections and destruction of the skin by the formation of holes [4].

A defect assessment done on rejected wet-blue cattle hide shows the following results, "ekek (48.6%), flying cuts (18.7%), putrefaction (16.7%), Scratch (10.7%), branding (1.7%), scar (0.3%), Wound (0.3%), and smoking (3%) were important major defects [5].

1.2 Statement of the problem

Raw cow hide are available in plenty to the Ethiopian tanners, however, producing quality leather to compete in international market is difficult. Owing to various ante mortem and post mortem defects, the quality of the cow hides gets affected. The present study aims to upgrade the cow leathers by adopting modified wet finishing and finishing processes so as to add value on the sale-ability of finished products.

1.3 Objective of the study

1.3.1 General objective

Developing wet finishing and finishing methods to produce high quality cow leather without affecting the natural look.

1.3.2 Specific Objective

- Study histological and chemical characteristics of the cow hide in different stages (raw, liming, wet blue, crust and finished)
- Systematic study on the fiber structure of Ethiopian cow hides in comparison with Indian cow hides.
- Identifying the possibility of looseness in liming stage if any
- Study the physical characteristics of the leather (crust and finished) stage
- SEM analysis of crust and finished stage
- Upgradation based on wet-finishing trial in post-tanning operation
- Using different finishing technique (snuffing, cationic finish) to overcome surface blemishes
- Standardizing process technology that improves overall quality of the finished leather.

1.4 Significance of the study

- Studying the nature of Ethiopian cow hide
- Identifying the main defects that alter the quality of the finished leather
- Devising a technology that suits to upgrade the leather
- Improving the selling price of the finished leather
- Used as secondary data for further research work on Ethiopian cow hide

1.5 Scope of the study

This project work covers the following activities so as to have an insight about Ethiopian cow leather quality problem and as per the result to standardize process technology.

- Grain surface pattern using stereo microscope (Ethiopian and Indian at crust and finished stage)
- Hair pore count –surface fineness or coarseness of Ethiopian and Indian cow leather at crust and finished stage
- Histological Examination of the Ethiopian raw material in comparison with Indian.
- Grain to corium ratio of the raw hide using light microscope after soaking
- SEM on crust and finished stage
- Chemical characterization at raw and wet blue
    - Fat content, nitrogen content, and hydroxyproline content of the raw hide
    - Chrome content the wet blue
- Process design in post tanning and finishing after trials due in consideration of the result of the mentioned study
- Physical characterization
    - Strength property(Tensile, tear and elongation at break)
    - Organoleptic property(fullness, smoothness, roundness, grain tightness, defect coverage, uniformity of color and overall appearance of the finished leather)
    - Fastness property (wet/dry rub fastness)

Chapter two

2. Review of the literature

2.1 Introduction

The story of leather is long and colourful. Many years before recorded history people wrapped themselves in dried animal pelts. The fact that the skins turned stiff and rotted was a problem, but ways of softening and preserving the hides were discovered. This was the beginning of leather processing. At first the hides or skins were probably dried in air and sun light. Later they may have been soaked in water and dried over a fire. Still later it was discovered that certain twigs, barks and leaves soaked with the hides in water helped to preserve them [6].

Through archaeologist’s findings, we know that primitive man used the skins of hunted animals for food as well as clothing. Nomadic tribes made shelters from the hides of larger animals, such as bison [6].

As civilization advanced, preserving hides and tanning them into leather became an important industry. In the 18thcentury tanning was an old and respectable trade and a tedious one. Nearly a year was spent manipulating a hide before it was delivered as leather to the saddle maker, harness maker or other craftsmen [6].

The history of making leather in old age also further recorded in religious Holly books among them we found the following in Holly Qur’an;”And Allah had made your home’s a place of rest for you, and made dwellings for you out of the hides of the cattle which you find so light when you travel and when you camp; and furnishings and articles of convenience out of their wool, fur, and hair - comfort for a while’’ [7].

Allah mentions His great blessings for His servant in that He has given them homes to dwell in and protect themselves with, in which they find all kinds of benefits. He has also given them homes from the hides of cattle, i.e., leather, which are light and easy to carry on journeys and can be erected wherever they stop, whether they are traveling or are settled.(out of their wool, fur and hair) refers to sheep, camels and goats respectively.

(Furnishings) meaning what you take from them, i.e., wealth. It was also said that it means articles of convenience, or clothing. The correct view is more general in meaning than this; it means that you make carpets, clothing and other things from their wool, hair etc., which you use as wealth and for trade [7].

Leather production is largely based on the utilization of the raw hides and skins which occur as a "waste" product in the slaughtering of domesticated animals that are kept for meat. From an ecological point of view, the tanner is therefore an "important utilizer" of putrescible matters which would otherwise contribute to an immediate increase in the release of CO_2 into the atmosphere and the much discussed heating up of the earth's climate [6].

Fresh hides or skins consists of water (64%), protein (33%), fats (2%), mineral (0.5%), and other substances like pigments etc (0.5%).Of theses, the most important for leather making is protein. This protein may consist of many types. The important ones are collagen, which on tanning gives leather and keratin, which is the constituent of hair, wool, horn and the epidermal structures [8].

Leather processing involves mainly four important operations, viz., pre-tanning, tanning, post-tanning and finishing. It includes a combination of single and multi-step processes that employs, as well as expels, various biological, organic and inorganic materials. As the main constituent of the raw skin and hides is protein, they are much susceptible to bacterial degradation. Thus, it is essential to preserve the protein matrix and to arrest microbial attack temporarily prior to processing. Several chemical, biocidal and physical methods have been advocated and adopted, preservation using salts (40-50% based on green weight of the hide/skin) remain popular worldwide due to ease, cost-effectiveness and quality of finished leather produced [9].

2.2 Pre-tanning operation

2.2.1 Trimming and sorting

Trimming is done to remove unwanted long Shank, horn, hooves, ears, tails etc and give a proper shape of hide/ skin. Then sorting is carried out according to size, weight, thickness, grade etc and formed into batches to maintain the quality of leather. The sorted hide/skin can be weight in order to take the weight of chemicals for the later processes [10].

2.2.2 Soaking

Soaking is the first operation carried out in drums, paddles or pits with subsequent water, wetting agent & bactericides to rehydrate and restore the hides/ skins to its natural condition and to remove adhering dirt, blood, curing agents & some soluble proteins. The method & duration of soaking varies according to the condition of raw stock, specifically, it depends on the type of curing of raw stock. Thus, fresh hides/skins require only a few changes of water, preferably cold water, to remove blood, dirt, etc. Wet salted stocks have to be soaked for longer period, depending on the degree of dehydration. In case of prolonged soaking, suitable preservatives are to be used. To reduce the time of soaking, wetting agents are used. For soaking dry salted stock, soaking aids and preservatives are to be necessarily used. Additives like sodium sulphide, caustic soda, soda ash may be required for proper rehydration. Enzymatic soaking aids have been found to be very useful to reduce the time of soaking. Dried hides require soaking for a period longer than that for dry salted stock, along with suitable wetting agents and preservatives. Enzymatic soaking aids have been particularly found to be useful in this case. Drums are useful in accelerating the soaking process. However, the R.P.M. of drum has to be controlled to avoid too much of beating action. Completion of soaking is tested by folding the skins/hides flesh side out, and feeling for uniform softness flexibility. These are taken as evidence of proper soaking [11].

2.2.3 Unhairing and liming

Loosening (depilation) or unhairing may be considered as an extension of soaking. Its purpose is to separate the two structural proteins keratin and collagen. The aim of un-hairing (depilation) and liming is to remove the hair, epidermis and to some degree the inter-fibrillary proteins, and to prepare the hide for removal of loose flesh and fat by the fleshing process [12].

In the process of un-hairing which follows soaking, the hides and skins are treated with lime, sodium sulphide (sharpener) and other additives in pit/paddle/drum. This is done depending upon the soaked material and final end-product. During this process, hair is loosened/pulled out, flesh loosened and removed, hides/skins suitably plumped for easy fleshing. Hair and flesh are removed by hand/machine to make the material free from any hair and loose flesh presenting a clean surface and the material is taken up for further processing.

Unhairing method depends upon the raw stock as well as the final leather required to be produced. In case of goat or sheep skins where the wool of hair has some value, a paint un-hairing system is to be adopted. In the case of cattle hide, hair pulping method is used in paddle/drum. Short liming is necessary to get tighter leather and less looseness in leather. For soft leather where good opening up of structure is required, a slightly longer liming is adopted to increase the swelling and splitting of fibres. Such process is dependent on the type of raw stock. Liming with the addition of soda ash/caustic soda is done to adjust the desired degree of plumping. The plumping is also regulated by the addition of materials like glucose, molasses and sodium thiosulphate. In all cases, it should be ensured that the flesh is sufficiently loosened for easy removal [11].

2.2.3.1 Paint Liming

In paint liming, the skins are painted with a paste of lime, sulphide and wetting agent (10% lime, 2% sodium sulphide, 15% water and 0.2% wetting agent) on the flesh side and piled flesh to flesh, kept overnight well covered with wet gunny cloth. Next day they are unhaired either over the beam using unhairing knife or by pulling out the hair by hand and re-limed (using 10% lime and 1-1.5% sodium sulphide for 2 days with occasional running of the paddle for 15’ every 2 hrs), taking care to prevent lime blast (Lime blast results when fleshed pelt is exposed to outside air with the formation of calcium carbonate in patches. The presence of calcium carbonate will affect subsequent de-liming and pickling, which in turn influence the tanning) [11].

2.2.3.2 Drum liming

In Drum liming**,** the soaked skins are put in the drum with suitable float. The required amount of lime and sodium sulphide is added during the drumming of the skin. The drum is run intermittently and the duration is determined by type of final leather. Here also hair is pulped out and the material is sent for fleshing.

The soaked hides after weighing are put in a paddle containing 300-400% water and well agitated for 15 min. 5% lime and 2.5-3% sodium sulphide is added to the paddle while running. Then the paddle is run 10 min every 2 hrs. and left overnight. When the hides are properly plumped they are taken for un-hairing and fleshing [11].

2.2.4 De-liming Bating, degreasing and pickling

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

The degreasing unit operation is primarily important to remove excess fat which otherwise alter uniform chemical distribution and penetration on the next unit operation. The process of degreasing is crucial for sheep skin which has more fat as well for fatty hides and goat skin from hilly origin. This can be done by using surfactants/emulsifiers such as non-ionic surfactant example is nonylphenol-etoxylate, solvent such as diesel and, lipase based enzymes also used for hydrolysis of fat.

The pickling process is primarily conducted to adjust the collagen to the conditions required by the chrome tanning reaction to have acidic PH around 2.5-2.8, an ideal PH condition, for the penetration of chrome salt in the skin matrix so as to form coordination covalent bond with the COO^- group of collagen during basification. The conventional recipe for pickling based on limed pelt weight is 100% Float, 10% salt, 1% Sulfuric acid [12].

2.3 Tanning

Tanning is the process of converting raw hide and skin, which is unstable and putricable, in to leather, with adequate strength properties and resistance to various biological and physical agents.

Tanning is a process of introducing a tanning agent in to the hide/skins. This is accompanied by introduction of additional crosslinks in to collagen, which binds the active groups of the tanning agents to functional groups of the protein.

A vast number of inorganic compounds used to treat collagen to increase its shrinkage temperature, among those salt of chromium is the very special one used to obtain light leather of high thermal and bacterial resistance. A usual procedure is to introduce Cr^{3+} in to the hide, adjusting a PH of about 3 by pickling, and then make the collagen-chromium complex cross-linking reaction to occur. [13].

2.3.1 Chrome tanning

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:-

- 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.
- Vegetable tanning creates hydrophilic leather, because of the chemical nature of the plant polyphenols that constitute the tanning material, but chrome tanning makes collagen more hydrophobic, so the tannage allows water resistance to be built into 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).
- Tanning with plant polyphenols has the effect of making the dyeing effect dull, whichever vegetable tannin or dye types are used- the leather is said to be „saddened‟.
- Vegetable tanned leather may exhibit poor light fastness, depending on the type of vegetable tannin, but chrome tanned leather is lightfast. Hence dyed chrome tanned leather will retain its color better.
- 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 ladie’s weight shoe upper, combat upper, soling, clothing, gloving, upholstery, etc. [13].

2.3.2 Vegetable Tanning

Vegetable tannins are extracted from plant materials that contain commercially viable concentrations: this may be done with water or with organic solvents. The extracts typically contain Non-tans, tans and gums. Vegetable tanning technologies use drums to facilitate rapid penetration. The reaction is typically conducted at about pH 3.5 and up to 38^{o}C [13].

2.4 Post tanning/wet-finishing operation

The processes that are performed after tanning but prior to finishing such as neutralization, dying, re-tanning and fat-liquoring are called post tanning or wet finishing operations.

The main objectives of this set of unit operations are to give a color to the leather as demanded by the market (dyeing), impart softness (fat-liquoring) and fullness and uniformity of substance (re-tanning). These operations assume great importance due to the fact that most of the times, one start from the wet blue and produce different types of finished leathers without having any knowledge about the beam house and tanning operations the leather has undergone. Needless to say, wet blue is an internationally traded commodity which is the starting material for many leather finishing units today. It is generally said the leather is made or marred in the lime yard. In the changed scenario where the tanner is forced to buy the material from the open market and adjust the post tanning processes to build the functional properties required in the different types of leathers in his product mix, the post tanning operations assume greater significance. Hence in-depth knowledge of the fundamentals and the understanding of the intricacies involved will go a long way for gaining mastery in the production of quality finished leathers. The processes that are performed in the drum in this set of unit operations are Acid wash, Re-chroming, Neutralization, Re-tanning, Dyeing, Fat-liquoring, Fixing [14].

2.4.1 Acid wash

Acid wash is the first process performed in the drum after adjustment of the thickness of the wet blue leathers by splitting (bovine hides) and shaving. This is performed to wash away any unfixed/loosely held chrome and also adjust the pH for re-chroming. The chemicals used include an acid, mostly acetic acid and a fat and chrome dispersing agent (an amphoteric agent most of the times). Sometimes, oxalic acid is also used to scavenge hexavalent chromium if any in the leather or in the case of white or pastel colored leathers [14].

2.4.2 Re-chroming

The purpose of re-chroming for chrome tanned leathers is to get more uniform chromium content in a pack of leathers procured from different sources and/or to get uniform layer-wise distribution of chrome in thicker bovine leathers or to get the required amount of chrome as required by the type of leathers or as demanded by the buyers. Another reason for re-chroming is to get fresh cationic charge in the aged wet blue leathers to improve affinity for dyes and fat-liquors. Certain types of leathers like stropping leather (used in sharpening razor blades) or oil seal leathers, more chrome content is necessary to impart heat resistance. Sometimes aluminum based tanning salts or syntans are used in re-chroming to improve dye-ability and get rich shades in dyeing. Zirconium tanning agents are used in certain types of leathers to get white leathers or to increase the dry heat resistance (pilot glove leather) or to reduce stretch in the leathers. It is necessary to basify the chrome in re-chroming to a pH of about 4.0 to increase the fixation and allow the re-chromed leathers to age overnight before the leathers are taken for further processing. This is to ensure completion of olation process. If the re-chromed leathers are taken for neutralization process without aging, there is a possibility of stripping out chrome in the bath and the more serious issue with respect to production of free mineral acid in the leather due to continuing olation process resulting in poor strength properties of the leathers [14].

2.4.3 Neutralizing

Neutralization is an important process in wet finishing operation to get the desired final product. This is the process in which the charge characteristics of the leathers are adjusted by the neutralization of the free acid present/liberated from the chrome complexes due to oxolation during aging in the chrome tanned leathers and the extend of neutralization will depend on the softness of the final leather and the extent of neutralization increases with the increase in the softness required. In chrome tanning, the cationic chromium complexes are used in tanning and that alone confers high amount of cationic charge to the chrome tanned leathers. Moreover, the chromium complexes are involved in co-ordinate covalent linkages with the charged side chain

$C00^-$ groups in the skin protein and hence the chrome tanned leather becomes highly cationic-ally charged due to the blocking of $C00^-$groups through reaction and the presence of charged side chain amino groups, NH^{3+} at the pH conditions prevailing in wet blue leather (~3.6). In such conditions if post tanning operations are performed without neutralization, the following things will occur.

- The dyes will get fixed only to the surface without penetration and the patchy and unlevel surface dyeing will result in
- The fat-liquors will not be able to penetrate well due to premature breaking of oil in water emulsion resulting in surface greasiness and hard and bony leather without the internal softness
- The penetration of re-tanning material will not be good and there will be more loading of the grain resulting in empty leather with coarse grain and in worst cases the grain might crack due to excessive surface loading.

Hence the neutralization is an important operation that should be performed with good process control to obtain quality leathers with required properties suitable for the intended end-uses. This is the process that should be carried out consistently to the same extent for a particular leather to get batch to batch consistency.

The extent of neutralization required for different types of leathers are as follows:-

Corrected grain upper leather (PH -4.8-5), Softy upper (PH-5.0-5.2), Suede leathers (PH -5.2- 5.5)

Nappa garment leather (PH 5.5-6.0), Glove leather (PH-6.0-6.2).

Apart from the type of finished leathers, the nature of raw material should also be taken into account to decide about the extent of neutralization. The loosely structured skins and hides should not be subjected to extensive neutralization; if otherwise may lead to further loosening of the leathers. Sometimes, it is better to use only neutralizing syntans and buffering salts in such cases.

The chemicals commonly used in neutralization are mild alkalis in combination with basic buffering salts. Sodium bicarbonate in combination with sodium formate is commonly employed for neutralization. Sodium formate is a buffering salt with slight alkalinity and performs the role of not allowing the pH to shoot up suddenly.

If the pH shoots up suddenly during the fast addition of alkali, there is a possibility of grain becoming coarse or non-uniformity in colour due to local precipitation of chrome or in worst cases chrome patches also can happen. Though presence of buffering salt to a large extent can avoid the problem, however care must be exercised to add the alkalis in feeds slowly to avoid such occurrence. The neutralization process should be completed as quickly as possible and the running time after achieving the pH should be kept short. The extended running time at high pH can lead to loosening of the fiber structure and may prove detrimental to leathers where the grain tightness is important.

After the end of neutralization process, it is necessary to wash the leathers well before commencing post tanning operations to remove the neutral salt formed during the acid-alkali neutralization. The neutralized and washed leathers should be taken for further processing immediately. Aging the neutralized leathers is a bad practice as the aging will alter the pH condition thereby the charge characteristics of the leathers as well and hence should be avoided. But if there is a delay in processing, the pH should be adjusted to the required level before commencing the post tanning operations [14].

2.4.4 Re-tanning

The skins and hides vary in their fiber structure not only from one species to another but within the same species also based on the breed, sex, age and nutritional status of the animals during their life time and also based on the climatic conditions in which they are bred. Butt and neck are compactly woven whereas the bellies and shanks are loosely structured. Hence, in leather processing, every effort should be made to bring about uniform fullness and fiber compaction not only in a pack of leathers but within the same skin/hide in order to be able to cut components for the intended article from any parts of the leathers. This is necessary to get the best out of the natural material and also to minimize the wastage.

It is well known that chrome tanning produces empty types of leathers and vegetable tanned leathers produce fuller leathers. Hence in the case of chrome tanned leathers, more efforts are necessary to bring about uniformity in fullness and fiber structure. Re-tanning is the process performed to achieve this objective. Sometimes, re-tanning of chrome tanned leathers or vegetable tanned leathers are carried out to impart special characteristics such as improved dyeing characteristics or improving the affinity for fat-liquors by altering the charge characteristics or bleaching or bringing about whiteness etc.

The main objectives of the re-tanning are:

- To improve the fullness and uniformity of substance
- To fill the looser areas in order to get uniform substance and fiber compaction

in all parts of the skins

- To impart body and round feel
- To avoid grain looseness and improve ‘’break’’ properties and grain tightness by filling the void spaces between grain and corium by selective filling
- To improve the overall cutting value by bringing about uniformity of substance and fiber compaction

Apart from the above objectives, in the case of some leathers, re-tanning needs to be given more emphasis as given below:

- ✓ To improve buff-ability in the case of suedes by improving fiber compactness
- ✓ To improve glazability in the glaze finished leathers
- ✓ To improve print retention in the case of printed/embossed leathers
- ✓ To improve burnish-ability in the case of burnish- able leathers

Since selective filling is required to get overall uniformity in fullness and fiber structure, there are different classes of re-tanning materials need to be used in combination to get the desired results in re-tanning. The main re-tanning materials used for imparting fullness (i) vegetable tanning materials (ii) phenolic syntans (iii) acrylic and other resin tanning materials (iv) protein based tanning agents (v) Whitening syntans (vi) polyurethane syntans (vii) aldehydes and their derivatives (viii) protein fillers and their derivatives

Some list even inorganic mineral tanning agents or mineral based syntans (chrome, aluminium, zirconium salts) as re-tanning agents as they are used in re-chroming (in the case of chrome leathers) and in semi-chroming (in the case of vegetable tanning) and have different objectives as would be elaborated little later (14).

2.4.4.1 Organic Re-tanning agents

Organic re-tanning agents are classified based on the effect they have on the treated leathers and they vary in terms of their selective filling effect or other additional properties imparted by them.

1. Replacement type Syntans (which were originally developed as replacements for vegetable tannins): condensation products of aromatic compounds like phenol, naphthalene sulphonic acid with formaldehyde or urea

2. Resins: condensation products from formaldehyde with amino and amido compounds like urea, melamine, cyanamide.

3. Polymeric or popularly known as acrylic syntans: mainly polyacrylics, i.e. polymerization products from acrylic acid derivatives.

Replacement type syntans as the name suggests, were developed as substitutes for vegetable tannins during the World War. They have similar filling action like vegetable tanning materials giving overall fullness to the leathers but the filling is relatively more in the butt area of the leathers than in the shanks and bellies whereas the resin tanning agents have preferable filling for the looser areas. Acrylics tend to fill the void spaces between grain and corium imparting grain tightness/reducing grain looseness and improved ‘break’ property. (Break is an important property for upper leather as it influences the durability of upper leather in use. Good upper leather should have fine break meaning when the leather is folded with the grain inwards, the number of creases formed should be more per unit area, so high they are not visible. On the contrary, leather with poor break will exhibit less number of visible creases and in the worst cases pipiness is seen indicating the lack of cohesion) (14).

2.4.5 Dying and fat-liquoring

Leathers are dyed to impart color as demanded by the fashion. Dyeing is the finishing operation for some of the finished leathers like suede and nubuck leathers. Some leathers or buyers want only surface coloration and certain leathers (glove leather, high quality garment and glaze kid) require not only through and through dyeing but also tone-in tone (grain, cut and flesh all in almost same shade and in the case of finished leathers, tone-in-tone with finishing as well).

Fat-liquoring of leathers are performed to impart softness, flexibility, feel, drape, run etc. The strength properties are also improved by fat-liquoring. In effect, what is being aimed at in fat-liquoring is to coat the individual fibers or fiber bundles (depending on the extent of fiber 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 fibers slide over one another to give the required softness and flexibility.

Since, water is the medium used in leather processing; the oil cannot be used as such but in the emulsion form to ensure ease of application in order to get the required diffusion of the oil into the interstices of the fiber structure. The oils in water emulsion called fat-liquors are used in fat-liquoring operation. The emulsions can be made by external emulsification of the chosen oils with the use of emulsifiers or building the emulsifying groups in the oil molecules through chemical reaction. Due to the fact that the emulsifying groups also function as reactive functional groups to substantively fixing the fat to the fiber structure, the fat-liquors used in leather processing are mostly based on oils with in-built emulsifying groups. The external emulsifiers (either non-ionic or anionic type) may be used in combination to adjust the emulsion stability against acids, salt and hardness in water used in processing. The natural oils based on triglycerides (with un-saturation in the molecule) are converted into fat-liquors by chemical reactions such as sulfation, sulfonation, sulfitation whereas the mineral oils, paraffinic oils are made into emulsion form through sulfochlorination route. Fat-liquoring is usually carried out in a drum at the highest temperature practical for the type of leather, or about 45°C for vegetable tanned leather and 60 to 65° C for full chrome tanned leather. The leathers are run in a drum for 30 to 40 minutes. After drumming, the leathers are usually struck out on the flesh side, carefully set out to smooth the grain, nailed or toggled out flat to dry, or paste dried [14].

2.5 Finishing

The objective of finishing is to give a treatment of coatings to the grain surface to protect it against dirt, staining, wetting, mechanical stresses like rubbing, scuffing, flexing etc., leveling or evening out the color of the grain surface, hiding grain blemishes and upgrading its quality, improving the aesthetic appeal and the sales value of the product. By the finishing process, the grain surface of the leather is coated with various substances and is then submitted to different mechanical operations, depending upon the purpose intended whereby the appearance of leather can be highly influenced to make it more useful, attractive and appealing to users. Finishing may be employed to impart colors, a uniform shade, special patterns, a smooth or grained or printed/embossed surface, luster (Matt or glossy) as well as opaque (covered) or transparent (aniline/semi-aniline) appearance to the leather surface. Finishing operation is the most vital part of the processing of leather as the final product is judged by its appearance, evenness of color and surface, feel, handle, break, gloss etc. Hence it is usually the finishers who have to face the complaints or blames, if anything goes wrong. They are also expected to correct whatever faults that have occurred during the earlier operations.

Finishing was once considered as an art and was kept a secret but today with the introduction and availability of a wide variety of leather finishing chemicals and mechanization, finishing is no longer that secret. However, in spite of the innumerable finishing auxiliaries available and marketed by the firms providing details like general composition and properties of the products, mode of application with formulation for different types of finishing of leather, finishing is still dependent upon the finisher's ability of judging and blending of different auxiliaries to make his own combination to give the best finishing effect. Also, he keeps in mind the high qualities required from finishing, like adhesion, flexibility, durability against weathering and aging, durability against dry and wet rubbing, resistant to pealing, cracking on flexing, light fastness, resistant to the various mechanical operations involved in finishing and permeability to water vapor and air thus ensuring the hygienic conditions.

These rigid requirements cannot be met by a finishing agent in a single coating. It is necessary to have various finishing agent with different properties applied in several coats. A normal finish essentially consists of 3 coats [15].

2.5.1 Bottom Coat

The bottom coat may be either sealing or impregnation coat and clearing coat. The object of sealing or impregnating coat is to seal the grain to control the penetration of the season coat. The season coat should give a leveled and uniform filmed color coating and not overload the grain. Sealing should uphold firmly on the leather surface. Impregnation coat is applied for soft grain tightening and filling effects. The objective of the clearing coat is to make the grain devoid of any oils or fats and to improve the absorbance of the season coat by the leather [15].

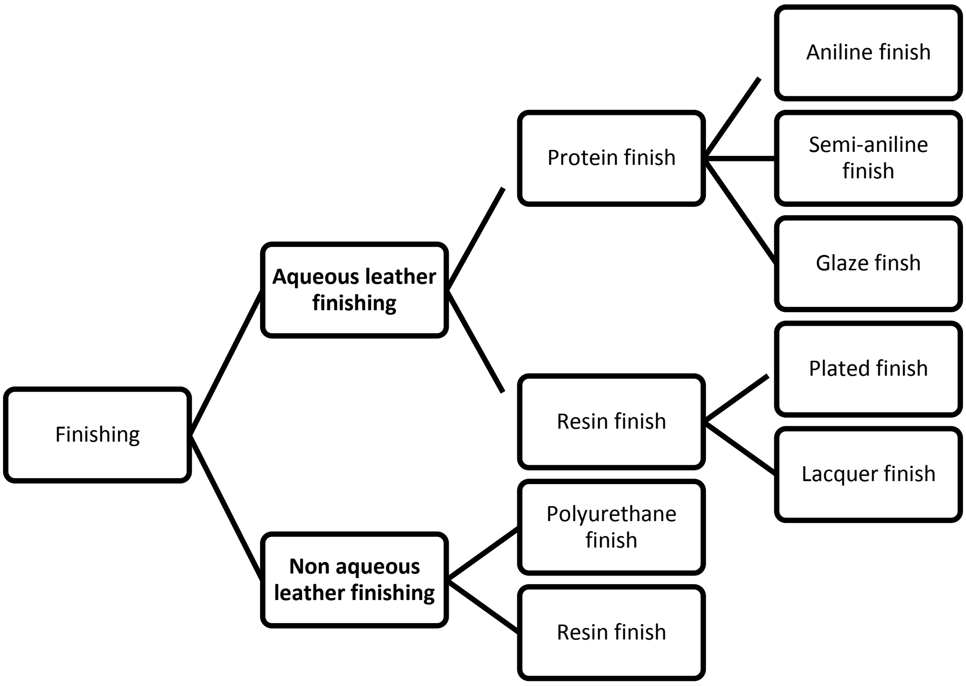
2.5.2 Season Coat

The season coat is to impart a desired color to the leather and level out the surface defects. The effects like glossy or matt, soft or hard feel can be brought about by proper choice of auxiliaries added to the season coat. This coat can be done either by pad or hand spray or Auto spray. By spraying on we can achieve levelness in film formation [15].

2.5.3 Top Coat

Top coat serves the purpose of protecting the season coat. It gives properties like appearance, handle, fastness to wet and dry rub resist to hot plating [15].

2.5.4 Classification or type of finishing system



[14].

2.5.4.1 Protein Finish (Aqueous)

Shoe uppers, lining leathers of goat, sheep, cattle any leathers of various types for leather goods which are protein finished and glazed still occupy an important position in the export demand of finished leathers. This type of finish uses binders mostly based on proteins. The film formed is not continuous, which facilitates the friction glazing at high temperature. The leathers will have a natural look and feel. The finish would also be resistant to cold weather [15].

2.5.4.2 Aniline Finish

In the recent years, the practice of coating leathers with a heavy opaque, plastic like finish has been abandoned due to the simulation of the leather imitation materials by their manufactures. The leather manufactures and finished goods manufacturers are anxious to preserve the natural look and handle of leather and hence finishing with thin coats are done through which the grain pattern is more or less visible. Leathers that were formerly buffed and heavily filled with film forming materials like polymers and covered with opaque/covering pigments is slowly replaced and given an aniline look subsequently. Aniline finish is a transparent/translucent finish, which keeps the natural appearance so that the original grain pattern of leather surface is easily visible. This is a lighter finish without loading the surface of the good quality leathers. It will have good fastness to light and bleeding. Most of the color matching is competed in the wet finishing stage itself. Aniline finish is done only in full grain leathers to retain the natural grain clearly visible.

Aniline leather need not have full grain. Buffed leather with aniline finish/look can also be produced. Aniline leather need not be completely free of pigments. The finish may be leered out with small amounts of finely dispersed pigments.

So the main feature of aniline leather is its natural appearance and handle so that the original grain pattern of the leather surface is best retained when the leather is dried out after uniform and level dyeing and fat-liquoring without any surface treatment of finishing coats. But surface of leathers are prone to staining, wetting and mechanical damage. It is therefore necessary to protect the grain surface by a finish that seals the transparent and light in application (not heavy) so that light rays are deflected by the grain surface, showing clearly the grain pattern. Though colorless seasons are the best to most these requirements besides improving the uniformity and liveliness of the grain surface add to brilliancy.

Full grain aniline finish is applicable only to good quality raw material without grain blemishes. The aniline finished leathers are expected to be full with mellow handle, springy and rubbery feel, heaving a natural look of grain. Not all available hides and skins can be finished into full grain aniline leathers. Not more than 15% of the available raw materials can be finished into full grain aniline leathers with a satisfactory uniform appearance good aniline leather depends upon the effect obtained in the previous operations of dyeing and finishing. In dyeing it is important to have the correct choice of dyestuffs which will give the neatest shade of the final finish required, having good fastness properties to light and bleeding. Uneven, patchy and cloudy dyeing is sometimes encountered with and such leathers are not possible always to be finished into aniline leathers [15].

2.5.4.3 Semi-aniline or aniline look or mock-aniline finish

These types of finishing are more adopted for plated finished leather. The leathers are more or less heavily re-tanned and invariably the leathers are snuffed on the grain lightly or deeply depending upon the defects in the grain surface. After initial impregnation the grain surface may be coated with a good covering of opaque pigments to hide the defects. The finisher then uses his skill to give a slightly darker tone on the top using sprits soluble dyestuff transparent organic pigments/colored lacquer emulsions etc., so that they look like aniline leather. Effects like pull up, speckle effect, smoky effect can be produced. Even full grain leather which is not good for aniline finish can be finished like this. Sometimes even in full grain aniline small quantity of pigment is used to hide the defects. Brilliancy as increased by adding suitable dyestuffs and/or transparent pigments to opaque pigments. This finish is in between real aniline and pigment (opaque) finishing.

Finishing based on transparent pigments and little of opaque (covering) pigments for hiding slight grain blemishes. Sometimes opaque finishing is done first to hide the grain defects and on which an aniline look/mock aniline effect is given by applying dyestuffs and/or transparent pigments etc. Full grain leather with slight defects is snuffed to even the surface. In case of deeper grain damages it is necessary to snuff the leather deeply. So heavy coating with season is required. This may result raised grain. Applying impregnation coat with medium hard resin can eliminate it. This treatment not only improves sealing it also tighten the grain. On this artificial grain patterns are printed after season coat [15].

2.5.4.4 Resin Finish (Aqueous or Aqueous Cum Non Aqueous)

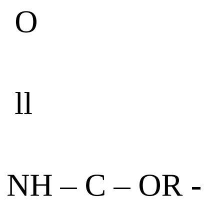
This finish is primarily based on polymer emulsions and top coated with lacquer. This has a continuous film which is thermoplastic. The resin finished leathers can only be plated at pressure and temperature and not capable of being friction glazed. The film has more filling effect than protein finishes. Unlike protein finish, the film is internally plasticized and hence possesses intrinsic elasticity. The new easier form of film forming products like acrylates or vinyl or butylenes polymers or polyurethane or nitrocellulose are offered by the chemical industry. The new modern finishes have been accepted by the tanner as it is possible to upgrade the poor quality raw material by this finishes [15].

2.5.4.5 Lacquer Finish

This finish is generally based on nitrocellulose or cellulose nitrate. Here both lacquers (solvent dilutable) and lacquer emulsions (water dilutable and solvent dilutable) are used. The film formed is firm, but may crack at low temperatures. Some of the lacquers with suitable plasticizers can be friction glazed. The leathers finished with nitrocellulose lacquers have no fastness to light. Hence, for finishing of white leathers special lacquers or lacquer emulsions based on cellulose acetate-Butyrate are preferred to cellulose nitrate as the former are more stable to light and yet yield a flexible film [15].

2.5.4.6 Polyurethane finish (non- aqueous)

Urethane finishes have come into extensive use in leather finishing in the current decade. Polyurethanes represent a class of versatile, high performing polymers. The reaction of poly iso-cyanates with polyols is the basis for polyurethane chemistry. Urethanes are amide esters of carbonic acid of the formula



$$NH - \overset{\overset{O}{\|}}{C} - OR -$$

The best known simple urethane is ethyl-carbonate. The most widely used method for the synthesis of urethane is the reaction of diamide polyisocyanates with polyols (polyether or polyester polyols). The characteristics of the finish film depends on the nature of the polymer binder used and hence the nature of the polyurethane system with respect to these characteristics have been dealt here with some of the polyurethanes, they are highly compatible both in cationic and anionic systems. This finish is based on urethanes (both reactive and non reactive polyurethane systems). This finish gives a film, which has exceptionally excellent abrasion resistance, balance of flexibility and toughness, high gloss, gloss retention, solvent resistance, covering, better handle, softness and levelness, brilliancy of the finish, dry and wet rub fastness, and better adhesion. At the same time, the finish has one disadvantage in that it makes the leather look like plastic. Urethanes are normally used as top coats for leathers finished with polymer emulsions. Urethanes are reactive finishes where the film is formed on the leather by the reaction of the isocyanate prepolymers containing residual OH groups with additives containing isocyanate groups. The polyurethane is formed with the development of high molecular weight by the reaction of NCO groups with OH groups. In polyurethane resins which are supplied in one component system the curing is affected by moisture from air. In using one pack system, it is always better to remember that the container once it is opened should be used quickly (within a day or two). Otherwise, the finish gets on changing in composition and becomes as solid. Two pack systems are better in this respect [15].

2.5.4.7 Opaque or Covering Finish

Finish using covering pigments for hiding the grain defects and damages or for covering the very uneven drum dyeing. Here covering pigments are used along with polymer (resin) dispersions and other auxiliaries. Sometimes little dye solutions is also added to brighten the finish. Finally they are top coated with lacquer emulsions or lacquers. In addition there are a variety of finishing systems and finishes like metallic finishes, pearl finishes, two tone finishing, antique finishing, rub off/brush off finishing, burnish type finishing, transfer of gold, silver and other metallic foils, transfer of PVC films, polyurethane films etc., marbled and fancy finishing and so on. The list is really inexhaustible. Once the finisher has a basic understanding of the various materials and finishing agents that go into making of finish and also their properties compatibility, mode of application etc., he can juggle with an endless combination of finishes, formulation and produce results that can be highly individualistic [15].

2.5.4.8 Various Constituents used in Finishing Formulations

Pigment paste

In leather finishing dry pigment colors (inorganic or organic), which are not miscible with water are normally dispersed using dispersing agents or with other vehicles like casein, plasticizers, wetting agents, preservative etc. The dry pigments are ground and dispersed using equipments like ball mill, cone mill, triple roll mill, uniroll mill or similar equipments. The vital properties required for leather pigment are; color, strength of staining, hiding power, texture, absorption, fastness to light, fastness to heat and temperature and resistance in various media in which the pigment pastes are likely to come into contact (viz., alkali, acid, formaldehyde, solvent, etc.)[15].

Dye solution

In protein finishes, only anionic dyestuffs can be used for brightening the aqueous finishes. Because of the opposite charge, basic dyes cannot be mixed with protein finishes as they may precipitate. As normal anionic dyestuffs contain additives, for finishing concentrated dyestuffs are marketed and used. Metal complex dyes with special molecular structure which are soluble in solvents like alcohol, di-acetone, alcohol, dimethyformanide, oxitol are used not only for coloring lacquers but also sometimes in protein finish [15].

Binders/ Gloss giving agents

Casein

This is a protein derived from milk. It is obtained by acidifying warm skimmed milk and allowing the precipitated casein to settle down. Usually lactic acid is used for acidifying. It is then washed, filtered and finally dried and later ground to obtain desired fineness of 30, 60 or 100 mesh. For leather finishing 30 meshes is used. Amongst the protein binders, casein is the most important and widely used finishing auxiliary. For leather finishing, casein dispersions of 10 to 18% in strength are made, dispersing casein in water using alkalis like liquor ammonia or borax. Other alkalis like triethanolamine and morpholine are also used which give casein dispersions having good polarity. Casein dispersions after application to leather and drying form a hard film with good adhesion to leather surface. As casein films are non-thermoplastic, they can be friction glazed in machine, which produces gloss and surface smoothness. Ammonia based casein dispersions are less viscous than borax based casein and also it gives better water resistance as the ammonia later evaporates from the system. Casein based finish is finally coated/fixed with an application of formaldehyde solution. Formaldehyde reacts with casein forming an insoluble mass known as ‘galalin’, which is taken advantageous of for fixing casein based finishes.

The formation of the insoluble mass is accelerated when the pH is lowered and as such very often to improve the water resistance, fixing is done on protein finishes using formaldehyde and water to which acetic acid is added. As casein is soluble in alcohol, the fixing coat of formaldehyde besides acetic acid may also contain methylated spirit, which may tend to soften the casein film and enable the formaldehyde and acid to act on casein [15].

Linseed

Linseed mucilage or solutions are prepared by soaking linseed seeds in water and boiling till the seeds are softened. It is then strained and made as 10% stock solution. A small amount of oil is also extracted from the seeds during boiling. The mucilage has good grain filling properties and may be used as sealer coats. Too much use, can cause dullness and make the film cloudy. The film formed is soft and flexible and hence its use with other finishing agents in glaze finishing, imparts films of good flexibility and elasticity by minimizing the brittleness and the feel is also improved. It is always better to prepare fresh solutions of linseed mucilage and use them [15].

Acrylic polymer

Acrylic resins are manufactured by reacting (polymerizing) various quantities and ratios of acrylic monomers. Each acrylic monomer will contribute to different properties. Different polymer combinations are possible resulting in products with different and specific characteristics. Acrylic emulsions are tiny insoluble resin particles uniformly dispersed in water. The acrylic emulsions used for leather are film forming (i.e.) on evaporation tiny resin particles flow together to form a durable uniform film. Acrylics can be emulsified with other resin monomer class to form co-polymers. Normally acrylic polymers have good light fastness. Some of the parameters, which influence the performance of the acrylic emulsion, are particle size, molecular weight, film formation, viscosity and reactivity.

Particle size of the acrylic emulsion ranges from 0.07 to 0.25 microns. Smaller sizes give good penetration or impregnation, bigger size gives good filling and covering with pigments also. Though the size of the acrylic is tiny they have high molecular weights. Each tiny molecule contains thousands of acrylic monomers. This facilitates a tough, durable and non-cracky film. Normally after spraying, the season coat will be dried through the steam chamber. During this time, the water evaporates and tiny resin particles in acrylic emulsion flow together to form a strong film. The characteristics of an acrylic film vary from resin to resin. Acrylic emulsions are used for impregnation and finishing with polymers, now self cross linked polymers are available. These give greater abrasion, solvent resistance and toughness to the final finish [15].

Plasticizers

Binding materials like casein, albumin, gelatin etc., do not give films sufficiently elastic to withstand natural movements and flexing of the surface on which they are applied. The film has to be plasticized in sufficient quantities to prevent it from cracking and flexing. Sulphated oils are popular and most popular amongst them are sulphated castor oil (TRO). TRO is also used in making aqueous pigment pastes from dry pigment powders. In protein finishes, TRO acts as not only a plasticizer but also as a wetting agent. It promotes uniform flow of the finish on less absorbent leathers but on highly absorbent leathers, it may cause the finish to penetrate too deep. An excessive amount of plasticizer may make the film very soft, make the grain surface tacky and also prevent gloss. Wet rub fastness is also affected. Normally in finishes, weakly sulphated castor oil, which is miscible with water is preferred to highly sulphated castor oil as besides on plasticizing effect, it does not have a pronounced setting effect.

High molecular alcohol or their derivatives like glycerine, diethylene glycol and polyglycol are also used as plasticizers both in casein based and polymer based finishes, because of the hygroscopic properties, they prevent the finish from drying out excessively and becoming brittle. In glazed finishes they promote smooth gliding of the glazing cylinder. However in very humid atmosphere, the hygroscopic nature may impair the glazing properties. These products have a true plasticizing effect on polymer films.

Emulsified water insoluble phthalate is also used as plasticizing both for glazed and plated finishes. In protein they act as non-gelatinizing and in polymer as gelatinizing plasticizer. Products based on fatty substances and wax dispersions are also marketed by firms. Though they may have pronounced plasticising effect on glaze and resin finishes, they are used more as filling cum flowing agents to impact suppleness, smoothness and a settled appearance to the finish. It reduces tackiness of plated finishes [15].

Wax emulsions

Wax emulsions are one of the most important leather finishing materials. Popular waxes are carnauba wax, micro crystalline wax, montan wax, shellac wax, paraffin wax etc., and other modern synthetic waxes of different hardness. In leather finishing, waxes as emulsions are used as aqueous dispersing agents along with other finishing agents to impair what is known as waxy feel in the trade. Hard waxes with high melting point are emulsified with triethanolamine soap and used in protein glaze finishing giving a pleasant waxy feel to touch. [15].

Fixing agents

Formaldehyde

It is generally used as a fixing agent on protein finishes or on finishes where protein binders are added. If used alone, it is used along acids like acetic and sometimes with chrome salts and methylated spirit. Fixing is brought about by chemical combination of formaldehyde with casein to form a hard resin ‘galalith’. A combination of 300 parts of formaldehyde (40%), 20 parts acetic acid and 680 parts water has proved to be more suitable mixture for fixing. [15].

Preservatives

Casein and other protein binders besides aqueous pigment pastes are required to be preserved against putrefaction. A small quantity of suitable preservative has to be used in stock solutions of binders, finishes and seasons to be used. The most commonly used are sodium tri-chlorophenate, sodium orthophenyl phenate, sodium pentachlorphenate etc. About 0.5 - 2.0 gm of preservative upon the dry weight of proteinous material is required [15].

Even if conventional anionic resin finish has advantageous in-terms of less investment in finishing equipment and use of less costly chemical, the disadvantages are ,the look of the finished low grade grain leathers are inferior because the normal finish doesn’t cover the defects and loads the grain heavily which reduces physical properties like rub fastness ,flexibility of the leather. Such finished leathers as well as splits can be used in the manufacture of low quality shoes, chapels, belts and cheap leather goods. The consumption of chemicals also very high. The consumption of leathers for making such products also very high because of the uncovered defects, non uniformity in the texture and non-uniformity in the grain pattern which will give less cutting value[16].

2.5.4.9 Compact Finishes

Now a day everything becomes sophisticated in the industry easy way of applying, handling and with less labor. The compact resin binder will be used as single binder for the finishing of garment leather, upper leather and upholstery leather. It give excellent wet/dry resistances and a soft and natural feel, good adhesion and long lasting film which remain unchanged even after dry drumming and staking. This can be used in the place of season coat but initially pre bottom or base coat should be given and normal topcoat [15].

2.5.4.10 Cationic finish

Cationic finishing products were first available for tanning and finishing leather from the time modern ideas on finishing began to take a hold on the industry in the 1930s. New technologies, including acrylics, copolymers and polyurethanes were all anionic in form and only recently has there been resurgence in the application of cationic technology in the leather industry.

Products such as pigments and fillers with an anionic charge have little natural affinity for leather and, therefore, call for the use of resins and binders to provide the necessary levels of adhesion to the leather surface. Nevertheless they provide excellent physical properties. In contrast, cationic finishes are meeting requirements for a finish which may be best described as a 'skin cosmetic' rather than a 'paint' while performing to the same high aesthetic standards as anionic finishes.

cationic finishing products now includes pigment colours, casein binders, fine particle aliphatic polyurethane resins, a fine non-ionic acrylic resin, a soft oily emulsion, a filler and a number of other special effect products. They are being used to give a soft, natural, well-filled look to leather while providing excellent coverage to mask defects such as pin-hole, scars, mange and others. In so doing, they offer an excellent means of upgrading a wide variety of full grain softy shoe upper leather and sheep nappa clothing leathers.

This early approach to the use of cationic products was to apply them as a sealer coat to regulate the absorption of subsequent finishing coats. Upgrading was achieved by sealing the parts of the grain surface where the enamel had been removed due to mechanical or natural causes. This resulted in relatively poor performance by today's standards, often with poor inter-coat adhesion, wet rubs and other physical properties.

Today, the chemistry is much better understood and results in a number of important advantages:

* The cationic charge gives better bonding with both chrome and vegetable retans with less need to use resins and binders to promote adhesion

* The pH of around 4.0 is close to the natural iso-electric point of leather, giving rise to gentle absorption of the finish by osmotic pressure without using wetting agents or solvents. This gives better penetration and adhesion of the finish

* All cationic products have a natural fine particle size and, with a Shore hardness of 10 or less, are softer than many of the anionic counterparts. This contributes again to improved penetration, good adhesion within the leather structure, a softer finish and often a tighter leather due to less wetting and, therefore, minimal swelling of the grain surface

* Less film loading is formed on the surface of the leather

* Cationic products can be used with less pigments and resin in the formulations. As pigments are generally dry and rough, they do not penetrate well into the leather and the ability to replace them with softer, fatty and waxy substances improves upgrading and aesthetics

* Cationic finishes improve tensile strength; lasting properties, softness, and fill In addition to the general range of cationic products for use in finish formulations.

There are two main disadvantages to using cationic finishes: the first is that wet-rub fastness does not measure up to the performance of anionic counterparts. This is not necessarily a problem provided that it is considered when deciding on the finishing system to be used.

The second is that, because of the softness of the finish film, print retention is usually poor. Where this is important to the continued good looks of the leather, the finish can be cross-linked to improve its Performance.

There are three choices of approach to final finishing of the leather:

* A fully cationic finish is achieved by using only cationic products in the base coat and subsequent conventional top coats.

* A semi-cationic or multi-charge finish using a combination of cationic, non-ionic and even anionic Products for upgrading using a more conventional type of finish.

* Sandwich finishes are finishes in which a fully cationic sealer coat is followed by anionic conventional finish coats to give maximum upgrading on very low quality leathers. For this type of finish, Butadiene resins must not be used in the base coat as these causes inter coat adhesion problems. The incorporation of non-ionic acrylic resins in the sealer coat is recommended for improving inter-coat adhesion as this reduces the possibility of over-sealing and acts as a 'chemical bridge' to subsequent anionic coats.

Using cationic technology, low selection crust material can be upgraded into a competitively priced, saleable article, natural looking and with acceptable physical properties [17].

Chapter three

3. Materials and Methods

3.1 Raw Materials Leather Chemicals and Reagents

Wet-salted Ethiopian and Indian raw hide, different leather chemicals from soaking to finishing (see Annex 3-8), laboratory grade chemicals such as sulphuric acid, nitric acid, hydrochloric acid, ethanol, diethyl ether, chloraminT, PDAB (paradimethyl amino benzaldehyde), sodium hydroxide pellet, potassium sulphate, copper sulphate, boric acid and different indicators which are necessary for determination of hydroxyprolin, nitrogen, fat and chrome content of the leather in different stages.

3.1.1 Equipments

Leather processing equipments from soaking to finishing such as pit, paddle, drum, fleshing machine, summing machine, splitting machine, shaving machine, setting out machine, overhead dryer, stacking machine, buffing machine ,spray gun, ironing machine.

And different laboratory equipments like Analytical Weighing balance, sample preserving refrigerator, thermometer, water bath shaker, desiccators, measuring cylinder, burettes, micro pipettes, heating mantle, Sohxelet apparatus, Hot air heating oven, Kel-plus apparatus for nitrogen determination, different sized standard measuring flasks, fume hood, UV-spectrophotometer, light microscope, scanning electron microscope (SEM), universal testing machine (for testing of tensile strength, %elongation, and tear strength),ball brust testing machine and rub fastness testing machine.

3.1.2 Methods

In order to have better understanding of Ethiopian cow hide nitrogen content of the raw hide will determine using "Standard Test Method for Nitrogen Content (Kjeldal) and Hide Substance Content of Leather", ASTM International, West Conshohocken, Hydroxyproline estimation using Woessner JF (1993), The determination of hydroxyproline in tissue and protein samples containing small portion of this amino acid, pp 440-447, fat content of the raw hide, chrome content of wet blue, Histological examination in raw and lime stage, scanning electron microscope analysis (SEM) for the crust leather, grain surface pattern for crust and finished leather using stereo microscope and many number of processing trials including physical test will be done to standardize suitable wet-finishing and finishing process technology.

3.1.2.1 Nitrogen Content Determination

KEL PLUS NITROGEN ESTIMATION SYSTEM

DIGESTION

1. Switch on the system
2. Initially pre-heat the digestion unit up to 350 °C
3. Take the sample in 250 ml Macro DTL tube
4. Liquid: - 2 g, powder: - 0.2 g to 0.3 g(in the case of raw hide the hair was removed by blade carefully and 0.5g was measured and put in the tube)
5. Liquid sample should be at room temperature
6. Powder sample should be moisture free
7. Note down the sample weight (W)
8. Then add 3 g to 4 g of catalyst mixture. [5:1 (Potassium Sulphate: Copper Sulphate)]
9. Add 20ml of Conc. H_2SO_4
10. Load the sample in the digestion unit with manifold.
11. Switch on the LEL VAC system or connect tap water with maximum pressure for KEL FLOW system
12. Now increase the temperature to 420 °C
13. Digestion will take 1 to 1.5 hour depending on the type of sample used.
14. A clear green color indicates that the digestion of the sample is over
15. Keep the sample in the cooling rack for cooling.
16. Cooling will take about half an hour

DISTILLATION

1. Switch on the system
2. Prepare the solution (4% Boric Acid, 40% Alkali, 0.1 N HCl)
3. Check the distilled water tank (Water level, Tap and Cap)

4. Load the alkali, Boric acid and $KMnO_4$ (KMnO4 was not necessary in the case of hide sample) to the system through silicon hoses provided at the back of the equipment while you wait for the READY signal.

5. Take 25 ml Boric acid with mixed indicator (Methyl red-Methylene blue mixed indicator) in a 250 ml conical flask and place at the receiver end.
6. Load the sample tube in sample side.
7. Before starting the sample testing open the tap water for cooling purpose (Check the INLET and OUTLET)
8. Start the sample testing after getting the READY signal.
   Add 40 ml of the 40% alkali (until dark brown color appears)
9. Now start the process. (Timing based on the sample's Nitrogen value,9 minute were taken for this particular sample),then after the dark brown color of the sample changes to green
10. During the process, liquid ammonia will collect in the Boric Acid and the Boric acid's color will change based on the indicator used, mix end indicator were used and green color was developed in the boric acid containing tube.
11. After completion of the process remove the conical flask from the receiver end and then titrate it.
12. The DTL tube from the sample side can now be removed.

TITRATION

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

3.1.2.2 Hydroxyproline estimation

20 mg of both Ethiopian and Indian wet salted cow hide were weighed after main soaking from butt, neck and belly area. Then it was placed in hydrolysis tube. To this 1 ml of 6N **HCl** was added. After this the tubes were sealed in glass blowing section and allowed to incubate at 100 ^{o}C in hot air oven for 20 hours. Then the hydrolysis tubes were disealed. The hydrolyzed samples were taken and placed in china dish and were allowed to evaporate in water bath at 60^{o}c. The evaporation of acid was continued by adding distilled water to the china dish until the full elimination of acid

smell (the pH reaches 7). The final solution was made to **10 ml** by adding distilled water using standard flask. From this solution **20µl** was taken and made up to 2000µl by adding distilled water, after this 1ml chloramine T was added. Then it was incubated for 20 min at room temperature. 1 ml of perchloric 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 then after it was allowed to cool by using tap water and this solution was taken for measurement of absorbance at 557 nm in UV Vis spectrophotometer.

Procedure for preparation of standards

10mg of L-hydroxyproline was measured and dissolved in 0.001N, 100 ml hydrochloric acid. From this stack solution different standard hydroxyproline solution was prepared from a known concentration (i.e. 0.1mg/1ml). From this known hydroxyproline solution 20, 40, 60, 80,100 and 120µl were taken and placed in test tubes. Each test tube was made up to 2000 µl 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 and allow to cool using tap water. 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: -** 1.41 g chloramine T, 20 ml water, 30 ml methyl cellosolve and 50 ml buffer solution.

PDAB: - 20 g PDAB dissolved in 100 ml of 2 methoxyl ethanol

Perchloric acid: - 27 ml of 70% percholoric acid and make up to 100 ml with distilled water.

3.1.2.3 Fat Content determination

5g of both Ethiopian and Indian raw hide from butt portion respectively were taken after carefully removing the hair by blade. Using sox-let apparatus the sample was allowed for the extraction of fats by petroleum ether as a solvent for 5-hour at 70^{o}c, the experiment was done in triplicate.

The weight of empty round bottom flask was measured and recorded. After extraction and fully evaporation of the solvent the weight was recorded also and the results were calculated using the following formula.

$$\%fat = \frac{weight\ of\ fat}{dry\ weight\ of\ the\ sample} x100$$

3.1.2.4 Chrome content Determination

0.5 gram of wet blue sample from butt portion of both Indian and Ethiopian leather was cut from trial one, and place in conical flask. To that the following acid are added for digestion.

Nitric acid =5ml

Sulphuric acid =3.5ml

Perchloric acid= 11.5 ml

Then using heating mantle, adjust temperature 90^{o}c digestion was continue inside hood till green color changes to orange. Allow to cool and add 10 ml distilled water and boil for another 5-minute fro fully digestion of the sample. switch off the heater and allow to cool, transfer to 100ml standard flask and fill distilled water till the mark, from this stack solution take out 10ml,add sodium hydroxide pellet till PH around 12 as well orange color changes to green. Then made the solution to 50ml. absorbance of the sample was read at 372nm wavelength.

Thus chrome content of wet blue, as $\%Cr_2O_3 = \frac{Od\ value\ x\ 152\ x52\ x100\ x\ \ 50\ x\ 100}{4820\ \ x\ \ \ \ 104\ x\ \ \ \ \ \ \ \ 0.5\ x\ \ \ 10\ x\ \ 1000}$

3.1.2.5 Histological Examination of Raw material

Samples for histological analysis were cut from butt portion of both Ethiopian and Indian raw hide after soaking and liming stage before fleshing. Samples before staining were preserved using 10% formalin solution. H and E (hematoxylin and

Eosin) staining was done at Indian veterinary college. The procedures for sample preparations are as follow:-

3.1.2.5.1 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 .

3.1.2.5.2 Dehydration

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

1. Sample tissue was removed from formalin
2. Washed in running tap water for 3 hours
3. Placed in 30% alcohol solution for 3 hours
4. Placed in 50% alcohol solution for 3 hours
5. Placed in 70% alcohol solution and was left for overnight
6. Placed in 90% alcohol solution for 3 hours
7. Placed in 95% alcohol solution for 3 hours
8. Placed in 100% alcohol solution for 1 hours
9. Placed in 100% alcohol solution for 1 hours
10. Placed in 100% alcohol solution for 1 hours

3.1.2.5.3 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.

3.1.2.5.4 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.

3.1.2.5.5 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.

3.1.2.5.6 Trimming

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

3.1.2.5.7 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.

3.1.2.5.8 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.

3.1.2.5.9 Mounting and spreading of ribbons

The long ribbon is cut in to pieces of small length which could be conveniently accommodated on a slide with sufficient space on the side of the slide for labelling. 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.

3.1.2.5.10 Staining

1. The slides were first deparaffinised by keeping them in xylene for nearly 2-3minutes with two changes

2. Hydration: the deparaffinised 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 alum haematoxylin of choice for nearly 2 to 5 minutes.

4. Wash well in running tap water. If over stained, distain 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.

3.1.2.6 Scanning Electron Microscope study for the crust leather (SEM)

Crust leather samples were cut from butt portion of both Ethiopian and Indian.

3.1.2.6.1 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.

3.1.2.6.2 Dehydration

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

After dehydration with acetone the tissues samples are further treated with different percent of Hexamethyl disilazane (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.

3.1.2.7 Physical Testing Method

3.1.2.7.1 Tensile Strength and Elongation at Break-ISO 3376/IUP6

Tensile strength is the ultimate strength of the leather that includes grain, corium and flesh layers. In this test elongation property of the leather can also be measured. Permanent elongation that is responsible for permanent set (plastic character) of the leather also can be tested.

Tensile strength

Tensile strength is defined as strength of material in terms of force per unit area of cross section while applying force in linear direction.

$$\text{Tensile strength} = \frac{\text{Force (N)}}{\text{Area (Width in mm x Thickness in mm)}}$$

Test Procedure:

Measure the thickness of each test piece to the nearest 0.01 mm using thickness gauge at three places on grain side of the leather test specimen and record the average thickness. Measure the width of the leather using a steel rule. Calculate the area of cross-section on the test specimen by multiplying its width and thickness. Set the distance between the grips of the tensile tester 50 mm for standard test specimen. Insert the test specimen between the grips, tight the grips with sufficient pressure. Operate the tensile testing machine at a speed of 100±2 mm/minute until the leather sample breaks. Stop the machine immediately, measure the distance between the two grips and record the maximum force found at leather break.

Calculation

$$\text{Tensile strength, N/mm}^2 = \frac{\text{Breaking load (N)}}{\text{Width (mm) x Thickness (mm)}}$$

$$\text{\% Elongation at break} = \frac{(b-a) \times 100}{a}$$

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

Tensile strength can also be expressed in metric units as Kg/cm^2 and in imperial units as lbf/inch^2.

Table 1 Guide lines for tensile and elongation at break

S.N	Property	Units	Upper	Lining	Furniture	Goods
1	Tensile strength	N/mm2	15.0	15.0	10.0	10.0
2.	Elongation at break	%	40-80	40-80	40-80	40-80

3.1.2.7.2 Tear Strength-ISO 3377/IUP 8

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

Double-edge Tear strength

Cut six test specimen (three test specimen from along direction and three test specimen from across directions) using a cutting knife 50 mm x 25 mm size having a central slot , Condition the test specimen for 48 hours and measure the thickness.

Insert one of the test specimen through the slit into the sample holding “L” clamps that are fixed to the tensile tester. Conduct the test by operating the tensile tester at the rate of 100 ± 10 mm/ minute speed until the test piece is torn apart. Record the maximum force. Continue the test for remaining test specimen.

$$\text{Tear strength} = \frac{\text{Maximum tear force (N)}}{\text{Thickness (mm)}}$$

Table 2 tear and elongation at break minimum requirements

S.N	Property	Units	Requirement
1	Tear strength		
	Light use upper	N	40
	Heavy use upper	N	100
	Safety shoe upper	N	120
	Lining leather	N	30
	Garment leather	N	15
	Furniture leather	N	50
	Goods leather	N	50
	Glove leather	N	15
2.	Elongation at break	%	40-80

3.1.2.7.3 Grain Crack Properties

The grain of the leather is subjected to more stain in shoe making process. Therefore the grain is liable to exhibit grain cracks on the shoe surface especially at toe area. This may be due to filling of more re-tanning materials into the leather matrix to give sufficient substance. Rapid tanning practices over loads the grain side instead of allowing the tanning chemicals, fat-liquors and dyes to move into the entire thickness of leather. This is also a reason for exhibiting grain cracks in shoe making process. This grain crack failure cannot be visualized by simple folding and flexing. Therefore selection of leather for shoe making has to be made after testing the leather for grain crack load and distension properties using standard test equipment called lastometer. In the shoe manufacturing places “instant lastometers: are used before cutting the components from the leather for making shoe upper.

LASTOMETER TEST – ISO 3379/ IUP 9 /SATRA TM 24

This test method is intended to determine the grain crack force and distension of leather when used for shoe upper.

Principle

Shoe upper leather often shows slight crack in the toe area at the time of lasting operation in-spite of the leather has good tensile and tear strength properties. This is due to weak grain surface characteristics of leather by more filling and loading of tanning and re-tanning materials in the grain side. Therefore a laboratory test is developed to determine the grain crack distension and load when a circular leather test specimen is secured in between two circular rings of 25 mm diameter and stretched with the help of a spherical head. Unto grain crack appears on the grain surface of leather.

Guide lines: - 1. Distension : Minimum 7 mm
2. Grain crack load: Minimum 200 N

3.1.2.7.4 Colour Fastness to Circular Rubbing - BS 1006 UK LC SLF 5

This method is intended to assess the degree of damage (marring) and transfer of a material's surface color or finish onto the rubbing felt during mild dry and wet rubbing.

A specimen of finished leather is rubbed in a circular fashion using a white wool felt of 25 mm diameter under force. After a specified number of cycles of rubbing, the extent of damage of the color/finish and color transfer to the rubbing felt are assessed with grey scales.

Dry-Rub fastness

Cut one test specimen about 75 mm square from the finished leather. Place the test specimen on the horizontal platform. Secure a felt pad on to the spindle and bring in contact with the test specimen. Adjust the weight to24.5±0.5N; operate the machine for specific number of revolutions. Stop the machine in between for a few seconds to avoid thermal damage caused to the finish of the leather. Continue the test until specified number of cycles. Remove the leather and felt pad from the machine. Place the test specimen and felt pad inside the light cabinet to view the materials at 45^o angle. Assess for change in color (marring) grade for leather and transfer of color (degree of staining) with the help of respective grey scales. Generally this test is conducted for the following order of cycles, 8,16,32,64,128,**256,512** and 1026.The number of cycles and grade of color change and color transfer are depend up to the type of leather and customer's requirement.

Wet-Rub Fastness

Immerse a felt pad in cold water; boil for 1 minute for complete wetting of the felt pad. Cool, remove excess water from the wet felt by slight squeezing, attach to the spindle, adjust the weight to 7.1 N forces, bring the spindle into contact with leather specimen, weight for 60 seconds, and operate the machine to the desired number of cycles. Assess for color change and color transfer after complete drying of the samples.

Chapter four

4. Results and Discussions

4.1. Resuts

4.1.1 Determination of Hydroxyproline in raw stage of both Ethiopian and Indian cow hides

20 mg of both Ethiopian and Indian wet salted cow hides were weighed after main soaking from butt, neck and belly area, and the hair was carefully removed by blade before weighing and the experiment was conducted based on the procedure mentioned earlier. The standard graph was prepared using 10mg/100mL stock solution. Different concentrations of hydroxyproline used and the respective OD values at 557 nm are provided in Table 3.

Table 3 concentration of hypo in the solution

µg/1000µl	**OD Value**
2	0.114
4	0.241
6	0.432
8	0.576
10	0.695
12	0.856

The calibration/standard graph for determining the hydroxyproline content in the hide sample is provided in Fig1.

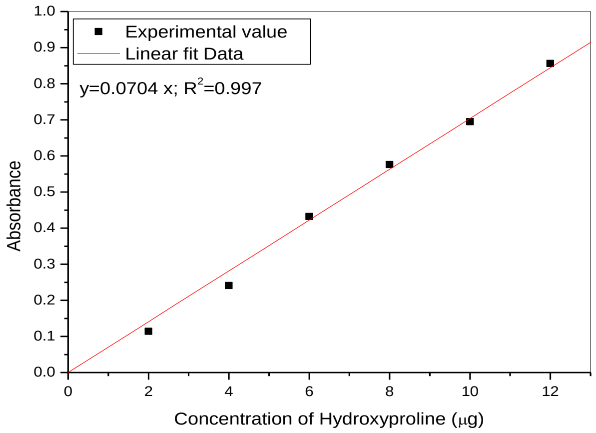


Fig1: Standard Graph for Hydroxyproline estimation

It could be observed from the figure that the hydroxyproline content can be determined using the following equation

From the formula y=0.0704x, where y is the absorbance value and x is the hydroxyproline concentration. R^2 is correlation coefficient it should be 0.997 for correct fit graph.Table 4 shows the hydroxyproline concentration of Ethiopian and Indian cow hides.

Table 4: Concentration of Hydroxyprolin in mg/mg of dry tissue

Samples	% moisture	Dry weight of the hides (mg)	OD at 557 nm	Hydroxyproline concentration (mg/mg of dry hide)	Collagen content (%)
E butt	51.68	9.664	0.177	0.063	47.3
E neck	51.68	9.664	0.153	0.055	41.5
E belly	51.68	9.664	0.132	0.047	35
I butt	52.34	9.532	0.136	0.048	36.4
I neck	52.34	9.532	0.096	0.034	26
I belly	52.34	9.532	0.112	0.04	30.2

It could be observed from the table that the average hydroxyproline content of the Ethiopian cow hides, taking in to account the values from neck, belly and butt was 0.055mg of hydroxyproline per mg of hides taken (dry weight). Similarly, the average hydroxyproline content of the Indian cow hides, taking in to account the values from neck, belly and butt was 0.041mg of hydroxyproline per mg of hides taken (dry weight). Thus, it could be seen that the collagen content (hypo conc. multiply by 7.54) of Ethiopian cow hide (41.5%) is higher than that of the counterpart Indian cow hide (30.7%) and it is possible to conclude that the former has more reactive site than the later one.

4.1.2 Nitrogen percentage estimation of Ethiopian and Indian raw cow hides

0.5 gm of both Ethiopian and Indian hides was cut for the determination of nitrogen content after main soaking and removing the hair by blade carefully. The nitrogen content of both raw hide samples was determined using the procedure mentioned before and the following average results were found.

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

Where TV- Titrant volume (volume of HCl consumed by the sample solution)

BV-blank volume (volume of HCl consumed by blank solution)

W- weight of the sample before digestion

Table 5 volume of HCl used for titration and %N of raw hides

S. No.	Sample	Dry weight of the sample(g)	Titrant volume (TV) in ml	Nitrogen (%)
1	E butt	0.2416	33.1	18.61
2	E belly	0.2416	29	16.24
3	E neck	0.2416	25.6	14.27
4	I butt	0.2383	33	18.81
5	I belly	0.2383	26.5	14.99
6	I neck	0.2383	25.4	14.35

It could be observed from the table that the average % nitrogen content of the Ethiopian cow hides, taking in to account the values from neck, belly and butt was 16.37% (dry weight). Similarly, the average % nitrogen content of the Indian cow hides, taking in to account the values from neck, belly and butt was 16.05% (dry weight). Thus, it could be seen that the hide substance (%N multiplied by 5.62 as conversion factor) content of Ethiopian and Indian cow hide is 92 and 90.2%, respectively. From the calculations, it could be inferred that increased hide substance value in Ethiopian cow hides reveals that it has more protein fiber content than that of Indian cow hides, which is in concordance with the earlier collagen content results.

4.1.3 Fat Content Determination of the Raw Material

5g of both Ethiopian and Indian raw hide from butt portion respectively were taken after carefully removing the hair by blade. Using soxhlet apparatus the sample was allowed for the extraction of fats by using petroleum ether as a solvent for 5-hour at 70^{o}C, the experiment was done in triplicate.

The weight of empty round bottom flask was measured and recorded, after extraction and fully evaporation of the solvent the weight was recorded and the following result were found. $\%\text{fat} = \frac{weight\ of\ fat}{dry\ weight\ of\ the\ sample} x100$

Table 6 fat content of raw hides

Sample name	Dry weight of the samples(g)	% of fats
Ethiopian raw hide	2.416	3.146
Indian raw hide	2.383	2.291

From the result of % fat it is clear that Ethiopian hide has more amount of fat content than the counterpart of Indian cow hides. Hence, it is required to do proper degreasing before tanning. Degreasing becomes a critical operation to have optimum penetration of post tanning chemicals so as to gain good finished product, which can fulfill buyer's requirement.

4.1.4 Process recipe from raw to dyed crust, Experiment 1

When the hide is processed in to leather, the subsequent removal of non-collagen components may create empty space or voids in the structure between fibrous layers, particularly between the grain and corium. These voids or open spaces may be exacerbated or enlarged by a number of leather processing factors such as bacterial degradation in the raw stack; excessive opening up in the beam-house and mechanical stressing this can produce a very loose structure called **Looseness** [18].

To assess whether Ethiopian cow hide has the problem of looseness or not Ethiopian wet salted raw hide and Indian wet salted raw hide were processed as upper crust employing conventional process (trial 1) as given in Annex 3. This trail was performed by skipping degreasing process in-order to see the effect of fat on the quality of wet blue as well it's consequence on post tanning process. An assessment on the wet blue leather shows that pink colors was developed due to reaction between fat and chrome salt. The crust also suffers with improper dye uniformity and less substance due to lack of penetration of re-tanning material because of the presence of fat. The organoleptic study reveals that no looseness found on the crust from Ethiopian hide.

Experiment 1

Details of the process carried out

- No degreasing
- Conventional chrome tanning was used
- Patches (pink color formed on the wet blue)
- Shaved thickness 0.9-1.0mm
- Crusting:16% re-tanning and 10% fat -liquoring

Observations

- Dye not uniformly distributed, which might be due to the presence of grease
- Less substance, due to improper penetration of re-tanning material
- No-looseness
- More defect
- Very soft leather

Suggestions

- Degreasing should be done
- Shaved thickness,1.2-1.3mm
- Re-tanning to be increased to 20%
- Fatliqour should be reduced to 8%
- Black dyestuff to be used.

4.1.4.1 Organoleptic properties

The properties of the cow dyed crust leather, such as general appearance, grain tightness, smoothness, fullness, softness, roundness and the uniformity of colours were assessed by experienced experts. The grade of 0-10 was fixed for each properties and the result are provided in Fig 2.

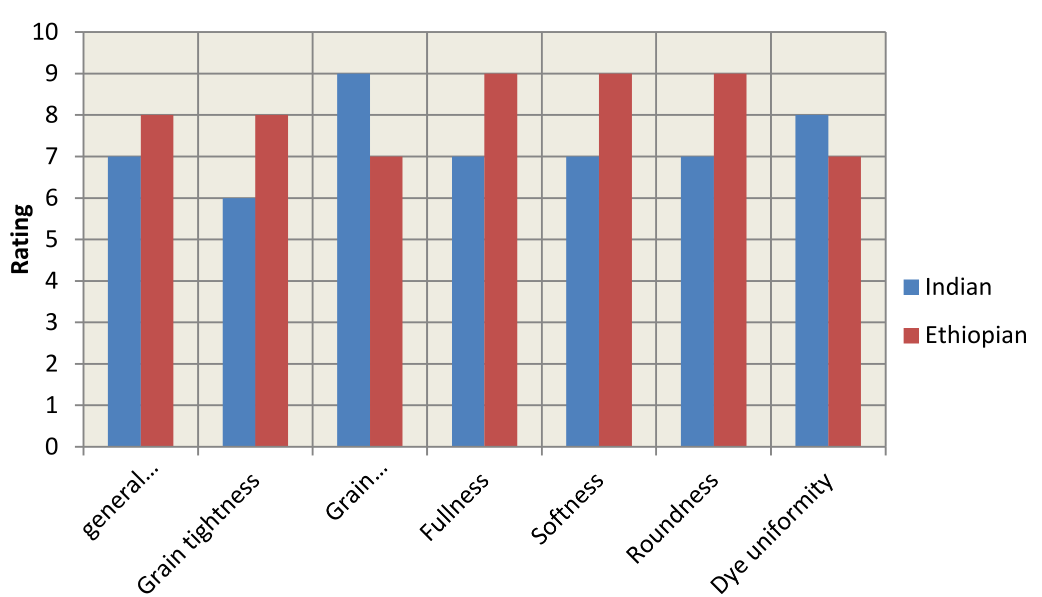


Fig 2 Organoleptic properties of both Indian and Ethiopian dyed crust

During comparison of the organoleptic properties for both crusts of Indian and Ethiopian cow leathers, dye uniformity is less for Ethiopian crust; this is mainly due to absence of degreasing in this trial. To overcome the problem, an experiment (trial 2) involving degreasing was suggested (**Annex-4**). In the case of grain smoothness it is better for Indian cow leathers owing to fine and more number of hair pore, which gives smooth grain, however Ethiopian cow has less number of hair pore, which results in less smoother surface when compared to the counterpart. In contrary, other properties for Indian crust are less mainly due to poor substance raw material. For Indian raw hide to be poor in substance different reason may be raised such as breed, climate, age etc, the increment for thickness after crusting was measured using thickness gauge and the following results were found.

Table 7 thickness of wet-blue and crust

Sample name	Wet-blue shaved thickness(mm)	Crust thickness(mm)	Gained thickness(mm)
Ethiopian	1.0±0.1	1.5±0.1	0.4-0.5
Indian	1.0±0.1	1.2± 0.1	0.1-0.3

Remarks: after crusting using 16% re-tanning and 12% fat-liquoring the increment for thickness in the case of Ethiopian cow crust is more than Indian this is because substance-wise the former is better than the later. Specifically, this result comply with the claim for higher content of collagen for Ethiopian raw material, the higher the collagen content the better in reaction with chemicals and the better in resulting full crust leather.

4.1.5 Grain surface pattern study

In-order to study the surface finesse or coarseness of the Hide, grain surface pattern was studied using stereo microscope. Samples were cut from butt portion of both Ethiopian and Indian crust leather. The grain surface pattern for the crust from experiment-1 was observed through stereo microscope, 40X magnification was used, and the following result was found.

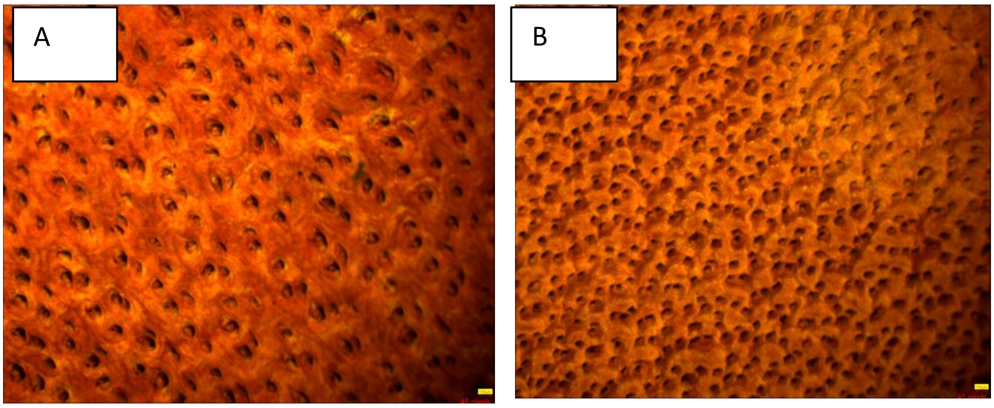


Fig. 3: Microscopic image of crust, Ethiopian (A) and Indian (B)

Dyed crust leathers were observed under the microscope and the number of hair pores were counted at three place and the average results are provided in Table. It could be observed that the Indian cow hides have more hair pores than the Ethiopan cow hides.

Table 8 Hair pore count

Crust leather	**Average hair pore per sq.inch**
Ethiopian crust	10,533±2
Indian crust	26,784±1

The number of hair pore for Ethiopian crust is lower than that of Indian per sq.inch indicating that it has not so smooth grain compared with Indian. From this result the type of choose-able product that can be made out of our raw material is upper and leather goods.

4.1.6 Chromic oxide (Cr_2O_3) content of the wet blue Leather

0.5 gram of wet blue sample from butt portion of both Indian and Ethiopian leather was cut from trial one, for the determination of chrome content in terms of chromic oxide as per the procedure mentioned in 3.3.3, the experiment was done in triplicate for both samples and absorbance of the prepared solution were found as follow:-

Absorbance of the sample solution were read at 372nm wavelength using uv-vis spectroscopy

$$\%Cr_2O_3 = \frac{ODValue\ x152\ x52}{4820\ x104\ x\ Sample\ weight\ x1000}\ x\ dilution\ \ factor\ x100$$

Table 9 absorbance value for chromic oxide content of wet blue samples

Sample name	Average Absorbance value	Dry weight of the sample(g)	$\%Cr_2O_3$ based on dry weight
Ethiopian wet blue leather	0.339	0.23	5.81
Indian wet-blue leather	0.8796	0.212	3.27

4.1.7 Histological Examination of the Hide at Raw and Liming stage

Samples for histological analysis were cut from butt portion of both Ethiopian and Indian raw hide after soaking and liming stage before fleshing. Hair is carefully removed by blade from raw sample, Samples before staining were preserved using 10% formalin solution. H and E (hematoxylin and Eosin) staining was done at Indian veterinary college and the following microscopic image was presented.

Ethiopian (A) and Indian (B) **raw hide**, **Entire cross section,** thickness of the slice sample was 25micron and the image was focused with 40x magnification of light microscope.

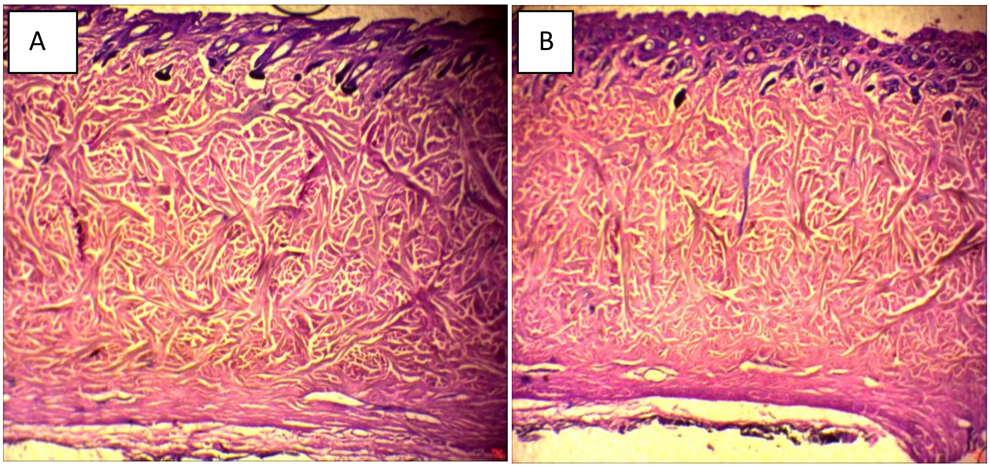


Fig-4: histological image of raw, Entire cross section

Table-10-thickness of the grain, corium and flesh as well as grain –corium ratio of both Ethiopian and Indian hide at raw stage.

The thickness for grain, corium and flesh were measured at three different region of the histological image using paint software and average of the three results were taken and converted to mm unit.

Sample origin	Grain thickness (mm)	Corium thickness (mm)	Flesh thickness (mm)	Total thickness(mm)	Grain to corium ratio
Ethiopian raw hide	0.41	1.87	0.41	2.68	0.22
Indian raw hide	0.42	1.69	0.44	2.54	0.25

Ethiopian (C) and Indian (D) **limed pelt, grain-corium image**, thickness of the sample was 15micron, and the image was focused with 40 x magnifications of light microscope.

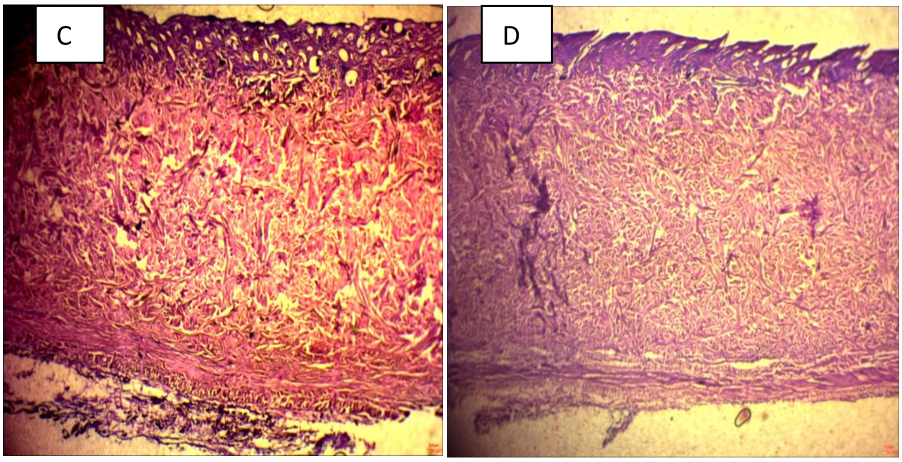


Fig-5: histological image of limed pelt, Entire cross section

4.1.8 SEM (Scanning Electron Microscope) Image of crust leather

4.1.8.1 Surface image of the crust using SEM

Surface Image of crust leather at butt portion was observed using scanning Electron microscope using 100 x magnifications, Ethiopian (K) and Indian (S).

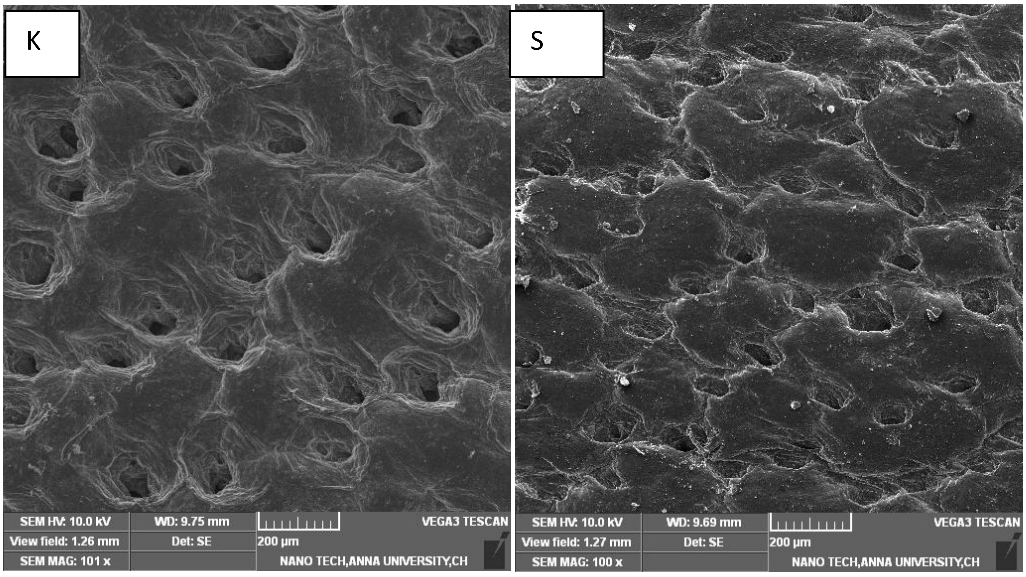


Fig-6: SEM image, crust surface

The surface image of the crust clearly shows that surface of the crust leather for Ethiopian has less number of hair pores and it seems course surface, whereas Indian crust has more number of hair pores and fine surface. The result of SEM complies with the result of grain surface pattern of stereo microscope study.

4.1.8.2 Cross-sectional image of crust using SEM

Cross-sectional image of the crust leathers were observed at 300x magnification for both Ethiopian (N) and Indian (R) crust at butt portion.

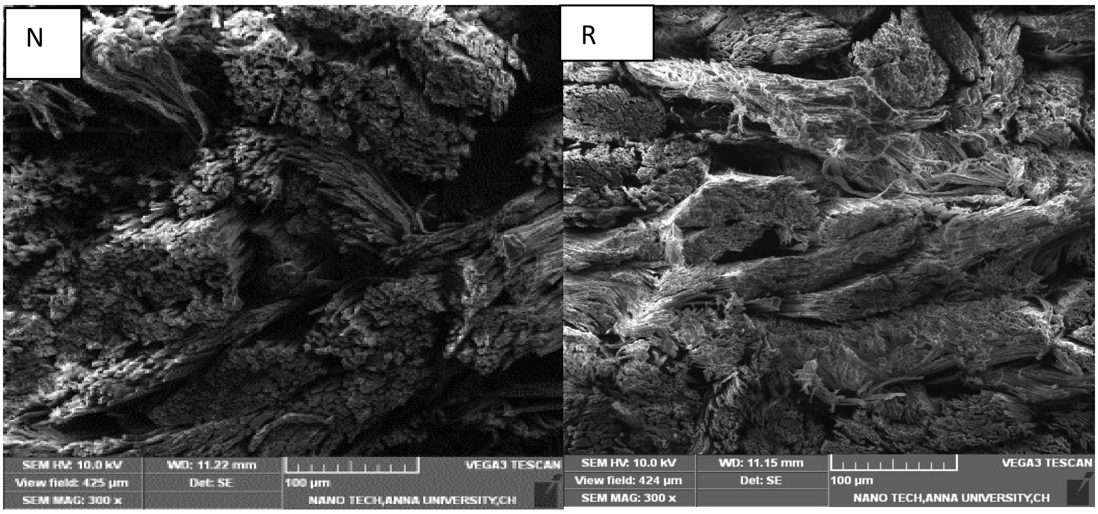


Fig-7: SEM image, crust cross section

The result of cross-sectional image of the crusts at 300x magnification reveals that the fibers are compact and less in finesse in the case of Ethiopian crust, but in the case of Indian fibers are fine and looks loose.

4.1.9 Process Recipe from Raw to Crust, Experiment-2

After a clear idea was developed about the nature of Ethiopian cow hide from the previous study in comparison with the counterpart Indian cow hide at raw, lime, wet-blue and crust stage it was arrived at to a conclusion that the main problem, which should be address is avoiding surface blemishes to upgrade the finished leather.

For the idea of upgrading the leather starting from the crusting stage cationic liquid pigment (2k black) and wet end protein filler (sellcomfill) were used to make upper leather. For the detail of the chemical (see annex 5).

1% pigment + 1% filler were used after fixation of all re-tanning chemicals before cationic topping for the experimental leather. To assess the degree of surface defect coverage for the experimental crust leather, samples were cut from butt portion of both experimental and control crust and observed using stereo microscope and the micrograph were presented as follow:-

Microscopic image for the control crust (P) in comparison with the experimental (Q), with 2x10 magnifications.

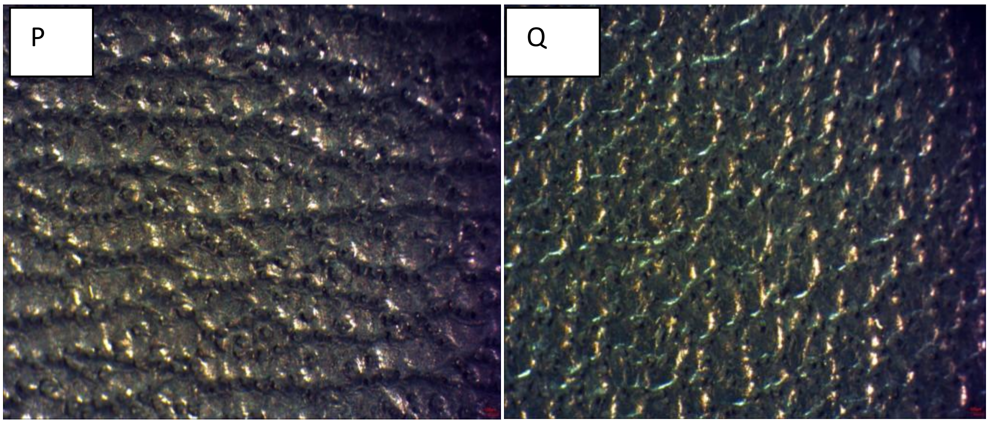


Fig-8: surface image of crust using stereo-microscope, control (P) and experimental (Q)

The micrograph image shows that a better coating of the surface was achieved in the case of experimental crust leather due to filler wax and pigment resulting in better defect coverage.

4.1.9.1 Organoleptic study for the crust from experiment-2

The following properties are assessed by experienced experts for the dyed crust.

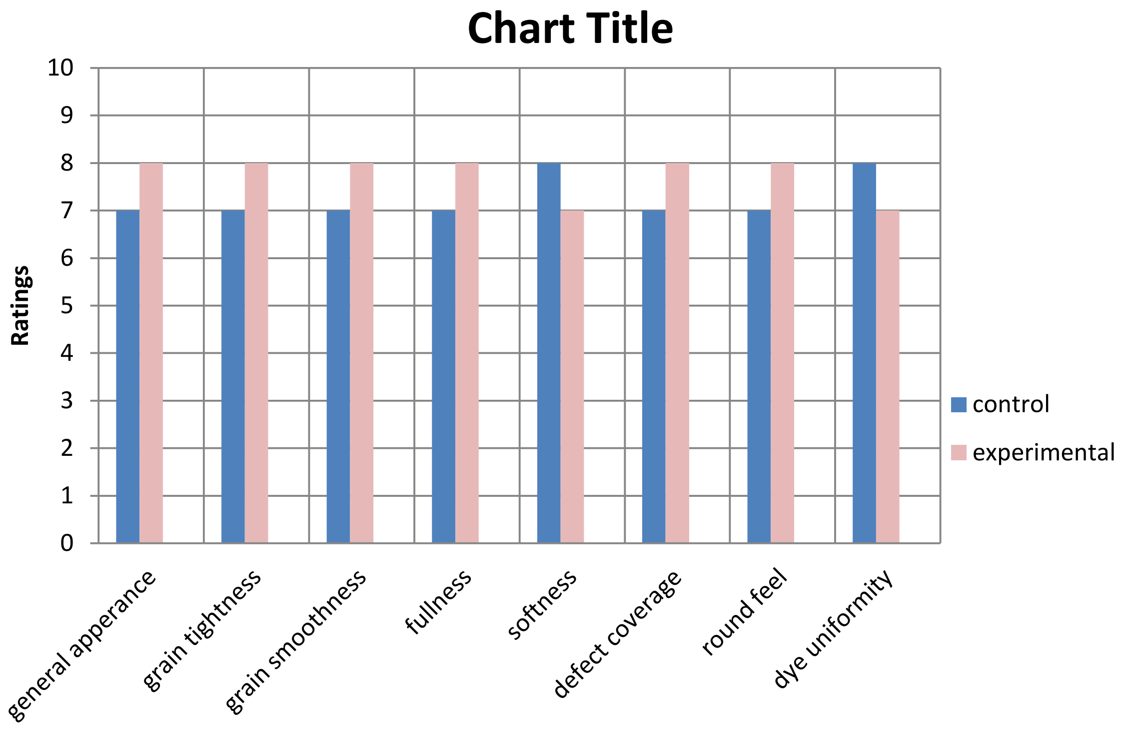


Fig -9 : organoleptic properties for the dyed crust from experiment -2

4.1.9.2 Physical properties for the dyed crust from Experiment-2

Tensile strength, % elongation, tear strength and grain crackiness were tested, for all physical test samples were conditioned for 48 hours at 20^{o}c temperature and 65% humidity, and the results are as follow.

4.1.9.2.1 Grain crackiness test results

Dyed crust from trail-2, both experimental and control as well Indian crust were tested for the grain crackiness and the following results were found.

Table-11 physical test result for the crust leather

Sample ID	Load(kg)	Distance(mm)
Ec1	42	6.08
Ec2	23	5.2
Ec3	30	5.9
means	31.67	5.73
Eexp1	19	5.44
Eexp2	42	7.34
Eexp3	28	6.10

means	29.67	6.3
Ic1	22	5.27
Ic2	24	5.53
Ic3	26	5.27
means	24	5.36

The physical test result of ball burst (grain crackiness) shows that the chemicals used to avoid surface blemishes have not adverse effect on the grain strength of the crust leather.

Where: - Ec- Ethiopian crust control

Eexp-Ethiopian crust experimental

Ic- Indian crust conventional process

4.1.9.2.2 Double-Edge tear strength test results

Table-12 Double edge tears strength test results

Sample ID	Maximum load(N)	Maximum load (Kgf)	Tear strength(N/mm)	Thickness(mm)	Direction
Ec1	100.47	10.25	55.82	1.80	Along
Ec2	96.57	9.85	52.48	1.84	Along
Ec3	120.78	12.32	67.10	1.80	Along
mean	105.94	10.81	58.47	1.8	
Ec4	84.11	8.58	45.22	1.86	Across
Ec5	97.54	9.95	51.61	1.89	Across
Ec6	98.28	10.02	53.70	1.83	Across
Mean	*99.62*	*10.16*	*54.32*	*1.84*	
Eexp1	108.05	11.02	60.70	1.78	Along
Eexp2	121.36	12.38	68.18	1.78	Along
Eexp3	95.85	9.77	52.09	1.84	Along
Mean	108.42	11.057	60.32	1.8	
Eexp4	93.23	9.51	50.12	1.86	Across
Eexp5	103.94	10.60	57.74	1.80	Across

Eexp6	101.51	10.35	55.47	1.83	Across
Mean	*99.23*	*10.15*	*54.44*	*1.83*	
Ic1	99.81	10.18	69.31	1.44	Along
Ic2	96.77	9.87	68.15	1.42	Along
Ic3	99.56	10.15	69.14	1.44	Along
Mean	98.71	10.07	68.87	1.43	
Ic4	130.55	13.31	89.42	1.46	Across
Ic5	110.65	11.28	74.26	1.49	Across
Ic6	112.64	11.49	74.59	1.51	Across
Mean	*108.33*	*11.05*	*74.15*	*1.46*	

Summary table –13 for double-edge tears strength test results

Sample name	**Average Maximum load(N)**	**Average Maximum load (Kgf)**	**AverageTear strength(N/mm)**	**Average thickness**
Ethiopian crust, control	102.78	10.49	56.5	1.82
Ethiopian crust, experimental	103.83	10.6	57.38	1.82
Indian crust, conventional	103.52	10.56	71.51	1.45

Both Controls (Ethiopian and Indian) and experimental crust leathers achieve more than the minimum requirement of light shoe upper tear strength of 40N/mm, even in the case of experimental crust it has better tear strength than that of the counterpart control crust leather.

4.1.9.2.3 Tensile Strength test results

Table-14 tensile and elongation at break test results

Sample Id	Maximum load(N)	Tensile strength(N/mm^2)	Elongation at break (%)	Extension at maximum load(mm)	Thickness	Direction
Ec1	342.69	19.25	47.67	23.83	1.78	Along
Ec2	333.58	19.62	42.33	21.17	1.70	Along
Ec3	337.55	19.74	44.33	22.17	1.71	Along
Mean	*337.94*	*19.54*	*44.78*	*22.39*	*1.73*	
Ec4	346.26	20.93	39.33	19.67	1.74	Across
Ec5	355.27	19.74	44.33	22.17	1.80	Across
Ec6	329.95	18.85	39.33	19.67	1.75	Across
Mean	*343.83*	*19.84*	*41.00*	*20.50*	*1.76*	
Eexp1	359.48	20.31	47.00	23.50	1.77	Along
Eexp2	262.55	14.59	37.00	18.50	1.80	Along
Eexp3	207.32	11.15	35.00	17.50	1.86	Along
Mean	276.47	15.35	39.67	19.83	1.81	
Eexp4	382.50	20.79	44.33	22.17	1.84	Across
Eexp5	327.41	17.42	41.33	20.67	1.88	Across
Eexp6	346.56	17.77	43.00	21.50	1.95	Across
Mean	*352.16*	*18.66*	*42.89*	*21.45*	*1.89*	
Ic1	308.93	21.34	39.00	19.50	1.45	Long
Ic2	318.37	21.37	45.00	22.50	1.49	Along
Ic3	288.53	19.24	44.33	22.17	1.50	Along
Mean	305.28	20.65	42.78	21.39	1.48	
Ic4	291.68	19.19	42.33	21.17	1.52	Across
Ic5	342.66	22.54	48.67	24.33	1.52	Across
Ic6	338.84	21.31	47.67	23.83	1.59	Across
Mean	*324.4*	*21*	*46.2*	*23.11*	*1.54*	

Summary table ---15 for the tensile strength test results

Sample name	Average maxi. load	Average tensile strength(N/mm^2)	Average elongation at break	Average extension at max. load	Average thickness
Ethiopian crust, control	340.89	19.69	42.89	21.45	1.75
Ethiopian crust, Experimental	314.32	17	41.28	20.64	1.85
Indian crust, conventional	314.84	20.83	44.5	22.25	1.51

Summary of the test result for tensile and elongation at break clearly shows that the result of the physical test for experimental crust of tensile and elongation at break (17N/mm^2 and 41.28%) are above the minimum requirement of 15N/mm^2 tensile and 40% elongation at break.

From all physical test of strength results for the experimental crusts it is convincible to conclude that the wet-end chemicals used for improving the leather quality at crust stage have not a negative effect on the strength property of the crust leather.

4.1.9.3 Finishing formulation for the dyed crust, Experiment-2

Both experimental and control crusts are finished using **cationic compact resin based** from **Sellam chemical company** and the formulations are as follow:-

Table 16 cationic compact resin based finishing formulation

Chemicals	**Solutions(in ml)**						**processes**
	1	2	3	4	5	6	
1. Clearing coat							2x spray

Anionic dye solution	50		30				Allow to dry
Water	900	350	540	495	895		
IPA	50	50	30				
2. Cationic base coat							3xspray,Roller haircell@100^{o}c and 120 pressure
SELCOM MK 6757		500					
CATIONIC PIGMENT		100					
3. Anionic season							2xspray, plate Haircell@80^{o}c,150 pressure
SELLCOM CA 1722			300				
ANIONIC PIGMENT			100				
4. Fixing							2xspray,Sandblast plate @80^{o}c,100pressure
MEDIUM SHINE LACQOR				200			
MATT LACQOR				300			
CROSS-LACQOR				5			
5. Top lacquer							1x spray plain plate @80^{o}c,100pressure
SELKHEM KW 0555					100		
SENSOL SW					5		

Where:-

- SELCOM MK 6757 - cationic compact resin
- SELCOM CA 1722 - anionic compact resin
- SELKHEM KW 0555 -cationic wax
- SENSOL SW- silicon Wax

4.1.9.3.1 Organoleptic properties for the finished leather

Experienced experts were assesed physically the following properties for both control and experimental finished leather. The average results were found and presented as follow:-

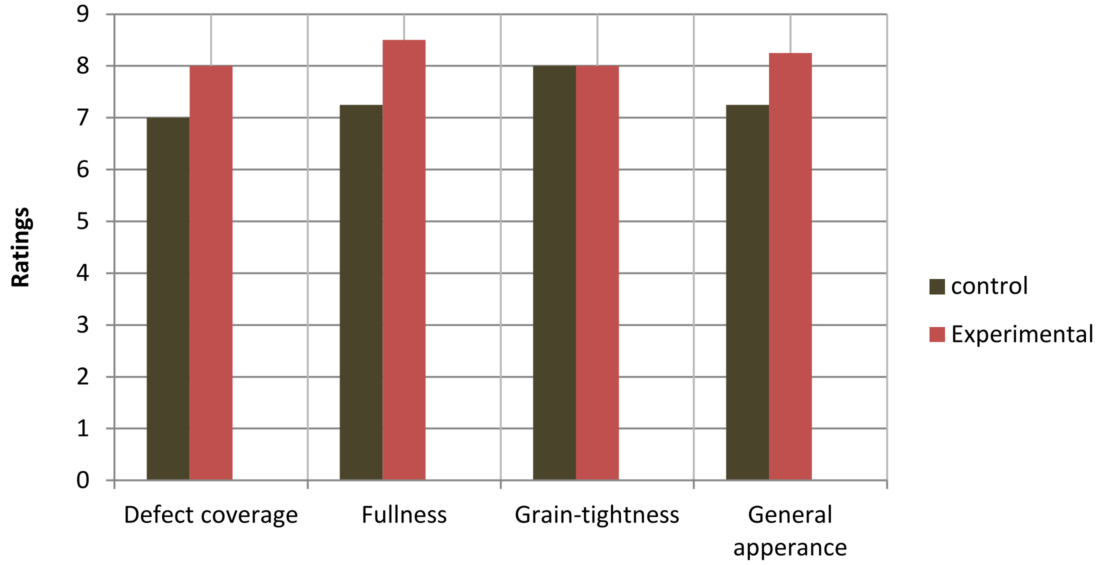


Fig-10: Organoleptic properties for finished leather from experiment-2

The major target of covering the defect as well as fullness and general appearance of the experimental finished leather was improved well compared to the control one with less number of coatings. Such types of finishes are viable for upgrading lower ends with keeping the natural look of the leather.

4.1.9.4 Process recipe from raw- dyed crust, trial-3(Experiment-3)

The main deference between this trial and the former one is 1%filler used along with chrome to try the idea of up-gradation even in the early stage of tanning. The detail of the process was presented at Annex 5. Cationic compact protein based finishing system was used and the microscopic image for the crust and study of organoleptic properties were presented as follow.

Microscopic Image for the crust

Control (L) and experimental (Y) crust micrograph are present as follow.

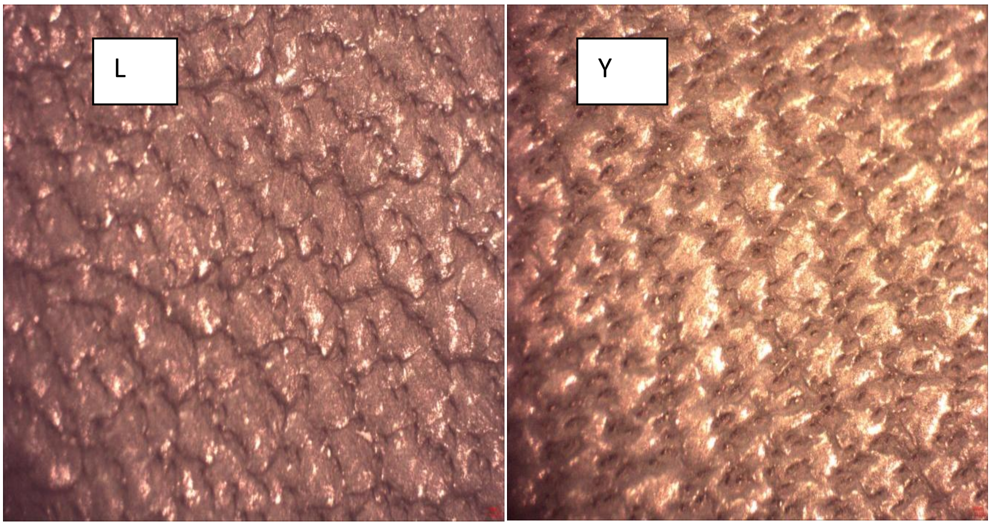


Fig-11 microscopic image for crust from experiment-3

The comparison of the experimental and control leather at wet-blue stage gives a minimal difference based on the result of this trial , this result leads to a conclusion that the idea of up-gradation will be visible if it is started in post-tanning and finishing unit operation.

4.1.9.5 Finishing formulation for the dyed crust from Experiment-3

Both experimental and control crusts are finished using cationic compact protein based finish from **SELLAM CHEMICALS**, Indian chemical company, and the formulations are as follow:-

Table-17 Cationic compact protein based finishing formulation

Chemicals	Solutions(in ml)						processes
	1	2	3	4	5	6	
1. Clearing coat							2x spray,dry
Anionic dye solution	50		50				
Water	900	350	620	750	500	895	
IPA	50	50	30				
2. Cationic base coat							3x spray, dry, Roller haircell@100°c and 120 pressure
SELCOM BK 3190		500					
CATIONIC PIGMENT		100					

3. Anionic season							2x spray, dry, plate Haircell@80^{o}c,150 pressure,Again1x spray
LUSTROBIN 1451			250				
ANIONIC PIGMENT			50				
CROSS-LINKER			5				
4. Top protein							2x spray
LUSTROBIN TOP 1214				250			
5. FIXING							1X spray, Sandblast plate @80^{o}c,100 pressure
BTX					500		
6. Top lacquer							1x spray plain plate @80^{o}c,100pressure
SELKHEM KW 0555						100	
SENSOL SW						5	

Where:-

- SELCOM BK 3190-cationic compact protein based.
- LUSTROBIN 1451-anionic compact protein based
- BTX- free formaldehyde fixing agent
- SELCHEM KW 0555- cationic wax
- SENSOL SW- silicon wax

4.1.9.5.1 Organoleptic properties for the finished leather

Experienced leather experts are assessed physically for the following properties, ratings are given 0-10 and average values were given.

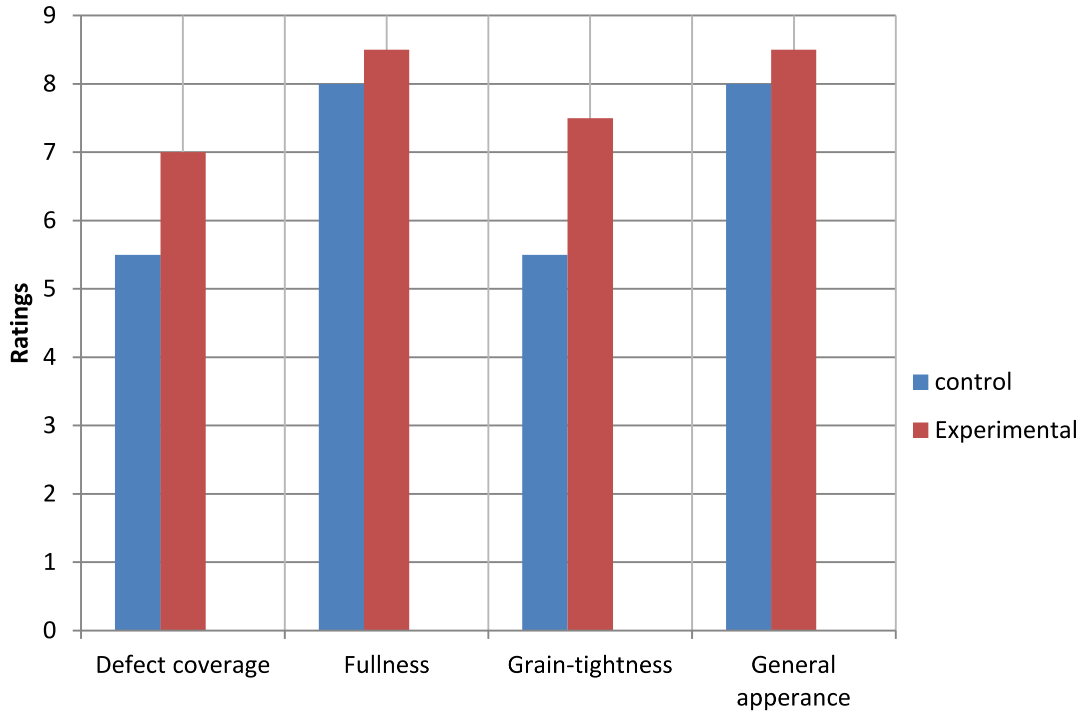


Fig-12: Organoleptic properties for the finished leather from experiment-3

The organoleptic study comparison of the former finished leather (cationic compact resin based) and the later finished leather (cationic compact protein based) reveals that, the main problem of surface defect was covered in a better manner with cationic compact resin, besides to this it gives better finished leather in terms of grain-tightness and general appearance. This is because generally resin has a better ability of covering defect than protein. In comparison between the two types of finishing techniques cationic compact resin based types of finish is much suitable finishing alternative than cationic compact protein based for up-gradation of lower ends.

4.1.9.6 Process recipe from raw to dyed crust, Indian cow hide (experiment 4)

Conventional crusting techniques were used (see annex 8) only for making a dyed crust to compare with Ethiopian cow crust in terms of physical properties. The crusts were finished using **anionic compact resin** finish from **Sellam chemicals** to compare the color fastness with the former cationic finishes used. The detail of finishing formulation was presented as follow:-

4.1.9.6.1 Finishing formulation for Indian crust

Anionic compact finish used from **sellam chemicals** for the finishing and the recipe is as follow.

Table-18 Anionic compact resin based finishing formulation

Chemicals	Solutions						Process
	1	2	3	4	5	6	
1. Anionic season							3X spray, dry, plate haircell @ 80^{o}c,150 pressure, Again 2x spray
SELCOM CA 1722	300						
ANIONIC PIGMENT	100						
ANIONIC DYE SOLUTION	30						
IPA	30						
WATER	540	495	895				
2. Fixing							2x spray, dry, sandblast plate @80^{o}c,100 pressure
MEDIUMSHINE LACQUER		200					
MATT LACQUER		300					
CROSS-LINKER		5					
3. TOP WAX							1X spray, plain plate @ 80^{o}c,100 pressure
SELCHEM KW 0555			100				
SENSOL SW			5				

SELLCOM1722- Anionic compact resin based.

4.1.9.7 Process Recipe from wet-blue to finishing, Experiment-5

Wet-blue leather was processed to crust with conventional method (see annex 7). The finishing was done using conventional finishing technique (anionic resin based).this experiment was done only for comparison of rub fastness with the experimental cationic finished leathers.

4.1.9.7.1 Finishing formulation for the crust from Experiment-5

Table 19 conventional (anionic resin based) finishing formulation

Chemicals	Solutions(in ml)				processes
	1	2	3	4	
1. Clearing coat					2x spray, dry
Ammonia	100				
Water	800	475	900		
IPA	100				
2. Season coat					3x spray, dry, haircell@100^{o}c and 120kg/cm^{2}pressure,again 3xspray Allow to dry.
Hard acrylic binder		125			
PU(hard resin binder)		75			
Medium soft casein(casein binder)		100			
wax		50			
Anionic pigment		150			
Dye solution		10			
3. Top lacquer					2x spray, dry well, Plating smooth plate, Temp=80^{o}c and 100kg/cm^{2} pressure
Lacquer emulsion			100		

4.1.9.8 Rub fastness test result for finished leather

Both dry and wet rub fastness were tested for the finished leather and the following results are found.

Table -20 Rub fastness test result for the finished leather.

No of cycles	E-exp-3(cationic compact protein based)	E-c-3	E-exp-2(Cationic compact resin based)	E-c-2	I-c-4 (anionic compact resin based)	E-c-5 (conventional finishing, anionic resin)
Dry 512 rubs	4/5	4/5	4/5	4/5	4	4/5

Wet 256 rubs	3	2/3	3/4	4	3	4

Where E-exp-3-Ethiopian experimental -3

E-c-3- Ethiopian control-3

E-exp-2-Ethiopian experimental-2

E-c-2- Ethiopian control-2

I-c-4 Indian control-4

E-c-5 Ethiopian control-5 (Conventional, anionic resin finish)

Rub fastness test results for all three types of finished leather, i.e. cationic compact resin based, cationic compact protein based, and anionic compact resin based reveals that wet rub fastness, which seems a problem for cationic finish in general, is above the minimum requirement in the case of cationic compact resin based.

Rub fastness and its capability to cover the defect was another important criterion to choose cationic compact resin based as best finishing technique.

Chapter five

5. Conclusion and Recommendation

5.1 Conclusion

Value addition on finished leathers from Ethiopian cow hides in terms of upgrading lower ends is possible. The chemical and physical characterization as well as study of the surface of Ethiopian cow hide leather found that it has coarse surface with less number of hair root that makes the material good for upper leather than clothing leather compared to Indian cow hide.

In the present project, drum based upgradation of the cow leathers have been established. Drum based pigments and fillers have been used during the post tanning stage and the leathers have been upgraded.

Also, cationic compact resin based finishing techniques have been used in order to have upgraded full grain finished leathers. This cationic finishing system provides good selection with least number of coating and easy unit operations for the finishing technician.

5.2 Recommendation

The result of the research work gives an inclusive idea about Ethiopian cow hide from raw to finishing processing stage. Drum up-gradation is a newer approach for Ethiopian tannery which is not used popularly so far. Cationic compact resin based finishing techniques are more suitable finishing types and it is advisable for our tanneries to look at as an alternation to overcome their problem of quality issue.

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Annexures

Annex 1 Lists of tanneries and their capacity

	NAME OF TANNERY	MAN POWER		MARKET IN %		CAPACITY				REMARK
						INSTALLED		ACTUAL		
		MALE	FEMALE	LOCAL	EXPORT	HIDE	SKIN	HIDE	SKIN	
1	China Africa Overseas	169	206	0	100	0	12,000	0	5,000	
2	Colba Tannery	230	54	10	90	500	6,000	400	6,000	
3	Ethiopia Tannery SC.	522	184	29	71	1,200	12,000	970	6,000	
4	Sheba Tannery	442	242	46	54	600	6,000	540	4,800	
5	ELICO	742	481	40	60	1,050	13,000		4,800	
6	Dire Tannery	274	191	30	70	600	6,000	350	4,000	
7	DX Industrious	48	58	0	100	0	8,000	0	3,500	
8	East Africa Tannery	83	55	0	100	0	8,000	0	3,500	
9	Batu Tannery	303	75	50	50	1,000	8,000	933		
10	Modjo Tannery	245	158	15	85	500	8,000	400	6,000	
11	Hafede Tannery	189	161	10	90	250	6,000	0	4,000	
12	Friendship	239	656	0	100	400	10,000	400	10,000	

	Tannery									
13	Bale Tannery	48	32	100	0	400	2,000	60	0	
14	Kombolcha Tannery	102	28	10	90	0	6,000	0	4,000	
15	Gelan Tannery	54	21	20	80	0	3,000	0	2,000	
16	Mersa Tannery	141	75	38	62	500	10,000	300	6,000	
17	Bahirdar Tannery	68	102	20	20	80	4000		1200	
18	Crystal Tannery									
19	New wing Leather Finishing Unit	399	167	0	100					
20	Wallia Tannery	180	155	5	95	1,000	5,000	500	2500	
21	Hora Tannery	40	40	30	70		3200		3200	
22	Addis Ababa Tannery	207	60	35	65	1,200	2500	900	2400	
23	Mesaco Tannery	23	6	100	0	0	3,000			
24	Debre Birhan Tannery	33	21	0	100	0	6,000	0	800	
25	Habesha Tannery	48	73	5	95	0	4,000	0	1,200	
26	Farida	36	56	0	100	0	7,000	0	2,500	

	Tannery									
27	United Vasn Tannery	25	85	0	100	0	5,000	0	2,000	
28	Blue Nile Tannery						4000			
29	Xiang Xin Xang	30	80	30	70	500	5,000	4,000sqft cow split per day		
30	Sun Industrial Tannery	4	0			0	3,500			
	TOTAL	4924	3522							
		8446								

Source: - Leather industry development Institute, Leather manufacturing technology directorate, Tannery profile.

Annex 2 Finished Leather exports follow up 2011/2012 LIDI

Finished leather	Quantity in kg	Values in USD
Sheep	893,274.92	39,051,574.65
Goat	418,189.91	9,840,066.61
Cow	157,226.28	2,564,948.44
Total	1,468,691.11	51,456,589.7

Annex 3 Process recipe from raw to dyed crust, Experiment-1

Two sides, one from Ethiopian(1R) and one from Indian wet salted raw cow hide was processed and the recipe was as follow:-

Soaking, liming and re-liming are done using pits.

process	percentage	Chemicals	duration	parameter
soaking	up- to covering the hide	Water	2-days	Hand check for full wetting of the hide in the neck and butt portion.
	0.5	preservative		
	0.5	Wetting agent		
Drain/ wash				
Liming	200	Water		
	10	Lime	1-day	
	3	Sodium-sulphide		
Un-hairing was done using beam				
Reliming	1	Lime	2-days	Checking the plumpness by hand
Drain/wash				
Fleshing, using fleshing machine and scudding by manually using knife.				
De-liming	100	Water	1.5 hour	Check cross-section for completion of de-liming using phenolphtalin indicator, colorless indicates complete de-liming.
	6	Ammonium chloride		
Drain /wash				
Bating	100	Water	1-hour	Check completion by thumb test
	1	Alkali bate		
Drain/wash				

Pickling	100	Water	20-minute	Baume check,6-7
	10	Salt		
	0.5	Formic acid (on to 5 dilution)	20-minute	
	0.7	Sulphuric- (one to ten dilution)	3x20-minute	PH=2.5-2.8
Leave overnight in the pickle bath, morning run 10-minute ,half drain and tanning started				
Tanning	50	Pickle bath		
	4	Basic chromium sulphate	1-hour	
	0.5	Sodium formate		
	4	Basic chromium sulphate	1-hour	
	0.5	Sodium formate		
Basification	50	Water		PH=3.8-4.0
	0.5	Sodium formate	20-minute	
	2	sodium-bicarbonate	3x20-minute	
Drain/pile for 2-days,sam,split,shave,for post-tanning process, shaved thickness=0.9-1.0mm, for **softy upper**				
Acid wash	200	Water	20-minute	
	0.5	Acetic acid		
	0.5	Wetting agent		
	Drain /wash			
Re-chroming	100	Water		
	3	Chrome syntan		
	5	Basic chromium sulphate	30-minute	
	2	Fish oil		
Basification	1	Sodium formate	20-minute	

	1.5	Sodium-bicarbonate	3x20-minute	PH=4.0-4.2,L/O/N
Morning,Run-20-minute,Drain/wash				
Neutralization	100	Water	20-minute	PH=4.8-5.0
	2	Neutralizing syntan		
	1.5	Sodium formate	20-minute	
	2	Sodium-bicarbonate	3x20’	
Drain/wash				
Re-tanning	100	Water	20-minute	
	3	Acrylic syntan (Relugan RE)		
	6	Mimosa	1-hour	
	4	Brown dye		
	3	Replacementsyntan (retinal FB18)		
	4	Melamine syntan (MR 70)		
Fatliqouring	100	Water	20-minute	
	3	Fish oil		
	4	Sulphited fatliqour (EA1)	40-minute	
	3	Semi-synthetic (EXP)		
Fixing	2	Formic acid	2x20’	
Drain				
Top-dye	100	Water	20-minute	
	2	Brown dye		
Fixing	1	Formic acid	20-minute	

Drain/wash/pile, morning set/over head dryer/stacking.

Annex-4 Process recipe from raw to dyed crust, Experiment-2, (best recipe)

One side (1L, left-side), from Ethiopian wet salted raw cow hide was processed and the recipe was as follow:-

Ethiopian raw wet salted hide weight=10kg

Soaking, liming and re-liming were done using pit

process	percentage	chemicals	duration	parameter
soaking	up- to covering the hide	water	2-days	Hand check for full wetting of the hide in the neck and butt portion.
	0.5	preservative		
	0.5	Wetting agent		
Drain/ wash				
Liming	200	water		
	10	lime	1-day	
	3	Sodium-sulphide		
Un-hairing using beam				
Re-liming	1	lime	2-days	Checking the plumpness by hand
Drain/wash				
Fleshing, using fleshing machine and scudding by manually using knife beam. taking fleshed weight, Ethiopian=15kg				
Deliming	100	water	1.5 hour	Check cross-section for completion of de-liming using phenolphtalin indicator, colorless indicates complete deliming.
	6	Ammonium chloride		

Drain /wash				
Bating	100	water	1-hour	Check completion by thumb test
	1	Alkali bate		
Drain/wash				
Pickling	100	Water	20’	Baume check,6-7
	10	Salt		
	0.5	Formic acid(ont to 5 dilution)	20’	
	0.7	Sulphuric- (one to ten dilution)	3x20’	PH=2.5-2.8
Depickiling	100	Water		
	1	Sodium bicarbonate	3x20’	PH=4.5-5,
Degreasing	**Dry float**			
	0.5	**Degreasing agent(Tergon ND 01)**	**1-hour**	**drain,2 times wash with salt and drain**
pickling	100	Water	20’	PH= 2.5-2.8
	10	Salt		
	0.5	Formic acid	20’	
	0.7	Sulphuric acid	3x20’	
Leave overnight in the pickle bath, morning run 10-minute ,half drain and tanning started				
Tanning	50	Pickle bath		
	4	Basic chromium sulphate	1-hour	
	0.5	Sodium formate		
	4	Basic		

		chromium sulphate	1-hour	
	0.5	Sodium formate		
Basification	50	Water		PH=3.8-4.0
	0.5	Sodium formate	20’	
	2	sodium-bicarbonate	3x20’	
Drain/pile for 2-days,sam,split,shave,for post-tanning process, shaved thickness=1.2-1.3 mm, and shaved weight 2.7kg for Upper leather				
Acid wash	200	Water	20’	
	0.5	Acetic acid		
	0.5	Wetting agent		
	Drain /wash			
Rechroming	100	Water	30’	
	3	Chrome syntan		
	5	Basic chromium sulphate		
	1	Cationic fatliqour(OK)		
Basification	0.5	Sodium formate	20’	PH=3.8-4.0
	1.5	Sodium-bicarbonate	3x20’	
Drain/wash/pile the leather was summed and cut in to two,$1L_1$ and $1L_2$, and weight was measured,$1L_1$=1.7kg and $1L_2$=1.9kg, $1L_1$ used for the **experimental trial-2** and $1L_2$ used as control.(the post tanning process are done in different drum)				
Neutralization	100	Water	20’	PH= 4.8-5.0 Drain/wash
	0.5	Sodium formate		
	1.5	Sodium-bicarbonate	3x20’	

Re-tanning	150	Water	20’	
	5	Acrylicsyntan (Relugan RE)		
	4	Black dye	40’	Check-penetration, by cutting the cross-section, it was penetrated well.
	7	Mimosa		
	3	Replacement syntan (FB-18)		
	5	Melamine syntan(MR-70)		
Fat-liquoring	100	Water	20’	
	2	Fish oil(BLSFO)		
	4	Sulphited fat-liqour	40’	
	2	Semi-synthetic fat-liqour		
Fixation	2	Formic- acid	2x20’	Drain/wash
Top-dye	100	Water	20’	
	2	Black-dye		
fixation	1	Formic acid	2x20’	Drain/wash
For the control,1L$_2$,cationic topping				
Cationic topping	100	Water	20’	Drain/wash/pile/set/hook/stack / trim
	1	Cationic fatliqour		
For the experimental,1L$_1$,after top dyeing and fixation, drain/ wash				
Pigment + filler	**200**	**Water**	**30’**	**Mix the filler with the liquid pigment and add as the drum running.**
	1	**Liquid pigment(2k black)**		
	1	**Sellcomfill 6718**		
fixation	1	Formic acid	20’	drain/wash
Cationic topping	100	Water	20’	

	1	Cationic fatliqour		
Drain/wash/pile/Set/hook/stack/trim				

Annex 5 Chemical Description

Cationic liquid pigment (2 k black):- Casein based viscous liquid containing both organic and Inorganic Cationic Pigments. Compatible only with cationic products.

Excellent tinctorial strength is useful for all types of leather.

Selchem cationic pigments are well suitable to use them along with Sellam protein filler in wet end final process after fixing the dyes .

Selcomfill MK 6718:- Cationic protein wet end filler for all types of softies and milled Leather. It is used to produce upgraded, soft, tight and fine grain with pleasant satin touch.

Practical values of Sellam wet end fillers

- Lower selection wet blue is upgraded to higher selection (crust) leather resulting in higher unit value realization.

- No need to load the grain in finishing; aniline look of finished leather is preserved even in the lower selections.

- Reduces the time in finishing; it takes only 30 minutes running time in the wet-end drumprocess.
- Diminishes the visibility of vein marks, growth marks, deep ticks and grain off .

- Marginal increase in the area of leather.

- If there is no rejection, no dead stock is a great relief for the tanners [19].

Annex 6 Process recipe from raw to dyed crust, (Experiment-3)

One side (1R, right-side), from Ethiopian wet salted raw cow hide was processed and the recipe was as follow: - Ethiopian raw wet salted hide weight=7kg

Soaking, liming and re-liming were done using pits.

process	percentage	chemicals	duration	parameter
soaking	up-to covering the hide	water	3-days	Hand check for full wetting of the hide in the neck and butt portion.
	0.5	preservative		
	0.5	Wetting agent		
Drain/ wash				
Liming	200	water		
	10	lime	1-day	
	3	Sodium-sulphide		
Un-hairing using beam				
Re-liming	1	lime	2-days	Checking the plumpness by hand
Drain/wash				
Fleshing, using fleshing machine and scudding by manually using knife. taking fleshed weight =10kg				
De-liming	100	water	1.5 hour	Check cross-section for completion of de-liming using phenolphthalein indicator, colorless indicates complete de-liming.
	6	Ammonium chloride		
Drain /wash				
Bating	100	water	1-hour	Check completion by thumb test Drain wash
	1	Alkali bate		
Degeresing	0.5	Degreasing agent(tergolND	1-hour	Salt wash twice

		01)		
Drain/wash				
Pickling	100	Water	20’	Baume check,6-7
	10	Salt		
	0.5	Formic acid(one to 5 dilution)	20’	
	0.7	Sulphuric- (one to ten dilution)	3x20’	PH=2.5-2.8
Leave overnight in the pickle bath, morning run 10-minute ,half drain and tanning started				
Tanning	50	Pickle bath	1-hour	
	4	Basicchromium sulphate		
	0.5	Sodium formate		
	1	**Sellcomfill (mk5718)**	**30’**	
	4	Basic chromium sulphate	1-hour	
	0.5	Sodium formate		
Basification	50	Water	20’	PH=3.8-4.0
	0.5	Sodium formate		
	2	sodium-bicarbonate	3x20’	
Drain/pile for 2-days,sam,split,shave,for post-tanning process, shaved thickness=1.2-1.3 mm, and shaved weight 3kg for Upper leather				
Acid wash	200	Water	20-minute	
	0.5	Acetic acid		
	0.5	Wetting agent		
	Drain /wash			
Re-chroming	100	Water	30’	
	3	Chrome syntan		
	5	Basic chromium sulphate		
	1	Cationic fatliqour		
Basificati	0.5	Sodium formate	20’	

on				PH=3.8-4.0
	1.5	Sodium-bicarbonate	3x20’	
Drain/wash/pile, the leather was summed and cut in to two,$1R_1$ and $1R_2$, and weight was measured,$1R_1$=1.4kg and $1R_2$=1.6kg, $1R_1$ used for the **experimental trial-3** and $1R_2$ used as control.(the post tanning process are done in different drum)				
Neutralization	100	Water	20’	PH= 4.8-5.0 Drain/wash
	0.5	Sodium formate		
	1.5	Sodium-bicarbonate	3x20’	
Re-tanning	150	Water	20’	
	5	Acrylic syntan (Relugan RE)		
	4	Black dye	40’	Check-penetration, by cutting the cross-section, it was penetrated well.
	7	Qubracho		
	3	Replacement syntan (FB-18)		
	5	Melamine syntan (MR-70)		
Fat-liquoring	100	Water	20’	
	2	Fish oil(BLSFO)		
	4	Sulphited fat-liqour	40’	
	2	Semi-synthetic fat-liqour		
Fixation	2	Formic- acid	2x20’	Drain/wash
Top-dye	100	Water	30’	
	2	Black-dye		
fixation	1	Formic acid	2x20’	Drain/wash
For the control,$1R_2$,cationic topping				
Cationic topping	100	Water	20’	Drain/wash/pile/set/hook/stack/trim
	1	Cationic fatliqour		
For the experimental,$1R_1$,after top dyeing and fixation, drain/ wash				
Pigment+filler	**200**	**Water**	**30’**	**Mix the filler with the liquid**

	1	**Liquid pigment(2k black)**		**pigment and add as the drum running.**
	2	**Sellcomfill (mk6718)**		
fixation	1	Formic acid	30’	drain/wash
Cationic topping	100	Water	20’	
	1	Cationic fatliqour		
Drain/wash/pile/Set/hook/stack/trim				

Annex-7 Process recipe from soaking to dyed crust trial-4

One side from Indian wet salted cow hide was taken for the process and the details are as follow

Wet- salted raw hide weight=7kg

process	percentage	chemicals	duration	parameter
soaking	up- to covering the hide	water	4-days	Hand check for full wetting of the hide in the neck and butt portion. The process was done using pit
	0.5	preservative		
	1	Wetting agent		
Drain/ wash				
Liming	200	water		
	10	lime	1-day	process done using pit
	3	Sodium-sulphide		
Un-haring using knife				
Re-liming	2	lime	10’/1hr for 1day	Process was done using drum , Checking the plumpness by hand
	1	Sodium sulphide		
Drain/wash				
Fleshing, using fleshing machine and scudding by manually using knife. taking fleshed				

weight =10kg				
De-liming	100	water	1.5 hour	Check cross-section for completion of de-liming using phenolphthalein indicator, colorless indicates complete de-liming.
	6	Ammonium chloride		
Bating	1	Alkali bate	1-hour	Check completion by thumb test Drain wash
Degreasing	1	Degreasing agent(tergol ND 01)	1-hour	Salt wash twice
Drain/wash				
Pickling	100	Water	20’	Baume check,6-7
	10	Salt		
	0.5	Formic acid(one to 5 dilution)	20’	
	0.7	Sulphuric- (one to ten dilution)	3x20’	PH=2.5-2.8
Leave overnight in the pickle bath, morning run 10-minute ,half drain and tanning started				
Tanning	50	Pickle bath	1-hour	
	4	Basic chromium sulphate		
	0.5	Sodium formate		
	4	Basic chromium sulphate	1-hour	
	0.5	Sodium formate		
Basification	50	Water	20’	PH=3.8-4.0
	0.5	Sodium formate		
	2	sodium-bicarbonate	3x20’	
Drain/pile for 2-days,sam,split,shave,for post-tanning process, shaved thickness=1.2-1.3 mm, and shaved weight --- for Upper leather				
Acid wash	200	Water		

	0.5	Acetic acid	20’	
	0.5	Wetting agent		
	Drain /wash			
Re-chroming	100	Water	30’	
	3	Chrome syntan		
	5	Basic chromium sulphate		
	1	Cationic fatliqour		
Basification	0.5	Sodium formate	20’	PH=3.8-4.0
	1.5	Sodium-bicarbonate	3x20’	
Drain/wash/pile (for two days), the leather was summed.				
Neutralization	100	Water	20’	PH= 4.8-5.0 Drain/wash
	0.5	Sodium formate		
	1.5	Sodium-bicarbonate	3x20’	
Re-tanning	150	Water	20’	
	5	Acrylic syntan(Relugan RE)		
	4	Black dye	40’	Check-penetration, by cutting the cross-section, it was penetrated well.
	7	Qubracho		
	3	Replacement syntan (FB-18)		
	5	Melamine syntan(MR-70)		
Fat-liquoring	100	Water	20’	
	2	Fish oil(BLSFO)		
	4	Sulphited fat-liqour	40’	
	2	Semi-synthetic fat-liqour		
Fixation	2	Formic- acid	2x20’	Drain/wash

Top-dye	100	Water	30’	
	2	Black-dye		
fixation	1	Formic acid	2x20’	Drain/wash
Cationic topping	100	Water	30’	Drain/wash/pile/set/hook/stack/trim
	1	Cationic fatliqor(ok)		

Annex-8 Process recipe from Wet-blue to dyed crust trail-5

One side wet-blue leather (Ethiopian) was taken and shaved to 1.2-1.4mm thickness. The post-tanning process was done using conventional technique for upper leather and the process technology is as follow.

process	percentage	Chemical	Time	Remark
Acid wash	200	Water	20’	
	0.5	Acetic acid		
	0.5	Wetting agent		
Re-chroming	100	Water	30’	
	3	Chrome syntan		
	5	Basic chromium sulphate		
	1	Cationic fatliqor		
Basification	0.5	Sodium formate	20’	
	1.5	Sodium bicarbonate	3x20’	PH= 3.8-4.0
Drain/wash/pile				
Neutralization	100	Water		
	0.5	Sodium formate	20’	
	1.5	Sodium bicarbonate	3x20’	PH=4.8-5.0
Re-tanning	150	water@40^{o}c	40’	
	5	Tafigal HK(sulfonic syntan)		
	4	Incoflor blackGTN(Black dye)		

	3	Donatan F(phenolic syntan)		
	5	Retanal MD 80(Melamin syntan)		
Fat-liquoring	100	water@60^{o}c		
	2	Fish oil(Nexofol NT)		
	4	Synthetic fatliqour (SE)	60’	
	2	Semi-synthetic fatliqour (fosfol AR 75)		
Fixation	2	Formic acid	2x20’	
Drain/wash				
Top-dye	100	Water	30’	
	2	Black dye (Incoflor black GTN)		
Fixation	2	Formic acid	20’	