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ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAiT)

SCHOOL OF CHEMICAL AND BIO-ENGINEERING

MANUFACTURE OF HIGH PERFORMANCE SHEEP UPPER LEATHER FROM LOW QUALITY SHEEP SKINS IN SELECTION THROUGH PROCESS UPGRADATION AND OPTIMIZATION

BY

WONDIMU WOLDE ZEGEYE

ADVISORS

Dr. Eng. ABUBEKER YIMAM

Dr. R ARAVINDAN RATHINAM

Dr. P THANIKAIVELAN PALANISAMY

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This is to certify that the Thesis prepared by Wondimu Wolde, entitled: ***Manufacture of high Performance Sheep Upper Leather from lower Quality Sheep Skins in selection through process Upgradation & Optimization*** and submitted in partial fulfilment of the requirements for Degree of Master of Science in Chemical Engineering (Leather Technology) complies with the regulations of the University and meets the accepted standards with respect originality and quality.

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Dr. Eng. Abubeker Yimam Dean, School of Chemical and Bio Engineering, Advisor	___________________ Signature	___________________ Date
Dr. R. Aravindhan Advisor	___________________ Signature	___________________ Date
Dr. Shegaw Ahmed Internal Examiner	___________________ Signature	___________________ Date
Dr. J. Kanagaraj External Examiner	___________________ Signature	___________________ Date

____

School Dean/Graduate programs Coordinator

ABSTRACT

The quality of a raw material for any manufacturing industry or firm is one of the decisive factors controlling its productivity and profitability. Leather processing industries are no exceptions to this fact. The decline of quality raw material supply for the leather processing industries is a great challenge to be competent and survive in the industry these days. The quality of the raw material is largely affected by different factors. The problems leading to lower selection of raw skins or semi-processed skins in industry are categorized as ante-mortem and post-mortem defects. Especially the ante-mortem defect caused by ecto-parasite attack on the skins surface is one of the major problems for downgraded selection of sheep and goat skins. In this research work, an attempt has been made to upgrade poor and reject wet blue leathers due to mange disease damage or “Ekeke” on sheep skin. The problem of lower quality selection of skins could be improved and upgraded into better quality shoe upper leather by working on suitable leather processing techniques for covering the defects of mange damaged skins in wet-finishing and finishing by upgradation and optimization. In wet- finishing process, filler waxes and pigments combination were employed for upgradation. This has resulted in improved coverage of defects on dyed crust leathers. Physical strength tests and organoleptic property assessments performed on the treated leathers are found to be good. The optimized process of dyed crust leather is taken further for finishing, where five finishing methods were chosen for upgrading the uncovered defects in wet-finishing. Waxy, metallic, corrected grain and cationic finishing were employed against the conventional resin finishing. With cationic finishing, an improved and upgraded leather was obtained with better natural look or appearance of grain, good covering and comparable physical and organoleptic properties and better grade.

DEDICATION

This work is dedicated to my all families

1. W/ro Genet Eshetie (My wife)
2. Emahoy Abebu Temesgen (My mother)
3. Yohanes Wondimu and Abraham Wondimu (my sons)
4. Nigist Wolde & Emebet Wolde (my sisters)
5. Cherkos Wolde and Dikon Yared Wolde (my brothers)

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List of Abbreviations and Acronyms

Al	Aluminum
CLRI	Central Leather Research Institute
CG	Corrected Grain
CSA	Central Statistical Agency of Ethiopia
cm	Centimeter
C^0	Degree Celsius
FG	Full grain
ISO	International Standard Organization
IUP	International Union for Physical Test
Kg	Kilogram
LIDI	Leather Industry Development Institute
mm	Millimeter
N	Newton
Psi	Pounds per square inch
SATRA	Shoe and Allied Trades Research Association
SEM	Scanning Electron Microscope
SYF	Synthetic Fatliquors
SSF	Semi- synthetic Fatliquors
Ti	Titanium
WBSS	Wet Blue Sheep Skin
Zr	Zirconium

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CHAPTER 1

INTRODUCTION

1.1. BACKGROUND

Leather manufacturing industry is one of the oldest and important economic backbone of countries for growth and development in generating foreign currency and creating employment opportunities for citizens. The leather industry occupies a place of prominence in the economy of countries in the world in view of its massive potential for employment, growth and exports. Ethiopian small ruminant skins, especially sheep skins traditionally have a very good reputation for quality in the world leather market due to their fine grain and compact structure [1, 2].

Ectoparasites are the major causes of skin diseases that hamper small ruminant production in many areas of Ethiopia. Studies conducted in different parts of the country in the past years have revealed that the occurrence and the spread of skin diseases have been shown to correlate with feed scarcity host, poor husbandry, climate factors and inadequate veterinary services including absence of national control strategies. Ectoparasites also have transmission ability for many infections due to blood sucking habits. Mange mites are common in Ethiopia in different agro climates. Reports show that mange mites are most prevalent in four national regional states of Ethiopia. In all reports, three genera of mites namely, Sarcoptes, Psoroptes and Demodex affects small ruminants in Ethiopia [3].

Raw material affects the end product of leather produced. Of those defects, which affect the quality of the end product is the defects that are caused by parasite on the skin surface. Especially defects that are seen on the skin surface that result poor selection result with its remedial action will be investigated in detail in this research work.

They are also very important to the country's economy as sheep and goat skins rank among the largest export commodities. Ethiopia has 24.2 million sheep and 22.6 million goat skins. Leather and leather products are supplied to domestic and international markets and contribute significantly the country's economy by providing 14-18% of foreign exchange earnings. Though Ethiopia has very good potential to produce substantial quantities of skins, the quality of skins supplied is decreasing from time to time. This has resulted in an ever-increasing number of complaints about the quality of skins available to local tanners and export market. The problem has adversely affected all aspects of the industry including the income derived from exports. Improvement of the quality of raw material is vital in expanding trade in the sector. Better-quality skins generate better prices. Eliminating or at least reducing defects that cause the down-grading and consequent rejection of the raw material will improve price received. Defects occur as a result of a variety of causes during the life of the animal, during slaughter and after slaughter. So, the defects resulted in any case has to get a remedy to improve the quality and the value of the final leather product by incorporating different up gradation techniques and process optimization through research. By studying the nature, type, distribution and depth of defects on skin surface that affect the quality of sheep skin develop suitable working processes in wet-post tanning and finishing to enhance the quality of the final product [4].

Physical properties of the leathers are directly related to the thickness of the leather, grain to corium ratios and corium collagen structure which in turn is related to the quality of the raw material. The thickness decreases due to parasitic attack on the skin, under nourishment etc. [5]

Factors Influencing Quality of Skins

Several reasons may contribute to low quality output: -

i. First, poor animal husbandry, including inadequate and poor-quality feeds, inadequate parasite and disease management, and branding with hot iron for identification purposes may lead to low quality of hides and skins.
ii. Second, a good proportion of hides and skin produced may be of poor quality, especially those produced in rural areas outside organized slaughter houses, due to inappropriate slaughtering, flaying, collection and initial processing methods used leading to spoilage and rejection in the market.
iii. Third, technology used at various stages in the processing chain from raw hides to finished leather products may be inappropriate or poor leading to poor quality products.
iv. Fourth, investment in both technology, infrastructure (physical, financial, information) and skill of manpower engaged in the sector may be very low in comparison to the need and potential leading to poor quality output [3,5].

1.2. Problem statement

Ethiopian Leather Manufacturing Industry is one of foreign currency earning sub-sectors next to coffee. So as to produce competitive and quality leather products for local and international market there has to be continuous supply of quality raw materials for the industries. Nowadays, the great challenge for leather processing industries is the quality of the raw material supply decline and no improvement has been made up to now. Today it is nearly impossible to find a perfect animal skin; this is due to carelessness and indifference in breeding, feeding, handling, diseases and parasite control, all of which result in leather defects.

This has made this sub-sector to be uncompetitive in international market due to poor quality of leather products. Large percentage of this problem occurred due to poor raw material of sheep skins attacked by parasite especially mange disease. Around 65-70% of raw sheep skin is poor quality. As a result, the leather manufacturing industries are facing great challenge to produce competent products. So, the major defect that contributed for low selection is parasitic damage seen on the surface of skin specifically mites' causes the skin disease known as mange or "Ekeke" in sheep and goat. Mites can cause extensive and visible damage but cannot be seen by naked eye. Mange is a serious cause of sheep skin disease in Ethiopia. So, a remedy has to be sought for this problem in order to improve poor quality raw materials attacked by parasitic diseases. This research is targeted to upgrade and optimize low(poor) grade sheep skins in selection to better grade shoe upper leather by studying and performing changes in the production processes of post-tanning and finishing operations.

1.3. Objectives

1.3.1. General Objective

- To investigate and develop suitable post-tanning and finishing processes for improving the quality of downgraded skins particularly focusing on ante-mortem defects such as Mange damage or ''EKEK'' occurred due to external parasitic diseases.

1.3.2. Specific Objectives

- to assess the defects caused by different parasites on the surface of skins.
- to identify the depth and distribution of parasitic defects that account for the downgrading of the skin in selection.
- to examine and study the skin structure and defects of wet blue and crust sheep skins surface through scanning electron microscope.
- to design suitable post tanning and finishing processes that absorb the appearance of defects and improve the quality of the products.
- to select the optimum process that utilize minimum resources and operations and comparatively which produce best quality of leather product.

1.4. Scope of the study

The scope of this research comprises different processes to be performed on low quality sheep skins due to parasitic damage and the relevant technologies to improve the quality of poor grade skins through process upgradation and optimization in post-tanning and finishing.

- Design suitable post-tanning process to improve defect coverage and upgrade the quality of the processed leather products.
- Devise compatible finishing process so as to cover keeping the natural look of the skin grain structure.
- Physical, visual and organoleptic evaluation of the leathers at various stages

1.5. Significance of the study

The importance of studying this research work is to develop an optimum leather processing and upgradation systems for poor quality raw materials of sheep skins attacked by parasitic diseases especially mites which caused by mange diseases and introduce consistent and compatible leather processing technology in post tanning and finishing to improve the performance of the end product.

- Design appropriate post-tanning and finishing process in order to produce better quality products.
- Improve the quality of the end product coming from poor quality raw material

- Brings foreign Currency for the country and enhance employment opportunity in the area and improve the productivity of the tanning industries.
- Enhances efficient utilization of resources
- Attract and encourage investment in the sector i.e. leather manufacturing industry.

CHAPTER 2

LITERATURE REVIEW

2.1. Skin Defects and Its Impact

Skins commonly exhibit defects caused by a variety of factors. Defects originating while the animals are alive are called *ante-mortem defects* while those originating after the death of the animal are called *poste-mortem defects*. While some defects are common to all animals, some are specific to some species [6].

Parasitic skin diseases caused by ecto-parasites such as mange mites, lice, keds and ticks are among these threats resulting in serious economic loss to the tanning industry and the country as whole. The economic impact of ecto-parasitism is not properly documented. Tannery's reported data shows that 40% of sheep skin and 56% of goat skins are rejected due to external parasites, and out of the reject groups of semi-processed skins, about 80% to 90% of defects were believed to be due to Ectoparasites. Information available so far in Ethiopia indicates that parasitic skin diseases of small ruminants are widely distributed in different agro-climatic areas, causing serious economic loss to the farming community and tanning industry seriously hampering the income generation and foreign currency flow to the country. The extent of the problem has increased continuously during long years ago having not yet got a solution [7].

The most common ante mortem and post mortem defects that affect the animals and skins/hide quality are depicted in Figure 2.1 [8]

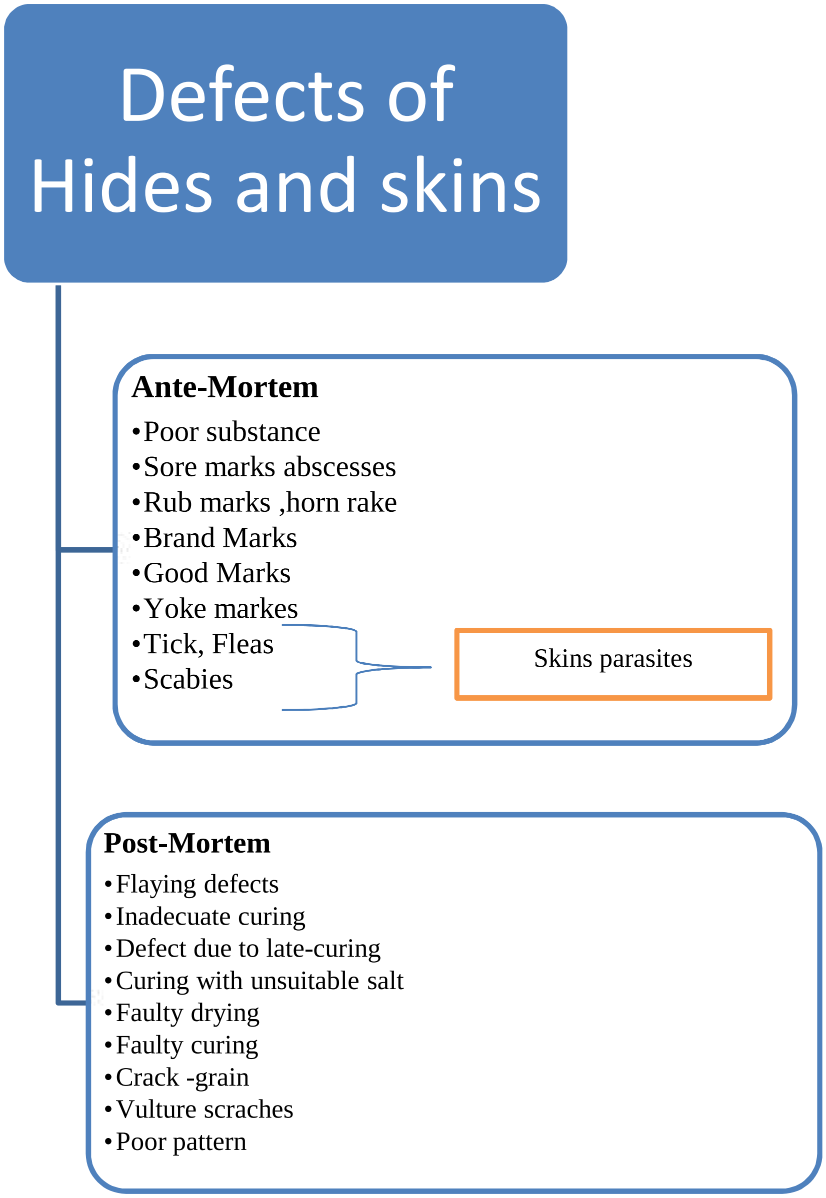


Figure 2.1 ante-mortem and post-mortem defects of skin

2.1.1. Ant-mortem defects

- Poor substance
- Sore marks
- Barbed wire and torn scratches
- Rub marks
- Goad marks and whip lashes
- Bite marks from ticks, flees, lice, leeches etc.
- Cockle
- Scars
- Dung damage
- Natural characteristics of the skin
- Injection punctures shearing cuts

The skin defects can be categorized as: -

- Environmental or Natural causes
- External parasites and diseases
- Pre-slaughter/ant-mortem defects due involving human activities.
- Post-mortem defects

Different external parasites and diseases are: -

Mange: - this is a skin disease, of which most common type is follicular demodectic mange.

Scabies: The mites multiply under the skin surface leaving a coarse grain, lesion and scratch where the animal scratches itself.

Ticks: Blood sucking parasites found attached to the thinner and tender part of the skin, the inner part of the thigh under the elbow and on the udder and scrotum. Ticks cause small holes marring the smoothness of the grain. Secondary, infections my lead to more extensive damage.

Sheep ked: a flat brown insect that sucks blood. Normally infests sheep and spends all its life on the host. It causes irritation resulting in scratching biting and damage to the fleeces. It causes skin blemishes downgrading the skin.

Warble flies: occur in dry and arid regions and are generally absent in moist regions. This is due to the fact that moist soil is not conducive to the growth of larvae into flies. Hairy goat breeds with short and drooping ears often attacked by these insects.

Cockle: A warty growth in wool sheep seen as rounded nodules scattered through the corium and appears to develop as fleece grows. The disease is due to a nutritional and digestive disorder.

Ringworm: A fungal disease that attacks the hair and its roots with circular inflammation leaving shiny scars.

Pox: An infectious disease forming inflamed spots usually on the udder and other tender parts of the skin. The spots become charged with pus. Apart from lesions, the animals rub the irritating parts causing further infection and damaged grain.

Diseases such as trypanosomiasis, streptothricosis, sweating sickness, etc., cause thickening and coarsening of the epidermis and hair follicles, especially in the neck. This causes hair follicles to protrude above the grain, giving a rough finish. Streptothricosis also causes lesions which break spontaneously. These cause blemishes on the superficial grain tissues.

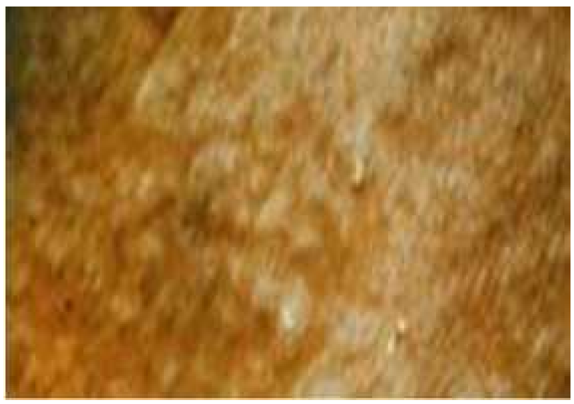


Figure 2.2 Salt dried Sheep Skins attacked by Mange Diseases.

Figure 2.3 Semi-processed pickled sheep skin from M/s Colba Tannery, Modjo showing defects due to infectious pox diseases causing a flamed spot on the entire skin surface

2.1.2. Post-mortem Defects

A large number of skins contain defects due to careless and inefficient use of the flaying knife. Cuts, holes and scores produced through faulty flaying greatly diminish the value of skins. Use of an improperly pointed knife adds to the problem. Flaying on the floor causes more cuts and delays in flaying which makes the carcass cold and more difficult to flay. Other defects are due to unnecessary use of a knife, insecure position of the carcass, bad lighting, and lack of skill. Using a fist wherever possible will improve the quality. If the ripping line is not properly cut, the final shape will not be symmetrical and may affect the usefulness of the skin for commercial production of quality leather, ultimately affecting the value of the leather itself. Improper fleshing allows fatty tissues to remain on the skin, resulting in poor curing both by salting and air drying. In tanning and finishing, improper curing results in patches of different quality leather during later processing [6,8].

All defects mentioned above largely contribute poor quality sheep skins and as a result the overall leather quality manufacturing in industry is affected. Especially in this project defects due to ecto-parasite and diseases on the surface of sheep skin will be assessed and studied in detail to improve the consequent leather products coming from this raw material through process optimization and up gradations [1,2].

2.2. Upgradation of Shoe Upper leather

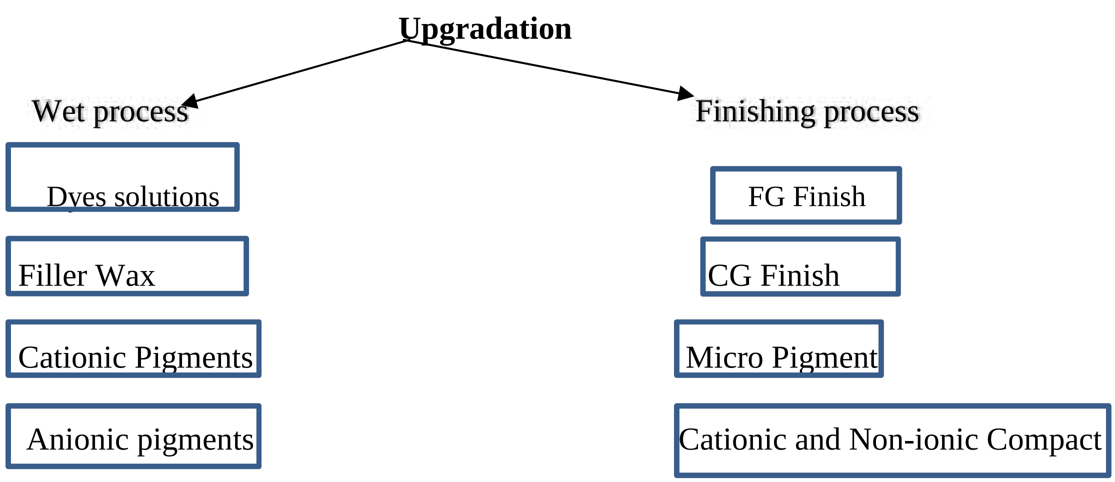
2.2.1. Upgradation of low grade skins

The ‘upgrading of leather’ in simple terms means: to make the best leather possible out of the available crust material. This includes the highest quality as well as the largest cutting yield while keeping the elegance and natural aspect of the final leather. Since the gap between supply and demand of high class raw material is increasing rather than decreasing, upgrading becomes more and more important. It does not seem to be so difficult to cover crust defects by applying a thick and heavy finishing layer, or even to remove the damaged grain by buffing – but that’s only half the solution. For heavily finished articles such as some automotive or furniture articles, upgrading by using mechanically created foams, special filling components, pre-base coats containing microspheres and/or heavily embossing can be used. For most of the shoe upper leathers these technologies are no alternative, because these leathers do not have thick finishing layers, so upgrading has to be achieved with thin coats. And, of course, there are lots of articles without any finishing coat at all. We'd like to upgrade them as well. Because of the spectrum of shoe upper leathers, it is not possible to deal with them all in the same way. Different defects in different sizes and on different leathers need different upgrading techniques and products/systems [9,10].

- This first part explores upgrading ideas and techniques for shoe upper leather types such as
  i. Corrected grain (CG) leather, box types
  ii. Corrected grain leathers, less covered
  iii. Full grain leathers (FG)

- The second article will concern some more details referring to:
  - Pre-base coat
  - Base coats and
  - Effects

2.2.2. Upgrading Techniques



i. Corrected grain shoe upper leather, box types

This is the only kind of shoe upper leather, where the upgrading procedures are not so far away from the procedures for furniture/automotive leathers.

To achieve a smooth and even surface and sufficient cutting yield, the crust needs to be well prepared before applying the base coat. Very common today is a pre-treatment of the crust with microspheres-containing pre-base products1 (‘stucco’) by reverse roller coating. This can be done either on the full grain crust and the subsequent buffing will then remove the surplus and even out the surface or, what’s far more effective in terms of upgrading, after a pre-buffing process.

These leathers do not get a deep grain correction. As a general rule the final article and the available crust must be evaluated, as with this kind of shoe upper leather sorting is value-adding! The intension here is to equalize the leather surface but the final leather may not look corrected. The goal is to achieve a full grain imitation. Therefore, the first and most important step is the grain restoration.

Two options are possible: either the leathers will be buffed in the finishing department or they enter the finishing department already buffed [11].

ii. Corrected grain leathers less covered

The more natural, less covered leathers don’t get a high viscous pre-base coat. More common is the more liquid pre-base coat with microspheres-containing products. These leathers get a careful sealing first instead of a heavily covering base coat. This sealing coat contains aqueous oil emulsions, selected resins and additives. The intention is to re-close the surface after buffing and creating an artificial grain. Therefore, this pre-base coat has to be treated by any melting process, commonly by hair cell embossing. For smooth leathers plating is recommended. After this initial step a further base coating is necessary. Since the leather has a new (but artificial) grain, the final base coating can be done as for full grain leathers. Away from the heavily finished articles is a method for lightly covered, almost semi-aniline leathers [12].

Soft and elegant upgrading with a soft pre-coat

A fine balanced mix of resins and additives needs to be used to ensure minimum hardness is introduced to the leather. Besides this penetration, some of the components should remain on the surface to seal it by the subsequent sand blasting or embossing. The following effects should result:

- The surface is sealed, an artificial grain is created
- The leather does not get harder, does not lose its natural appearance and feel.

- No looseness or double-grain effect
- Print retention is improved
- Good adhesion properties

iii. Full grain shoe upper leather

For upgrading full grain leathers special products and systems have been developed based on the experience made on the corrected grain leathers. Upgrading corrected grain leathers by using microspheres in the pre-base is a very effective state-of-the-art technology. The use of microspheres in the pre-base coat for full grain leathers seemed to be no way to go, but today it's found to be a really helpful upgrading tool. Those pre-base coats are applied either by spraying or reverse roller coater. Unlike corrected grain leathers these pre-base coats do not get a subsequent buffing. Polishing is more suitable, or alternatively plating could be done.

For full grain leathers this kind of application is used as a very strong covering and polishing coat. The idea is to apply only a little surplus on the leather surface that will be removed from the undamaged parts and pushed into the smaller remaining defects such as pin holes. It's obvious that a very well-balanced mix is necessary to: Cover the defects, adhere to the leather, be easily polishable and ensure good adhesion to the subsequent finishing layer. After the application of such a pre-base coat the filling components will remain on the leather surface, so this layer is touch-sensitive. Polishing will remove the filling components from the surface and will simultaneously move the components into the small defects. If no polishing follows this kind of pre-base makes the handling of these leathers difficult. In order to avoid scratches or finger prints some resin should be added into the pre-base coat mix.

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials and Chemicals

Raw Material and Chemicals

Raw material and chemicals used in this project work

- Low grade (reject) wet blue sheep skins (WBSS), especially affected by mange diseases was chosen as a raw material.
- Analytical grade chemicals for analysis and industrial grade chemicals for leather processing was employed.

Machineries or Equipment

Different types of leather processing machines or equipment used during the research work for improving quality of low grade skins are as below:

Weighing balance for skins and chemicals, pH meter, testing drums (tanning and dyeing), shaving and Samming machines and thickness gauge, sam-setting out machine, drying machines vacuum and overhead driers, staking (rotary and vibrator), buffing machine and emery paper with grit number 480,600 or 800, toggling, spraying, Roto press and Ironing machines, area measuring machines.

Laboratory testing and analysis equipment, optical microscope, SEM (Scanning Electron Microscope), tear and tensile strength testing, lastometer, flexing endurance measuring, rub fastness (wet and dry), finishing adhesion are used to test the sample specimens of leather products against standards required for the product.

3.2. Experimental Methods

3.2.1. Wet-Finishing Techniques

Different experimental and control processes were designed by employing different combination of chemicals such as dyestuffs, cationic pigments, dye solution and filler waxes in order to cover up the defects and upgrade the poor quality raw material. Five experimental techniques were employed for improving the quality of the low-grade sheep skins. For each experiment a respective control experiment was also conducted. The dyes and auxiliaries used for the five experimental techniques are given in Table 3.1.

Table 3.1 variation in the wet finishing process

Sl. No	Experiment	% offer of the chemicals
1	Brown FBR	2
	Ink dye (brown IFL)	1
2	Brown FBR	3
	Brown pigment	2
3	Brown FBR	3
	Brown pigment	2
	Filler waxes	3
4	Brown FBR	3
	Brown pigment	2
	Filler wax	5
5	Brown FBR	2
	Ink dye (brown IFL)	1
	Brown pigment*	2
	Filler Wax*	3
In all control leathers, 3% of Brown FBR was employed *Chemical offered in fresh bath after fixation		

- In the first experiment, in addition to the conventional dye stuff, concentrated ink dye (dye solution) was employed for dyeing of the leathers.
- For the second experiment, additional offer of conventional dye stuff along with a brown pigment was employed during the process.
- For the third experiment, in addition to the conventional dye stuff, brown pigment and filler were employed during the process.

- For the fourth experiment, in addition to the conventional dye stuff, brown pigment and increased quantity of filler wax were employed during the process.
- For the fifth experiment, in addition to the conventional dye stuff, dye solution, pigment and filler wax were employed during the process. In this experiment, brown pigment and the filler wax were used in the fresh bath after fixation of the post tanning bath.

3.2.2. Finishing Techniques

After optimizing the wet finishing techniques, different finishing techniques were conducted to cover up the defects and upgrade the low-quality skins. Here again, five different types of finishing techniques were evaluated for its efficiency, in covering up the defects. The different types of finishing employed are crunch effect, corrected grain finish, metallic finish, cationic finish and waxy finish. Conventional resin finish was used for control leathers for comparison. The process recipes are provided in the following tables (Table 3.2 to 3.7)

Table 3.2 Wax finish (crunch effect) mix formulation

Chemical description	Parts				Application
	1	2	3	4	
Wax ME	100				3 x coat the season, dry properly
Glitter wax LL	30				
Polyurethane binder	25				Transparent foil plated on to the leather at 80^{o}C temperature and 100 psi pressure
Dye solution	20				
Water	50				

Table 3.3 Corrected grain finishing formulation

Chemical description	Parts				Application
	1	2	3	4	1 x spray coat on the crust leathers, and dried properly, plated at 90 ^{o}C temperature and 100psi/pressure
Compact burnish, levelonte binder	150				
Pigment	50				
Water	150				

Table 3.4 Metallic finishing formulation

Chemical description	Parts			Applications
	1	**2**	**3**	
Luster UT	100			3X spray coated, dried properly and plated with temperature 85 ^{o}C and 100psi pressure
RPU 048	100			
Comp A086	50			
Wax	50			
Alpatop L101	50			
Slip 100	10			
Metallic pigment	50			
Dye solution	10			
Akral RF 905	50			
Water based lacquers		500		2x spray coated, dried properly, and plated with 100 psi pressure and at 85 ^{o}C temperature
Water		500		

Table 3.5 Cationic finishing formulation

Chemical descriptions	**Parts**			**Applications**
	1	2	3	
Prefondal K-78	100			3x spray coated, dried properly and polished. And same season 2x spray coated dried properly and plated with temp. 90 ^{o}C and pressure 100 psi
Cational VFC	100			
Cational GN	50			
RPU SW 260	60			
Cational PK -wax	60			
Cationic pigment	30			
Water	100			

Table 3.6 waxy finishing formulation

Chemical descriptions	Parts			Applications
	1	2	3	
Alpatop BS	50			3x spray coated and dried properly.
Alpatop L101	40			
Alpatop F143L	30			
Alpatop F73V	20			
Pigment	20			
Dye solution	20			
Water	50			

Table 3.7 Resin finishing formulation

Chemical description	Parts			Applications
	1	2	3	
Protein binder	100	30		1. 3 x spray coated, dried properly and plated at a temp. 95c^0 and 100psi pressure. 2. 3 x spray coated, dried properly. 3. 2 x spray coated, dried properly and plated at temp. 95c^0 and 100psi pressure.
Resin binder	100	60		
MSR PU 92	100	75		
Soft PU	50	5		
BM binder	200			
Slim S 134	5			
Pigment	100			
Wax	40	20		
Water	485			
Water based nitro cellulose lacquer			500	
Water			500	

All these finishing techniques use different types, amounts and combination of chemicals and will be applied on the defective leathers to upgrade the leather by covering the uncovered defects. An optimized process that resulted having better covering was selected and additional processes using wet blue leather was conducted to further ensure its performance and scaled up for bulk production.

3.2.3. Scanning Electron Microscope (SEM) study of surface defects and features of leathers

The surface defect due to mange in both wet blue and crust leathers were examined optically in order to understand the degree of the defects. Based on the extent or degree of defects distribution on the surface of leather, compatible leather processing strategy were designed so as to improve the quality of the end product, which is used for making shoe upper. A sample was cut on the butt area of the skin for SEM examination. Before examination of wet blue leather by scanning electron microscope, the moisture content of samples was removed using different concentrations of acetone and alcohol. The SEM samples were coated with a thin layer of metal (usually gold or gold-palladium). The metal coating makes samples conductive.

3.2.4. Physical testing methods and Requirements

Physical testing is one of the measure of a given leather product meet certain standard requirements developed for the product. It is one way of evaluating the quality of the leather. Only those physical tests are carried out for a particular leather which have similarities with its use as a leather product. Since the physical testing results of a leather varies with atmospheric conditions, all experiments are carried out after conditioning the test specimens in a standard atmosphere, internationally recommended ($27 \pm 2^{o}C$) dry bulb temperature and $65 \pm 2\%$ relative humidity [13]. In this research work, the crust leathers after the wet finishing experiments were assessed for tensile strength, % elongation, tear strength and grain crack strength as per the standard procedures [14-16].

3.2.5. Grading of Leather

Grading of leather is carried out at either after wet finishing or after finishing of leather, before area measuring and packing. In fact, grading of leather starts in a semi-processed stage, pickle/wet blue or crust in leather manufacturing industries. The sales price of a finished product is based on the grade of the leather, on the other hand, grading is a measure of whether a product is a good quality or not or grading shows whether an improvement in quality had been made with technologies employed in leather manufacturing processes [17,18]. Therefore, grading of a leather is done by experienced experts. A leather is graded based on the type and size of defects and also the distribution on the surface of the leather. Here, it is graded based on Ethiopian standard work directives sated for each individual product type. It could be graded from Grade I, II, III, IV, V up to reject depending on the quality of the products. These days, grading is done as I- IV as TR (table run) in one category, V & reject because the quality of the leather is declining due to different factors and reasons. The major problem which contribute for low selection result is Ecto-parasite damage of skin surfaces specially mange disease on sheep and goat skins. Grading is based on the useable area of a leather, improvement in defects coverage, natural appearance or look of leather surface grain a leather that has large useable area will have higher grade which means less defects on the surface. The description of grading of chrome tanned crust leathers is provided in Table 3.8.

Table 3.8 Grading of chrome tanned dyed crust for upper leather

Grade	Useable area by % of total area	Description of visual assessment defects
I	85- 100	The skin/hides should have well filled flanks and even substance with smooth and light grain appearance. The crust leather could have closed surface defects randomly spread-out which could be covered on light finishing. The closed defects could be healed snatches, tick, small scar
II	70 - 84	The crust will have good grain with well filled blanks and could have few open defects as well as closed defects which could arise from thick ekeks, scars, and scratches which eventually will be covered on finishing.
III	55 - 69	This crust leather will have similar grain pattern and filled as grade II and similar defect including one or two cuts on skins/hides surface randomly scattered over major portions.
IV	40 - 54	The chrome tanned crust leather will have similar defects as in grade III with some more open defects like open scratches, licks, wound, grain indentation, and grain damages as well as some loose flanks.
V	25- 39	This skins/hide chrome crust leather will be similar to grade IV but will include brand marks, holes, deep knife cuts.
R (Reject)	< 25	Chrome crust leather will have useable area of < 25

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Upgradation and Optimization of Wet-Finishing Process

In wet-finishing, different experiments were conducted to upgrade and optimize the quality of skins attacked by parasites especially mange diseases. In control process, a conventional dyestuff was employed. For experiment and control process low-grade wet blue leathers of thickness 0.8-0.9 mm were employed.

Experiment 1

In this process, conventional dyestuff, brown FBR and dye solution were used in dying for experiment and conventional dye stuff brown FBR only was used for control. Then the defect coverage on the leather surface and subjective properties of the dyed crusts were visually assessed. Figure 4.1 depicts the wet blue and crust leathers from control process. Figure 4.2 depicts the image of wet blue and the experimental crust leathers.

Figure 4.1 Wet blue leather with surface defects and dyed crust leather control

Figure 4.2 Wet blue leather with mange disease and dyed crust leather experiment 1

From figure 4.1 and 4.2, it can be observed that in both control and experimental leathers the defects were not covered as expected. The ink dye used for the experiment, did not have sufficient covering power, rather highlighted the defects and resulted non-uniform shade on the leather surface. The pits which are seen on the skin surface is shown as blacked spot on the dyed crust leather surface, which still needs further treatment in order to hide or to cover the defects. However, it could be seen that the experimental leathers were darker in shade than the control leather. This could be attributed to the use of ink dyes/ concentrated dye solution. Also, in control crust leather, the leather surface was lighter and the defects were seen without having any pronounced difference from the wet blue leather defects.

Experiment 2

In this process, conventional dyestuff, brown FBR and brown pigment were used in dying for experiment and conventional dye stuff brown FBR only was used for control. The defect coverage on the leather surface and subjective properties of the dyed crusts were visually assessed. Figure 4.3 depicts the wet blue leathers and the crust leather from control process and Figure 4.4 depicts the image of wet blue and the experimental crust leathers.

Figure 4.3 Wet blue leather with surface defects and dyed crust leather control

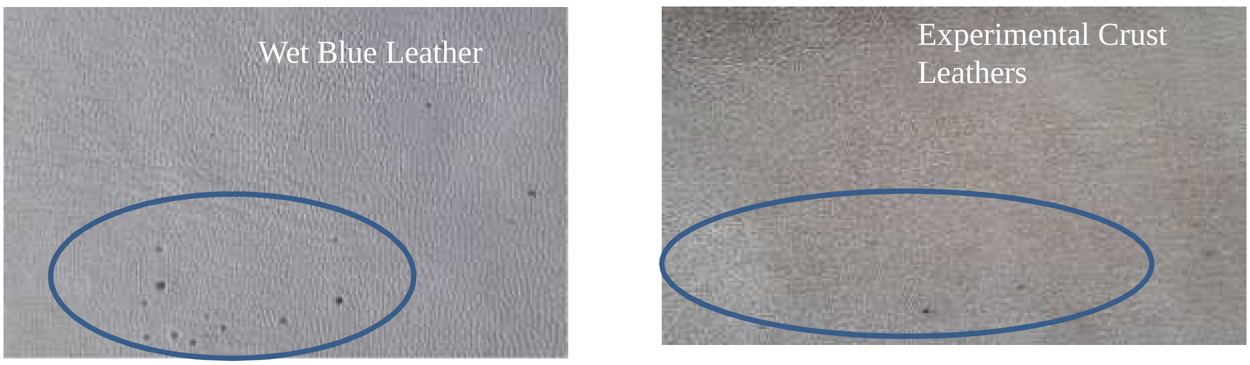


Figure 4.4 Wet blue leather with mange disease and dyed crust leather Experiment 2

From the figures 4.3 and 4.4, it can be observed that in both control and experimental leathers the defects were not covered as expected. The use of pigment resulted in darker shade of dyed crust leather surface. When compared to control leathers, the experimental leathers showed better covering of defects. This could be due to the effective hiding power of the pigment used in the study.

Experiment 3

In this process, conventional dyestuff, brown FBR, brown pigment and filler wax were used in dying for experiment and conventional dye stuff brown FBR only was used for control. Figure 4.5 depicts the wet blue leathers and the crust leather from control process and Figure 4.6 depicts the image of wet blue and the experimental crust leathers.

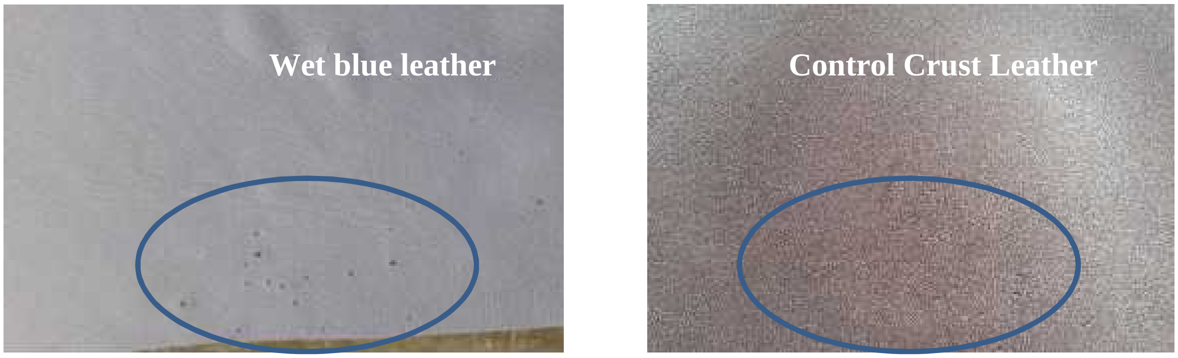


Figure 4.5 Wet blue leather with surface defects and dyed crust leather controls

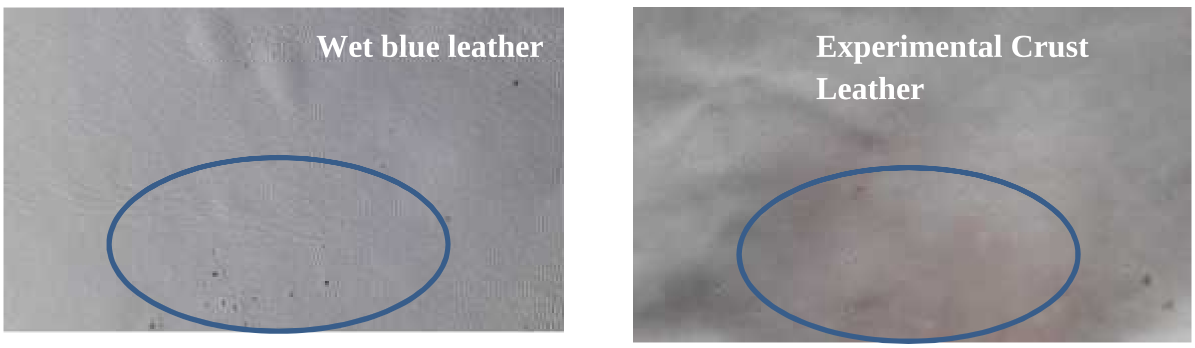


Figure 4.6 Wet blue leather with surface defects and dyed crust leather Experiment 3

From the figures 4.5 and 4.6, it could be seen that in the experimental leathers the defects were almost covered. The use of pigment resulted in darker shade of dyed crust leather surface. When compared to control leathers, the experimental leathers showed better covering of defects, without highlighting the defects. Use of filler wax has improved filling of pits that were seen on wet blue leather. the defects were hidden and some sort of covering is achieved through this process. Whereas on the control dyed crust leather the defects are more highlighted.

Experiment 4

In this process, conventional dyestuff, brown FBR, brown pigment and filler wax were used in dying for experiment and conventional dye stuff brown FBR only was used for control. Figure 4.7

depicts the wet blue leathers and the crust leather from control process and Figure 4.8 depicts the image of wet blue and the experimental crust leathers

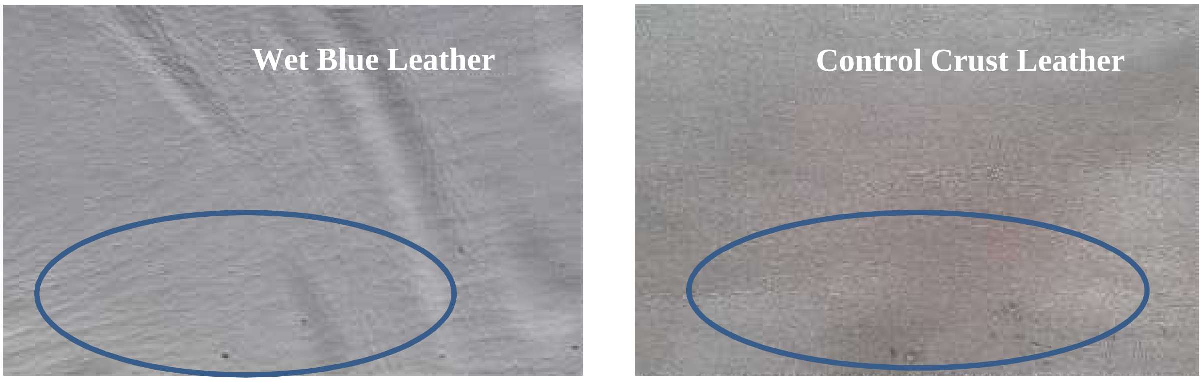


Figure 4.7 Wet blue leather with surface defects and dyed crust leather control

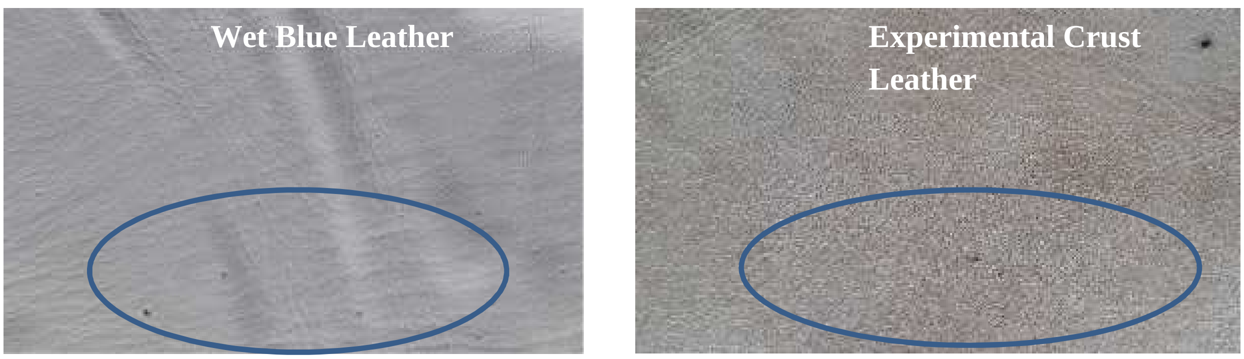


Figure 4.8 Wet blue leather with surface defects and dyed crust leather Experiment 4

From the Figures 4.7 and 4.8, it could be seen that in the experimental leathers the defects were almost covered. The use of pigment resulted in darker shade of dyed crust leather surface. When compared to control leathers, the experimental leathers showed better covering of defects, without highlighting the defects. Use of increased amount of filler wax has improved filling of pits that were seen on wet blue leather. The defects were hidden and covering is achieved through this process. However, owing to the increased use of wax, the final crust leather was seen pale in color.

Experiment 5

For the fifth experiment, conventional dyestuff, brown FBR 2%, and dye solution 1% were used during the main dyeing process. After fixing the post tanning bath using formic acid, the bath was drained. In the fresh bath, brown pigment 2% and filler wax 3% were employed for improving the covering of surface defects of wet blue sheep skins damaged by mange disease and the following picture shows how the defects were there before and after wet-finishing on the leather surface. For control process, only conventional dye stuff (brown FBR) was employed. Figure 4.9 depicts the wet blue leathers and the crust leather from control process and Figure 4.10 depicts the image of wet blue and the experimental crust leathers.

Figure 4.9 Wet blue leather with surface defects and dyed crust leather control

Figure 4.10 Wet blue leather with surface defects and dyed crust leather Experiment 5

From the Figures 4.9 and 4.10, it could be seen that in the experimental leathers the defects were almost covered. The use of pigment on top after fixing has resulted in darker shade of dyed crust leather surface. When compared to control leathers, the experimental leathers showed better covering of defects, without highlighting the defects. Use of increased amount of filler wax has improved filling of pits that were seen on wet blue leather. The defects were hidden and covering is achieved through this process. Whereas in control leathers, the pits were not filled and the colour of the crust leather was also lighter. The overall observations from all the five experiments are tabulated in Table 4.1.

Table 4.1: Visual observations on crust leathers after all five wet finishing experiments

Processes	Observations	Remark
Experiment1	As can be observed, the processed dyed crust leather for sheep upper of experiment1 and control1, in experiment1 dye solution was used together with the conventional dyestuff, here the dye solution resulted in poor hiding of defects, rather highlighted the defects and resulted in lighter and non-uniform shade of the leather surface. The pits which were seen on the skin surface was shown as blacked spot on the dyed crust leather surface which still needs another leather processing techniques and mechanism to hide or to cover the defects further. The control1 dyed crust leather, the leather surface is lighter, darker shade and defects were seen having without any pronounced difference from the wet blue leather defects.	No covering of defects has been observed, rather the defects are more highlighted
Experiment 2	- Use of pigment resulted for darker shade of dyed crust leather surface. - Good covering without highlighting defects resulted for experiment dyed crust leather - The dye used caused some sort of non-uniformity of color or irregularity in dyed crust leather.	No improvement in defect coverage

Processes	Observations	Remark
Experiment 3	• Use of pigment resulted in darker shade in the experiment crust leather. Good covering without highlighting defects have be observed on experiment with brown FBR, pigment and filler wax combinations on the dyed crust leather • Use of filler wax has improved filling of pits that are seen on wet blue leather. • Defects are hidden and some sort of covering is achieved through this process • Whereas on the control dyed crust leather the defects are more highlighted	Improved defect coverage
Experiment 4	• Use of higher quantity filler wax improved the covering of pits	Improved defect coverage
Experiment 5	• The filler wax used in dyed crust leather has covered or filled the pits on the crust leather whereas in the control crust leather the pits remain unfilled or uncovered	

4.1.1. Optimized Process Recipe

Out of five experiments conducted, Experiment 5, was found to be efficient in covering the defects in a better way. In this experiment, as like control process, 3% of brown FBR was used. However, in addition to Brown FBR, brown pigment and filler wax were employed after the fixing of the post tanning bath. This particular experiment was very much efficient in covering of the defects and could upgrade the leather. Leathers prepared by following this optimized process was further taken for finishing experiments. The optimized process recipe is provided in Table 4.2.

Table 4.2 An optimized process recipe for wet- finishing

Process	Description	%	Tem.	Amount Kg or L	Total time	Time		Control parameters	Remark
						From	to		
Neutralization	Water	100	28ºC		3x10'+30				
	Sod. bicarbonate	0.50							
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
Retanning	Acrylic resin	3			30'				
	Replacement syntan	4			40'				
	Melamine syntan	3							
	Veg.syntan	2							
	Dye leveling agent	2			10'				
Dyeing	Brown FBR	3			45'			Check cross-section	
Fatliquoring	SYF	5			2x30'+60'				
	SSF	4							
	LecithinFatl.	3							
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15'				
Fixing	Formic acid	3			5x10'+30'			Check ph	D/w/w
Top dyeing & retanning	Pigment	2			30'				
	Filler wax	3							
Fixation	Formic acid	1			2x10'+15'				D/w/o/pile

4.1.2. Organoleptic property assessment

Organoleptic properties measure the subjective properties of the leathers. Dyed crust leathers from the optimized experimental process were assessed for softness, grain tightness, defect coverage, fullness, grain smoothness, shade and surface properties through experienced expert evaluation by tactile assessment and compared with that of the control leathers.

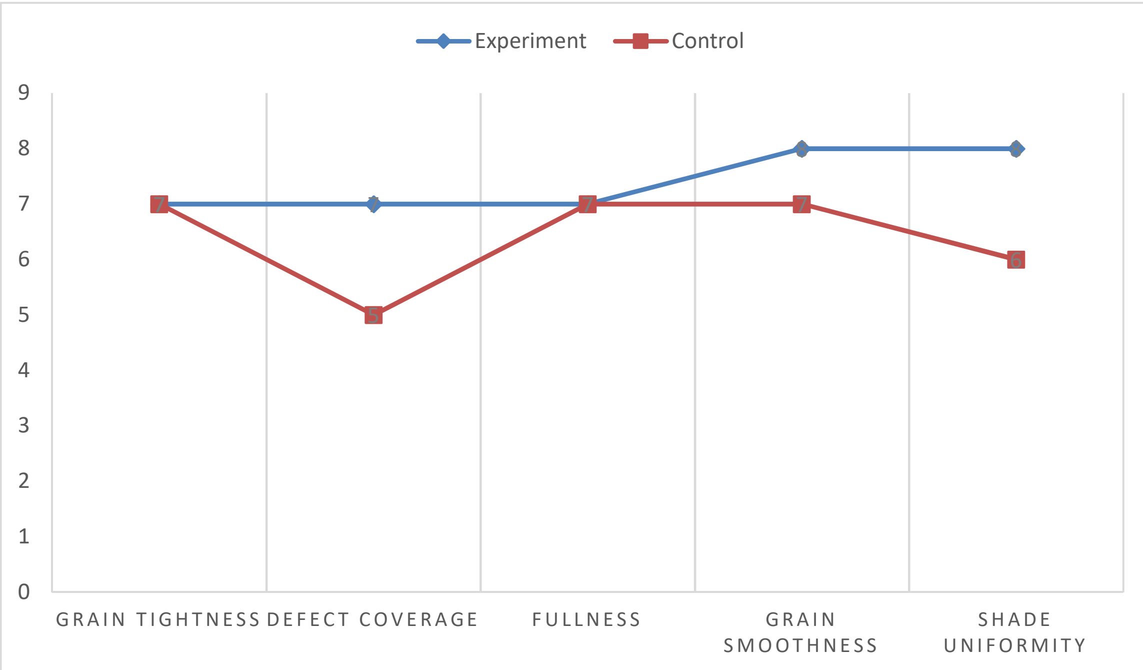


Fig 4.11. Organoleptic properties of dyed crust leather from optimized process against the control leather

From Fig 4.11, it can be pointed out the differences in organoleptic properties, defect coverage, grain smoothness and shade uniformity has shown an improvement for the leathers made using optimized process. Because the filler wax and pigment used most of the defects and pit holes and where as other organoleptic properties remain the same for both experimental and its respective control leather. Both the dyed crusts had the same fatliquoring and retanning process. Filler wax and pigment combination used in processing wet blue leather into dyed crust leather gave better coverage of the defects. Hence the pigment and filler wax used in post tanning has improved the quality of the dyed crust by hiding and filling surface defects on the leather. So, they can be used for upgradation of lower grade wet blue skins surface damaged by mange diseases. Still additional work has to be done in finishing to enhance the upgradation process to cover up the uncovered defects.

4.1.3. Microscopic Examination of Leather

A surface examination of wet blue and dyed crust leathers were carried out by employing optical microscope to see the defects before and after wet-finishing of defective wet blue leather, to do that a sample of small pieces of wet blue and dyed crust leather were cut from the butt area with defects from skin and dyed crust leathers. The sample surfaces were examined through magnifying microscope. 4X magnification were done for both samples and the degree of defects coverage was assessed.

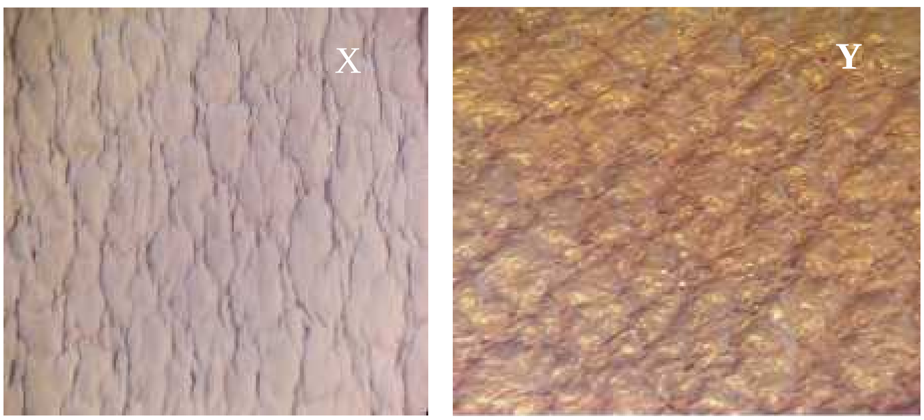


Fig 4.12.: **Microscopic surface picture of wet blue (X) and dyed crust (Y) leathers, experiment**

From magnified microscopic image of the dyed crust leather it could be observed that the defects were hidden and pits were covered by the pigment and filler wax, also uniformity of the dyed crust leather was achieved too.

4.1.4. Physical Test strength results of dyed crust leathers

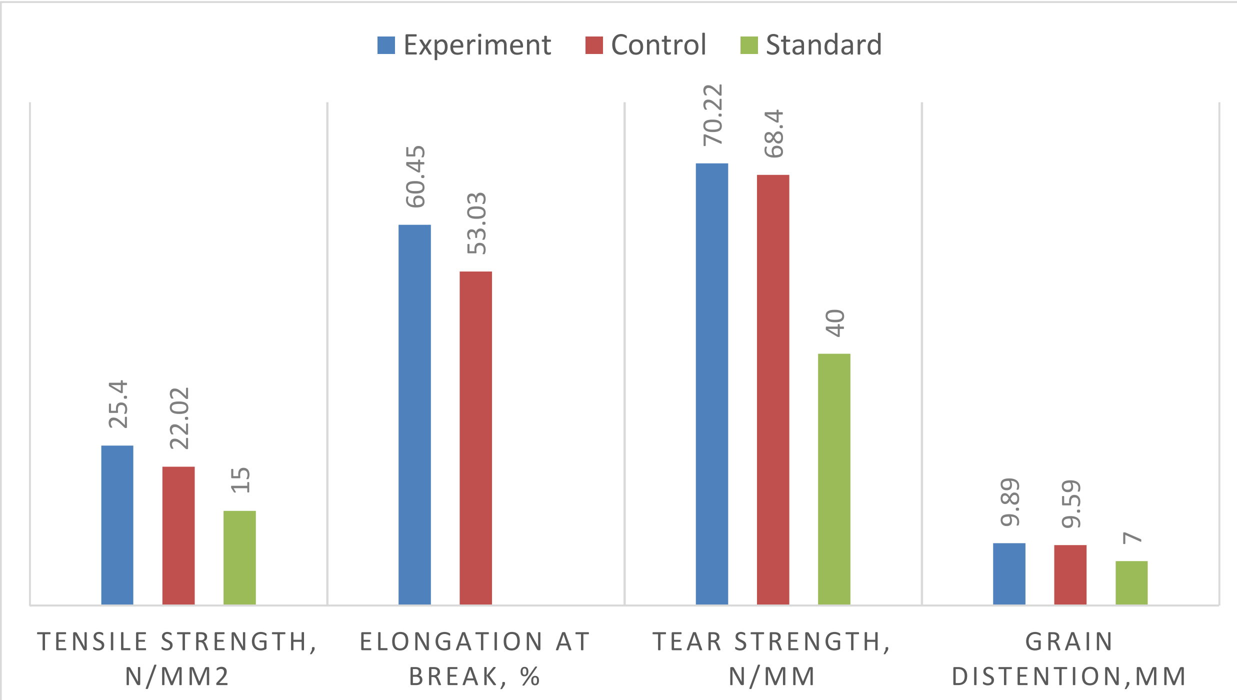


Figure 4.13 Strength properties of dyed crust experiment and control

The average physical testing results of dyed crust leathers from experiment and control trials for tensile, % elongation, tear strength and grain distention at break are depicted in Figure 4.13. The average tensile strength for experiment and control was 25.4 and 22.02 N/mm^2, respectively which was better than the standard 15N/mm^2 values. From these values, it could be inferred that the chemicals used for upgradation had no influence on the tensile strength properties of dyed crust leather. Similarly, the average elongation at break, tear strength and distention test results of dyed crust of the experiments and their respective controls were better than the standard requirements, which again confirms strength properties are not affected by the use of chemicals in upgradation.

4.2. Finishing Techniques for Upgradation Lower end Leathers

In this section, different kinds of finishing techniques are employed to cover up the defects which were not covered through wet-finishing process. Five finishing types were selected for improving the performance of dyed crust leather which were taken as experiments and were compared against the conventional resin finishing as control process. Finishing methods employed are: -

1. Crunch effect
2. Corrected grain finishing
3. Metallic finishing
4. Cationic finishing
5. Waxy finishing

The above finishing methods were carried out on dyed crust leather with defects on skin surface. Resin finishing was used as a control process.

4.2.1. Crunch Effect- Aniline Finishing

Leather was treated with a clear aniline dye and wax finish so that the colour and the natural grain pattern of the leather is visible. Aniline finishing was applied to preserve the natural look or appearance and handle of the final product. In this experiment, the defective leathers were sprayed with thin coats of the chemical formulation having aniline dye and wax emulsion.

a) Dyed crust leather b) Wax finished leather

Fig. 4.14: - Dyed crust leather (a) and (b) crunch effect leather

It could be seen from the Figure 4.14 that application of wax resulted in darkening of shade and pull up effect. Due to the darkening of shade, the defect coverage was obtained. In addition, application of transparent foil provided high gloss to the final leather. However, some sugariness of the finish film was observed on the leather surface.

4.2.2. Corrected Grain Finishing

The dyed crust leather was slight surface snuffed using 480 grit emery paper by buffing machines to level out the surface defects and avoid surface irregularities.

a) snuffed dyed crust leather

b) Corrected grain finished leather

Fig 4.15: - a) Snuffed dyed crust leather, and b) Corrected grain finished leather,

Corrected grain leathers have a lesser-known grain. It is a special type of leather, which is corrected and fixed to better its functionality aesthetic qualities. From Figure 4.15, it could be observed that in corrected grain finished leather complete covering of all surface defects was achieved. The imperfections were sanded off and then corrected, corrected grain is used to make pigmented leather. However, the natural look or appearance was not seen.

4.2.3. Metallic Finishing of Leather

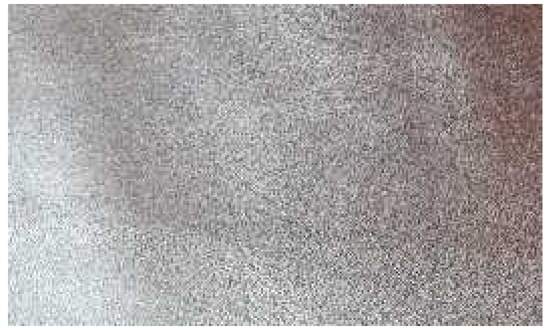
 

Fig 4.16 a) Dyed crust leather ready for metallic finishing and b) Metallic finished leather

From Figure 4.16, it could be seen that in metallic finishing, the finished leather is more glossy and shiny. A slight improvement was observed with respect to defects coverage, in case of metallic finishing. Metallic finished leathers are sensitive to water and it is important to lightly water proof with water and stain protector.

4.2.4 Cationic Finishing

Cationic finishing technology is a new technology applied in improving low-grade skins/hides raw materials to better quality leather. Cationic finishing products includes pigment colors, casein binders, a fine non-ionic acrylic resin, a softy oily emulsion, a filler and a number of other products.

Fig4.17 a) Dyed crust leather ready for cationic finishing and b) Cationic finished leather

From figure 4.17, it could be observed that Being cationic finishing, the defects coverage was better even with a little amount of pigment. The leather was not too much glossy and the natural look or appearance of the finished leather grain is better. The cationic charges gave both chrome and retans with less need to use resins and binders to promote adhesion. This gave better penetration and adhesion of the finish.

In addition, less film loading is formed on the surface of the leather. Cationic products were used with less pigments and resins in the formulation. Furthermore, the cationic finishes had improved softness, fill and lasting properties.

4.2.5. Waxy Finishing

Fig 4.18 a) Dyed crust leather for waxy finishing and b) Waxy finished leather

Waxy finishing is a newer type of finishing, where anionic waxes in combination with polyurethane binders are used. From the Figure 4.18, it could be clearly observed that the defects are completely covered and the natural appearance of the leather is also maintained. It has the advantage of being moisture resistant, and generally does well in poor weather without the leather becoming water saturated and having to dry as normal leather does.

4.2.6. Resin Finishing- Control process

Resin finishing is the conventional process, it uses quite a lot of finishing chemical combinations, it is loading type of finish used to cover the defects.

Fig 4.19 a) Dyed crust leather for resin finishing and b) Resin finished leather

From the Figure 4.19, it could be observed that the control leather with resin finishing recipe showed better defect coverage and had good appearance but there is too much load on grain with poor flexing endurance since it uses more chemicals in the season.

In conventional resin finishing the defects were covered but there is too much loading of finish on the grain surface, poor flexing endurance, and since it had used more finishing chemicals and in addition to physical test quality problems it incurs relatively more cost for producing the product than the other finishing experiments discussed above. Out of the five finishing techniques cationic and waxy finishing was found to be better in terms of improving quality of leather, degree of defects coverage and its appearance to natural look. Also, employs less amount of chemicals as compared to the control conventional resin finishing. Cationic and waxy finishing technologies were the preferred finishing processes optimized in upgrading low selection results of leather with defects with variety of Ecto-parasitic damages specially mange.

4.2.8. Microscopic image of Dye crust and Finished Leathers

The control and experiment dyed crust and finished leathers were examined using stere-microscope for surface defects before and after post-tanning. The images are shown as below. From the microscopic image of dyed crust leather experiment (a) and control (b) above it could be seen that the surface pit hole that were there in wet blue leather have been covered in the experiment (a) and still existed in the control (b). This showed that filler wax had the tendency of filling or covering the defects on the skin surface. Thus, the filler wax and pigment when applied together in wet-finishing, it could upgrade lower selection skins by covering the defects. Here, different techniques and finishing methods to improve the quality of low grade sheep skin crusts that were not covered by wet-finishing had been done. For experiment, five methods of finishing were performed. But, based on the tendency of covering defects and maintaining the natural look or appearance of the finished product quality out of the 5(five) finishing processes methods, one is optimized. The selected finishing method had resulted better quality in upgrading poor grade of skins.

First, two finishing method had resulted an improvement for better performance of the product for upper leather, but after further evaluation of the products with other quality measure parameters, like organoleptic assessment, adhesion and other tests the one with cationic finished product was found to have a better in covering the defects on the leather surface.

The microscopic images of the resin finished leather and the leather finished with cationic finishing are shown in Fig 4.20(a) and(b), respectively. It could be observed that resin finishing had achieved more coverage of defects as more amount chemicals are used. But at the same time, more loading of the finish was observed, when compared to the cationic finished leather. Whereas for the cationic finished leather less amount of chemicals was applied and the natural look or appearance of the finished leather was maintained, also better improvement in quality was achieved. Hence, it could be inferred that the cationic finishing could be efficiently used for improving the lower end selection.

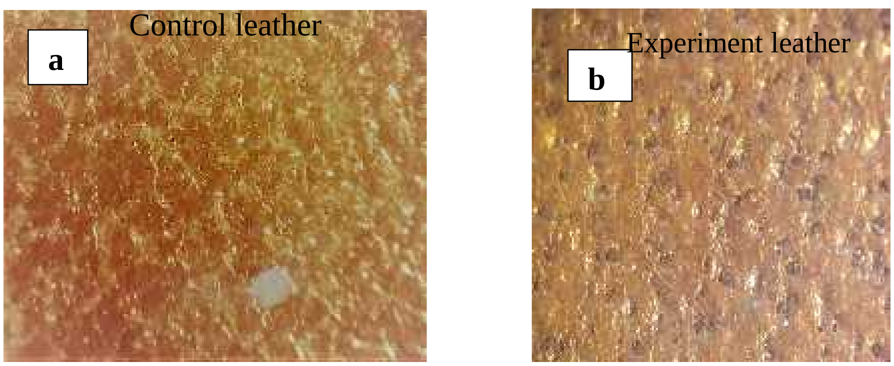


Fig 4.20 a) Resin finished leather and b) Cationic finished leather

4.2.9. Scanning Electron Microscope (SEM) assessment of leathers

A sample around the butt area of the dyed crust leather was cut, prepared for SEM analysis and seen using a scanning electron microscope with 250 x magnification power. The SEM images are shown in Figure 4.21. Similarly, the sample from the finished leathers were also cut from the butt area seen using a scanning electron microscope with 100 x magnification. The SEM images are shown in fig 4.22. The surface image shown using SEM for the dyed crust leather control and experiments depicts that there was a sort of surface coverage of defects achieved in the experiments where in the control still existed. The surface of the control crust leather was uniform, signifying surface uniformity, where the defects were covered in wet-finishing operation to some extent.

From Fig 4.22, it could be observed that the surface of resin finished leather was found to be more sealed and hair pores were not visible owing to the fact that more amount of finish is deposited on the surface. This indicates resin finishing had more loading effect on the surface as discussed in the previous sections due to more amount of chemicals used in the formulation. Whereas in cationic finishing, surface covering is achieved still keeping the natural look or appearance of the leather grain surface.

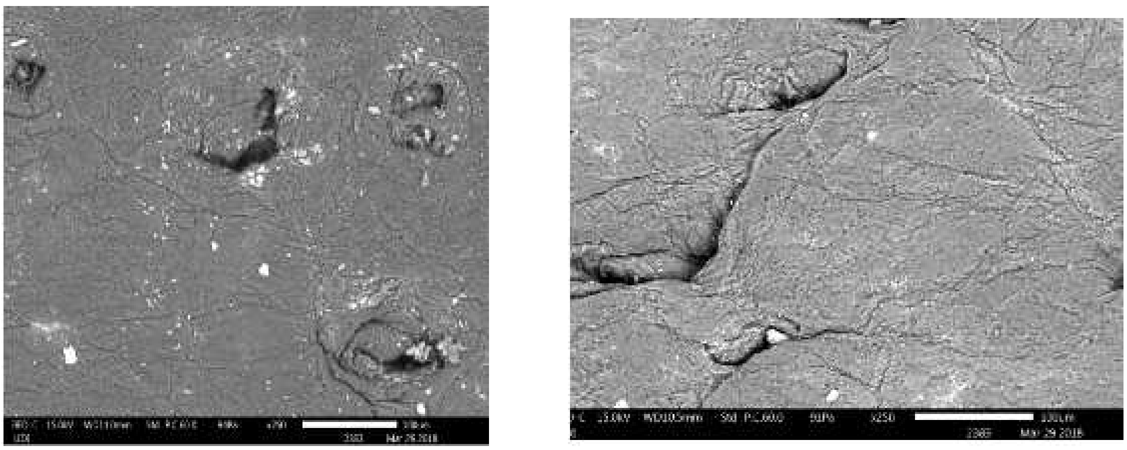


Fig 4.21 a) SEM. Surface image of experiment, dyed crust leather and b) SEM surface image of control dyed crust leather

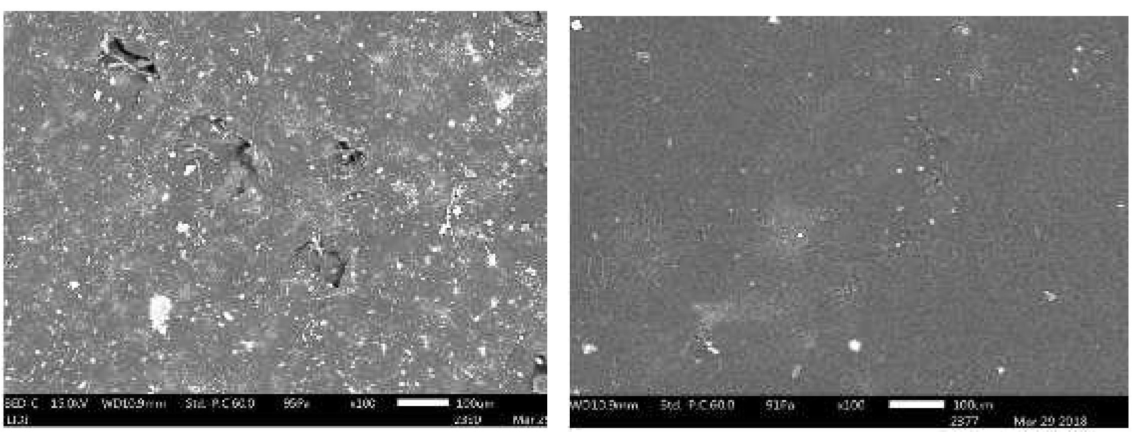


Fig 4.22 a) SEM surface image of cationic finished leather, Experiment and b) SEM surface image of resin finished leather, Control

A specimen of experiment leather that was cut on the butt area of the dyed crust leather was examined for its cross-sectional image using scanning electron microscope (SEM) 100 x magnification, the cross section could be seen in the Fig. 4.23. It could be seen from the figure that the voids in the experimental crust leather are filled with wax, whereas the cross section of the control leathers are empty. Hence, it could be inferred that the filler wax and the pigments used in the post tanning process, not only resulted in smooth grain, but also had a filling effect, which improved the handle properties of the final leathers.

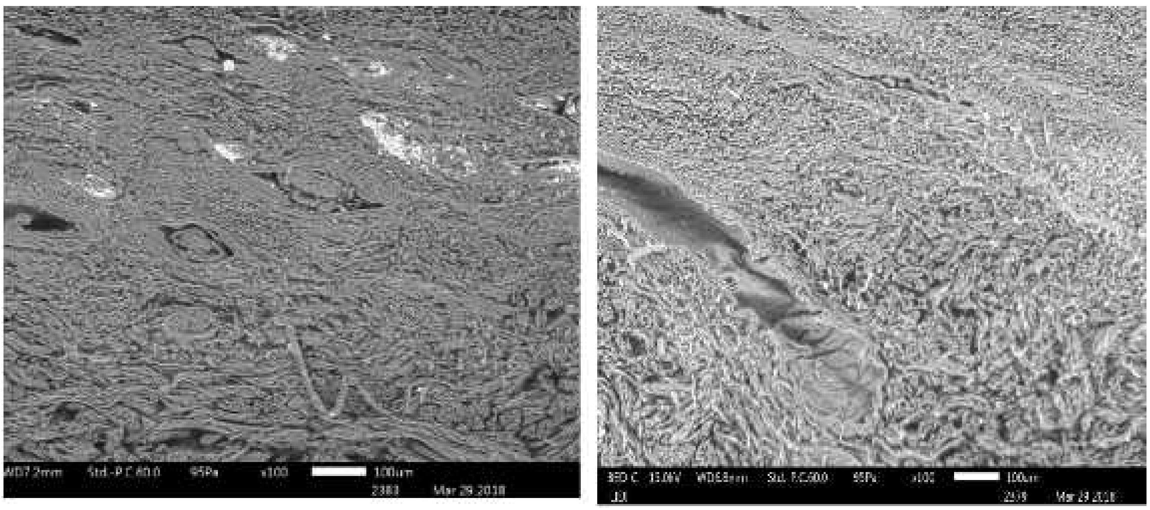


Fig 4.23 a) SEM cross section image of experiment crust leather and b) control dyed crust leather

4.2.10 Organoleptic property Assessment of Finished Leathers

An organoleptic properties assessment was done for cationic, wax (crunch effect), waxy, metallic and corrected grain finished leathers among experiments and the one with better or improved organoleptic property assessment was optimized and finally compared with the control, resin finished leather and rated 0-10 by tactile method by experienced experts from the tanning industry. The properties that were assessed were softness, defect coverage, maintaining natural look or appearance of the finished leather, shade uniformity and improved lasting properties

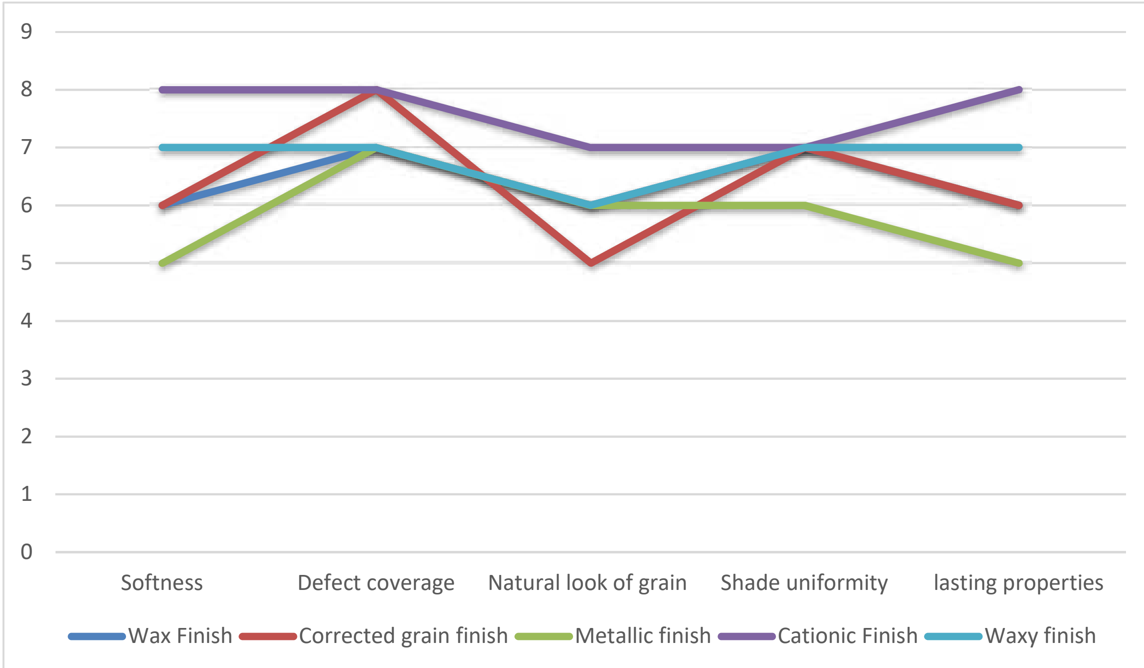


Fig4.24: - Organoleptic assessment of the five finishing methods

The organoleptic assessment performed on the five finishing methods for experiment showed that cationic and waxy finishing had shown better improvement, especially cationic finished leather had shown good defects coverage, natural look of the grain and good lasting properties which is selective property of upper leather. Therefore, from the five experiments that had been done, cationic finishing was selected as optimum finishing process, in handling the defective low-grade skins for better upgradation. From the above figure 4.24, the cationic finishing, with pink line had shown improvements i.e. the pink line goes up, had the highest value showing better in defects coverage and lasting properties.

Both cationic finished leather, experiment and resin finished leather, control organoleptic properties were assessed through tactile by industry experienced experts, rated from 0-10. Those assessed organoleptic properties were softness, defect coverage, natural look or appearance of grain and shade uniformity of the finish. The observations are depicted in Fig. 4.25

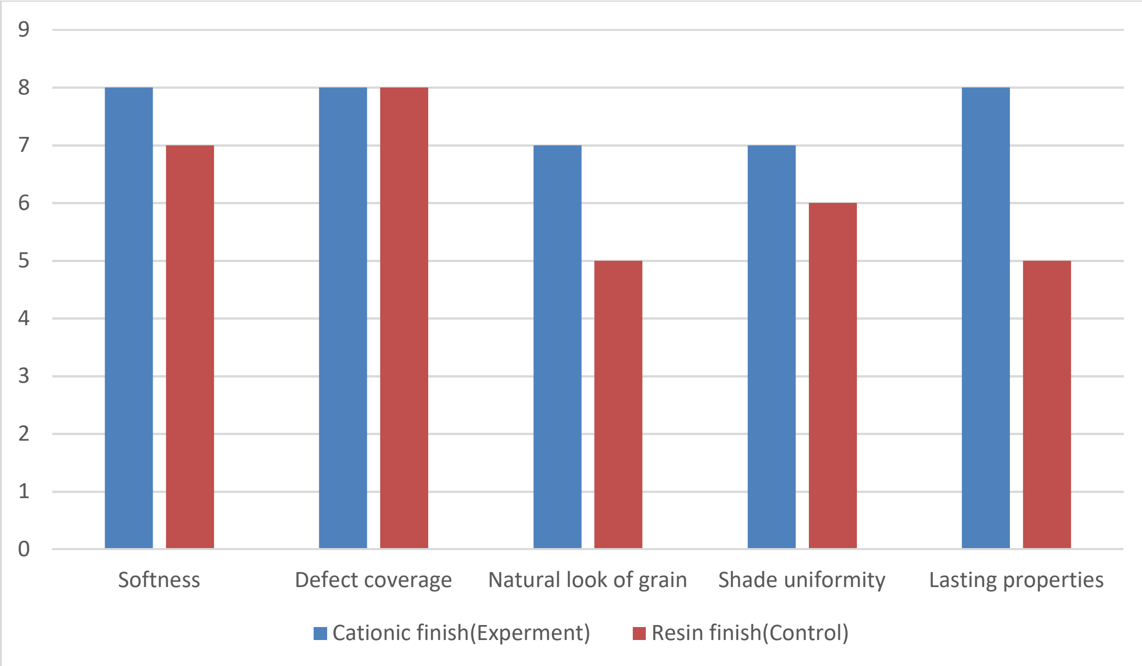


Fig. 4.25: - Organoleptic property assessment of Experiment and control

Comparing the organoleptic properties of cationic finished leather, experiment with resin finished one, control those properties natural look of the grain surface, shade uniformity and lasting properties had shown better improvements for cationic finished leather whereas other property such as defect coverage had been shown to be same. As it had been discussed in the previous sections of finishing, resin finished leather had better coverage but there was more loading of finish, poor flexing endurance and adhesion of the finish. As a result, cationic finished leather had better performance in improving and upgrading the quality of low selection of skins with different ecto-parasitic attack on the skin surface.

4.3. Evaluation of the Final Finished Leather through Grading

After wet-finishing and finishing processes and operations grading had been done on leather finished in the five different finishing types through upgradation and process optimization of lower grade wet blue skins by experienced experts. Grading is one measure of quality of a leather.

Higher grade indicates best quality in terms of defect coverage, appearance, sales value, having large useable area and good organoleptic properties whereas lower grade leather is poor in quality and those mentioned above will not be there. Having this in mind experiments and control finished leathers were grade to ensure how far improvement had been made in those finished leather experiments.

Grade of Original raw material wet blue skins: Reject

Dyed crust leather grade: 5^{th}

Table 4.3 Grade of finished leather by different finishing methods

S/N	**Finishing Types**	**Crust Grade**	**Grade after finishing**				**Remark**
			I-II	**III**	**IV**	**V**	
1	Wax (crunch effect) finishing	5^{th}					
2	Corrected grain finishing	5^{th}					
3	Metallic finishing	5^{th}					
4	Waxy finishing	5^{th}					
5	Cationic finishing	5^{th}					
6	Resin finishing	5^{th}					
	Grade of original wet blue:- Reject						

It could be observed from the Table 4.3 that after crusting, the grade of all the leathers has been improved to grade 5th from reject. However, by proper choice of finishing, the grade was probably improved still further. The grades of metallic and crunch finished leather did not improve further. But, corrected grain leather and the cationic finished leather got upgraded to Grade 3rd. Except for wax and metallic finished leather in the other finishing methods upgrading were found from the input raw material crust grade was 5th. The waxy finished and the resin finished leather were only upgraded to grade 4th.

Good quality and natural look or appearance was attained only by cationic finished leather. But, resin finished and corrected grain leather had too much loading of finish on the surface. In addition, in corrected grain leather the natural appearance or grain is lost due to snuffing and too much covering of the grain was achieved. Hence upgradation of lower selection, poor quality raw materials were made to be improved in cationic finishing keeping the natural look or appearance of the grain surface.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The quality of finished leather, highly depended on the quality of raw material, is a key factor in leather manufacturing industries to be competent in local and international markets. In this work, poor quality sheep skins (reject grade) due to parasitic mange diseases were chosen and studied for improving the quality through process innovation unusual from conventional leather processing from wet-finishing and finishing. As can be seen from the results, low grade reject sheep leathers are upgraded in terms of quality and value of leather after processing with filler wax and cationic pigments in drum based wet-finishing process, which covers surface defects without loading on the grain. Notably, the application of these specialty chemicals on the top immediately after fixing provided better upgradation in comparison to the application in the middle of wet-finishing. Nevertheless, the obtained crust leather still possessed partially covered defects. Hence, we studied the ability of different types of finishing on the coverage of defects without affecting its natural look and other physical properties. Of the different finishing techniques employed, cationic finishing resulted in better quality upper leather with natural look in comparison to the conventional resin finishing and other types of finishing methods. In addition, physical and bulk properties of the upgraded leathers are also better than the leathers obtained from other finishing techniques. The improvement in quality and defect coverage of the leathers was also ensured from light and scanning electron microscopic (SEM) analyses. Hence, the results of this study suggest that high performance shoe upper leather can be produced from low grade sheep skins damaged by mange diseases through upgradation with proper process and chemicals in wet-finishing and finishing processes.

5.2 Recommendations

- Low grade reject sheep skins are improved by working on the proper wet-finishing process using selective chemicals, which covers surface defects without loading on the grain. As can be seen from the results, leather processed with filler wax and cationic pigments are upgraded in terms of quality and value of leather since most of the defects were covered. Here, drum wet-finishing process had been performed with the above mentioned chemicals, consequently, improvement in coverage of defects was achieved.

- Cationic finishing method employed in this work had resulted in better quality upper leather in comparison to the conventional resin finishing method. In addition, physical test results such as flexing endurance were found to be poor in conventional resin finishing due to high amount of chemical consumption, which also added to the cost.
- Based on these results, filler wax and cationic pigments based on wet-finishing followed by cationic finishing method can be used for upgrading the skins attacked by mange diseases.
- The quality of sheep skins is being affected by different factors and hence the raw material supply and the subsequent processed semi-products in tanneries are found to be lower grade in selection. The lower grade wet blue skins are mostly stored in tanneries for a long period resulting in economic burden to the tanners. Hence, instead of processing this lower selection skins in conventional manner, it is recommended to use the result of this research work in achieving quality upper leather with minimum cost.

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Annex1: - Information on the Leather Sector of Ethiopia

1. **Livestock**

Variable	**Number**	**Remark**
a. Population	**CSA (2011/2012)**	**CSA, Central statistical agency of Ethiopia**
Cattle	52,129,017	
Sheep	24,221,384	
Goat	22,613,105	
Camel	979,318	
Others	None	
b. Off –take rate	**ELIA**	**ELIA, Ethiopian leather Industries Association**
Cattle	10%	
Sheep	31.7%	
Goat	32%	
Camel	--	
Others	None	
c. Slaughter facilities		
Industrial/Commercial	Industrial	
Municipal	--	
Slab Houses	168	
Others, If any	Traditional Slab Houses	

Source: -

2. **Production of Hides and skins**

Variable	**Number**	**Remark**
a. Annual production in ton	FAO	
Cattle Hides	75,600	
Sheep skins	15,300	
Goat skins	13,860	

b. Annual collections (in %)	ELIA	
Cattle hides	78.6%	
Sheep skins	84.65%	
Goat skins	82.9%	

3. Tanning Industry

Variables	**Number ITC-2011/2012GC or 2004 E.C**	**Remark**
Number of tanneries in the country	25	
Tanneries in operation	23	
Installed tanning capacity	173,075	
Utilized Capacity	76.73%	
Output of the industry	Pickle, Wet blue, Crust and Finished Leathers	
Number of Employees	6,515	
Market, Local vs International(in %)	Local 23% -export 77%	
Estimated annual export value(in USD)	100.2 Million	

4. Footwear

Variable	**Number/2004E.C**	**Remark**
Footwear factories	17	
In Operation	14	
Manufacturing/production capacity	16,450pairs/day	
Employees	4,654	
Market, Local vs International	Local 42%- Export 58%	
Estimated annual export value(USD)	10.2 Million	

5. Leather Goods

Variable	Number 2011/2012(ERCA) Export Data	Remark
Number of leather goods and garment factories	8	
Numbers in production	8 Engaged in but only 3 export	
Production capacity	3063 pcs/day	
Number of employees	746	
Market, local vs international(in %)	Local 86.6% -Export 13.4%	
Estimated annual export value(inUSD)	184,066.32	

Annex 2: - Recipes used in leather process for experiments and controls for wet-finishing processes

A. Experiment1

2% Dyestuff and 1% ink dye combinations process recipe

Process	Description	%	Tem.	Amount Kg or L	Total time	Time		Control parameters	Remark
						From	to		
Neutralization	Water	100	28c^0		3x10'+30				
	Sod. bicarbonate	0.50							
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
Retanning	Acrylic resin	3			30'				
	Replacement syntan	4			40'				
	Melamine syntan	3							
	Veg.syntan	2							
	Dye leveling agent	2			10'				
Dyeing	Brown FBR	1			45'			Check cross-section	
	IFL brown(ink)	2							
Fatliquoring	SYF	5			2x30'+60'				
	SSF	4							
	LecithinFatl.	3							
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15'				
Fixing	Formic acid	3			5x10'+30'			Check ph	D/w/o/pile

B. Control:

3% Brown FBR process recipe

Process	**Description**	**%**	**Tem.**	**Amount Kg or L**	**Total time**	**Time**		**Control parameters**	**Remark**
						From	**to**		
Neutralization	Water	100	28c^0		3x10'+30				
	Sod. bicarbonate	0.50							
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
Retanning	Acrylic resin	3			30'				
	Replacement syntan	4			40'				
	Melamine syntan	3							
	Veg.syntan	2							
	Dye leveling agent	2			10'				
Dyeing	Brown FBR	3			45'			Check cross-section	
Fatliquoring	SYF	5			2x30'+60'				
	SSF	4							
	LecithinFatl.	3							
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15'				
Fixing	Formic acid	3			5x10'+30'			Check ph	D/w/o/pile

C. Experiment 2

3.5% Brown FBR, 2% cationic pigment and 3% filler wax combinations process recipe

Process	Description	%	Tem.	Amount Kg or L	Total time	Time		Control parameters	Remark
						From	to		
Neutralization	Water	100	28c^{0}		3x10'+30				
	Sod. bicarbonate	0.50							
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
Retanning	Acrylic resin	3			30'				
	Replacement syntan	4			40'				
	Melamine syntan	3							
	Veg.syntan	2							
	Dye leveling agent	2			10'				
Dyeing	Brown FBR	3			45'			Check cross-section	
Fatliquoring	SYF	5			2x30'+60'				
	SSF	4							
	LecithinFatl.	3							
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15'				
Fixing	Formic acid	3			5x10'+30'			Check ph	D/w/w
Top dyeing and filling	Cat. pigment	2			30'				
	Filler wax	3							
	Brown FBR	0.5			15'				
Fixing	Formic acid	1			2x10'+15'				D/W/pile

D. Control

Process	Description	%	Tem.	Amount Kg or L	Total time	Time		Control parameters	Remark
						From	to		
Neutralization	Water	100	28c^0		3x10'+30				
	Sod. bicarbonate	0.50							
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
Retanning	Acrylic resin	3			30'				
	Replacement syntan	4			40'				
	Melamine syntan	3							
	Veg.syntan	2							
	Dye leveling agent	2			10'				
Dyeing	Brown FBR	3			45'			Check cross-section	
Fatliquoring	SYF	5			2x30'+60'				
	SSF	4							
	LecithinFatl.	3							
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15'				
Fixing	Formic acid	3			5x10'+30'			Check ph	D/w/w

E. Experiment 3

Process	Description	%	Tem.	Amount Kg or L	Total time	Time		Control parameters	Remark
						From	to		
Neutralization	Water	100	28c^0		3x10'+30				
	Sod. bicarbonate	0.50							
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
Retanning	Acrylic resin	3			30'				
	Replacement syntan	4			40'				
	Melamine syntan	3							
	Veg.syntan	2							
	Dye leveling agent	2			10'				
Dyeing	Brown FBR	1.5			45'			Check cross-section	
	Dye solution	2							
Fatliquoring	SYF	5			2x30'+60'				
	SSF	4							
	LecithinFatl.	3							
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15'				
Fixing	Formic acid	3			5x10'+30'			Check ph	D/w/w
Top dyeing & retanning	Pigment	2			30'				
	Filler wax	3							
Fixation	Formic acid	1			2x10'+15'				D/w/o/pile

F. Control

Process	Description	%	Tem.	Amount Kg or L	Total time	Time From	Time to	Control parameters	Remark
Neutralization	Water	100	28c^0		3x10'+30				
	Sod. bicarbonate	0.50							
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
Retanning	Acrylic resin	3			30'				
	Replacement syntan	4			40'				
	Melamine syntan	3							
	Veg.syntan	2							
	Dye leveling agent	2			10'				
Dyeing	Brown FBR	3			45'			Check cross-section	
Fatliquoring	SYF	5			2x30'+60'				
	SSF	4							
	LecithinFatl.	3							
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15'				
Fixing	Formic acid	3			5x10'+30'			Check ph	D/w/w

G. Experiment 4:

Process	Description	%	Tem.	Amount Kg or L	Total time	Time		Control parameters	Remark
						From	to		
Neutralization	Water	100	28c^0		3x10'+30				
	Sod. bicarbonate	0.50							
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
Retanning	Acrylic resin	3			30'				
	Replacement syntan	4			40'				
	Melamine syntan	3							
	Veg.syntan	2							
	Dye leveling agent	2			10'				
Dyeing	Brown FBR	3			45'			Check cross-section	
Fatliquoring	SYF	5			2x30'+60'				
	SSF	4							
	LecithinFatl.	3							
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15'				
Fixing	Formic acid	3			5x10'+30'			Check ph	D/w/w
	Pigment	2			30'				
	Brown FBR	0.5			15'				
	Formic acid	1			2x10'+15'				D/w/o/pile

H. Control

Process	Description	%	Tem.	Amount Kg or L	Total time	Time		Control parameters	Remark
						From	to		
Neutralization	Water	100	$28c^0$						
	Sod. bicarbonate	0.50			3x10’+30				
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
	Acrylic resin	3			30’				
Retanning	Replacement syntan	4							
	Melamine syntan	3			40’				
	Veg.syntan	2							
	Dye leveling agent	2			10’				
Dyeing	Brown FBR	5			45’			Check cross-section	
Fatliquoring	SYF	5							
	SSF	4							
	LecithinFatl.	3			2x30’+60’				
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15’				
Fixing	Formic acid	3			5x10’+30’			Check ph=	D/w/0/pile

Experiment 5

Process	Description	%	Tem.	Amount Kg or L	Total time	Time From	Time to	Control parameters	Remark
Neutralization	Water	100	28c^0		3x10’+30				
	Sod. bicarbonate	0.50							
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
Retanning	Acrylic resin	3			30’				
	Replacement syntan	4			40’				
	Melamine syntan	3							
	Veg.syntan	2							
	Dye leveling agent	2			10’				
Dyeing	Brown FBR	3			45’			Check cross-section	
Fatliquoring	SYF	5			2x30’+60’				
	SSF	4							
	LecithinFatl.	3							
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15’				
Fixing	Formic acid	3			5x10’+30’			Check ph	D/w/w
	Pigment	2			30’				
	Filler wax	5							
	Formic acid	1			2x10’+15’				D/w/o/pile

I. Control

Process	Description	%	Tem.	Amount Kg or L	Total time	Time		Control parameters	Remark
						From	to		
Neutralization	Water	100	28c^0		3x10'+30				
	Sod. bicarbonate	0.50							
	Neutralizing syntan	0.50						Check PH=5.2/5.5	D/W/D
Retanning	Acrylic resin	3			30'				
	Replacement syntan	4			40'				
	Melamine syntan	3							
	Veg.syntan	2							
	Dye leveling agent	2			10'				
Dyeing	Brown FBR	3			45'			Check cross-section	
Fatliquoring	SYF	5			2x30'+60'				
	SSF	4							
	LecithinFatl.	3							
	Vegetable Fatl.	2							
Top retanning	protein filler	2			15'				
Fixing	Formic acid	3			5x10'+30'			Check ph	D/w/w

Annex 3: Organoleptic Property Assessment of Dye Crust and Finished Leather for Experiments and Controls

A) Rating 0-10 organoleptic properties of dyed crust of Ex3, Control and Ex5, Con5

S/N	properties	grain tightness	Defect coverage	Fullness	Grain smoothness	Shade uniformity
1	Experiment2(Ex2)	8±0.3	7±0.4	7±0.5	8±0.5	8±0.5
	Control12(Con2)	8±0.3	5±0.3	7±0.5	7±0.5	6±0.5
2	Experiment5(Ex5)	8±0.5	8±0.3	8±0.5	8±0.5	8±0.4
	Control5(Con5)	8±0.5	6±0.4	7±0.5	6±0.5	6±0.4

B) Organoleptic Property Assessment of Leather with Different Finishing Methods

S/N	Finishing methods	Softness	Defect coverage	Natural look of grain	Shade uniformity	Lasting properties
1	Wax finish(crunch effect)	6	7	6	7	6
2	Corrected grain	6	8	5	7	6
3	Metallic finish	5	7	6	6	5
4	Cationic finish	8	8	7	7	8
5	Waxy finishing	7	7	6	7	7

Annex 4: - List Wet-finishing & finishing chemicals used for leather processing with their characteristic properties

A) Wet-finishing chemicals

S/N	Chemical description	Chemical nature	Remark
1	Sodium bicarbonate	Alkaline, neutralizing agent	
2	Sodium formate	Neutralizing agent	
3	Neutrigan	Neutralizing syntan	
4	Novaltan MAP	Acrylic resin(polymer)	
5	DLA	Dye leveling agent	
6	Brown FBR	dyestuff	
7	IFL brown	Dye solution(ink)	
8	Tanigan Os	Replacement phenolic syntan	
9	Protein filler	Fillers with protein nature	
10	Filler wax	Cationic protein waxy filler for wet-finishing	
11	Cationic pigments	Cationic pigment used for filling of defects. Cat. In nature	

B) Finishing chemicals

S/N	Chemical description	Origin/Company	Properties	concentrations	Remark
1	Alpatop L 101	ALPA chemicals	Appearance: - viscous opalescent liquid Synthetic waxy-protein based.	17% ± 1 PH= 8.5 ± 0.5	
2	Cational VFC	ALPA	Waxy modified protein cationic	Conc.=7% ± 0.5 PH(10%soln)=2 .5± 0.5	
3	Alpatop BS	ALPA	Burnish wax anionic	Conc.=22%±0.5	
4	Alpatop F143L	ALPA	High shine Pu anionic		

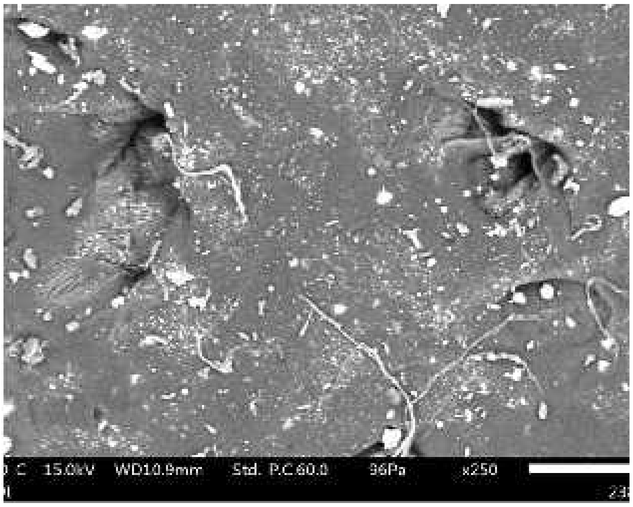
5	RPU 92	STAHL	Medium shine/ soft polyurethane		
6	Bm931	STAHL	Compact binder non-ionic		
7	Alpatop F73V	ALPA	Anionic patent Pu water based		
8	Cational GN	ALPA	Modified protein cationic based		
9	RA 1079	STAHL	Resin binder anionic		
10	FI- 50	STAHL	Season wax anionic		
11	S 134	ALPA	Feel Modifier Non-ionic		
12	LW 653		Lacquer		
13	Akral RF 905	ALPA	Acrylic binder anionic		
14	Lustral UT		Anionic glaze protein		
15	Comp A086		Compact non-ionic		

Annex 5: 2017/18 year's Expert performance of Ethiopian Leather and leather product Industries categorized by product

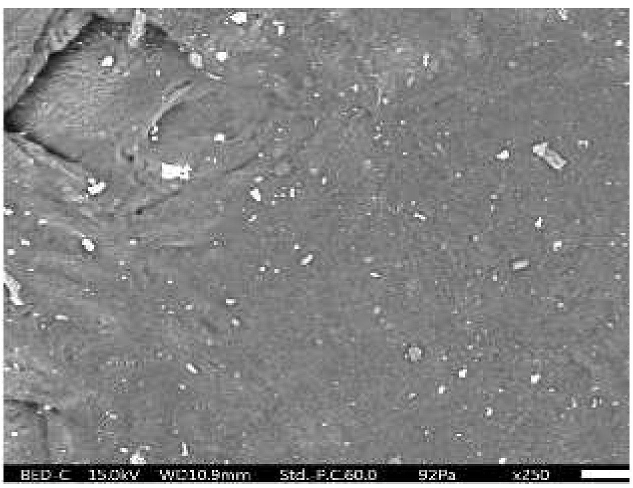
Product category	FOB value in USD	FOB value in BIRR	QUANTITY	Remark
Finished leather(total)	69,055,971.61	1,567,768,490.08	59,007,666.57	
F- Sheep				
Camo	1,606,103.13	36,490,417.52	708,095.45	
Dress glove	8,368,863.44	189,651,285.40	4,823,735.32	
Finished	5,207,865.71	117,934,346.03	2,306,234.45	
Garment	66,730.87	1,492,993.62	19,217.05	
Golf/sport glove	5,812,289.92	131,679,525.08	2,702,925.00	
Lining	2,633,047.32	59,666,124.04	2,989,627.36	
Nappa	597,933.94	13,559,865.15	357,677.39	
Premium	1,204,258.86	27,362,017.23	561,671.59	
Suede	2,366,184.49	53,327,717.27	5,822,820.61	
Upper	5,271,820.50	119,262,951.06	3,803,146.57	
vegetable	1,550,831.50	35,723,263.93	1,794,620.45	
Finished leather sheep Sum	**34,685,929.70**	**786,150,506.33**	**25,889,771.25**	
F-Goat				
Finished	253,706.26	5,790,748.62	113,608.27	
Glove	175,986.08	4,011,558.54	42,300.00	
Lining	3,694,769.14	83,697,765.51	3,917,520.00	
Suede	21,600,008.79	491,835,432.59	20,564,518.22	
Upper	2,896,942.76	65,361,015.74	2,291,726.67	
Finished leather- Goat sum	**28,621,413.03**	**650,696,521.00**	**26,929,673.16**	
F-Cow				
Asa	312,475.82	7,116,516.93	268,428.00	
Cairo	467,101.57	10,781,006.99	362,832.00	
Dyed	3,400.50	77,123.00	5,268.00	
Finished	1,306,299.82	29,915,417.76	1,261,263.00	
Garment	85,591.50	1,916,213.94	149,436.00	
Glove	480,236.55	11,029,269.60	173,037.60	
Lining	2,540,568.29	57,620,008.75	3,279,832.80	
Nappa	11,677.10	264,832.16	10,221.00	

Pull up	7,741.73	176,874.55	7,608.00	
Upper	493,168.67	11,084,834.24	644,843.76	
Vegetable	6,531.00	152,349.29	2,856.00	
waxy	33,805.35	757,015.54	22,596.00	
Finished Leather- Cow sum	**5,748,597.88**	**130,891,462.75**	**6,188,222.16**	
Goods and Garment Total	**2,527,681.85**	**57,030,356.67**	**106,735.00**	
Glove(Total)	**5,023,072.50**	**114,057,028.20**	**1,428,849.00**	
Footware(Total)	**38,566,552.36**	**874,111,292.42**	**4,168,707.00**	
Sandal	**4,517,663.46**	**102,164,907.93**	**528,809.00**	
Shoe	**33,844,204.68**	**767,310,479.81**	**3,613,620.00**	
Sole	**51,861.89**	**1,177,185.68**	**13,671.00**	
Traditional Shoe	**648.00**	**15,076.69**	**1,080.00**	
Upper	**152,174.32**	**3,443,642.31**	**11,527.00**	
Total Sum	**115,173,247.32**	**2,612,937,167.37**	**64,711,957.57**	

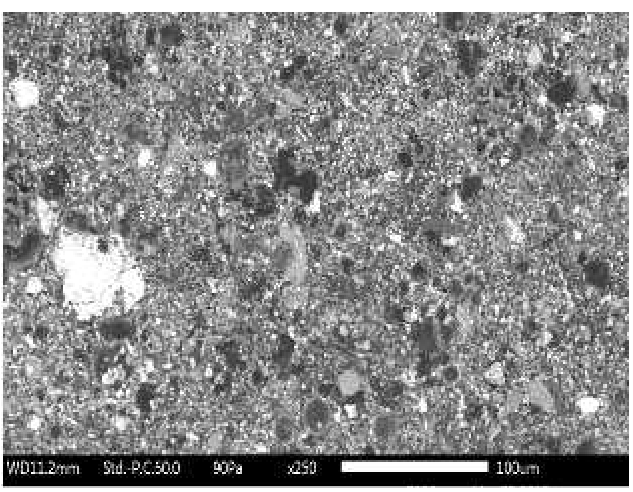
Annex 6: Scanning Electron Microscope Image of Leathers Finished with different Finishing Methods



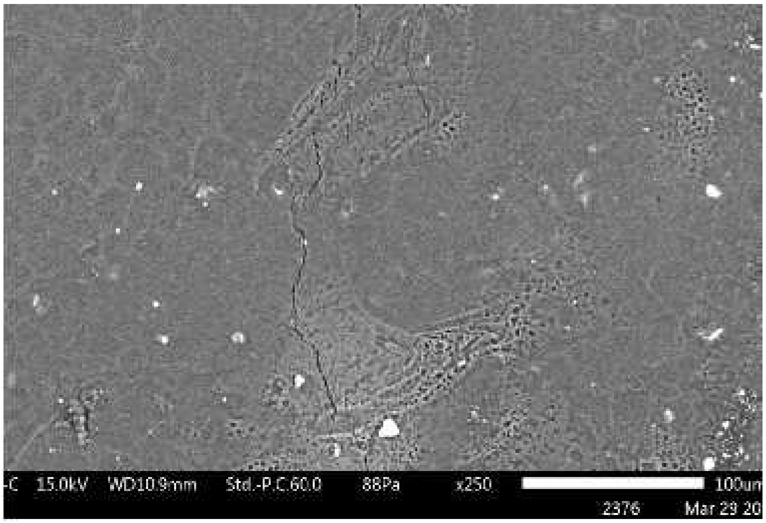
A) **SEM image of cationic finished leather**



B) **SEM image of Wax finished leather**



C) **SEM image of corrected grain finished leather**



D) SEM image of resin finished leather