ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF BIO AND CHEMICAL ENGINEERING

CHARACTERIZATION AND OPTIMIZATION OF CHROME FREE TANNING SYSTEM USING COMBINATION OF CHESTNUT AND TETRAKIS HYDROXYMETHYL PHOSPHONIUM SULFATE

BY

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SEPTEMBER, 2021

ADDIS ABABA, ETHIOPIA

ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF GRADUATE STUDIES
SCHOOL OF CHEMICAL AND BIOENGINEERING

Characterization and Optimization of Chrome Free Tanning System Using Combination of Chestnut and Tetrakis Hydroxymethyl Phosphonium Sulfate

A Thesis submitted to school of graduate studies of Addis Ababa university, Addis Ababa institute of technology, School of chemical and bioengineering in partial fulfilment of the requirements for the attainment of the degree of masters of chemical and bio engineering under leather stream.

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Declaration

The thesis entitled "Characterization and Optimization of Chrome Free Tanning System Using Combination of Chestnut and Tetrakis Hydroxymethyl Phosphonium Sulfate" is conducted by Mr. Haftom girmay under supervision of Dr.P.Thanikaivelan (Senior principal scientist, CSIR-CLRI, India) and Dr-Ing. Berhanu Assefa, AAIT/AAU, Ethiopia. I hereby declare that the information reported in the current paper is the result of my own work, except where work which has formed part of jointly-authored publications has been included. The thesis has not been accepted for any degree and is not concurrently submitted to any candidature for any other degrees or diploma. I have attempted to identify all the risks related to this research that may arise in conducting this work, obtained the relevant ethical and/or safety approval (where applicable), and acknowledged my obligations and the rights of the participants.

Signature

25/10/2021
Date

Abstract

Currently, chrome tanning accounts for more than 90% of global leather manufacturing. This tanning system result in significant material loss and considerable environmental concerns. In the present work, chrome free combination tanning system using a combination tanning system based on Chestnut and THPS is presented. The processing method for Experimental tanning trials were carried out with different percentages of Chestnut as a tannage followed by varying percentages of THPS as a re-tannage for process optimization. The leathers obtained were characterized for their physical strength characteristics, comfort & organoleptic properties, scanning electron microscopic analysis, reflectance measurements and environmental characteristics. The Chestnut-THPS leathers tanned using 20% chestnut followed by 2% THPS resulted in shrinkage temperature of 95^{O}C. The hydrothermal stability of the combination has been found better than the Chestnut alone and THPS alone tanned leathers, respectively. The strength properties and comfort properties of leathers obtained are on par with or better than the control chrome, Chestnut alone and THPS alone tanned leathers. The organoleptic properties of the experimental crust leathers exhibit good grain smoothness, fullness, grain tightness, general appearance compared to control chrome tanned crust leathers. Environmental impact assessment shows the combination tanning system results a significant reduction in TS, TDS, TSS and BOD in the waste water when compared to that of control tanning system. The study presented in this paper established the use of Chestnut and THPS combination tanning system as an effective alternative cleaner tanning methodology.

Keywords: Combination tanning, Chestnut, THPS, Chromium sulfate, Upper leather, Shrinkage temperature.

Acknowledgment

First and foremost, all glory belongs to the almighty God and His Mom Saint Merry for giving me the fortitude, strength and courage to accomplish this graduate thesis work successfully.

I would like to express my deepest appreciation and respect to my external advisor Dr.P.Thanikaivelan (Senior principal scientist, CSIR-CLRI, India) and internal advisor Dr-Ing. Berhanu Assefa for Their invaluable supervision, direction, constant encouragement, and never-failing intellectual support of my studies with lots of energy, excitement, and patience enabled me to complete my research work effectively. This thesis project would not have been possible without their advice and constant assistance.

I am really appreciative for the scholarship opportunity granted by Ethiopia's Leather Industry Development Institute (LIDI) as part of the CLRI-LIDI twinning program, which has provided considerable support for the study.

My heartfelt gratitude also goes to Dr.R. Aravindhan for his valuable contribution by providing all the necessary facilities required for the successful completion of the research work.

I would also want to thank the staffs at the Center for Leather Research Institute (CLRI), especially the technicians and laboratory assistants, for their support and assistance in carrying out my research by providing all of the necessary supplies.

My sincere gratitude also goes to Mr wondu Legesse, former Director General, LIDI, Dr. Shegaw Ahmed, coordinator, AAIT/AAU, Ethiopia, for allowing me to pursue my Masters degree through the Twinning program, Dr. B. Chandrasekaran, former Director, CLRI, and Dr. Madhan, Twinning Project coordinators, for their efforts in ensuring the success of my M.Sc. program.

Finally, I would like to express my gratitude to my loving parents and all of my friends, whose constant inspiration, unwavering support, and sacrifice enabled me to complete this research.

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List of Acronyms

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
ETP	Effluent Treatment Plant
ISO	International Organization of Standard
IULTCS	International Union of Leather Technology and Chemists Society
IUP	International Union of Physical
RH	Relative Humidity
SATRA	Safety and Technical Rescue Association
SD	Standard Deviation
SEM	Scanning Electron Microscope
TDS	Total Dissolved Solids
THPS	Tetrakis hydroxymethyl phosphonium sulfate
Ts	Shrinkage Temperature
TS	Total Solids
TSS	Total Suspended Solids
UV-Vis-Spec	Ultraviolet Visible Spectroscopy
WPR	Water Penetration Resistance
WVA	Water Vapor Absorption
WVP	Water Vapor Permeability

Chapter One

1. Introduction

1.1. Background

Chrome has been utilized as a traditional tanning ingredient in the past. Chromium forms a large number of complexes in its trivalent state, the majority of which are octahedral in shape. Hexavalent chromium, a metal ion, is a strong oxidizer. In the presence of suitable ligand environment, chromium iv and v are intermediate oxidation states [58]. In humans and animals Cr(VI) is highly toxic, mutagenic, and carcinogenic, causing damage to the skin, mucous membranes, and respiratory system [44]. Scientists are putting more effort into creating chrome-free tanning agents due to a growing interest in clean technologies and strict regulatory requirements [57]. They studied new tanning processes in an effort to find a replacement for traditional chrome tanning [26]. Some of the studies shows that the environmental effect of chromium may be mitigated by substituting all or part of the bid with other metal tanning salts. In last several years, techniques have been developed to minimize the use of chrome in the tanning process of leather production as well as to substitute it.

Different tanning systems, such as titanium, silicon, and aluminum tannings, have been developed over the last 15 years to avoid toxic chromium compounds [17, 69]. However, since these leathers contain organic salts, they have their own set of drawbacks. Other tanning options are oxazolidine, polyphenols, formaldehyde, aldehydes, etc. Combining organic (vegetable tannins) and inorganic tannins such as zinc sulfate, sodium silicate, and aluminum sulfate seems to be the most environmentally friendly tanning technology [8, 62 and 63].

THPS is a colorless organic liquid that produces leather with excellent light fastness, very good pelt penetration, light shades, good tanning effect, and white appearance, allowing for the production of leathers with a variety of colors, excellent aesthetic properties, and high physical properties [12, 13, 16].

Chestnut is a type of glucosidic tannin derived from chestnut wood (Castanea sativa). It is pyrogallol in origin and belongs to a group of glucosidic tannins that are easily hydrolysable. Chestnut extracts have a high concentration of acid groups and natural organic acids, which contribute to their astringency and ability to fix larger scales from the hide. These properties allow chestnut extract to produce a leather which is compact, firm, versatile or flexible, and waterproof as well as a high affinity for pelt, allowing for a high tannin fixation. A combination tanning system is a method carried out by use of two or several different tanning agents in the same tanning process which follow each other immediately. In this work, Chestnut in combination with THPS as an alternative tanning system to that of chrome tanning has been studied.

1.2 Statement of the problem

In leather industry, the conventional chrome tannage is still the most commonly used tanning system because of chrome (III) enjoys several advantages as d^3 ion it is related to the stability for both redox and substitution reactions as well as ability of coordinated aqua ligands to ionize in to hydroxyl and polymerize in to larger species in the PH range of 4-6. More than 90% of the 2 billion m2 of leather produced worldwide is tanned using chrome [3, 73]. The potential oxidation of Cr(III) to Cr(VI) or hexavalent chromium, which has been shown to be carcinogenic, mutagenic, highly toxic [2, 24] and causing allergic dermatitis as well as damage to the skin, mucous membranes, and respiratory tract [44]. The dumping of liquid and solid waste containing residual chromium poses the main threat to the environment. Leather products have received a lot of attention as a source of chromium allergy and dermatitis since the 1990s [5, 76]. After nickel and cobalt allergies, contact allergy to chrome is the third most common metal allergy, affecting 1-3 percent of the adult population [75]. Cr III) is supposed to stay in the leather, whereas Cr (VI) is soluble; chromate Cr(VI) is a more potent allergen, and Cr (VI) compounds can cause allergy and dermatitis at lower levels than most Cr(III) compounds [21, 28, and 52]. Skin allergies, dryness, fissured skin, skin ulcers, and puffiness are all symptoms of prolonged skin exposure [78]. In another way, some employees may acquire allergic sensitization, in which a modest amount of exposure causes a severe skin reaction. Dizziness, development issues, reproductive issues,

discolorations, and tooth erosion are some of the other side effects of chromium [60]. Over the last 25 years, Different technologies have been developed, including chromium exhaustion, recycling of basic chromium sulfate and partially replacing it with other organic tanning ingredients, and so on. These approaches, however, have limitations, such as inadequate chromium removal and the potential for human and animal health hazards. In this thesis, a study is presented to investigate an ecofriendly combination tanning system based on chestnut for the production of upper leather.

1.3 Objectives

1.3.1 General objectives

The general objective of this study is to characterize and optimize the chrome free tanning system using combination of chestnut and tetrakis Hydroxymethyl phosphonium sulfate.

1.3.2 Specific objectives

The specific objectives of the study are:

- To investigate the effects of the developed combination tanning system on fiber structure and to comprehend fiber compaction on the surface and in cross-section.
- To characterize Chestnut-THPS combination, Chestnut alone and THPS alone tanned leathers.
- To optimize chemical inputs of the combination tanning system.
- To develop beamhouse and post tanning process recipe.
- To analyze environmental characteristics of spent liquor.

1.4 Significance of the study

The new eco-benign combination tanning system developed completely replaces the conventional chromium tanning which is potentially harmful to the human health. Manufacturing a chrome-free, high-performance shoe upper is needed for diabetic patients because they are not supposed to wear a shoe made of chrome tanned leather. Compared to individual tanning systems, the optimized combination tanning system

produces leather with higher hydrothermal stability, good physical strength characteristics and improved organoleptic and comfort properties. No potentially harmful or dangerous substances were discharged, resulting in a healthy and secure climate. Effluent may be biologically processed at a low cost. During this combination leather manufacturing operations, it significantly reduces unit processes, use of chemicals and water, as a result, the chemical efficiency reduces manufacturing costs and waste water discharge emissions.

1.5 Scope of the research

The developed tanning system were assessed for quality and environmental aspects in comparison to conventionally adopted tanning systems uses for processing of skin in to leather and comparing quality of final leather product by taking under consideration of effluent discharge standard. The technical issues of an alternative system of tanning were compared with the conventional tanning system (chrome & vegetable tanning) as control by taking the chemical parameters like moisture content, fat content and ash content as well as comfort properties such as, water vapor absorption, water penetration resistance and water vapor permeability, hydrothermal stability determination, scanning electron microscopic analysis, measurement of leather reflectance and the physical strength characteristics for tanned as well as post tanned leathers. Then, the environmental issues of an alternative system of tanning will be compared with the conventional tanning system for the pollution load parameters. The limitation of this combination study is, it provides a leather with high yield of weight, then it becomes difficult to produce garment and glove leather product because this final product demands light weight and flexibility.

Chapter Two

2. Literature Review

2.1 Cross-sectional structure and composition of hides and skins

Water, protein, fatty components, and certain mineral salts make up fresh hides and skins. Of these, protein is the most essential for leather. This protein can come in a variety of forms. Collagen, which produces leather when tanned, and keratin, which is the main component of hair, wool, horn, and epidermal structures, are the most significant. A fresh-flayed hide's approximate composition is shown in Figure 2.1.

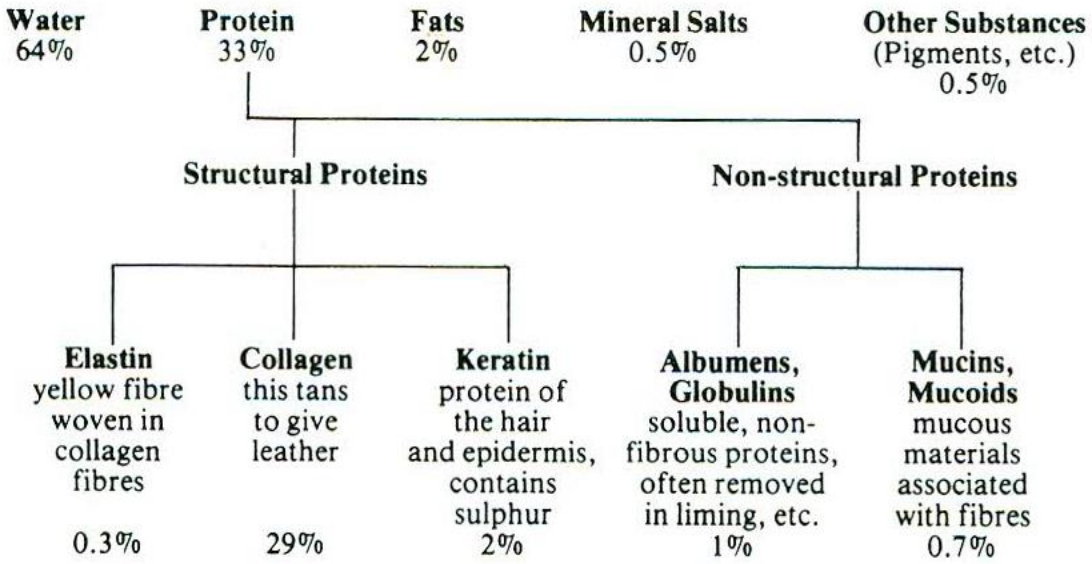


Figure 2.1 Constituents of skins and hides

However, the keratin figure can differ greatly depending on the amount of hair present, and the amount of the fat also vary.

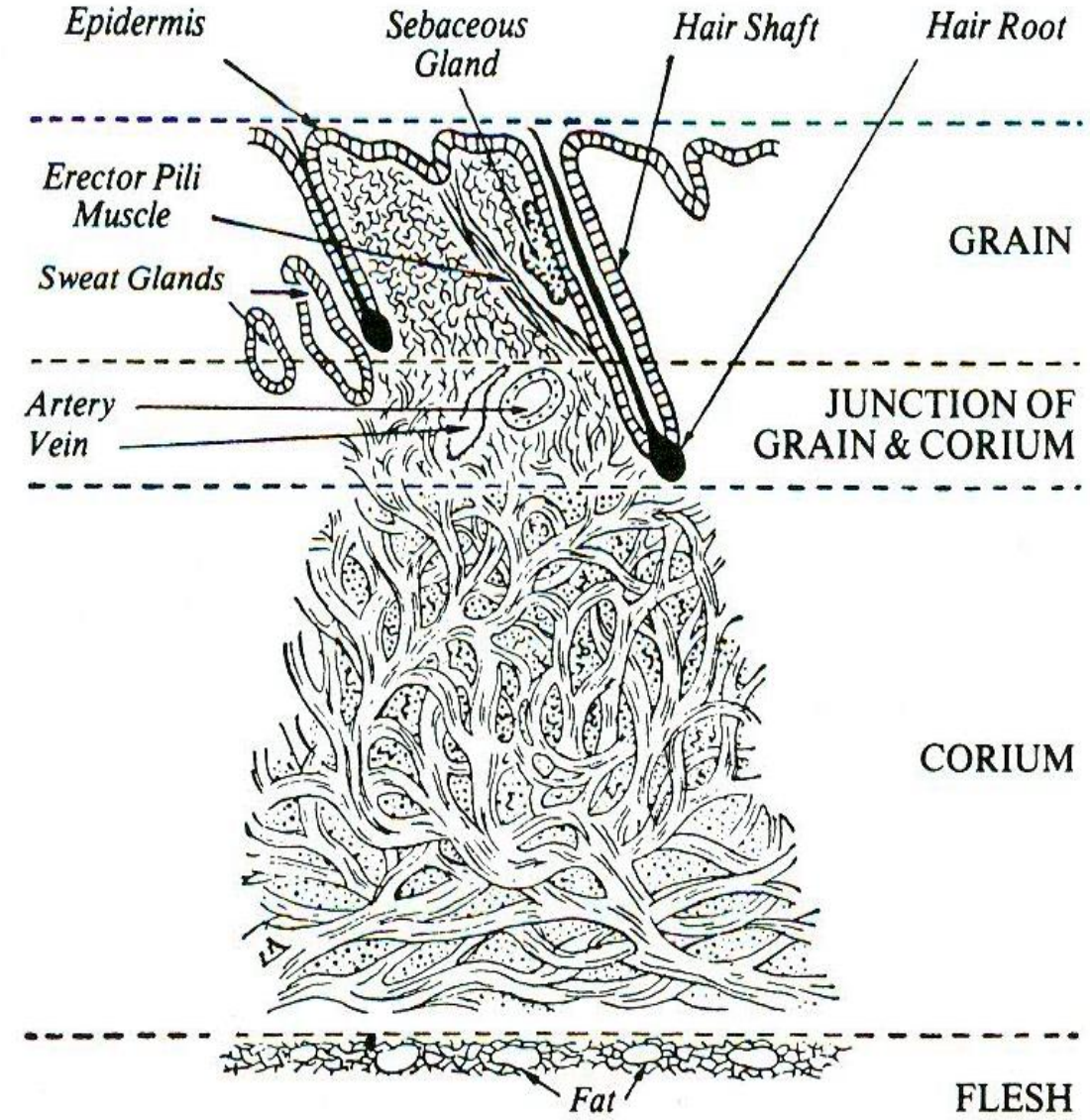


Figure 2.2 Cross-sectional view of hides and skins

A hair follicle pattern inside the skin surface that is uniformly sized and spaced along the grain layer with no distinct pathways distinguishes skin. The skin has relatively straight and shallow hair shafts that do not obstruct the grain-corium junction, with uniform fiber bundles passing through the corium and through the grain to add strength into the leather. However, since the fibers are set at an acute angle, paring can minimize the final leather's strength at the grain and corium junction. Cow-based leathers are the most widely used in the leather industry due to their intrinsic benefits.

2.2 Chrome tanning

Chrome-tanned leather is softer and more flexible than vegetable-tanned leather, has higher thermal stability, is water resistant, and is produced in less time [10]. Chrome tanning provides a very stable fiber that is resistant to bacterial attack and high temperatures due to the reaction with chromium salts. For two reasons, chrome tanning is preferable over other tanning methods: a). It may be completed in a significantly shorter time; and b). It provides leather that combines most of the chemical and physical attributes needed by leather consumers to the best advantage. Despite the fact that the chemistry involved in chrome tanning is extremely complicated, an attempt to simplify it has been investigated. Chromium salts, such as chromium sulphate ($Cr_2(SO_4)_3$) or chromium chloride, exhibit tanning properties. The chrome salt must contain a hydroxyl (OH) group in the complex directly connected to the chromium atom to have tanning characteristics. These chromium compounds are referred to as basic chrome compounds because when dissolved in water, they hydrolyze and produce an intensely acidic solution. The most polluting substance, on the other hand, is emitted following the tanning process. Basic chromium salts are used to ensure the quality of the leather produced, preventing microbial degradation, but they have a considerable environmental impact [8]. At 33% of basicity, 25% of the chromium is present as Cr_2O_3, causing significant pollution [49].

In the tanning process's outgoing fluid stream, about 30% of the initial salt level remains [23]. When this chromium leather waste is released into the air as a gaseous pollutant during the cremation process, it causes environmental difficulties. The creation of the very stable chromium leather waste will be discussed in the following paragraph. (figure 2.4.a) depicts the response of the tanning agent chromium with skin collagen, resulting in the stabilization of the collagen matrix's triple helical structure [27].

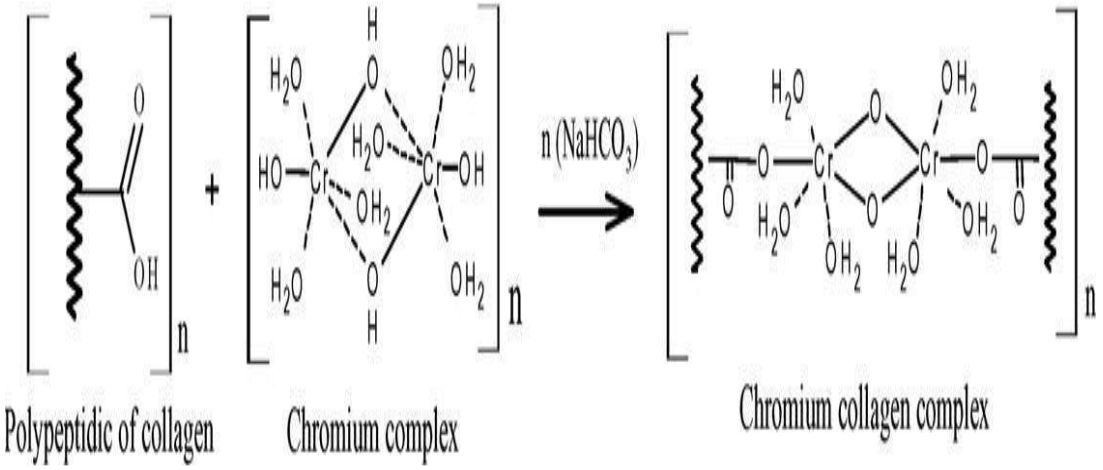


Figure 2.4.a Covalent linkage of the chromium complex with the polypeptidic chain of skin collagen

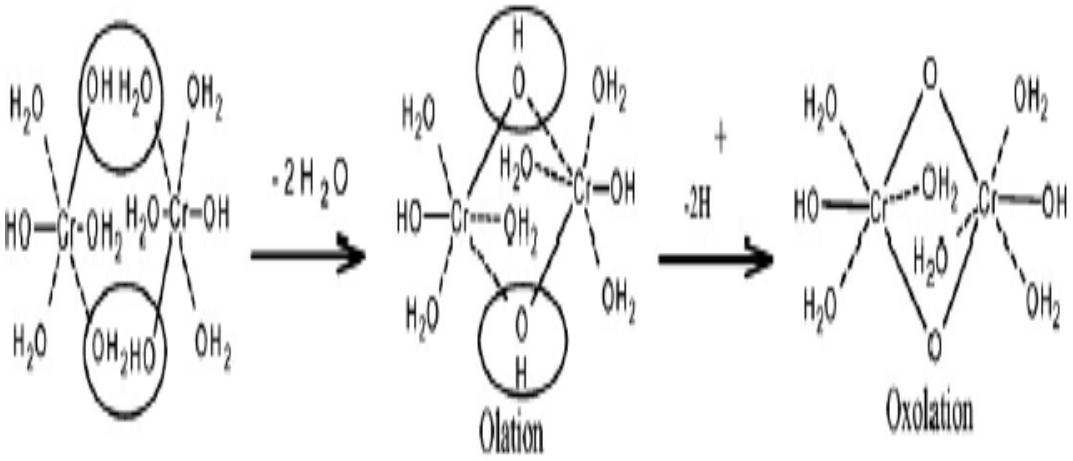


Figure 2.4.b Olation and Oxolation process

The chemical reactions that follow are referred to as "olation and oxolation." as the alkaline milieu of the tanning solution increases, olation occurs, resulting in dehydration Following that, a dehydrogenation phase occurs, leading in the discharge of two hydrogen atoms, culminating in the covalent bond of the oxygen-chrome, as shown in (figure 2.4.b). Because of the non-degradable hazardous substance, the resulting oxolation bridges result in high stability of the chromium – collagen complex, which has a negative environmental impact [61].

The classic procedure involves precipitating chromium as chromium hydroxide ($Cr(OH)_3$) in a sodium hydroxide solution and then dissolving it in sulfuric acid. Acidic hydrolysis [77] and enzymatic hydrolysis are two alternative methods for recovering chromium [71]. However, those procedures generate new low-quality waste products, such as chrome cake, a chromium-protein mixture.

2.3 Vegetable tanning

Vegetable tannins are natural products found in the leaves, fruits, exudations (gall nuts), bark, wood, and roots of trees and plants [42]. Tannins are polyphenols that are derived from plant materials in commercially viable concentrations, using either water or an organic solvent. Content fractions are commonly found in extracts. The benzene rings in vegetable tannins have two or three hydroxy -OH groups. The size and number of phenolic OH groups on the particle increase the affinity of tannin for the fiber structure. The size of the large particles prevents tannin diffusion into the fiber structure at molecular weights above 3,000. Fixing causes the penetrated tannins to link with collagen and produce a stable substance, whereas penetration entails tannins diffusing into the skin. Several elements influence it, including temperature, PH, mechanical actions, and particle size [33,55]. The ability of collagen fibers to swell is increased when the PH of tanning fluid is reduced, as does the likelihood of tannins to bind with collagen [59]. Another key factor that influences vegetable tanning is temperature. Increased temperature causes tannin diffusion to increase, resulting in a higher degree of tannage [74]. Chestnut, Wattle, Quebracho, Myrobalan, Gambier, Tara, and other plants are commonly used in vegetable tannings.

2.3.1 Mechanism of vegetable tanning

Tanning skins or hides using tannins derived from barks and leaves is known as vegetable tanning [46]. Tannins are astringent, water-soluble polyphenolic compounds that can precipitate proteins and have molecular weights ranging from 500 to 20,000. The physical strength of leather from the same origin are likewise affected by the tannins [56]. Vegetable-tanned leathers known to have good water resistance, shaping characteristics, solidity, and flexibility endurance [65].

If tannin is physically accumulated on collagen fibers, the ratio of tannin concentrations in the protein phase to the liquor phase should be constant at equilibrium. However, this is not the case. Only if one fiber is chemical combination theory of vegetable tanning can the experimental findings be clarified in part. However, the chemical mixture hypothesis has the downside of being unable to understand why the composition of collagen and tannin compounds varies. As collagen is treated with tannins solution, it is now thought that both physical deposition and chemical mixture occur simultaneously. As a result, scientists have recently concluded that positively charged collagen neutralizes the negative charges of negatively charged colloidal tannin molecules in vegetable tanning.

Vegetable tannins are polyphenols and polymeric materials, and their chemical composition allows for the creation of a crosslinking hydrogen bond network structure, which stabilizes or tans the raw hide structure to produce leather.

The interaction of basic groups of collagen protein with the acidic group of tannins via polyfunctional cross-linking is the process of vegetable tanning [54]. They create hydrogen bonds between collagen peptide oxygen and polyphenolic -OH groups, or between phenolic -OH group oxygen atoms and protonated amino groups [68, 27 and 50].

2.3.2 Classifications based on chemical nature

Freudenberg was the first to propose this grouping. The reaction of these tannins with mineral acid determines their classification [29, 45].

2.3.2.1 Hydrolysable tannins

Gallic acid esterified with glucose is an example of hydrolysable tannins with a molecular weight of 500 to 3000 Da [1]. Hydrolysable tannins are gallic acid derivatives (3,4,5- trihydroxy benzoic acid). They have a central core of sugar molecules, such as glucose, that are connected to phenol carboxylic acid molecules, gallic acid, and derivatives. The alcoholic -oh group on sugar molecules interacts with the acids -COOH groups on phenol carboxylic acid molecules to form ester connections. The number of

ester links in a tannin molecule is proportional to the number of sugar molecules in its nucleus.

Table 2.1 The number of sugar molecules and ester links

No. Of sugar molecules in central core	No. Of ester links
5	1
8	2
11	3
14	4

Acids and enzymes easily hydrolyze the ester bonds, releasing sugar and phenol carboxylic acid molecules. These are yellow-brown in color, as opposed to catechol's. During long tannage, their sugar content can cause acid fermentation, resulting in a deposit of sand-colored sludge known as "bloom." the latter is caused by enzyme action, which causes hydrolysis of the ester bond, releasing insoluble acids from the tannins, such as ellagic and chebulinic acids. They are generally less astringent than catechol tannins in terms of astringency.

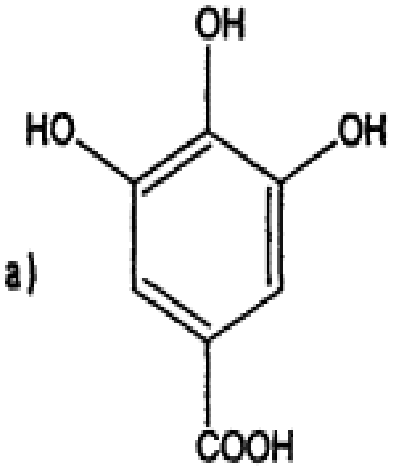
2.3.2.1.1 Types of Hydrolysable tannins

a) Gallotannins: when gallotannins are hydrolyzed, gallic acid (figure 2.5.a) and glucose are produced. Gallic acid and meta gallic acid are generated when gallotannin molecules are hydrolyzed. One molecule of glucose is esterified to five molecules of gallic acid or meta gallic acid in a standard gallotannin molecule. A semi-tannin is a glucose molecule esterified to gallic acid molecules in three positions.

b) Ellagitannins: on hydrolysis, the ellagitannins contain ellagic acid (figure 2.5.b) in addition to gallic acid and glucose. Hexahydroxy diphenic acid is an essential phenol carboxylic acid in ellagitannins (i.e., a derivative of gallic acid). This acid is released when the ellagitannin ester is hydrolyzed, and it reacts with itself to form an internal ester (this is known as lactonization).

Ellagic acid is a water-soluble ester. This group of hydrolysable tannins is known as ellagitannins. Bloom is the term used by tanners to describe the insoluble deposits that settle out in ellagic tannin liquors.

c) Tannic acid: Tannic acid is the most hydrolysable tannin, generated by a Penta galloyl glucose molecule esterified by five gallic acid units.



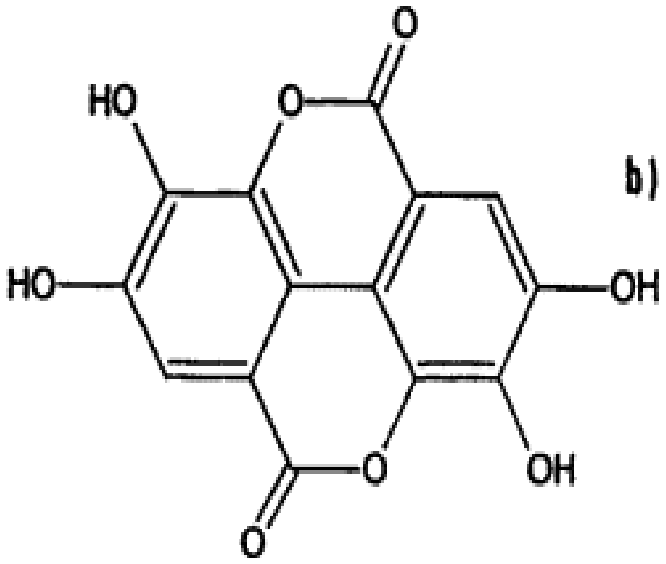


Figure 2.5.a Gallic acid's chemical structure

Figure2.5.b Ellagic acid's chemical structure

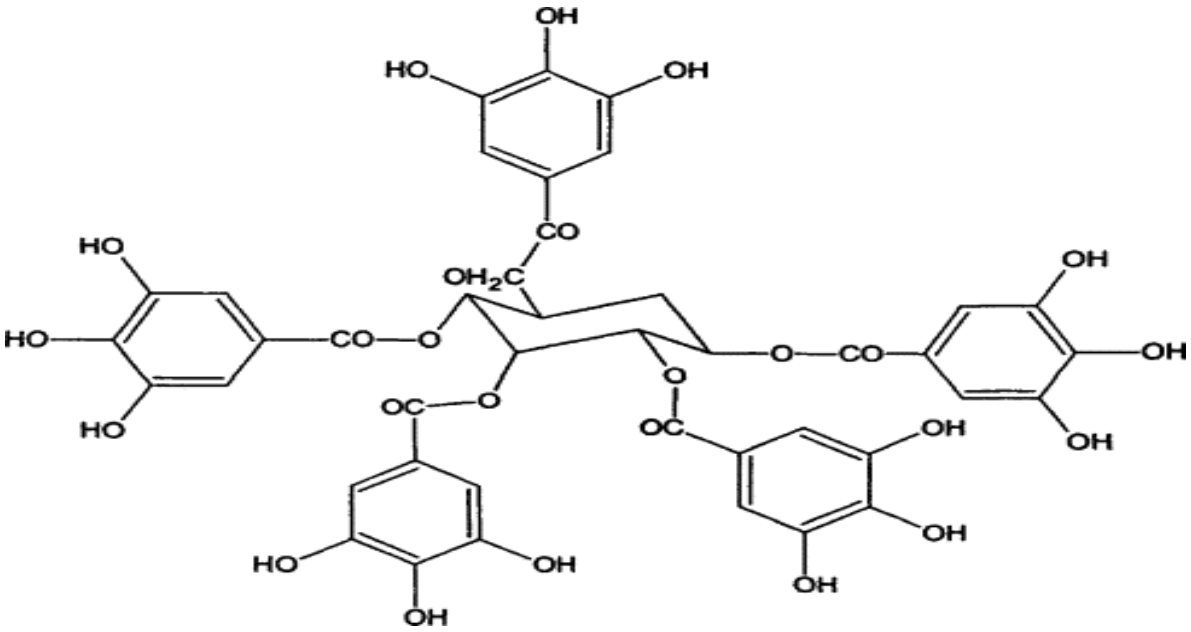


Figure 2.5.c Chemical structure of tannic acid

2.3.2.2 Condensed tannins

The non-branched flavanol polymer condensed tannins has a molecular weight of 1000-20,000 Da [22]. In an acidic atmosphere, several natural compounds may tan and have the remarkable ability to condense. Condensed tannins are the name for these compounds. The polymerized structure created by the polymerization of monomers is a distinguishing feature of condensed tannins. Catechin and epicatechin are two monomers of condensable tannins [1]. The structures of some of the flavonoids present in condensed tannins are shown below. Catechol's are flavonoid compounds with a complicated chemical structure [43]. A skeleton of 15 carbon atoms and one oxygen atom makes up the fundamental structure (monomer). A heterocyclic ring, which is a short chain consisting of one oxygen and three carbon atoms, connects two benzene rings containing phenolic –oh groups. Heat, acids, or oxygen open up the heterocyclic ring, releasing an active site for polymerization (cross linking) to a second monomer [31]. Condensed tannins (Proanthocyanins) are polymeric flavonoids. The flavonoids are a complex group of metabolites that are powered by phenylalanine (b) and polyketide biosynthesis and (a)

have heterocyclic ring systems [66]. The flavonoid skeleton, standard letters for ring identification, and the numbering scheme are all depicted here.

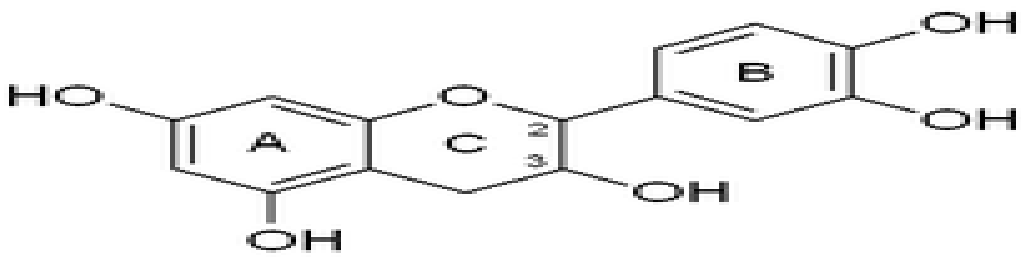


Figure 2.6.a The flavonoid skeleton of condensed tannins

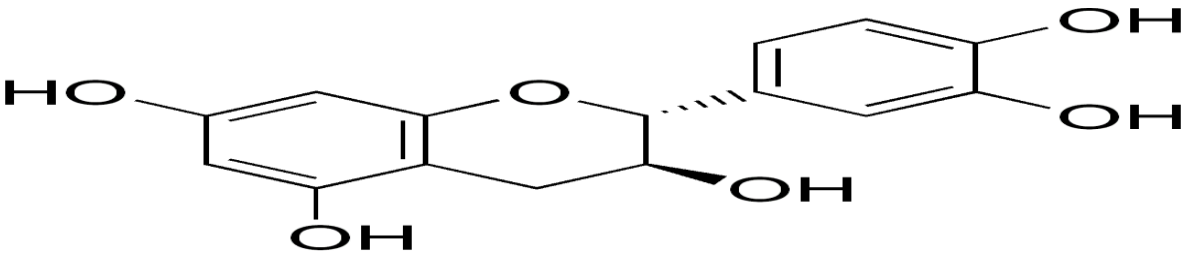


Figure 2.6.b Chemical structure for (+) catechin

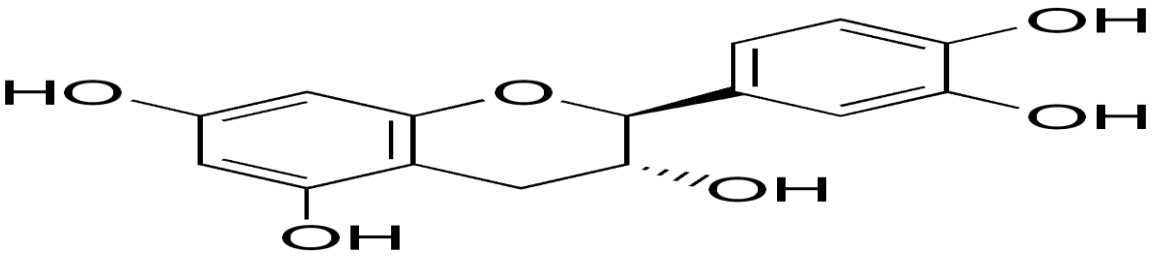


Figure 2.6.c Chemical structure (-) epicatechin

A third phenolic group is added to the b ring to produce epigallocatechin. Flavan-3-ols with only a single phenolic group on the b ring, in contrast to c-2, are much less common (Epiafzelechin, afzelechin with stereochemistry corresponding to epicatechin, catechin respectively).

2.3.2.2.1 Properties of Condensed tannins

Owing to strong covalent bonding between individual carbon atoms and the absence of ester links and biologically degradable content, it has a high resistance to hydrolysis and microorganisms. Catechol tannins have a PH range of 4.1-5.2 in general. Condensed tannins do not contain buffer salts, As a result, they are less effective at keeping leather from rotting. Leather's hue ranges from pinkish brown to reddish brown and phlobaphenes are deposited (reds), and it darkens when it is exposed to light.

2.4 Chestnut tanning system

Chestnut is a glucosidic tannin that extracted from chestnut wood (Castanea sativa). It is a pyrogallol tannin that belongs to a category of easily hydrolysable glucosidic tannins [19]. The high concentration of acid groups and natural organic acids in chestnut extracts contributes to their astringency and ability to remove larger scales from the hide. These characteristics allow chestnut extract to produce a leather that is lightweight, firm, versatile or flexible, and waterproof, as well as a high affinity for pelt, resulting in a high tannin fixation. With elastics, light fastness, traction and abrasion resistance, and a pleasing color, chestnut tanned leathers are highly durable and water resistant.

Chestnut tannins are large ester molecules (polyesters). They have a central core made up of sugar molecules like glucose that are connected to phenol carboxylic acid molecules like gallic acid and its derivatives. The number of ester interactions in a tannin molecule is calculated by the number of sugar molecules in the central center. The esters bonds are readily hydrolyzed by acids and enzymes, releasing sugar and phenol carboxylic acid molecules. The chemical composition of the phenol carboxylic acid released further divides chestnut tannins. These chestnut tannins are found only in dicotyledonous plants. Gallo tannins and ellagitannins are two types of tannins [25]. When gallotannin molecules are degraded, gallic acid and meta gallic acid are released. One molecule of glucose is esterified to five molecules of gallic acid or meta gallic acid in a typical gallotannin molecule [67]. A semi-tannin is a glucose molecule that has three locations of esterification to gallic acid molecules [20]. In ellagitannins hexahydroxy diphenic acid is an essential phenol carboxylic acid i.e. A derivative of gallic acid [32].

When the ellagi tannin ester is hydrolyzed, this acid is released, and it reacts with itself to form an internal ester this is known as lactonization. Ellagic acid is a soluble ester in liquids. The ellagitannins are a class of hydrolysable tannins. Tanners use the word "bloom" to describe the insoluble deposits that settle out in ellagitannin liquors.

2.4.1 Characteristics of chestnut tannins

phenol carboxylic acids or other hydroxyl acids mutual esters: the -COO- group is typical of this class of depsides (depsides are substances formed from two or more molecules of one molecule (s-component) with the hydroxyl group of a second (a-component), for example digallic acid.

Glucosides: The most common phenolic components are gallic acid and ellagic acid glucosides. Enzymatic assault on tannins is possible, for example from tannase a hydrolytic enzyme that breaks down molecules into sugars and polyphenols (gallic acid). Gallotannin (Chinese gall tannins) is the best representative. Chinese galls is also known as pentadigallyl glucose, which produces gallic acid and glucose when treated with mineral acids.

Low stability to hydrolysis and microbes: the deposition of bloom (yellow-brown colored sludge) and tannin loss are caused by the hydrolysis of the ester ties by acids and enzymes, i.e. Esterase's. The presence of sugars causes fermentation. Yeasts convert glucose to ethyl alcohol, which is then converted into weak organic acids, such as lactic acid and acetic acid, by particular bacteria, such as micrococci and bacilli. Fermentation is inhibited when the tannin concentration rises above 6%. These shifts are affected by both time and temperature. Tannin loss occurs after a long time of tanning, as was the case in the past. When tannins are leached rather than extracted, more enzymes and other substances may be present. Valonea and myrobalan, for example, produce more bloom than chestnut. Valonea is primarily composed of ellagic acid, while myrobalan contains both ellagic and chebulinic acids.

High concentration of acids: the acids are classified into three categories:(i) acid groups on the tannin, which are primarily phenolic -OH groups with a limited group of free carboxyl -COOH groups (as in chebulinic acid), (ii) acids formed by fermentation, such

as acetic acid or lactic acid, and (iii) naturally occurring acids, such as oxalic acid, citric acid, dphosphoric acid, or tartaric acid. Pectins - acids based on large sugar molecules - constituents of myrobalan, uronic acids - acids based on basic sugar molecules (gluconic acid) - constituent in chestnut the PH of chestnut tannin solutions ranges from 2.8 to 3.6. The rate of penetration into the matrix is slow.

2.5 Tetrakis hydroxymethy phosphonium sulfate(THPS) tanning

THPS is a colorless, transparent liquid organic substance having a broad range, quick biodegradability, and high bactericidal properties. Tetrakis hydroxymethyl phosphonium sulphate has been used in a variety of applications, including clothing flame retardants, bacterial growth control agents in oil fields and industrial waste water treatment, leather tanning agents, and disinfectants [11]. THPS salts, which were used as flame retardants, were the most common chemical assistants, and textiles treated with THPS salt had the following properties: good washability, excellent dyestuff absorption, and resistance to constringency.

Its main advantage is that it degrades quickly into completely harmless substances after use, and it is widely used in water treatment, the oil field, the paper industry, and other fields, minimizing the environmental impact of these industries significantly. It's a promising chrome-free tanning agent because the four hydroxymethyl groups in THPS molecular structure cross-link with amino groups in collagen fibers to achieve tanning effect. It is well known that in leather tanning, amino groups in collagen fibers can react with carboxyl or hydroxyl groups, resulting in a good tanning effect.

In recent years, tetrakis hydroxymethyl phosphonium sulfate has been investigated as a chrome tanning alternative [16, 70]. The effects of THPS on lambskin shrinkage temperature, as well as their interactions with aluminum salts were investigated [13]. This chemical has been found to make leathers of equivalent grade to chromium when combined with other metals. Wet white leathers of good quality were produced using a combination of silica alum and phosphonium [18]. Tannic acid and Tetrakis hydroxymethyl phosphonium sulfate were used to create a metal-free organic tanning

[15]. Using a combination of zirconium and THPS, wet pink leather has been created as an alternative for wet blue leather [14].

2.6 A new eco-friendly combination tanning system based on chestnut

A combination tanning system is a tanning method that involves the simultaneous application of two or more separate tanning agents in the same tanning procedure. The aim of a combination tanning system is to create a synergy between two or more tanning systems in order to achieve a minimum set on final leather. Combination tanning includes competition, reactive, and complementary tanning. When the tanning materials used operate on different functional types, the combination type is referred to as complementary type. When tanning materials compete for the same functional category of collagen, a competition form of combination tanning device is developed. Reactive type of combination tanning occurs when tanning materials bind with one another, the skin matrix's overall stability improves.

Currently, chrome tanning chemicals are employed in the production of 90% of all leathers [72]. Because of its exceptional qualities, chrome salt is widely utilized in the leather industry; no other tanning chemical can totally replace it. Researchers provide excellent explanations of chrome tanning's basic chemistry [27]. Tanners, on the other hand, are having a harder time complying with new requirements on effluent chrome content and the disposal of chrome-containing solid wastes such as sludge, shavings, leather trimmings, and buffing dust [47]. The majority of research into potential chrome tanning alternatives has focused on decreasing tannery effluent contamination. On the other hand, its toxicity to the human body and the environment is a contentious issue [53]. As a result, a number of researchers have looked at alternative chrome tanning methods [51].

Vegetable tanning, which is an organic tanning process, does not produce extremely hydrothermally stable leathers. Vegetable tanning systems are often used to give the leather a base color. Vegetable (Chestnut) tanned leather has a shrinkage temperature (Ts) of 70^{o}C to 80^{o}C [9, 43]. Re-tanning with metals like Tetrakis hydroxymethyl phosphonium sulfate will increase the shrinkage temperature (Ts) of vegetable (Chestnut)

tanned leather. High hydrothermal stability, strong organoleptic properties, high strength, and good tannin uptake are all advantages of combination tanned leather. Effluent can be treated biologically at a low cost. Chemicals can be used less often.

2.7 Waste water treatment process

Tanning agents, in particular, have a significant environmental effect and should be avoided during the cleanup process. Wastewater plants, wastewater plants that clean the released water from the leather industry have about ten times higher biomass concentrations.

2.7.1 Physio-chemical treatment

To remove the coarse material that can clog/block pumps, drains, and probably sewage lines when raw wastewater is present, to properly mix and match various tannery streams, resulting in homogenized "raw material" that can be handled consistently, PH must be adjusted, poisonous substances (sulfides) must be removed, to protect the biological treatment, shock loads must be avoided., which is very delicate, to reduce the bod/cod load by a considerable amount, simplifying and lowering the cost of the biological treatment process (UNIDO Vienna, 2011,12-13).

2.7.2 Biological treatment

The main goal at this stage is to reduce the amount of organic waste. This needs discharge standards/limits into surface waterways, as well as extra pollutants remaining present in the effluent after basic treatment (rivers, lakes). Almost all aerobic systems are employed in practice; facultative (ideally aerated/facultative) lagoons are used in rare circumstances in nations with a hot temperature and a lot of area.

2.7.3 Advance or tertiary treatment

The consistency of the final effluent in some cases does not meet the promulgated discharge limits, despite a well-designed ETP's thorough physical-chemical and biological treatment. The most prevalent cause is recalcitrant COD, or chemicals that the microorganisms in the floc are unable to breakdown. Additional, typically more complex

and costly treatments, such as mineralization of organic compounds by oxidation with H_2O_2 in the presence of ferrous sulphate, are needed in such cases (Fenton process and its derivatives). Ozonation is often used to remove some of the remaining cod, rather than to kill potentially harmful microorganisms. (Zenon environmental b v,1995).

Chapter Three

3.Materials and Methods

3.1 Experimental set up

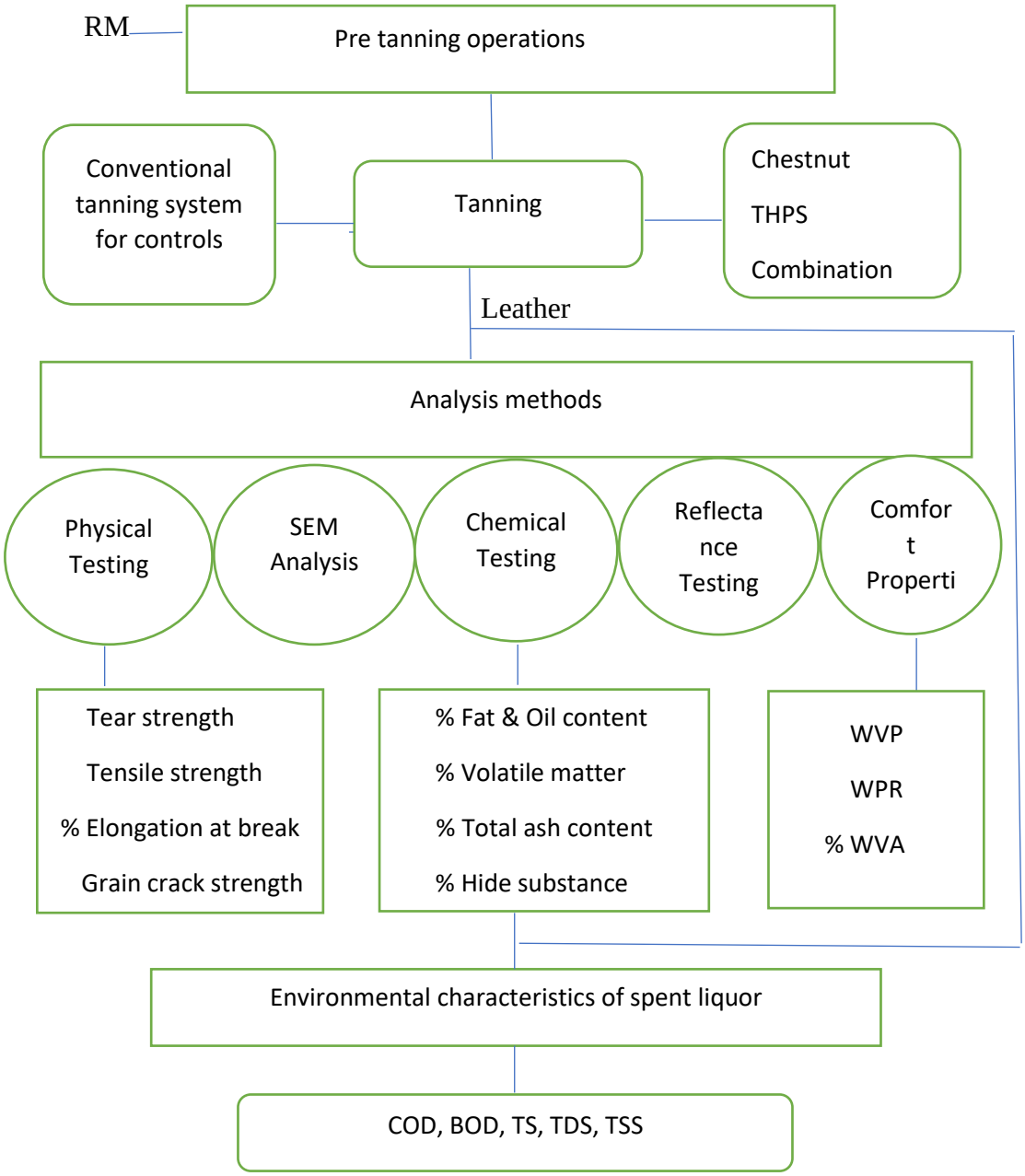


Figure 3.1 Experimental design of the whole process

The experimental set up of the study describes the leather processing and laboratory analysis of control and experimental leathers. wet salted sheep skins were used as raw materials for leather processing and laboratory analysis, then the skin was treated and preserved for tanning process in pre-tanning operation. The conventional and Experimental tanning trials were carried out with different percentages of Chestnut as a tannage followed by varying percentages of THPS as a re-tannage for process optimization. The leathers obtained were characterized for their physical strength characteristics, comfort & organoleptic properties, scanning electron microscopic analysis, reflectance measurements, chemical analysis and environmental characteristics.

3.2 Materials

3.2.1 Raw materials

Wet salted hair sheep skins from the central leather research institute (CLRI) model tannery slaughter house in Chennai, India, were chosen as raw materials for upper leather manufacture. The collected skins were employed for conventional beam house operations, wet finishing processes, as well as control and experimental leather processing trials.

3.2.2 Chemicals and Reagents used for leather processing and laboratory analysis

The leather processing chemicals were all commercial grade, while the reagents and chemicals employed in the analysis were analytical grade. The list of chemicals used in leather processing and laboratory analysis are listed in Table 3.1 and Table 3.2

Table 3.1 List of chemicals used in leather processing

Chemicals	Use
Sodium carbonate (Na_2Co_3)	Used as an alkaline soaking aid.
Sodium silico fluoride (Na_2SiF_6)	Used as a preservative to prevent putrefaction
TRD-H	Used as active soaking and non-ionic wetting agent auxiliary.

Sodium hydroxide (NaOH)	To improve swelling to obtain better opening up of fiber structure of skin.
Sodium sulfide (Na_2S)	To get rid of hair on the skin/hide
Calcium hydroxide ($Ca(OH)_2$)	To loosen fiber structures and remove hair and skin
Ammonium chloride (NH_4Cl)	To remove lime from the surface of leather for soft leathers
Ammonium sulfate ($(NH_4)_2SO_4$)	For upper leathers, to eliminate lime from the surface.
Acetic acid (CH_3COOH)	To adjust PH prior to tanning process
Oropon ON_2 (enzyme)	Purify the pelts by eliminating interfibrillar proteins, epidermis, and scud, as well as other undesired components.
Sulfuric acid (H_2SO_4)	To lower the PH so that chemicals can penetrate faster and be distributed evenly in the tanning process.
Sodium chloride (NaCl)	To prevent acid swelling caused by a reduction in PH during the pickling process.
Sodium formate (HCOONa)	To prevent not to shoot up the PH increment
Sodium Bicarbonate ($NaHCO_3$)	To balance out the excess acid in the tanned leather
Formic acid (H_2CO_2)	Used as a fixative at the end of the tanning process.
Chestnut	Used as a vegetable tanning agent
THPS	Used as an organic tanning agent
Acrylic syntan, Melamine resin syntan, Phenolic syntan	To improve uniform fullness in re-tanning process
Synthetic fat liquor (Softnol100)	To coat individual fibers and fiber bundles to

Semi-synthetic fatliquor (fosfol51) Lecithin based fat liquor	minimize internal friction of leather in fat liquoring process.

Table 3.2 Chemicals and reagents used in laboratory analysis

Chemicals and Reagents	**Use**
Glycerol	To determine the hydrothermal stability of leather
Anhydrous copper sulfate ($CUSO_4$), Potassium sulfate (K_2SO_4)	Used as reagents in estimation of hide substance
Phenolphthalein, Methyl red	Used as indicators in estimation of hide substance
Ammonium nitrate (NH_4NO_3), Sulfuric Acid (H_2SO_4)	Reagents used in determination of total ash
Dichloromethane (DCM)	Reagents used in analysis of fat and oils
Calcium chloride ($CaCl_2$), Ferric chloride ($FeCl_3$), Magnesium sulfate ($MgSO_4$)	Chemical chemicals used in manufacture of dilution water for determination of BOD
Sodium hydroxide (NaOH)	For caustic acidity pretreatment in BOD analysis
Sodium sulfite or Sodium thiosulfate ($Na_2S_2O_3$)	For residual chlorine pretreatment
Sulfuric acid (H_2SO_4) solution	For caustic alkalinity pretreatment
Potassium Dichromate ($K_2Cr_2O_7$)	In COD analysis, they are used as oxidants.
Silver sulfate (Ag_2SO_4)	In COD analysis, it's used as a catalyst.
Mecuric sulfate ($HgSO_4$)	Added to remove chloride interferences in COD analysis
Ferrous ammonium sulfate	

$(Fe(NH_4)_2(SO_4)_2)$	In COD analysis, it's used as a reducing agent.
Phenanthroline Ferrous Sulfate (Ferroin)	In COD analysis, it's used as an indication.
Potassium hydrogen phthalate (KHP)	Used as conventional COD reference substance

3.2.3 Equipment, Instruments and Apparatuses

Equipment, instruments and apparatuses used for leather processing and laboratory analysis are listed in Table 3.3 and Table 3.4.

3.2.3.1 Leather processing equipment and instruments

Equipment's and apparatuses used in leather manufacturing are listed in Table 3.3.

Table 3.3 List of leather processing equipment and instruments

Equipment and instruments	Model	Use
Fleshing machine	CE-B321	After the liming process, to eliminate the unnecessary flesh when creating leather
Unhairing machine	AO1.O7	During the liming and unhairing stages, to remove the skin hair.
Sammying machine	BBSM-3000	To reduce the amount of leather by applying pressure
Shaving machine	RDPA	To precisely bring the leather to a uniform thickness.
Setting out machine	B1200	It flattens and smoothes the leather while also removing creases.
Buffing machine	BHARAT	To remove loose fibers after crust preparation.

Vibratory stacking machine	DCH	Mechanically flex and soften the leather
Toggling machine	SGS	To flatten and increase the yield area of leather
Vacuum dryer	Hydraulic CNC	To sucked out of water vapor form leather in drying process
Overhead dryer	-	Leather can be dried by hanging it on hooks or over bars at room temperature.
Surgical blade	-	To cut a cross-section of leather to check for chemical penetration during tanning
Weighing balance	-	To weigh skins before going to processing
Thickness gauge	-	To attain the desired final product, measure the thickness of tanned leather.
PH paper	-	Used to measure the acidity or alkalinity of liquor

3.2.3.2 Laboratory Equipment and Apparatuses

Apparatuses, instruments and equipment used in laboratory analysis are listed in Table 3.4.

Table 3.4 List of laboratory equipment and apparatuses.

Equipment	Model	Use
Scanning electron	JSM-IT700HR	To investigate the grain surface

microscope		and fiber structure of crust leathers in cross-section.
Techkon Spectro Drive	TKSDEB	To measure the reflectance or color of leather samples
Soxlet apparatus	LTSW-5	Used to determine the chemical composition of crust leathers, such as fat and oil levels.
Kjeldhal apparatus	IK-194	To determine the hide substance of leather samples
UV-VIS Spectroscopy and Artificial Neutral Networks	V-730 UV	To compare COD and BOD estimates obtained using established procedures.
Shrinkage temperature tester	-	To determine leather's hydrothermal stability
Dynamometer	INSTRON-2519	Used to determine the tensile strength, elongation at break, and rip strength of crust leathers.
Lastometer	GW-002B	It measures grain fracture and distension at grain crack in crust leather samples.
Pentrometer	TO-512	To measure water penetration resistance of crust leather samples
Water vapor permeability tester	F-1249	Used to determine the rate of water vapor permeability in crust leathers.

Water vapor absorption tester	GT-KC51	To determine the water vapor absorption coefficient of crust leathers.

3.3 Methods

3.3.1 Processing methods

3.3.1.1 Optimization Chestnut-THPS Combination tannage

Nine experimental trials were randomly selected to optimize the combination tanning system based on the response parameter to hydrothermal stability, with the procedure that gave the greatest shrinkage temperature being chosen as the best offer. Six wet salted sheep skins were chosen for process optimization to examine the chestnut-based combination tanning system. By using the conventional process, wet salted sheep skins were treated to the deliming stage. Twelve delimed skin halves were taken. Each trial employed with one half skin. Delimed pelts were tanned with three different percentages of chestnut (PH was corrected to 5 using 0.5% diluted acetic acid) were added separately to each trial viz., 10, 15 and 20% and drummed for 60 minutes. After that, each experiment was re-tanned with three different percentages of THPS trial viz., 1, 1.5 and 2% and drummed for another hour. Basification was performed by combining 0.5 percent sodium formate with 0.75 percent sodium bicarbonate (1:10 dilution and three feeds separated by 10 minutes) and pounding it for 30 minutes. After running the drum for two hours, the PH was discovered to be between 3.8 and 4.0. The tanned skins were cleaned with 200% of water. The leathers were then piled for 24 hours.

Table 3.5 The tanning trial runs in percentage offer of experimental and control leathers

Trial's order	Percentage offers of chestnut **(%)**	Percentage offers of THPS **(%)**
1	15	1
2	10	1
3	20	1.5

4	20	1
5	10	2
6	15	2
7	10	1.5
8	20	2
9	15	1.5

Controls	Percentage offers of controls (%)
Chestnut alone	20
THPS alone	2
Chromium	6

3.3.1.2 Wet-finishing operations for control and experimental leathers

The wet-finishing process of upper involves a variety of operations comprising, neutralization, re-tanning, filling, dyeing, fat-liquoring and fixing. For the manufacturing of upper leather, post-tanning operations have a PH range of 5-5.2. In this study, a common wet-finishing operation was carried out for all the experimental (chestnut-THPS combination), chestnut (alone) and control chrome tanned leathers. Setting out operation was performed to minimize moisture content and shaved at 1-1.2 mm to reduce the thickness for upper leather. Finally, the weight for wet-finishing was taken for all of the experimental and control leathers. Here the post tanning operation carried out from neutralization to the end process fixing for all the experimental and control leathers.

3.3.2 Analysis methods

3.3.2.1 Measurement of Hydrothermal stability

The resistance of a material to wet heat is measured by hydrothermal stability. It is the action of heat on water saturate material in the case of collagenic materials, such as pelt or leather. The shrinkage temperature of control and experimental leathers was measured using a shrinkage tester.

3.3.2.1.1 Materials

- **Sample:** For the control and experimental tanned leathers, a 2x0.5 cm2 piece of tanned leather was taken as a sample.
- **Reagent:** Glycerol and water was taken as a reagent for analysis of hydrothermal stability of both experimental and control tanned leathers.
- **Apparatus:** A shrinkage temperature tester is a device that measures hydrothermal temperature.

3.3.2.1.2 Method

From the sample position, a 2x0.5 cm2 piece of tanned leather was cut and clamped between the clamp's jaws before being soaked in a 3:1 glycerol:water solution. A mechanical stirrer connected to the shrinkage tester was used to constantly mix the solution. The solution's temperature was gradually raised, and the temperature at which the sample shrank was recorded as the leathers' shrinkage temperature.

3.3.2.2 Scanning electron microscopic analysis

Control and experimental tanned crust leathers were analyzed using SEM to examine the influence of combination tannage on the fiber structure and better understand surface and cross-section fiber compaction.

3.3.2.2.1 Materials:

- **Sample:** Crust leather samples were taken for both experimental and control purposes in order to examine the fiber structure of the skin matrix.
- **Reagents:** ethanol and methanol are the reagents used for the crust leather specimen.
- **Equipment:** The grain surface and cross-section of the fiber structure of crust leathers are studied using a scanning electron microscope (JSM-IT700HR).

3.3.2.2.2 Method

Cutting samples from experimental and control crust leathers was done at the official sampling location. A Quanta 200 series scanning electron microscope was used for the

investigation. A scanning electron microscope (SEM) in low vacuum with a 20kv accelerating voltage and various magnification settings was used to produce grain surface and cross-section micrographs.

3.3.2.3 Reflectance Measurements

A Techkon Spectro drive instrument was used to assess the reflectance of experimental and control crust leathers. Hue, chroma (or saturation), which refers to the color's "colorfulness" or "richness," and brightness, which refers to how much light is reflected, are the three important aspects of color perception when employing reflectance measurements. Hue, chroma, and brightness are three properties that can be specified using the concept of color space. The L, a, and b* parameters are used to specify color in the CIELAB color space.

3.3.2.3.1 Materials

- **Sample:** Crust leather samples were obtained for both experimental and control leathers in order to quantify the color of the leathers.
- **Equipment:** Techkon Spectro Drive (TKSDEB) is an equipment used to measure the reflectance or color of leather samples.

3.3.2.3.1.2 Method

The L*, a*, b*, c* and Hue* values are the parameters used to assess and evaluate the color of leather samples. L* represents whiteness, which on scale of 0-100, the value 100 indicates pure white, a* represents red and green axis, where a*< 0 means green and a* >0 mean red, b* represents yellow and blue axis, where b*< 0 means blue and b*> 0 means yellow, c* represents the chromacity of the color, which means the intensity of the color. The values reported are average of three values.

3.3.2.4 Analysis of spent liquors from tanning trials

The wasted tannin liquor from the control and experimental tanning operations was collected, filtered, and COD, BOD5, TDS, TSS, and TS were measured according to the procedures [10]. The amount of effluent (lit) per tonne of raw skins processed was

multiplied by the concentration (mg/l) to calculate emission loads. The average of three experiments were reported based on their standard deviations.

3.3.2.4.1 Chemical oxygen demand (COD)

When a sample solution is susceptible to a powerful chemical oxidant, COD is defined as the amount of dissolved oxygen required to oxidize and stabilize organic or inorganic materials. The mass of oxygen required to oxidize carbon in the effluent per liter of solution is measured in milligrams per liter (mg/l). The quantity of pollution in the water sample grows as the chemical oxygen demand rises.

3.3.2.4.1.1 Materials

- **Sample:** Both the experimental and control tanning trails yielded a sample of tanning liquor.
- **Reagents:** Potassium dichromate (K2Cr2O7), silver sulfate (Ag2SO4), mecuric sulfate (HgSO4), ferrous ammonium sulfate (Fe(NH4)2(SO4)2), phenanthroline ferrous sulfate (Ferroin), and potassium hydrogen phthalate are some of the chemicals used in COD analysis (KHP).
- **Equipment:** UV-VIS Spectroscopy and Artificial Neutral Networks (V-730 UV) are used to estimate COD to those estimated using standard methods.

3.3.2.4.1.2 Method

In the method, potassium dichromate is utilized to determine COD levels. The amount of dichromate is measured by direct titration with ferrous ammonium sulfate (FAS) as the titrant and ferroin (1, 10 phenanthroline ferrous sulfate) as the indicator. During the titration, the titrant (Fe2+) quickly interacts with hexavalent chromium (cr6+) to form trivalent chromium (Cr3+) and ferric ion (Fe3+), as illustrated below:

$$3Fe^{2+} + Cr^{6+} \rightarrow 3Fe3^{+} + Cr^{3+}$$

By subtracting the final hexavalent chromium level from the beginning level, the amount of hexavalent chromium lost during digestion may be estimated.

Calculation

$$COD, mg/l = \{(C_1\text{-}C_2) \times (N \times 80) / ml \text{ of sample}\}$$

Where, C_1 is the ml FAS required for the blank titration, C_2 is the ml FAS required for the sample titration, and N is the FAS normality.

3.3.2.4.2 Biological oxygen demand (BOD)

BOD is the amount of oxygen required by bacteria to stabilize decomposable organic matter at a given time and temperature. If a small amount of biomass (mainly bacteria) seed is mixed in wastewater (containing organic matter such as carbohydrates, proteins, and lipids) and provided nutrients for biomass development, organic matter degradation will be increased and dissolved oxygen will be reduced.

3.3.2.4.2.1 Materials

- **Sample:** A sample of tanning liquor was obtained from both the experimental and control tanning trails.
- **Reagents:** Chemicals used in BOD analysis include calcium chloride ($CaCl_2$), ferric chloride ($FeCl_3$), magnesium sulfate ($MgSO_4$), sodium hydroxide (NaOH), sodium sulfite, or sodium thiosulfate ($Na_2S_2O_3$).
- **Equipment:** UV-VIS Spectroscopy and Artificial Neutral Networks (V-730 UV) are used to estimate BOD to those estimated using standard methods.

3.3.2.4.2.2 Method

The five-day technique is used to calculate BOD. A tiny sample of the wastewater to be studied, together with dilution water, is placed in a bod container in this conventional bod test (300 ml). The dissolved oxygen (DO) concentration in the mixture in the bottle is determined. Before the do concentration is measured again, the bottle is incubated at 200C for 5 days. The difference is utilized to compute how much oxygen the organics require, and the bod is calculated as follows:

Calculation

$$BOD, mg/l = \{(B_1\text{-} B_2) \times V_2/ V_1\}$$

Where, B_1 is the initial concentration of DO, mg/l in the dilution water prepared

B_2 is concentration of DO, mg/l in the diluted sample after 5 days incubation

V_1 is the volume of diluted sample, V_2 is the volume of the bod bottle, ml.

3.3.2.4.3 Determination of Total solids, Total dissolved and suspended solids

"Total solids" refers to the material residue left in the vessel after the sample has evaporated and been dried in an oven at a specific temperature. As a result, total solids are simply the sum of total dissolved and total suspended solids. Suspended particles are particulates from wastewater that adhere to the filter paper during filtering. After filtering the sample on filter paper, dissolved solids are included in the solids contained in the filtrate. After the appropriate handling methods have been performed, weighing is employed to determine the various types of solids. A sample's total solids content can be determined quickly by weighing it before and after drying at 103°C. TDS and TSS, on the other hand, necessitate filtration of the sample.

3.3.2.4.3.1 Determination of Total solids (TS)

3.3.2.4.3.1.1 Materials

- **Sample:** Both the experimental and control tanning trails yielded a sample of tanning liquor.
- **Apparatus:** clean porcelain dish, hot air oven, evaporating dish and analytical balance are the apparatuses used in analysis of TS.

3.3.2.4.3.1.2 Method

Use a clean porcelain dish that has been washed and dried for three hours in a hot air oven at 105^{o}C to measure total solids. Using analytical balance, Weigh the empty evaporating dish and give it (W_1). Pipette 20 ml of sample into the porcelain plate, then dry for 3 hours in the oven to get a uniform mass by evaporating the moisture. Cool the container (dish) in a desiccator after drying to avoid mass loss.

Calculation

$$\text{Total solids (TS)} = \{(W_2-W_1)/ V\} \times 1000$$

Where, W_1 = the dried dish's weight, W_2 = the dried dish weight + dried sample

3.3.2.4.3.2 Determination of Total suspended solids (TSS)

3.3.2.4.3.2.1 Materials

- **Sample:** A sample of tanning liquor was obtained from both the experimental and control tanning trails.
- **Apparatus:** filter paper, hot air oven, autoclave are the apparatuses used in analysis of TSS.

3.3.2.4.3.2.2 Method

The methods described below can be used to determine the total suspended solids (TSS) in waste water. Calculate the filter paper's weight (W3), then pour 10ml of waste water onto it, filter it, and dry it. After the dry sample has dried, weigh the filter paper with the dry sample (W4).

Total suspended solids (TSS) = (W_4-W_3) x1000/Volume of sample

Where, W3-weight of filter paper, W4-weight of suspended solid + filter paper

Total dissolved solids (TDS)

Total dissolved solid (TDS) is determined by subtracting Total suspended solid from Total solids.

Total dissolved solids (TDS) = Total solid (TS) - Total suspended solid (TSS)

3.3.2.5 Physical Characterization

3.3.2.5.1 Conditioning

IULTCS procedures were used to obtain samples for various physical tests from experimental and control crust leathers [34]. Specimens were conditioned at 20±2°C and 65±2% RH for 48 hours. Standard techniques were used to determine tensile strength, % elongation at break, grain fracture strength, and tear strength [35, 37, and 38]. Each value were calculated based on an average of four samples (two along the backbone and two across the backbone).

3.3.2.5.2 Measurement of Tensile strength

3.3.2.5.2.1 Materials

- **Sample**: samples were taken parallel and perpendicular to the backbone of crust leather.
- **Apparatus and Equipment:** apparatus used for tensile strength are thickness gauge, steel ruler, hydraulic cutting machine, Dynamometer (INSTRON-2519).

3.3.2.5.2.2 Method

The samples were sliced parallel and perpendicular to the backbone using a dumbbell shape. A conventional thickness gauge and vernier calipers were used to measure the thickness and width of the specimen in the same spot, i.e., one at the midpoint and the other two at midway. The average thickness (in mm) is then calculated. A press knife was used to cut the specimens into a rectangle that was 50 mm long and 10 mm wide. Multiplying the breadth by the thickness of each specimen yielded the area of cross section [35]. The tensile machine's jaws were positioned 50 mm apart, and the sample was clamped in the jaws so that the jaws' edges were parallel to the midline. The machine was run until the specimen was broken, and the breaking load was calculated using the highest load reached. The tensile strength load is measured in Newtons, and the Newton per millimeter square (N/mm^2) is the unit of tensile strength (IUP/6: BS3144).

Calculation

$$\text{Tensile strength} = \text{Force (N)} / \text{Cross-sectional area } (mm^2)$$

3.3.2.5.3 Percentage of Elongation at break

3.3.2.5.3.1 Materials

- **Sample:** For experimental control, samples were collected from the backbone of crust leather.
- **Equipment:** Dynamometer (INSTRON-2519) is an equipment used to measure the % of elongation at break for experimental and control leathers.

3.3.2.5.3.2 Method

The initial free length between the clamps was measured before the load was applied, and the ultimate free length between the clamps at the moment of break was measured. The machine's standard technique (IUP/6: BS3144) was used to calculate the elongation. The initial free length was set to 5 cm.

Calculation

Elongation at break, % = {Final free length – Initial length} / Initial length

3.3.2.5.4 Measurement of Grain crack

3.3.2.5.4.1 Materials

- **Sample:** test specimens were taken from the butt area for both the experimental and control leathers.
- **Apparatuses and equipment:** circular cutting knife, hydraulic cutting machine, Lastometer (GW-002B) are the apparatus and equipment used in grain crack measurement.

3.3.2.5.4.2 Method

A circular cutting tool was used to cut three test specimens with a diameter of 44.5 mm for the control and experiment [38]. The test specimens were conditioned for 48 hours at a temperature of 20±2^{o}C and a relative humidity of 65±2 percent. One test specimen was tightly clamped between the machine's circular rings, grain side facing upwards. To start the machine, the plunger was driven at a rate of 0.2 0.05mm/s. The surface of the specimen was constantly scrutinized for an initial crack in the grain at the center. At this location, the maximum distance and force were measured.

The technique was repeated for the remaining two test specimens. The following formula was used to obtain the mean values of the test results:

a. Grain crack load (N), b. Grain crack distension (mm).

3.3.2.5.5 Measurement of Tear strength

3.3.2.5.5.1 Materials

- **Sample:** The butt area provided samples for both the experimental and control leathers.
- **Apparatuses and equipment:** thickness gauge, paper clip with wire diameter, universal tensile meter are the apparatuses and equipment used to measure tear strength.

3.3.2.5.5.2 Method

The Tear strength test method can be used on any type of leather. The official method determines the tear load on a specimen cut with a slot and slipped over the turned-up ends of a pair of holders attached to the jaws of a tensile strength machine [37]. The forces applied during holder separation are recorded, and the maximum force is designated as the tearing load and given in Newtons. By dividing the force by the sample thickness, the tearing load may be computed. Using a cutting knife, cut six test specimens as a rectangle 50 mm long and 25 mm wide using a press knife that cuts out the specimen with a central three test specimens in one operation (three test specimens in one direction and three test specimens in the opposite way) (template machine). To perform the test, run the tensile tester at a speed of 100–10 mm/min until the test specimen is ripped apart, The highest load reached during tearing is recorded as the tearing load. Carry on with the test for the remaining specimens. The load readings fell into the portion of the scale that has been calibrated to be accurate to within 1%. The tearing load is measured in kilograms or newtons.

There are two types of tear strength test methods. a). Single edge tear strength (Tongue/trouser tear strength), b). double edge tear strength (Baumann tear strength).

Calculation

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

3.3.2.5.6 Determination of Water vapor permeability

3.3.2.5.6.1 Materials

- **Sample:** Samples were taken from the butt area for the experimental and control crust leathers.

- **Equipment:** The water vapor permeability tester is used to measure the water vapor permeability rate of crust leathers (F-1249).

3.3.2.5.6.2 Method

A square piece of leather with at least 50mm side length was cut from the sampling location and the surface coating of the leather was shattered using 180 grit papers and 0.2 kgf/cm2 pressure. The leather sample was pushed against the leather using 180 grade emery paper under a 200-gram weight and drawn across 10 times in various directions. A circular cutting knife with a 34 mm diameter was used to cut three test specimens from this grain buffed leather. Freshly dried desiccant silica gel was placed in a jar half its size (cooked in an oven at 125±5^{o}C for at least 16 hours and cooled for at least 8 hours in a closed container). The circular cut test specimen was placed grain side inward in the open end of the top screw type bottle lid for upper leather (flesh side inward for lining leather).

The test jar was placed in the holder of a machine that measures water vapor permeability [40]. The test started and lasted at least 16 hours. The goal of this procedure was to establish a continuous penetration and absorption process between the leather and the desiccant. These three leather samples were weighed independently after 16 hours in three different jars filled with dry desiccant silica gel. These bottles were placed in the test machine's holders, and the machine was run for at least 8 hours. The bottle was taken out and weighed to see if it had gained weight. The period in minutes between these two weighing's was recorded.

Calculation

$$\text{Water vapor permeability (WVP), mg/cm}^2\text{.h} = \{7639 \times m\} / (D^2 \times t)$$

Where, m = gain in weight in mg, t = time in hours between the two weighing's

D = the bottle's neck average internal diameter in millimeters

3.3.2.5.7 Determination of Water penetration resistance

3.3.2.5.7.1 Materials

- **Sample:** Samples were taken from the butt area for both the control and experimental crust leathers.
- **Apparatus:** The penetrometer is a device that is used to test the water penetration resistance of crust leather samples (TO-512).

3.3.2.5.7.2 Method

A total of four-square test specimens measuring 150 mm on each side were cut [39]. The test specimen (150 mm x 150 mm) was placed between the stationary and moving clamps to form a trough in the middle of the leather without creasing it. To prevent water from entering the test piece's ends, the clamp ends were tightened. The remaining three test specimens were placed in the test stations. The trough was filled with steel balls. The water tank was filled with water before being elevated to make contact with the test specimen, with the water level remaining about 1 cm below the leather's edges.

After connecting the machine to the electronic digital counters, start the motor. The vibrations of the movable clamp component bend the leather at a 30^{o} angle. Once water had breached the counter, it was switched off. This depicts water penetration cycles. The equipment was turned off after four samples indicated water penetration cycles. The number of cycles for water penetration was mentioned.

3.3.2.5.8 Determination of Water vapor absorption

The maser test was used to measure a material's resistance to water penetration. This approach is most commonly employed with upper outer fabrics in footwear, but it can be applied with any flexible sheet material [41].

3.3.2.5.8.1 Materials

- **Sample:** Samples were taken from the butt area for the experiment and control crust leathers.
- **Apparatus:** Water vapor absorption tester is the apparatus used to determine the coefficient of water vapor absorption of crust leathers.

3.3.2.5.8.2 Method

Rectangular pieces of leather measuring 75 mm x 60 mm were collected from the sampling area (two in each direction) and conditioned. Using 180 grade emery paper and the following method, the grain surface was somewhat scoured. On a table, the finished leather was placed side up. A piece of 180 grit paper was placed on top of the finish and gently scrubbed it with 1 kgf force to break the surface coat use a to-and-fro motion for 20 strokes. The water resistance testing machine (penetrometer) was set to deliver the required amplitude after determining the amplitude of crank motion as mentioned above. The trough-like test assembly was formed between two cylinders with the grain side of the leather facing outward and a 40-mm distance between them to weigh the test specimen (W1). This assembly was placed in the testing machine's holds. The water tank was increased, and the level was adjusted to be 1 cm below the cylinders' tops. The power was turned on, and the amount of time it took for the first sign of water penetration through the leather specimen to appear on the indicator lamp or partial counters was recorded. If any sign of water penetration was detected before the 60-minute mark, the test was continued until the 60-minute mark, at which point the test assembly was removed from the water trough, the leather specimen was separated, the excess water adhered to the leather surface was blotted, and the weight was taken (W2).

Calculation

$$\text{Water vapor absorption (WVA), \%} = (W_2 - W_1) / W_1$$

Where, 1. Time for water penetration in minutes, 2. Water absorption in percent for 60 min

3.3.2.5.9 Organoleptic properties of crust leathers

Visual and hand evaluation were used to assess the softness, fullness, grain smoothness, grain tightness (break), general appearance, and dye uniformity of experimental and control crust leathers. For each functional attribute, three professional tanners graded the leathers on a scale of 0-10 points, with higher numbers indicating greater quality.

3.3.2.7 Chemical Characterization

For control and experimental leathers, chemical testing methods such as percentage of moisture content, percentage of oils and fats content, percentage of hide substance, and percentage of total ash content were carried out according to standard procedures.

3.3.2.7.1 Preparation of sample

To pass through a screen with circular perforations of 4 mm, leather was sliced into small pieces. By storing the parts in a sealed container for at least one night, the parts were thoroughly combined and homogenized. They were placed in a jar for further investigation once the moisture content was measured.

3.3.2.7.2 Fat and Oil content determination

3.3.2.7.2.1 Materials

- **Sample:** sample positions for experimental and control crust leathers were taken from the butt area.
- **Apparatuses:** the apparatuses used for this analysis were Soxhlet apparatus, filter paper, hot air oven, crucibles, round bottom flask, stove, desiccators.
- **Reagent:** Dichloromethane (DCM)

3.3.2.7.2.2 Method

Solvent extraction was used to determine fat content. The fat content must be determined in order to build the process recipe for the end product's production. By taking samples (5gm) from the post-tanned crust leather, the fat content of the chestnut-THPS tanned crust leather and the chrome tanned control crust leather for the upper was determined. The leather sample is precisely weighed on an analytical balance and transported to a Soxhlet thimble, In a Soxhlet extraction system, oils and fats are extracted for 5 hours using dichloromethane. It is the official fat extraction method, which is a standard Soxhlet extraction method using dichloromethane as the solvent. The fat was extracted in the Soxhlet, dried, and the solvent separated and collected in the Soxhlet tank for

recovery. The extract in the round flat bottomed flask was dried at 103^{o}C to constant weight in the oven after recovering the solvent from the Soxhlet tank.

Calculation

$$\text{Fat and oil content, \%} = (W_f / W_s) \times 100$$

Where, W_f = extracted fat weight, W_s = sample weight

3.3.2.7.3 Moisture content estimation

Moisture content is an important feature of leather that varies depending on the temperature and relative humidity of the environment. Moisture content is calculated using moisture and small amounts of volatile oils or solvents. Because the oils or solvents represent only a minor part of the total weight loss during this test, the amount of volatile materials detected can be regarded a decent indication of the moisture content.

3.3.2.7.3.1 Materials

- **Sample:** samples were taken from the butt area for the experimental and control crust leathers.
- **Apparatuses:** the apparatuses used for this analysis were china dish, hot air oven and weighing balance.

3.3.2.7.3.2 Method

IS 582-L-2: 1970 was the method used to determine moisture content. In this case, the mass loss is calculated after a sample of ground leather is dried to a constant mass at a temperature slightly above 100^{o}C. The objective is to determine how much moisture is present in a crust leather sample. A 5-gram leather sample was carefully weighed, then dried for 3 hours at 105^{o}C in an air oven, cooled and weighed it again, continuing the drying, chilling and weighing process until it attained an uniform weight. A material's moisture content is frequently expressed as a percentage of its dry mass.

Calculation

$$\text{Moisture content, \%} = (M_1\text{-}M_2 / M_1) \times 100$$

Where, M_1 = wet sample weight in gram, M_2 = dry sample weight in gram

3.3.2.7.4 Total ash content determination

3.3.2.7.4.1 Materials

- **Sample:** Samples were taken from the butt area for the experimental and control crust leather.
- **Apparatuses:** the apparatuses used in this test are crucible, hot plate, filter paper.
- **Reagents:** Ammonium nitrate (NH_4NO_3) and sulfuric acid are the chemicals used to determine total ash (H_2SO_4).

3.3.2.7.4.2 Methods

The sample's known weight was placed in a ceramic crucible. To get an uniform weight, the sample was first carbonized on a hot plate in a fume cabinet before being placed in an 800^oC furnace [36]. If all of the carbon could not be burned off, a concentrated ammonium nitrate solution was added to the residue and heated again. If a complete burn off was not obtained after this stage, hot water was added to the residue, the solution was filtered, and the residue was washed over ashless filter. It was the dried to the same consistent weight in the same crucible. The working environment had a temperature 21.9^oC and a humidity of 50%.IS 582-LC-3: 1970 was the method used to determine moisture content.

Calculation

$$\text{Total ash content, \%} = (T_1\text{-}T_2 / T_1) \times 100$$

Where, T_1 = wet sample weight in gram and T_2 = dry sample weight in gram

3.3.2.7.5 Determination of Hide substances

3.3.2.7.5.1 Materials

- **Sample:** samples were taken from the butt, neck, and belly for the experimental and control crust leathers.
- **Apparatus:** kjeldahl apparatus (IK-194), weighing balance, conical flask, funnel, titration stand and burette are the apparatuses used in hide substance determination.

3.3.2.7.5.1 Method

The leather sample was thoroughly dried after the total matter soluble in water determination, and 0.6 g were collected and placed in a dry 250 ml Kjeld Hal flask with 15 to 20 ml concentrated sulfuric acid, as well as some glass beads. In the tilted position, the flask was gently heated. The flask was filled with 5 g potassium sulphate and 5 g copper sulphate, which were heated to boiling until the solution became clear and the color changed no longer. This treatment took about 30 minutes to complete. The solution was quantitatively put into an ammonia distillery after chilling. A dropping funnel was used to add sodium hydroxide solution (0.05 m) until the solution turned black. In the presence of methyl orange as an indicator, the ammonia was distilled into 100 ml of 0.05 m sulfuric acid. It is usually assumed that all ammonia has been distilled after collecting roughly 150 ml of distillate, and this technique takes around 40 minutes. 0.05m NaOH was used to back-titrate the surplus acid. IS 582 (LC-5): 1970 was the method used to determine hide substance.

Calculation

$$\text{Hide substances, \%} = (a / b) \times 100$$

Where, a = hide substance weight in gram,

b= leather sample weight in gram

Chapter Four

4. Results and Discussions

4.1 Optimization of Chestnut-THPS Combination tannage

A shrinkage tester was used to determine the hydrothermal stability of samples of experimental and control leathers. Combination tanning trials using Chestnut-THPS with a different percentage offers of Chestnut (10,15,20%) and THPS (1,1.5,2%) were carried out. Combination tanning using Chestnut- THPS was successful after many trials. Nine trials were conducted at random to optimize the combination tanning system based on the response parameter shrinkage temperature, with the process that gave the largest shrinkage temperature being chosen as the optimal process recipe. The shrinkage temperature of experimental combination tanned leather at different trial and the control leathers keeping at constant percentage offer are given in Table 4.1.

Table 4.1 Shrinkage temperature of Chestnut-THPS combination tanned and control tanned leathers

Trial's order	Percentage offers of Chestnut **(%)**	Percentage offers of THPS (**%**)	Shrinkage Temperature **(ºC)**
1	15	1	88
2	10	1	86
3	20	1.5	92
4	20	1	90
5	10	2	87
6	15	2	91
7	10	1.5	87
8	20	2	95
9	15	1.5	89
Controls	Percentage offers **(%)**		Shrinkage temperature **(ºC)**

Chestnut (alone)	20	82
THPS (alone)	2	84
BCS	6	105

As shown in the table, The Chestnut-THPS combination leathers tanned using 20% chestnut followed by 2% THPS provides hydrothermal stability of 95ºC. Chestnut and THPS individual tanned leathers have shrinkage temperatures of 82°C and 84°C, respectively. According to the findings, the chestnut-THPS combination tanned leather had a shrinkage temperature increase of more than 11oC and 13oC, respectively, when compared to the chestnut and THPS individual tanned leathers. It is seen from the table that with increase in the amount of chestnut and THPS there is increase in shrinkage temperature. The 20% of Chestnut followed by 2% of THPS has been optimized as best offer with a view to increase the hydrothermal stability of tanned leather.

4.2 Scanning electron microscopic studies on crust leathers

Scanning electron microscopic analysis of Chestnut-THPS (experimental) and chrome (control) tanned crust leathers was carried out to investigate the influence of optimized combination tanning system on the fiber structure and to understand the surface and cross-section fiber compaction. Figure 4.1 shows a scanning electron microscopic image of the grain surface and cross-section of control and experimental tanned leathers. Figure 4.1.d shows a SEM micrograph of the cross-section of the optimized experimental tanned upper leathers at a magnification of 500x, the presence of THPS inside the leather matrix causes fiber coating, which leads to good structural stability and smoothness. The grain surface of the experimental tanned leather at a magnification of 250x, as seen in Figure 4.1.b shows there is no surface deposition of tannins on the grain surface of the experimental tanned leather, a crust leather with good fiber compaction and grain tightness properties has been examined by hand and visual inspection. The filling nature of chestnut also give us an admirable fullness as observed from the figure given.

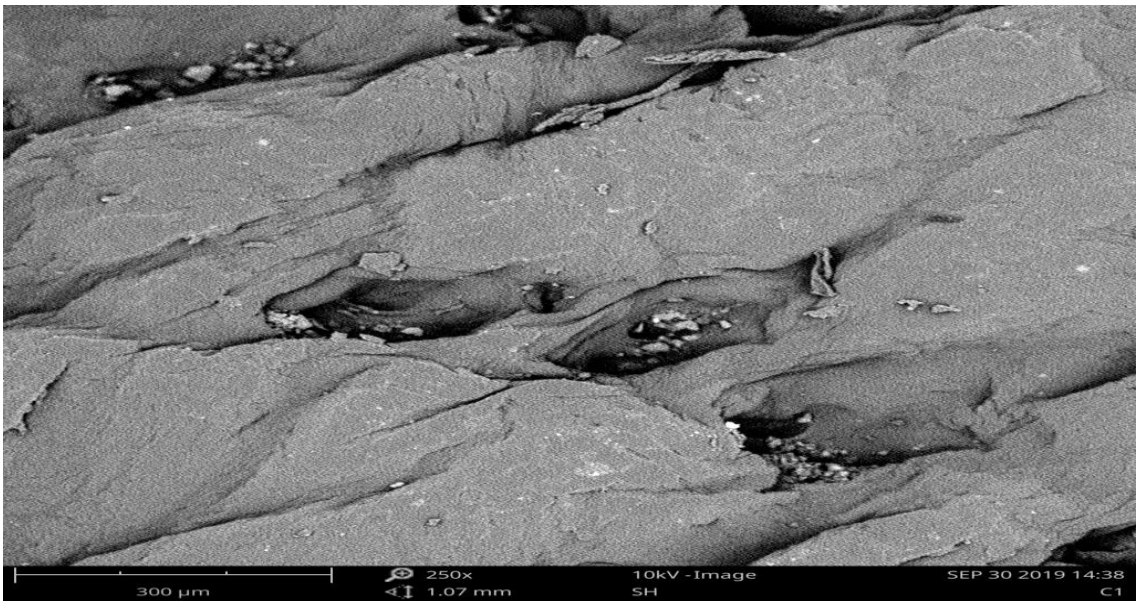


Figure 4.1.a Scanning electron micrographs of the grain surface (x250) of upper crust leather control

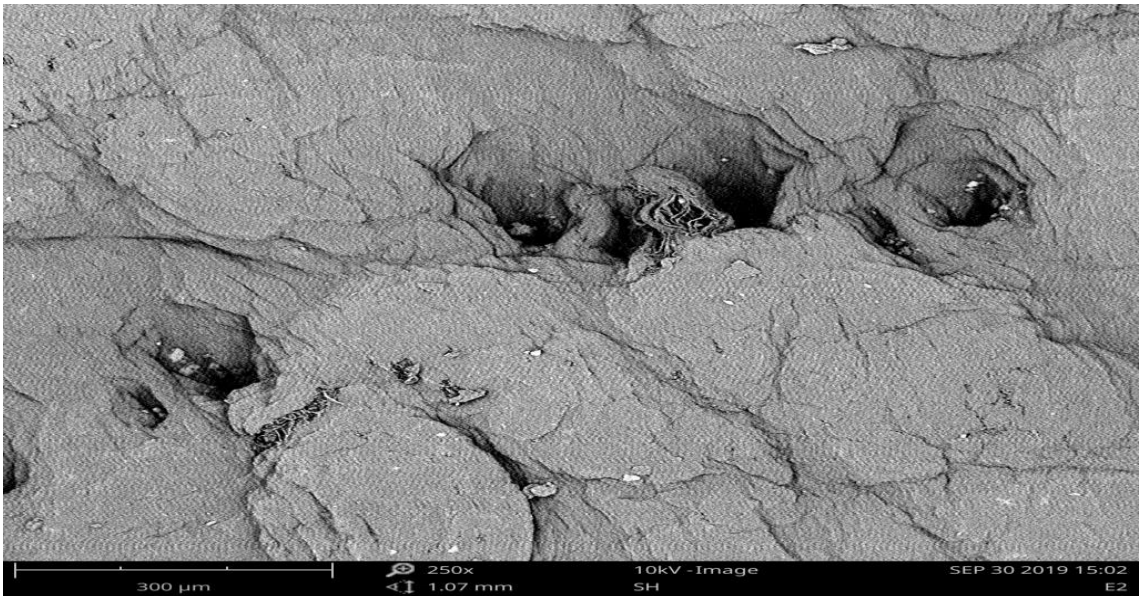


Figure 4.1.b Scanning electron micrographs of the grain surface (x250) of upper crust leather for experimental

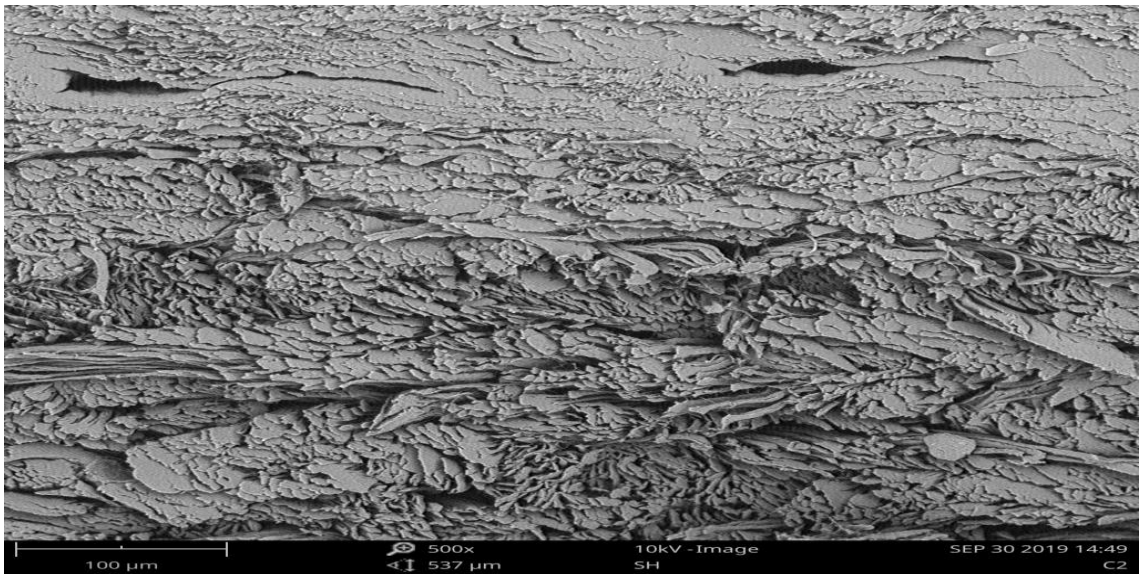


Figure 4.1.c Scanning electron micrographs of the cross-section (x500) of upper crust leather for control

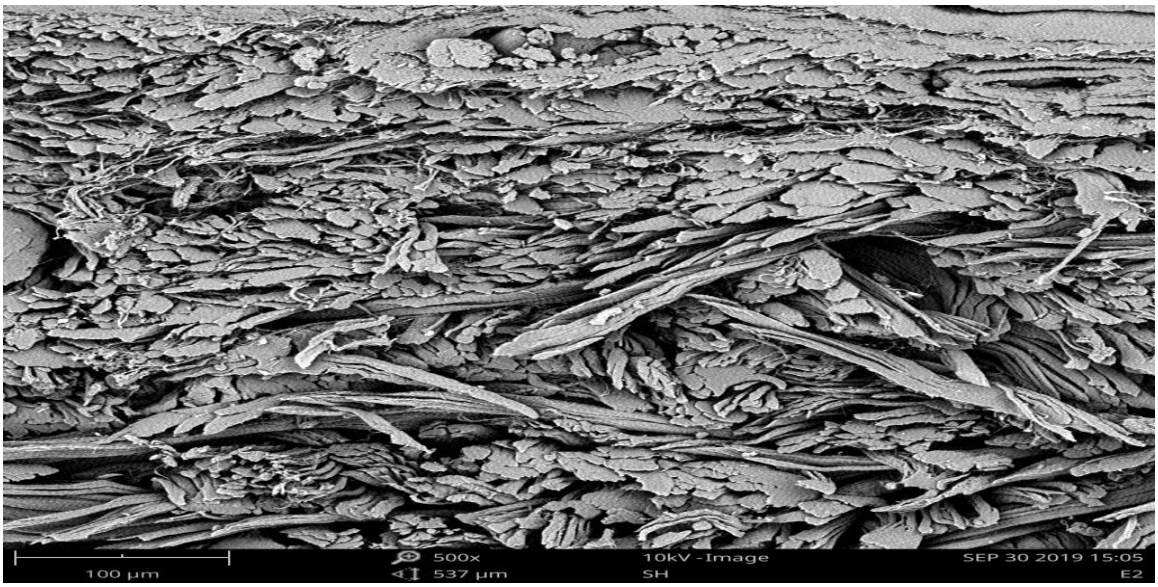


Figure 4.1.d Scanning electron micrographs of the cross-section (x500) of upper crust leather for experimental

4.3 Evaluation of Reflectance measurements of the upper crust leathers

The reflectance measurements were carried out for the chestnut-THPS (experimental) and control chrome & chestnut crust leathers. The L*, a*, b*, and hue* values are the parameters used to assess and evaluate the color of leather samples are given in Table 4.2. L* represents whiteness, then the L* values for chestnut-THPS tanned crust leather (E), chestnut tanned (alone) , THPS (alone) and control chrome tanned (C) crust leather are 34.559, 32.793, 67.164 and 37.363 respectively. The THPS alone crust leather hue is the lightest in shade compared to the experimental and control leathers. a* represents red and green axis, where a*< 0 means green and a* >0 mean red. In this case the experimental (E) and chestnut tanned (alone) and THPS alone leathers have a value of 0.178, 0.144, 0.101 respectively, then it means this leathers color obtained have a red shade. Though control chrome (C) leather has a green shade. b* denotes the yellow and blue axes, with b* 0 denoting blue and b*> 0 denoting yellow. The b* values for experimental, chestnut (alone) and control chrome leathers are greater than zero, then it indicates these leathers have a yellow shade. c* represents the chromacity of the color, which means the intensity of the color. The value of c* for experimental (E), chestnut (alone), THPS alone, and control chrome (C) indicates that the color obtained has less depth shade and intensity, making it appropriate for pastel hues, as shown in the table.

Table 4.2 Reflectance measurement results for experimental and control crust leathers

Leather samples	**Parameters**				
	L	a*	b*	c*	Hue
Chestnut-THPS (E)	34.559	0.178	2.480	2.490	85.977
Chestnut (alone)	32.793	0.144	2.009	2.014	84.905
THPS (alone)	67.164	0.101	0.841	0.651	94.103
Chrome (control)	37.363	-0.302	1.042	1.085	86.851

4.4 Environmental Characteristics of spent tan liquor

The measurements of chemical oxygen demand (COD), biological oxygen demand (BOD), total solids (TS), total suspended solids (TSS), and total dissolved solids (TDS) in spent tan liquors from experimental and control leathers are shown in Table 4.3. The average of three experiments are reported based on their standard deviations.

Table 4.3 Environmental characteristics of spent liquor from experimental and control leather process

Parameters (mg/l)	**Leather samples**			
	Chestnut-THPS (E)	Chestnut (alone)	THPS (alone)	Chrome (control)
TS	10540±16	12092±19	12239±16	14731±21
TDS	8014±14	11276±18	11402±10	16426±12
TSS	4912±13	9017±16	5961±8	6431±18
BOD	1485±21	6531±12	2125±14	1809±10
COD	3241±10	17310±13	3873±11	2750±16

As shown in the table, TS, TDS, TSS, and BOD of spent liquor processed with the chestnut-THPS combination tanning system (experimental) are lower than spent liquor processed with the chrome tanning system (Control), whereas COD is slightly higher. This could be due to the fact that vegetal tannins (chestnut) have been reported to increase the COD level of liquor. When compared to spent liquor from chestnut alone and THPS alone tanning liquor, COD, BOD, TS, TDS, and TSS were dramatically reduced in chestnut-THPS experimental tanning experiments. This could be owing to the chestnut's greater exhaustion during tanning.

4.5 Physical strength characteristics of crust leathers

For both experimental and control upper leathers, physical characteristics such as tear strength, load at grain crack, distension at grain crack, tensile strength, and percent elongation at break were measured using standard procedures, and the findings are provided in Table 4.4.

Table 4.4 Physical strength characteristics of experimental and control upper crust leathers

Parameters	**Leather samples**			
	Chestnut-THPS (E)	Chestnut (alone)	THPS (alone)	Chrome (control)
Tear strength (N/mm)	54.1±2	53.5±3	46±3	47.3±2
Load at grain crack (N)	456.2±5	398.7±5	387±1	408.4±3
Distension at grain crack (mm)	12±0.5	10.6±1.5	10±0.5	11±1
Tensile strength (N/mm^2)	26.9±1	30.7±2	27±2	28±1.5
Elongation at break (%)	66.0±2	62.8±2	62±1	64±1

The strength characteristics of Chestnut-THPS combination (E) tanned crust leathers, such as tear strength, load at grain crack, distension at grain crack, and percent elongation at break, are found to be higher than those of Chestnut tanned (alone), THPS (alone) and control chrome tanned (C) crust leathers, as shown in the table above. This could be owing to a higher level of crosslinking between the skin matrix fiber structure and the tannins utilized in the combination tanning system. whereas, tensile strength of Chestnut-THPS tanned (E) crust leathers were found to be marginally lower than control chrome , chestnut (alone) and THPS alone crust leathers. When compared to control chrome tanned leathers, chestnut tanned leathers have superior tensile and tear strength. The strength parameters such as tear strength and grain crack strength are an important factor particularly towards the durability of upper leather. Thus, due to this, the optimized combination tannage (E) is a preferable tanning system in the production of upper leather.

4.6 Comfort properties of crust leathers

Water vapor permeability (WVP), water vapor absorption (WVA), and water penetration resistance (WPR) are the most often used tests to determine the comfort qualities of shoe upper leather (WPR). Standard protocols were used to analyze the comfort qualities [39, 40, and 41]. Table 4.5 shows the results of testing the hygienic properties of experimental and control upper leathers.

Table 4.5 Hygiene properties of control and experimental upper crust leather

Parameters	**Leather samples**			
	Chestnut-THPS	Chestnut (alone)	THPS (alone)	Chrome (control)
WVP (mg/cm^2.h)	7.8	5.1	4.1	6.02
WPR (min)	0.9	0.8	0.7	1
%WVA (60 min)	58.9	48.7	46.5	51.2

The above hygienic features are known to be the most significant criterion for any type of leather because they are the sole way to distinguish natural leather from synthetics. According test results, it was revealed that the Chestnut-THPS (E) leathers have a higher water vapor permeability and percent of water absorption than control chrome tanned (C), chestnut tanned (alone) and THPS alone leathers. The presence THPS, which has a high-water vapor permeability, could explain this.

The chestnut tanned leather (alone) gave the lowest value of water vapor permeability. This result can be clarified with the higher density of the chestnut tannin particles that cause lower vapor permeability. Whereas, water penetration resistance of both experimental (E) and chestnut control found to be slightly lower than control chrome tanned.

4.8 Assessment and Hand evaluation of bulk properties of crust leathers

The bulk properties like softness, grain smoothness, grain tightness, fullness, dye uniformity, and general appearance of control and experimental leathers were assessed by touch and eye inspection. The average of the ratings for the leathers used in the experiment was calculated for each functional attribute, and the findings are shown in Figure 4.2. For each functional characteristic, three senior specialist tanners assessed the leathers on a scale of 0-10 points. Higher result numbers indicate better property.

In comparison to control chrome tanned (C), Chestnut (alone), and THPS (alone) crust leathers, Chestnut-THPS combination tanned (E) crust leathers have good grain smoothness, fullness, grain tightness, and general appearance. This is primarily due to the high tannin fixation and high affinity for pelt of the experimental combination tannin materials. This Chestnut softness problem can fix by proper mix of syntans along with the usage of penetrative synthetic fat liquors in post tanning leather processing to impart the desired result. The general appearance of optimized experimental combination tanned crust leather found to be better than of the control tanned leathers. The graphical representation of organoleptic properties of Chestnut-THPS (experimental), Chestnut (alone), THPS (alone) and control chrome tanned crust leathers are shown in Figure 4.2.

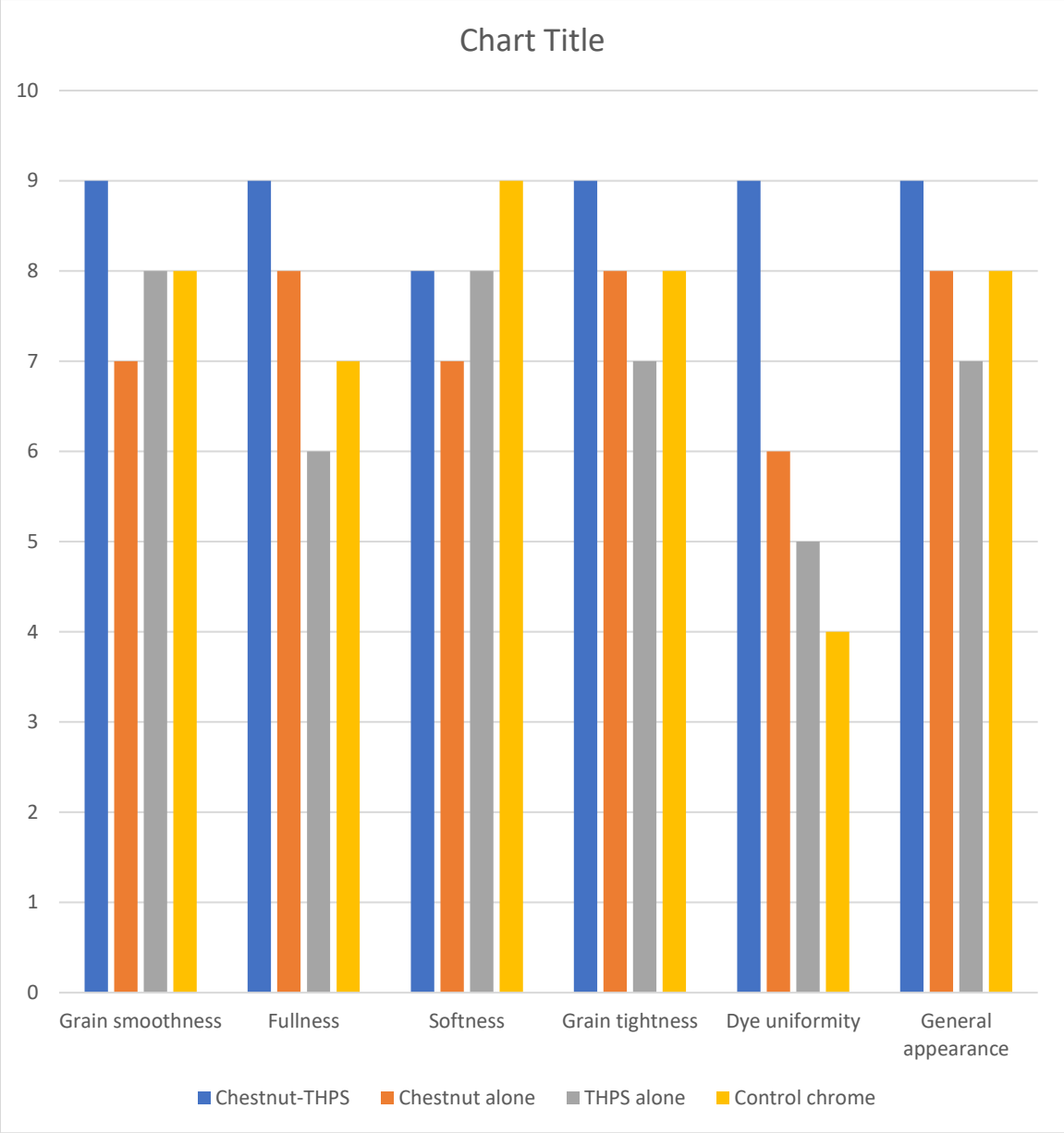


Figure 4.2 Graphical representation of organoleptic properties of crust leathers

4.8 Chemical characteristics of crust leathers

Chemical characteristics such as percent of fats and oils, percent of moisture content, percent of total ash content, and percent of hide substance were determined using standard procedures for control and experimental leathers and the results are presented in Table 4.6. Three trials were carried out for each sample, with the average values calculated. The chemical constituents like fat and oil content, moisture content and hide substance for Chestnut-THPS experimental (E) leathers are comparable to that of chestnut (alone), THPS alone and control chrome (C) tanned leathers. Although, the total ash content for control chrome tanned leather is higher than the experimental combination (E) and control chestnut tanned leathers. This means the chrome tanned leathers contains more amount of non-volatile matter this may be in the form of oxides and salts of the elements. The chemical properties of the experimental combination tanned leathers are found to be quite normal, and they meet the chemical analysis requirements as shown in Annex 2.

Table 4.6 Chemical characteristics of experimental and control crust leathers

Parameters	**Leather samples**				
	Chestnut-THPS (E)	Chestnut (alone)	THPS (alone)	Chrome (control)	Standard value
% Fat & oil content	6.7	8	7	8.6	15, Min
% Moisture content	14.9	13.4	14.2	14.4	-
% Total ash content	2.1	3.6	2.4	11.2	3 - 6
% Hide substance	70.9	68.6	69.1	71.5	64, Min

Chapter Five

5. Conclusion and Recommendation

5.1 Conclusion

In the present study, an attempt has been made using an eco-friendly combination tanning process based on Chestnut and THPS. The combination tanning using 20% of Chestnut followed by 2% of THPS provides a leather with shrinkage temperature of 95^{o}C. The SEM micrograph of the cross-section of the optimized experimental tanned leathers shows the presence of THPS inside the leather matrix causes fiber coating, which leads to good structural stability and smoothness. The micrograph of grain surface of the experimental tanned leather shows there is no surface deposition of tannins on the grain surface of the experimental tanned leather, a crust leather with good fiber compaction and grain tightness properties has been examined by hand and visual inspection. The filling nature of chestnut also give us an admirable fullness.

The organoleptic qualities of the leathers processed with this combination tanning agent are comparable to or better than the chrome-tanned control leather. The physical strength characteristics of Chestnut-THPS tanned leathers are significantly enhanced due to the presence of THPS. This could be owing to a higher level of crosslinking between the skin matrix fiber structure and the tannins utilized in the combination tanning system. The hygiene properties are the most necessary parameter for any type of leather since those parameters only distinguish or separate the natural leather from synthetics. According test results it was revealed that the Chestnut-THPS tanned leathers have higher water vapor permeability and % of water vapor absorption than the chrome and chestnut tanned leathers. The chemical constituents like fat and oil content, volatile matter and hide substance for Chestnut-THPS experimental leathers are comparable to that of chestnut and control chrome tanned leathers. The wasted liquor processed using the Chestnut-THPS combination tanning system has lower TS, TDS, TSS, and BOD than spent liquor processed using the chrome tanning system. The Chestnut-THPS tanned leathers can meet the mandatory and voluntary conditions specified by environmental protection organizations in terms of allowable waste water discharge limits.

5.2 Recommendation

- In this study cost analysis, market demand, or marketability of this product did not evaluated. It is suggested that these aspects be thoroughly examined.
- In the future, it is recommended to find out another alternative tanning system which are chrome and mineral free tannages occurring naturally with zero toxicity and to give a light weight and pastel shade leathers which are absent in the present study.
- The Chestnut-Tetrakis hydroxymethyl phosphonium sulfate combination tannage for upper leather fabrication is recommended as an alternative ecofriendly tanning due to its superiority in terms of quality and availability.

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Annexes

Annex 1: Physical and chemical test standard requirements of shoe upper leather

S.no	Characteristics	Requirements (Minimum)
1	Crackiness of grain	Shall not crack in single folding
2	Tensile strength Min. N/mm^2	15
3	Elongation at break %, Min.	40 – 60
4	Tearing strength, kg/cm, Min.	40
5	Distension at grain crack, in mm. Min	7
6	Thickness, mm	1-1.2
7	Air vapor permeability, $g/m^2/h$	20

Source central leather research institute (CLRI), India.

Annex 2: Chemical constituent test standards for the manufacturing of upper leathers

S.no	Characteristics	Requirements
1	PH of water soluble	Not below 3.5
2	%Oils and fats, Max	15
3	Hide substance % by mass, Min.	64
4	Total ash percent by mass, Max.	3-6

Source central leather research institute (CLRI), India.

Annex 3: Effluent discharge standards for different parameters in leather processing

S.no	Characteristics	Before treatment (mg/l)	After treatment (mg/l)
1	PH	-	6-9
2	Temperature	-	40^oc
3	Bod_5 at 20^0c	1200-3000	200
4	COD (Total)	2500-8000	500

5	Total solids (TS)	12000-20000	-
6	Total dissolved solids (TDS)	9000-18000	2100
7	Suspended solids (TSS)	2000-5000	100
8	Chromium (as Cr_2O_3)	120-200	3
9	Chromium (as Cr VI)		0.1
10	Sulfide (as S)	30-150	50
All values except PH and temperature are expressed in mg/l			

Source central leather research institute (CLRI), India.

Annex 4: Formulation of Chestnut-THPS tanning system (experimental)

I. Formulation of Trial number 1

Process	%	Chemicals	Duration (min)	Controls
Deliming	80 1 0.5	Water Ammonium sulfate Sodium bisulfate	Run 60’	Check completion using phenolphthalein
Adjustment of PH	1 0.5	Water Acetic acid	3x10 +15’	Check PH=4.8 Drain 70% of liquor
Bating	0.4	Bating agent (Oropon ON_2)	50’	
Degreasing	3	Degreasing agent	45’	
Tanning	30 10 5 1	Water (liquor) Chestnut Chestnut THPS	30’ 30’ 60’	Check penetration And record PH
Adjustment of	0.5	Sodium formate	15	Check the PH to be

PH	0.75 15	Sodium bicarbonate Water	3x10' 120'	3.8 – 4
Drain the bath and pile overnight. Next day sammed and shaved to 1.1 to 1.2 mm.				

II. Formulation of Trail number 2

Process	%	Chemicals	Duration (min)	Controls
Deliming	80 1 0.5	Water Ammonium sulfate Sodium bisulfate	Run 60'	Check completion using phenolphthalein
Adjustment of PH	1 0.5	Water Acetic acid	3x10 +30'	Check PH=4.8 Drain 70% of liquor
Bating	0.4	Bating agent (Oropon ON_2)	50'	
Degreasing	3	Degreasing agent	45'	
Tanning	30 10 1	Water (liquor) Chestnut THPS	30 +30' 60'	Check penetration And record PH
Adjustment of PH	0.5 0.75 15	Sodium formate Sodium bicarbonate Water	3x10' 120'	Check the PH to be 3.8 – 4
Drain the bath and pile overnight. Next day sammed and shaved to 1.1 to 1.2 mm.				

III. Formulation of Trial number 3

Process	%	Chemicals	Duration (min)	Controls
Deliming	80 1 0.5	Water Ammonium sulfate Sodium bisulfate	Run 60’	Check completion using phenolphthalein
Adjustment of PH	1 0.5	Water Acetic acid	3x10 +15’	Check PH=4.8 Drain 70% of liquor
Bating	0.4	Bating agent (Oropon ON_2)	50’	
Degreasing	3	Degreasing agent	45’	
Tanning	30 10 10 1.5	Water (liquor) Chestnut Chestnut THPS	30’ 30’ 60’	Check penetration And record PH
Adjustment of PH	0.5 0.75 15	Sodium formate Sodium bicarbonate Water	3x10’	
Drain the bath and pile overnight. Next day sammed and shaved to 1.1 to 1.2 mm.				

IV. Formulation of Trial number 4

Process	%	Chemicals	Duration (min)	Controls
Deliming	80 1 0.5	Water Ammonium sulfate Sodium bisulfate	Run 60’	Check completion using phenolphthalein

Adjustment of PH	1 0.5	Water Acetic acid	3x10 +15’	Check PH=4.8 Drain 70% of liquor
Bating	0.4	Bating agent (Oropon ON_2)	50’	
Degreasing	3	Degreasing agent	45’	
Tanning	30 10 10 1	Water (liquor) Chestnut Chestnut THPS	 30’ 30’ 60’	 Check penetration And record PH
Adjustment of PH	0.5 0.75 15	Sodium formate Sodium bicarbonate Water	3x10’ 120’	Check the PH to be 3.8 – 4
Drain the bath and pile overnight. Next day sammed and shaved to 1.1 to 1.2 mm.				

V. Formulation of Trial number 5

Process	%	Chemicals	Duration (min)	Controls
Deliming	80 1 0.5	Water Ammonium sulfate Sodium bisulfate	Run 60’	Check completion using phenolphthalein
Adjustment of PH	1 0.5	Water Acetic acid	3x10 +15’	Check PH=4.8 Drain 70% of liquor
Bating	0.4	Bating agent		

		(Oropon ON_2)	50’	
Degreasing	3	Degreasing agent	45’	
Tanning	30 10 2	Water (liquor) Chestnut THPS	 30 +30’ 60’	 Check penetration And record PH
Adjustment of PH	0.5 0.75 15	Sodium formate Sodium bicarbonate Water	 3x10’ 120’	Check the PH to be 3.8 – 4
Drain the bath and pile overnight. Next day sammed and shaved to 1.1 to 1.2 mm.				

VI. Formulation of Trial number 6

Process	%	Chemicals	Duration (min)	Controls
Deliming	80 1 0.5	Water Ammonium sulfate Sodium bisulfate	 Run 60’	Check completion using phenolphthalein
Adjustment of PH	1 0.5	Water Acetic acid	 3x10 +15’	Check PH=4.8 Drain 70% of liquor
Bating	0.4	Bating agent (Oropon ON_2)	50’	
Degreasing	3	Degreasing agent	45’	
Tanning	30 10 5	Water (liquor) Chestnut Chestnut	 30’ 30’	 Check penetration

	2	THPS	60’	And record PH
Adjustment of PH	0.5 0.75 15	Sodium formate Sodium bicarbonate Water	 3x10’ 120’	Check the PH to be 3.8 – 4
Drain the bath and pile overnight. Next day sammed and shaved to 1.1 to 1.2 mm.				

VII. Formulation of Trial number 7

Process	%	Chemicals	Duration (min)	Controls
Deliming	80 1 0.5	Water Ammonium sulfate Sodium bisulfate	 Run 60’	Check completion using phenolphthalein
Adjustment of PH	1 0.5	Water Acetic acid	 3x10 +15’	Check PH=4.8 Drain 70% of liquor
Bating	0.4	Bating agent (Oropon ON_2)	50’	
Degreasing	3	Degreasing agent	45’	
Tanning	30 10 1.5	Water (liquor) Chestnut THPS	 30 +30’ 60’	 Check penetration And record PH
Adjustment of PH	0.5 0.75 15	Sodium formate Sodium bicarbonate Water	 3x10’ 120’	Check the PH to be 3.8 – 4
Drain the bath and pile overnight. Next day sammed and shaved to 1.1 to 1.2 mm.				

VIII. Formulation of Trial number 8

Process	%	Chemicals	Duration (min)	Controls
Deliming	80 1 0.5	Water Ammonium sulfate Sodium bisulfate	Run 60’	Check completion using phenolphthalein
Adjustment of PH	1 0.5	Water Acetic acid	3x10 +15’	Check PH=4.8 Drain 70% of liquor
Bating	0.4	Bating agent (Oropon ON_2)	50’	
Degreasing	3	Degreasing agent	45’	
Tanning	30 10 10 2	Water (liquor) Chestnut Chestnut THPS	 30’ 30’ 60’	 Check penetration And record PH
Adjustment of PH	0.5 0.75 15	Sodium formate Sodium bicarbonate Water	3x10’ 120’	Check the PH to be 3.8 – 4
Drain the bath and pile overnight. Next day sammed and shaved to 1.1 to 1.2 mm.				

IX. Formulation of Trial number 9

Process	**%**	Chemicals	Duration (min)	Controls
Deliming	80 1	Water Ammonium sulfate		Check completion using

	0.5	Sodium bisulfate	Run 60’	phenolphthalein
Adjustment of PH	1 0.5	Water Acetic acid	3x10 +15’	Check PH=4.8 Drain 70% of liquor
Bating	0.4	Bating agent (Oropon ON_2)	50’	
Degreasing	3	Degreasing agent	45’	
Tanning	30 10 5 1.5	Water (liquor) Chestnut Chestnut THPS	30’ 30’ 60’	Check penetration And record PH
Adjustment of PH	0.5 0.75 15	Sodium formate Sodium bicarbonate Water	3x10’ 120’	Check the PH to be 3.8 – 4
Drain the bath and pile overnight. Next day sammed and shaved to 1.1 to 1.2 mm.				

Annex 5: Formulation of control tanning systems for sheep skin to produce upper leathers

Process	%	Chemicals	Duration (min)	Controls
Chestnut tanning	30 10 10 0.5	Water (liquor) Chestnut Chestnut Formic acid	30’ 30+30’ 3x10 +30’	Check penetration And record PH
THPS tanning	50 2	Pickle liquor THPS	50’	

	1 1.5	Sodium formate Sodium bicarbonate	15' 3x10 +30'	Check PH to be 3.8-4.
Chrome tanning	50 6 1 1.5	Pickle liquor Chromium Sodium formate Sodium bicarbonate	 60' 15' 3x10 +1 hr	Check penetration and PH to be 3.8-4.
Check the PH to be 3.8 - 4. Drain the bath and pile overnight. Next day sammed and shaved to 1.1 to 1.2 mm. The shaved weight noted.				

Annex 6: Wet-finishing recipe for both experimental and control upper leathers to produce upper leathers

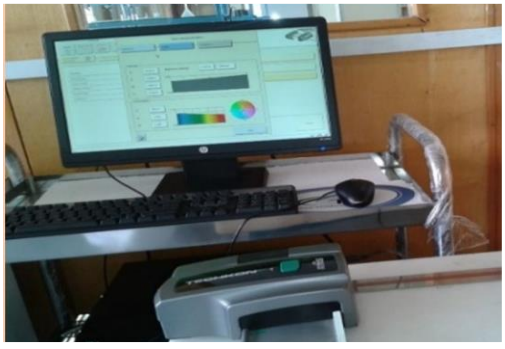
Process	%	Chemicals	Duration (min)	Controls
Neutralization	150 1 0.75	Water Sodium formate Sodium bicarbonate	 3x10 +30'	Check PH to be 5-5.2
Re-tanning	100 2 6 5	Water Acrylic syntan (Relugan RE) Melamin resine syntan (Basyntan FB6) Phenolic synatn (Basyntan DI)	 20' 60'	
Fat-liquoring	100	Water		

	5 4 2	Synthetic fat-liquor Semi synthetic fat-liquor Lecithin fat-liquor	 45’	
Dyeing	4	Acid black dye	50’	Check penetration
Fixing	1	Formic acid	3x10 +30	Check fixation
Pile overnight & next day go to setting, hook to dry, stacking, trimming and buffing.				

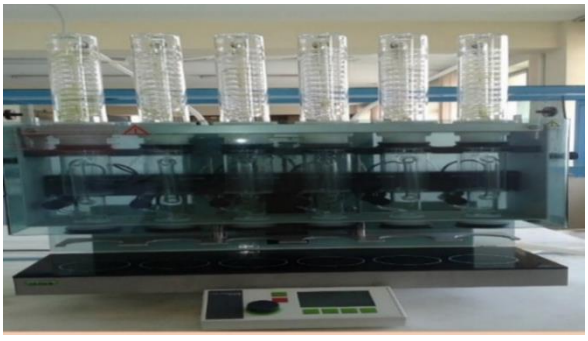
Annex 7: Laboratory Equipment and Apparatuses used in the study

Scanning electron microscope (SEM)

UV-vis spectrophotometer



Techkon specrodrive



Soxlet apparatus

Dynamometer

Lastometer

Hot air oven

Desicactors