
ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAiT)

SCHOOL OF GRADUATE STUDIES

DEPARTMENT OF CHEMICAL ENGINEERING

(LEATHER TECHNOLOGY STREAM)

# Quebracho-zinc sulphate combination as chrome-free tanning agent

A Thesis Submitted to the School of Graduate Studies of Addis Ababa University, Institute of Technology, in Partial Fulfilment of the Requirements for the Degree of Masters of Science in Chemical Engineering (In Leather Technology)

By

Melkamu Kassahun Mequannint

Advisor

Dr.B. Chandrasekaran (PhD)

AddisAbaba, Ethiopia

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SEPTEMBER, 2014

**DEDICATION**

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

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Signature Date

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## List of Abbreviations

| | |
|---|---|
| WVA | water vapour absorption |
| WVP | water vapour permeablity |
| WRP | water vapour resistances |
| Vc | quebracho control |
| Zv | quebracho-zinc |
| Zc | zinc control |
| Ts | shrinkage temperature |

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**ABSTRACT**

Leather has remained a unique material for a long time. visco-elasticity and pore size distributions are two important properties of leather that have rendered it a unique material. The ability to breathe and readjust to volume fluctuations of the foot has made leather a unique material of choice in footwear industry. The environmental pollution problems pressures on chromium and forced the leather industry to find the possible alternatives. In the present study, a combination tanning system based on a quebracho – zinc tannage for the production of versatile leathers as a cleaner alternative is presented. A combination tanning system based on qubracho and zinc sulfate. (quebracho-Zn) leathers tanned using 8% quebracho followed by 6% $ZnSO_4.7H_2O$; resulted in shrinkage temperature is 87°C. The uptake of quebracho-zinc combination tanning system with quebracho (8%) and zinc (6% $ZnSO_4.7H_2O$) has been found to be better than the tanning system of quebracho and zinc tanning systems. The combination tanning system provides significant reduction in the discharge of COD, $BOD_5$ and TDS in the wastewater. Quebracho-Zn combination tanning system resulted in leathers with good hygienic, bulk and strength properties. The work presented in this paper established the use of quebracho and zinc combination tanning system as an effective alternative cleaner tanning technology.

**Keywords**: combination tanning system, zinc sulfate, quebracho, shrinkage temperature, hygienic, bulk and strength properties.

# CHAPTER ONE

## INTRODUCTION

### 1.1 Background

Leather making is one of the oldest crafts performed by humankind. Although there is world-wide trend to exploit alternative materials derived from other sources, leather still finds widespread use[1].

The tanning effect of chromium salt was discovered by Friedrich Knapp[9] in 1858. But this idea that chrome alum has a leathering effect was then largely ignored. It was not until the end of 1870s and the beginning of 1880s that a leather manufacturing process was industrialized where the need was felt for a faster tanning method than the prevalent vegetable tannages. In 1850s, Carl Cavallin[10] patented a tanning process which involved impregnating the delimed hide with a mixture of potassium dichromate and alum and then immersing the hide in a solution of ferrous sulphate. The hexavalent salt was reduced by the ferrous ion to give a combined iron-chromium tannage. In 1851, Rene de Kercado Molac[11] patented a similar process but indicated the importance of basification of chromium and iron salts to function as a proper tanning agent. He was also the first to indicate that the chrome tanned leather had a tendency to give a hard cracky grain. In the leather manufacturing, phenolic compounds have an important role, particularly in the tanning process. They are used as materials for the production of synthetic tanning agents (syntans) and in the form of vegetable tannages.

Phenols are used in syntan production, i.e. exchange syntans, which are related to the natural polyphenol tannins. Syntans contain phenolic hydroxyl groups and have the ability to react with collagen to produce leather. The first successful development of a commercially feasible syntan capable of producing leather was by Stiasny [2, 3]. The syntan called Novolac was prepared by condensation of phenol or cresol (methylphenol) with formaldehyde by heating at elevated temperatures[2].

Plant polyphenols, also called vegetable tannins, have been used for many thousands of years to convert animal skins and hides to leather[4], because they can interact with collagen and increase the hydrothermal stability of the collagens[5]. They are extracted from a wide variety of plants, found in wood, leaves, nuts, twigs, and bark. From the early work of Freudenberg

in 1920's and 1930's, they can be classified into two groups based on the chemical nature and structural characteristics, i.e. hydrolysable tannins and condensed tannins [6]. Another group of vegetable tannins called complex tannins was introduced in 1980's. The tannins contain both hydrolysable and condensed tannins. They are tannins in which a catechin unit is bound glucosidically to a gallotannin or an ellagitannin unit[7]. Their actions towards hydrolytic agents, particularly acids, illustrate the main distinction between the two groups. Hydrolysable tannins are readily hydrolysed by acids or enzymes into a sugar or related polyhydric alcohol and phenol carboxylic acids. Condensed tannins undergo progressive polymerisation under the action of acids to produce tannin reds or the amorphous phlobaphenes[4, 8].

**1.2 Statement of the problem**

Up to now, leather tanning is dominated by the use of chromium(III) salts, because it gives leather with unmatchable hydrothermal stability and excellent organoleptic properties. The chromium salt tanning system, which is still the most popular leather tanning procedure, is under continuous pressure from environmental groups and international regulations due to pollution and toxicology reasons unfairly associating the commonly used Chromium(III) with hazardous Chromium(VI).

Chrome tanning has some negative attributes, posing serious challenges to our continued reliance on it. As a limited resource, chromium(VI) is a well-known carcinogen, but chromium(III) is considered as non-toxic. The chromium(III) existing in leather might be transformed into chromium(VI) in some extreme conditions. Therefore, the chrome remaining in wastewater and the solid wastes may be harmful to the environment[51].

Tanners are finding it increasingly difficult to comply with ever emerging regulations with respect to the chrome content of effluent as well as the chrome containing solid wastes such as sludge, shavings, leather trimmings, and buffing dust. The disposal of solid wastes brings many difficulties for the leather industries in complying with the emerging regulations. In fact, some countries have restricted the use of chrome-tanned leather for certain purposes.

Several methods were developed to reduce pollution by chromium salt like methods of exhaustion of chromium, partially replacing chromium with other tanning material, recycling basic chromium sulphate, zero waste or discharge concepts etc. and are employed to minimize the amount of chromium in tannery waste of effluent. These methods have major

disadvantage such as incomplete chromium removal, expensive equipment and monitoring system requirement and zero discharge principle is an ideal method[49, 50].

In this work, the development of cleaner production of leather based on quebracho-zinc sulphate was attempted as an alternative chrome-free tannage. The tanning conditions of the new combination system, physical-chemical characteristics of leathers and the environment impact of this tannage was presented.

## 1.3 Objectives

- **General objective**

The general objective of the research was to study quebracho-zinc sulphate combination as chrome-free tanning agent

- **Specific Objectives**

Specific objective of the research was to:

- ✓ Determine hydrothermal stability of quebracho-zinc sulphate tanned leather
- ✓ Analyse ZnO exhaustion
- ✓ Analyse total solids, BOD and COD of spent liquor
- ✓ Determine mechanical strength and comfort properties of final leather
- ✓ Assess bulk properties and colour of the tanned leather

## 1.4 Significance of the study

The significant of this work were:

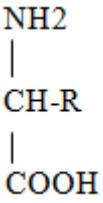
- ✓ Introducing quebracho-zinc sulphate tanning as alternative tanning agent
- ✓ Combination tanning is a promising option that produces leather with high hydrothermal stability compared to individual tanning agents.
- ✓ Quebracho-zinc sulphate is environmental friendly tanning agent and the product is ecological leather.
- ✓ Eco-friendly leather production, in which no potentially toxic, noxious and harmful chemicals were used and discharged.
- ✓ Producing chrome free shoe upper for diabetic patients

# CHAPTER TWO

## LITERATURE REVIEW

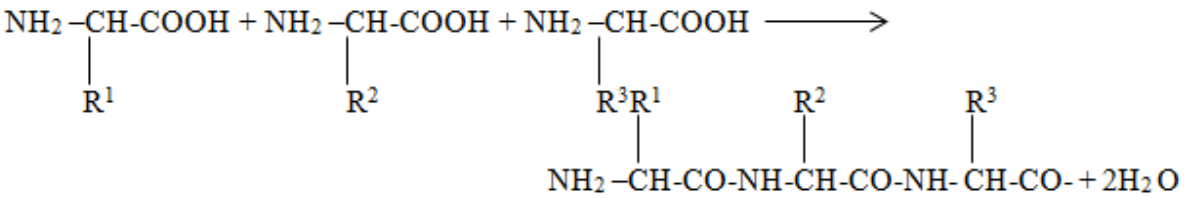
### 2.1 Nature of raw hides and skins

Hides and skins are made of proteins, fats, carbohydrates, mineral matters and water. In tanning, the protein which is of foremost importance is collagen. At present at least 19 different types of collagen are known[12]. Structure and function of collagen type I through type X are collected in a monograph edited by main and Burgeson[13]. Nimni[14] has published a more comprehensive collection of data. Heideman[12] has recently published an excellent review of our present knowledge of collagen. All proteins including collagen are made up of eighteen to twenty different amino acids. Collagen contains a number of basic and acidic groups. Macro molecules of a protein is made up of polypeptide chains which are formed by elimination of water between the carboxyl (-COOH) and amino ($-NH_2$) groups of large number of alpha acids.



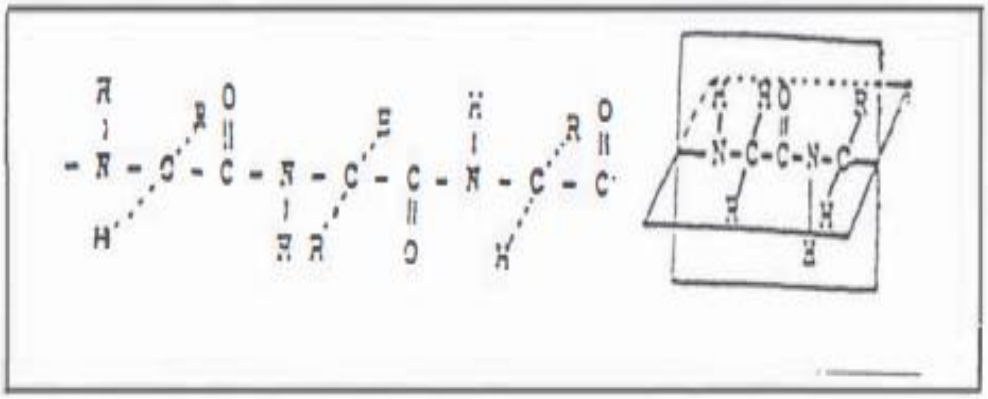

Informing the protein molecules the –COOH groups of one amino acid combines with the $NH_2$ group of the second amino acid. The two molecules are thus linked up together by

–CO.NH- or amide linkage with elimination of one molecule of water. A large number of amino acids are linked up in this way forming a long chain, known as polypeptide chain which constitutes the structure of protein that may be represented as follows:

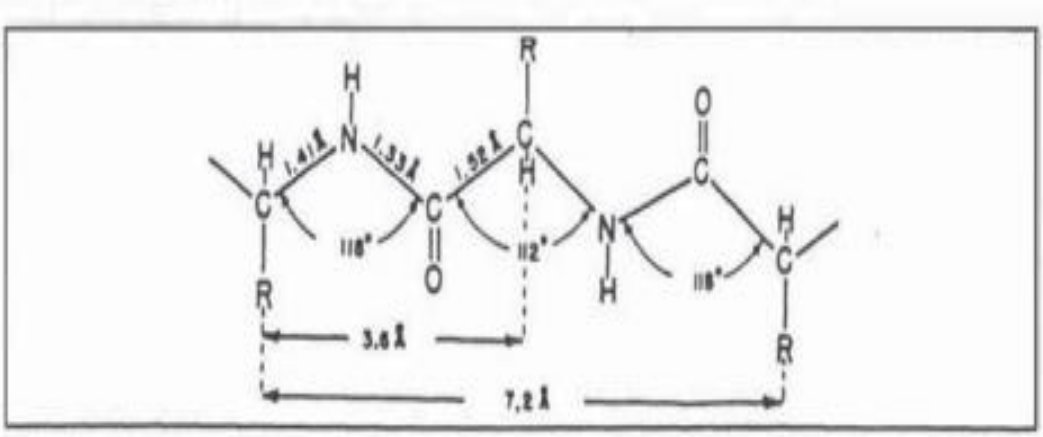



The groupings –CO-NH- within the chain are respectively called “amide link” and “amino acid residue.” A large number of these are present in the protein molecule. The polypeptide chains are three dimensional structures, the hydrogen and oxygen atoms of the amide groups

form a two dimensional plane with the N-C-C- chain. The side chain and hydrogen atoms attached to alpha-carbon atoms form another two dimensional plane which is linearly at right angle to the former. This is represented in the diagram below

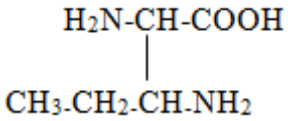


The special configuration of the amino acids residues in the protein chain is a zigzag structure with R groups alternately above and below the -N-C-C- plane. The bond distance and the bond angles are also fixed. This zigzag structure is represented by the following formula:-

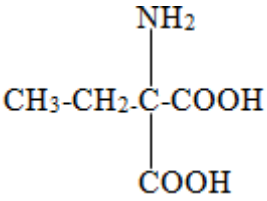



The repeated –N-C-C- unit forms the backbone of the polypeptide and is the characteristics for the structure of all kinds of protein. In the generalized polypeptide formula of protein stated above, R is representative of individual and distinctive portion of the amino acid molecule. The R group of the side chain may be widely different in chemical character, from R=H to strongly polar group of acidic or basic functions. Thus, when a polypeptide is composed of a single amino acid like glycine $NH_2CH_2COOH$, the R group consists of a H atom only. But when a polypeptide chain is composed of a complex amino acid, R may be containing many radicals of either aliphatic or aromatic compounds having free amino ($NH_2$) or carboxylic (COOH) groups. Thus, when a polypeptide is composed of the amino acid

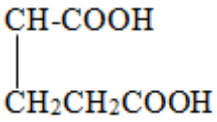
lysine, $NH_2.CH_2.CH_2.CH_2.CH\text{-}CH(NH_2)\text{-}COOH$, R will consist of the long side chain $NH_2CH_2CH_2CH_2CH_2$ and there will be a free $NH_2$ group in this which is positively charged:-



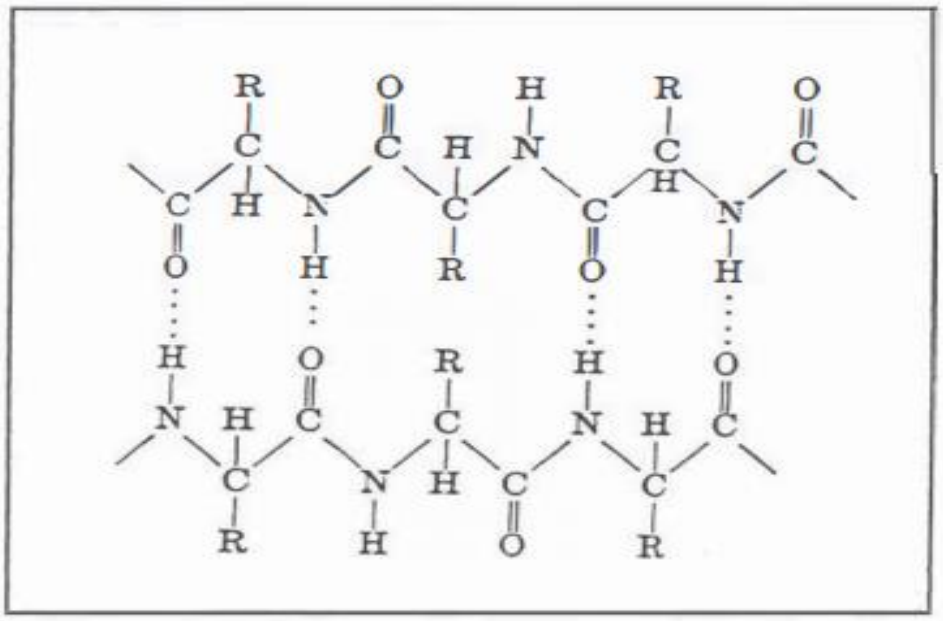
Similarly, when a polypeptide chain is composed of the amino acid glutamic acid,



R: will consist of $CH_2CH_2COOH$ containing a free carboxyl group which is negatively charged.

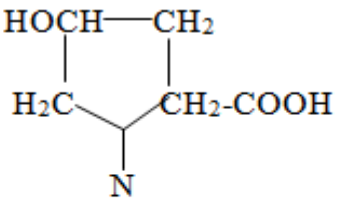


The polypeptide chain of protein molecules are oriented parallel to the fibre axis and are also parallel to one another. They are held tightly together by means of coordinate bonds or hydrogen bridges between –CO- and –NH- groups of the peptide chains. This arrangement is represented by the following graphic formula:-

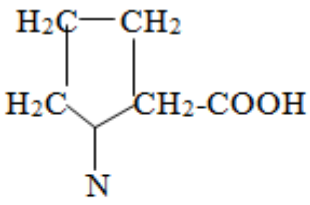


Arrange in this way the peptide chain forms a two dimensional plane. Such individual planes are again held tight by crosslinking formed between the projected side chains of the different planes.

The amino acid composition, first reported in full in 1948, is now well established. It has been shown that, regardless of species and the tissue from which they come, all mammalian collagen fibres have a similar and characteristic composition in which glycine, the simplest amino acid constitutes one third of the total residues and the amino acids proline and hydroxyproline a further 25% [15; 16].




Hydroxyproline




proline

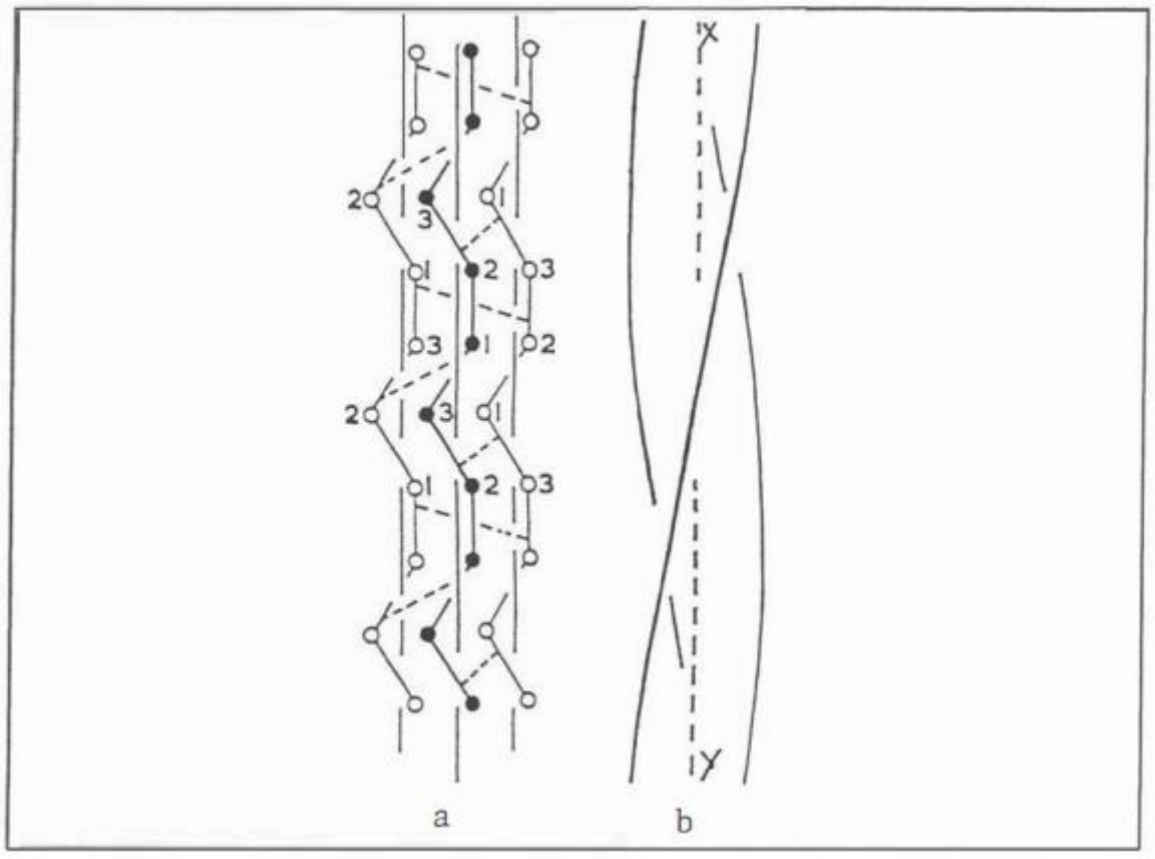
With these, the ring structure is built into the chain when the peptide bond is formed. This leads to certain restrictions on the findings of the chain and is responsible for the specific configuration of collagen molecule. The high hydroxyproline (14%) is characteristic of collagen which contains no cystine (the amino acid characteristic of wool and hair), no tryptophan and only small amount of other essential aromatic amino acids, tyrosine and phenylalanine. Considerable information is now available on the sequence of the amino acids in the three polypeptide chains which make up the collagen macro molecule.

Studies of the partial degradation of collagen with acids and enzymes has demonstrated the wide spread distribution of glycine, which has been found to be linked to all the amino acids including itself, and the frequent occurrence of a peptide, Gly-Pro-X, where X is often hydroxyproline. The general picture is of a chain built up of alternating sequence 3s of peptides containing predominantly neutral amino acids with Polar Regions containing acidic and basic residues.

Collagen gives a characteristics X-ray diffraction pattern and shows a specific banded appearance in the electron microscope. Both of these have been instrument in arriving at the present accepted structure of this protein. It is now accepted that the collagen macro molecule, referred to as tropocollagen, is a stiff rod-like structure about 2800Å long and 14-

15 Å in diameter with a molecular weight of 280,000 to 300,000 Daltons. It is composed of three polypeptide chains of approximately equal length with their terminal amino acid residues [17; 18; 19; 20] ,two of these chains designated $\alpha_{1,}$ are the same in composition and the third $\alpha_2$ is slightly different. The restriction imposed by their high proline and hydroxyproline content causes each of these individual chains to coil into a helix characteristics of the polymer. Poly-1-proline. Each chain has a left handed helical twist taking approximately 3.3 amino acid residues to make one complete ($360^o$) rotation about the polypeptide helical long axis. The three chains are then twisted about a central axis to give a slight right handed super helix as shown in figure 2.1.

Figure 2.1: coiled structure of the collagen molecule




a). Three polypeptide chains each twisted into a helix. The two outer chains are in the plane of the paper and the central one is place in front of these. The circles represent amino acid residues and the lines peptide bonds. The number 1, 2 and 3 indicates different types of side chain positions; for steric reasons position 1, which is located near the main axis X-Y, must be occupied by a glycine residue in which the side chain is hydrogen. Dotted lines represent hydrogen bonds. b). shows the deformation when the three chains are twisted about the common axis XY to give the super helix. The lines represent the axes of the three individual chains.

The small amino acid, glycine, which occurs at every third residue and which for steric reasons must occupy position1, allows the three chains to come close enough together for hydrogen bonding to occur between the –C= group of one chain and –NH- group of the other as in the polymer polyglycine. In this way a very stable and compact structure is obtained. The main feature of the collagen triple helix was defined mainly from the wide angle X-ray by Ramachandran and by Rich and Crick[21]. It takes 27-29 amino acid residues depending upon the model used for a single polypeptide chain to make one complete rotation about the triple helical axis. At the amino terminal end of each of the three chains of the molecule there is a length of uncharacteristic amino acid composition containing some fifteen residues.

These telopeptides contain no proline or hydroxyproline and this area is therefore, no in the specific helical configuration of the main bulk of the molecule. Both intra and intermolecular crosslinks have been shown to be located in this area. There have been suggestions that similar non helical peptides also protrude from the body of the molecule but so far no direct evidence for this has been obtained. Soluble collagen obtained from extraction of skins of young animals with neutral salts or dilute acetic acid, when heated at 37-40$^{o}$C shows a sharp change of properties due to collapse of helical structure.

Tropocollagen aggregate in a highly specific way to give native fibrils, each molecule overlaps its neighbour by one quarter of its length.

### 2.2 Crosslinking of collagen

Collagen cross-linking contributes to the tensile strength of tissues such as tendon and is important in stabilising the collagen fibrils. It can be classified into two types, i.e. natural and artificial crosslinkings.

#### 2.2.1 Natural crosslinking

The action of the enzyme lysyl oxidase on collagen causes formation of covalent cross-links[22, 23]. The cross-links are based on aldehyde formation and condensation involving specific peptidyl lysine and hydroxylysine residues. The process is catalysed by lysyl oxidase, which oxidatively deaminates the amino group of certain lysyl and hydroxylysyl residues in the telopeptide regions of collagen molecules to form reactive allysyl and hydroxylysyl aldehydes, respectively. These aldehyde groups then react with the amino group of lysyl and hydroxylysyl residues and other aldehydes to form a variety of di-, tri-, and tetra functional cross-links (Figure 2.2)[24].

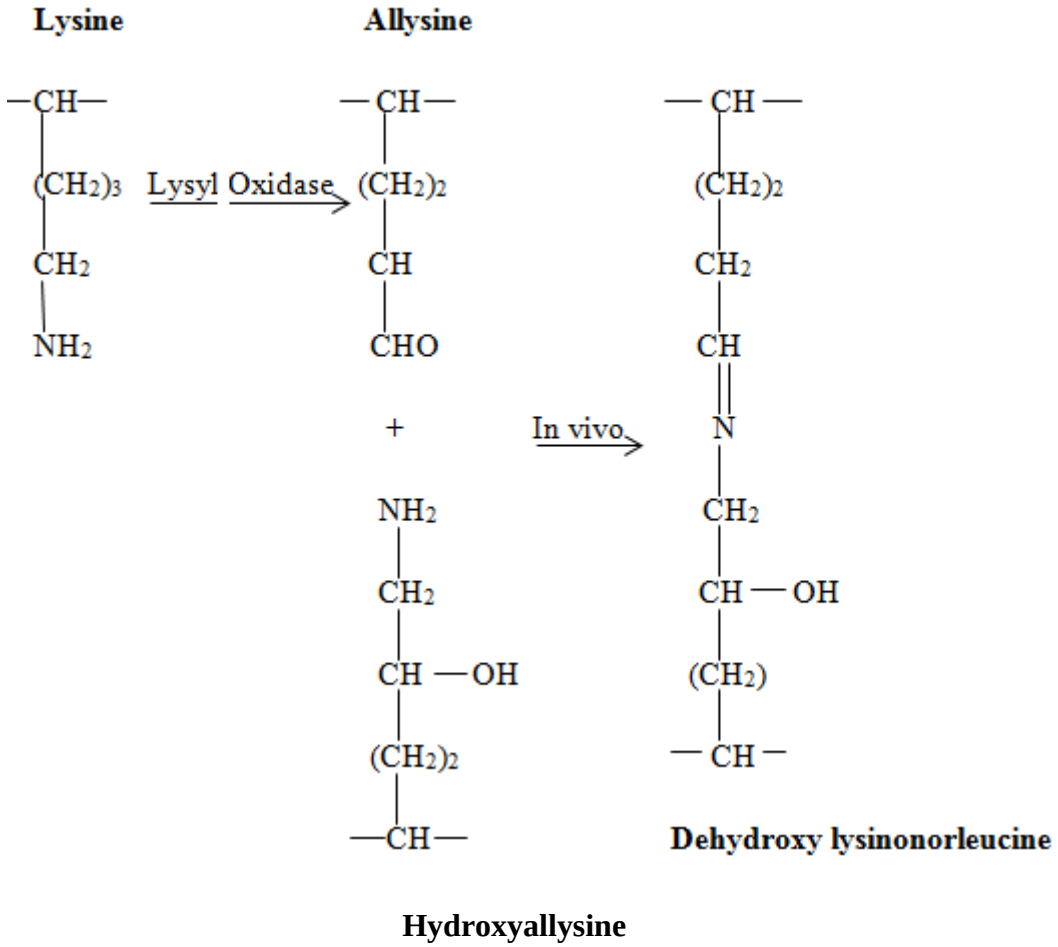



Figure 2.2 Oxidative deamination of lysyl and hydroxylysyl residues by lysyl oxidase[24]

The monomeric molecules in the supramolecular aggregates of collagen molecules are stabilised by two different pathways. Cross-linking initially takes place through an enzymatic mechanism involving oxidation of specific lysine hydroxylysine residues, providing divalent cross-linking which subsequently matures to multivalent cross-links. It is followed by a non-enzymatic pathway [25, 26].

Cross-links between the molecules making up the fibrils and between the fibrils making up the fibres determine the strength of the collagen fibres. These cross- links are covalent bonds formed between the individual molecules within the fibre at highly specific points, controlled by the precise alignment of the fibre. They are very important for the optimal functioning of collagen fibres as a framework structure in the body[25, 27].

### 2.2.2 Artificial cross-linking

Reconstituted forms of collagen, such as films, fibres or sponges, can lack strength and may disintegrate on handling or collapse under the pressure from surrounding tissue in vivo, due

to dissociation of cross-links in the isolation processes. As a consequence, mechanical resilience and collagenase resistance of the collagen is often necessarily conferred by introducing artificial cross-linking into the molecular structure of collagen[28]. This basic principle is used in leather tanning.

Trivalent chromium salts are used as cross-linking agents to form covalent bonds with collagen[29]. Aluminium and other polyvalent cations can also be used as cross-linkers[30]. Covalent cross-links in collagen can be created in a number of ways. Aldehydes are the most commonly utilised reagents, with formaldehyde and glutaraldehyde (GTA) being the most well-known examples. As an alternative to aldehyde treatment, strong, and resistant collagen can be obtained using hexamethylenediisocyanate (HDC) as a cross-linker[31].

Recently, a matrix theory of collagen-tannin cross-linking mechanism was proposed by Covington and Song[32]. The theory described that a matrix is composed of the primary tanning agent, covalently bound to collagen, interacting with the supramolecular water and any other secondary tanning or auxiliary. The matrix may be regarded as cross-linking the fibre structure, it is not necessary to consider cross-linking by individual components of the matrix as a fundamental requirement of the stabilising mechanism; cross-linking may occur depending on the tanning reagent and the availability of reaction sites. The theory indicates that hydrothermal stability derives from a matrix interaction at the triple helix.

### 2.3 Leather manufacturing

Leather is made by subjecting the protein of animal skin or hide to a process known as tanning, whereby the skin or hide becomes more durable and capable of being used for a wide range of purposes. The leather industry may be regarded as a bridge between production of the hide as a byproduct of the food industry and its manufacture into shoes and wearing apparel, for which it provides basic raw materials[3]. The practice of leather manufacture varies considerably from tannery to tannery and from country to country, so that there is no single universally applied process. The main sequences of operations and their aims are the same, but there are wide differences in detailed techniques[33].

The production of leather can be regarded as taking place in three steps. The first step is to remove unwanted components, hair, fats, etc., leaving the fibrous network of the hide protein. The second step is react this network with tanning materials to produce a stabilised fibre structure. The third step is to build in the characteristics of fullness, colour, softness, and lubrication, and to finish the surface, to make a practically useful product[3].

Cattle, sheep, goat, calf, and pig are the primary sources of hides and skins used for leather. After hides and skins are removed from the animal (flaying), they undergo curing or preservation, in which they receive either long term or short term protection against bacteria. The most common method of preservation of hides and skins is curing with sodium chloride[30, 33].

The typical tanning process starts in the beamhouse. Classical operations of the beamhouse are the following: (1) soaking and mechanical removal of scud from hides; (2) fleshing, splitting, smoothing of hides; (3) removing the hair, splitting hide fibres and degradation of the epidermis (liming); (4) removal of lime (deliming); (5) enzymatic loosening of hide fibres (bating); and (6) pickling[34]. The purpose of these operations is to increase the amount of water in the hide to the amount close to that of the living hide, remove non-collagenous components and loosen the structure. This loosening makes it easier for the tanning agents, fats, dyestuffs, and other substances to penetrate into the hide. In the beamhouse, the non-collagenous proteins are removed from the hide, so are the epidermis, hair, globular proteins, and melanins, while the collagen fibre skeleton remains practically untouched[34].

### 2.3.1 Soaking

Leather manufacture commences with the soaking of cured stock in water to rehydrate and to cleanse it. The soaking of cured hides has as its aim the removal of salt and part of the soluble protein content and imparting an adequate plumpness to the hide. Another purpose of soaking is to remove remaining blood, urine, and dung[33, 34].

### 2.3.2 Liming

Opening up of the structure may be considered as an extension of soaking; its purpose is to separate two structural proteins: keratin and collagen. Methods of hair removing can be divided into two groups: (1) methods based on destruction or modification of the epidermis tissue surrounding the hair, so that this may be loosened and mechanically removed, and (2) methods in which hair itself is attacked and its structure destroyed. This more drastic method is in practice connected with use of alkalis (calcium or sodium hydroxide) and of sulphide[34]. The hides and skins are chemically unhaired and the fibre structure is opened up by alkaline swelling in saturated lime at pH 12.5[30].

### 2.3.3 Deliming and bating

The removal of combined alkali is achieved by treating the goods with acids or acidic salts, typically ammonium salts[33]. Bating is a treatment of the hide with proteolytic enzymes to remove additional non-collagenous proteins from the surface of the hide[30].

### 2.3.4 Degreasing

Degreasing is the last step in the beamhouse operations. In the majority of technological processes applied there is no need for degreasing, as the fat contained in raw hide becomes saponified and is washed out by the use of surfactants[34].

### 2.3.5 Pickling

Pickling prepares raw hide for tanning. The purposes of this operation are to stop enzymatic bating and to adjust the pH of the hide for subsequent processes, e. g. storage or chrome or vegetable tannage. To pickle the pelts means to acidify it in such a way as to prevent it from simultaneous swelling under the action of acid: this is usually done by salt (sodium chloride) addition[34].

### 2.3.6 Tanning

Tanning is the process of introducing a stabilising or tanning agent into the hide or skin. Tanning is usually done with basified trivalent chromium salts. The reaction of chromium salts with carboxylic groups of the hide protein, collagen, and leads to high hydrothermal stability and stability against microbial action. After chrome tanning, hides and skins are called wet blue or blue crust[30, 35].

### 2.3.7 Retanning

Most leather requires retanning, using a variety of tanning materials. In general, retannage gives specific properties to the leather such as tightness and fullness. Various tanning agents are used for retanning, including chromium compounds. Retanning with chrome tanning agents makes the leather soft. Vegetable and synthetic tannins also fill leather well in its weaker parts (bellies) [34].

### 2.3.8 Dyeing

Leather dyeing is a transition process between tanning and finishing. It is colouration of leather usually with synthetic dyes typically either acid or direct dyestuffs. The former is used when a penetrating dyeing is required and the latter when surface dyeing is required[33]. The

result of dyeing depends not only on the tanning agent and method used, but also on reaction with fat, surfactant and water[3].

### 2.3.9 Fatliquoring

The process of fatliquoring entails the treatment of leather with a warm dilute emulsion of oil in water. The principle of fatliquoring is the application of an oil- in-water emulsion, which is subsequently induced to break, thus depositing a film of fatty matter over the fibre structure. The functions of the process are lubrication, adjustment of physical properties, waterproofing, and filling[33].

### 2.3.10 Drying

Before drying, leathers are stacked and sammyed (squeezed). Leather is dried usually at relatively low temperature in order to prevent structural and chemical changes. The initial temperature is lower (usually 40-50°C for chrome leather, 35-45°C for vegetable tanned leather), and then, as the water content decreases, temperature is increased, however, never higher than 8-10°C below the shrinkage temperature. It is done so to avoid local overheating and deterioration of components introduced in tanning and finishing[34].

### 2.3.11 Finishing

The final operation in leather manufacturing is finishing. The functions of leather finishing are to produce leather with constant and uniform physical properties and standardised colour and appearance, to protect the leather against adverse chemical and physical influences, and to satisfy fashion and colour fastness requirements[33].

## 2.4 Chemistry of tanning

Tanning is the most important step in leather production. It is typically carried out in an aqueous environment in rotating drums. During tanning, collagen will fix the tanning agent to its reactive sites, as a result stopping the putrefaction phenomenon[30, 36]. Tanning can be classified into three groups: mineral tanning, vegetable tanning, and other organic tanning (aldehyde, quinone, and synthetic tanning).

### 2.4.1 Mineral tanning

Four elements play a significant role in the modern leather tanning industry, i.e. chromium (III), aluminium(III), titanium(IV) and zirconium(IV)[35], of which chromium (III) is the most important. Nowadays, more than 90% of the world's leather is tanned with chromium, which is a consequence of the easy processing, the broad achievability and the excellent properties

of leather. Tanning using Cr(III) sulphate can achieve shrinkage temperatures above 120°C. However, it also has considerable potential for environmental pollution. The interactions of collagen with chrome have been extensively investigated since the end of the nineteenth century. The fundamental reaction is the formation of complex bonds with the ionised carboxyl groups of aspartic and glutamic acid residues on collagen fibres[35, 37] (Figure 2.3).

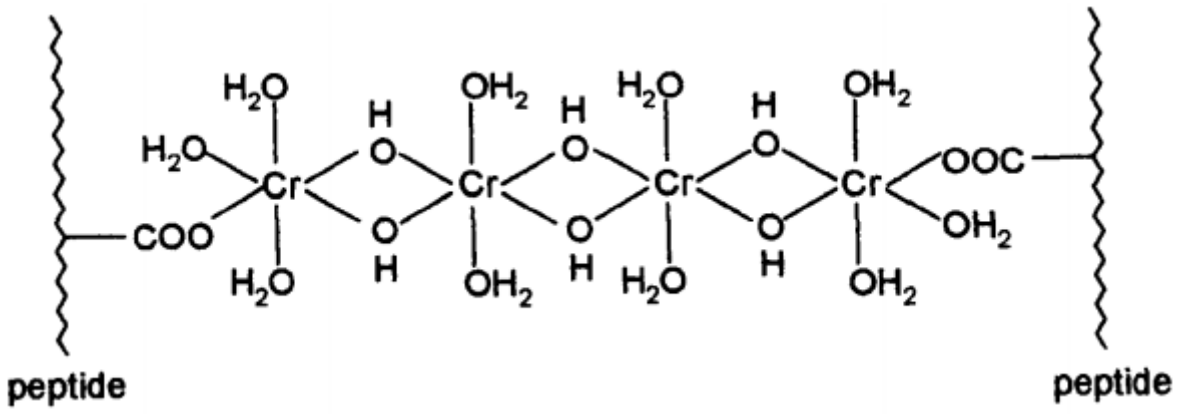



Figure 2.3. Model of chrome complexation with carboxyl groups of collagen

Other mineral tannages (Al(III), Ti(IV), and Zr(IV)) have similar reaction mechanisms to chromium, although reaction is dominated by electrovalent bonding, thus much lower shrinkage temperature is obtained than with chrome[35]. The maximum shrinkage temperatures of leather tanned with Al(III), Ti(IV), and Zr(IV) salts are 79,90, and 97°C respectively[30]. The development of titanium and zirconium tannage is relatively new[35]. Empirically, the chemistry of Ti(IV) is dominated by the titanyl ion $TiO^{2+}$ and the species in the tanning agent are chains of (Ti-O)n. Zirconium salts are characterised by eight-coordination and high affinity for oxygen, resulting in a tetrameric core structure; the basic unit of structure is four Zr(IV) ions at the corners of a square[30, 35]. The tanning powers of titanium and zirconium are similar and both are better than aluminium.

### 2.4.2 Vegetable tanning

Vegetable tannins or natural polyphenols are complex higher plant secondary metabolites. They are water soluble, have relative molecular masses in the range 500-3000 and besides giving the usual phenolic reactions, they are able to precipitate some alkaloids, gelatine, and other solution from protein, from solution. They may be extracted from plant material containing polyphenols[38]. They can be classified into three major groups: hydrolysable (pyrogallol), condensed (catechol), and complex tannins[7, 35, 38].

**Hydrolysable tannins** are sugar derivatives, based on glucose, but may be larger polysaccharides. Depending on the polyphenolic acids that are obtained as products of hydrolysis, hydrolysable tannins can further be divided into gallotannins (a) and ellagitannins (b) (Figure 2.4)[6]. Gallotannins yield gallic acid and glucose on hydrolysis. The ellagitannins produce ellagic acid in addition to gallic acid and glucose on hydrolysis. The hydrolysable tannins give good filling effect and typically raise the shrinkage temperature of collagen to 75-80°C[35]. Commercially used hydrolysable tannins are listed in Table 1.

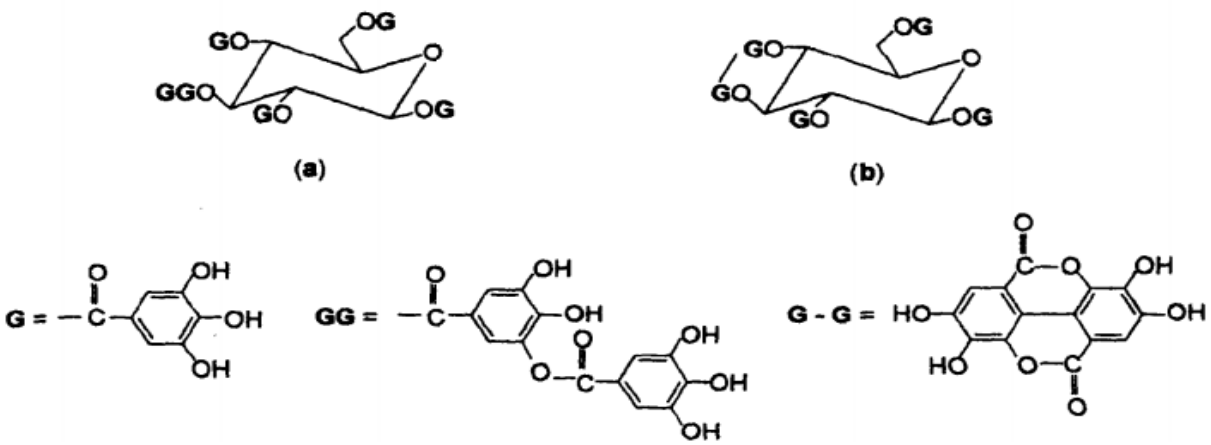



Figure 2.4. Indicative molecular structures of hydrolysable tannins: (a) gallotannin, and (b) ellagitannin

Table 1. commercially used hydrolysable tanning[6, 7]

| Tannin | Type of tannin | Plant | Part of the plant | Tannin Content (%) |
|---|---|---|---|---|
| Chinese tannins (tannic acid) | Gallotannin | Rhus semialata | Galls, leaves | 34-71 |
| Turkish tannin | Gallotannin | Quercus infectona (Aleppo galls) | Galls | 25-45 |
| Sumach | Gallotannin | Rhus coriana, R. typhina | Leaves | 26-27 |
| Tara | Gallotannin | Caesalpinia spinosa | Fruit pod | 45-59 |
| Myrobalan | Ellagitanni | Terminalia chebula | Fruit | 30-50 |
| Valonea | Ellagitanni | Quercus valonea | Acorn cups | 15-3 |
| Chestnut | Ellagitanni | Castanea sativa | Wood | 10-12 |

**Condensed tannins** are referred to as polyflavanols or proanthocyanidins; they are based on the flavonoid ring system (Figure 2.5)[6, 35]. The A ring usually contains one or two phenolic hydroxyl groups; the B ring, which typically has a catechol structure, has different reactivity[35]. The fundamental structure of the tannins is the phenolic flavan-3-ol, present in catechin (cyanidin), gallocatechin (delphini-din), fisetinidol, and robinetinidol. The flavan-3-ol units are linked through the C- 4 to C-8 positions and C-4 to C-6 positions. General structures of the condensed tannins are shown in Figure 2.6[8, 39, 40, 35]. Sources of condensed tannins are given in Table 2. They typically raise the shrinkage temperature of collagen to 80-85°C[35].

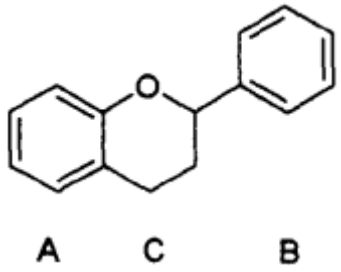
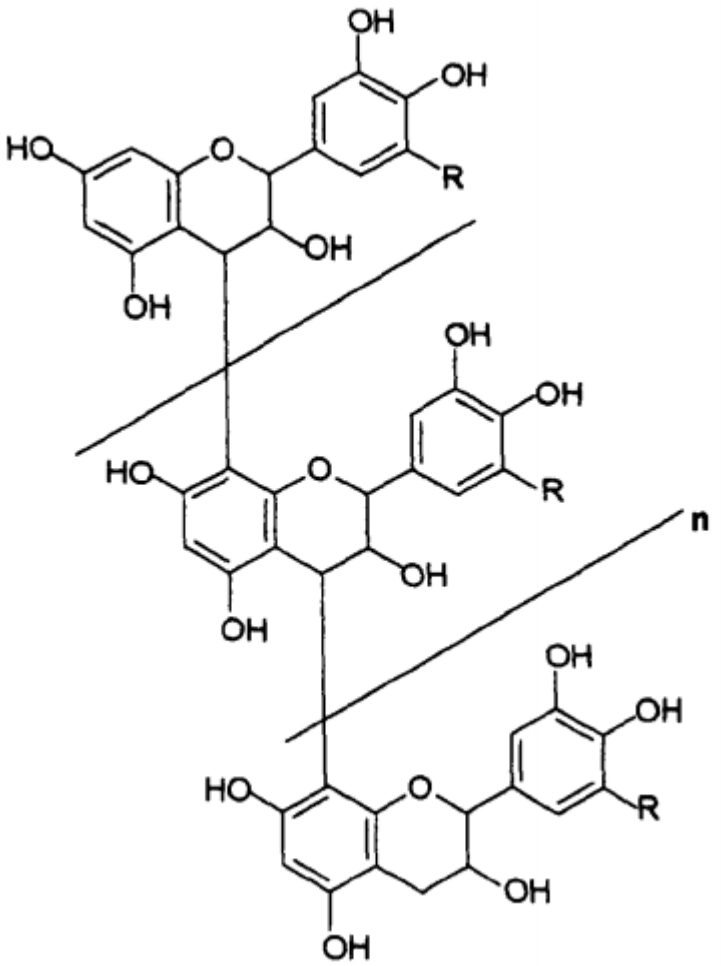



Figure 2.5 The flavonoid ring system of condensed tannins[8, 39, 40, 35]

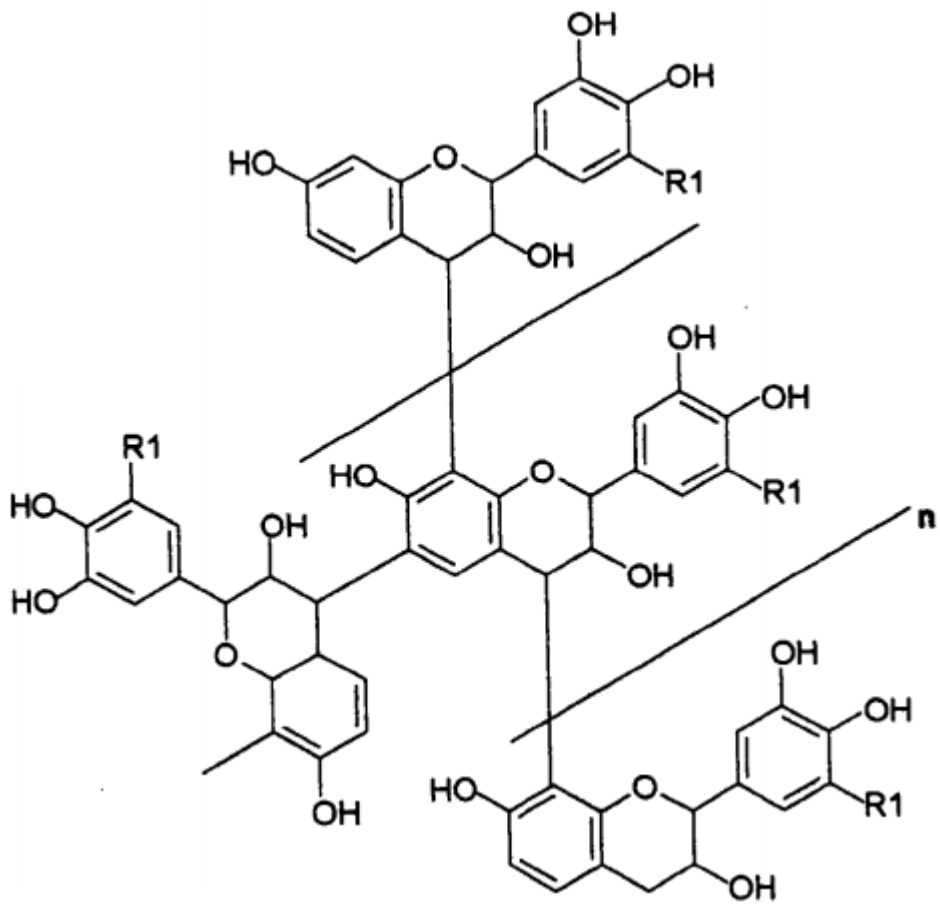



R=H, procyanidin

R= OH, prodelphinidin

Linear

Figure 2.6 General structures for condensed tannins[8, 39, 35]




R1 = H, pronseiniain Angular

RI = OH, prorobinetinidin

Figure 2.6 Continued

Complex tannins are built up from a gallotannin unit or an ellagitannin unit and a catechin unit. One example of this group is acutissimin A, having a flavogallonyl (nonahydroxytriphenoyl) unit bound glucosidically to C-1, and linked via three further hydrolysable ester bridges to the D-glucose derived polyol[7].

Vegetable tannins react with collagen primarily via hydrogen bonding, as demonstrated in the model in Figure 2.7[35]. Hydrophobic interactions have also an important role, particularly in hydrolysable tannins. Condensed tannins are more resistant to removal by hydrogen bond breakers because they have an additional mechanism for reaction, which is covalent reaction between the protein and aromatic carbon in tannin molecules via quinoid structures. Quinone itself can tan collagen effectively[35].

Table 2. Sources of condensed tannins[6, 7]

| Family (Tannin) | Plant | Part of the plant | Tannin content (%) |
|---|---|---|---|
| Myrtaceae | Eucalyptus astringens | Bark | 40-50 |
| Myrtan/ (Eucalyptus) | Eucalyptus wandoo | Bark, heartwood | 12-15 |
| Leguminosae | Acacia mollisima | Bark | 35-40 |
| (Wattle/mimosa | Acacia catechu | heartwood | 15 |
| | Robinia pseudacacia | Bark | 7 |
| Anacardiaceae | Schinopsis balansae | Heartwood | 20-25 |
| (Quebracho | Schinopsis lorentzii | Heartwood | 16-17 |
| Rhizophoracea | Rhizophora candelaria | Bark | 25-30 |
| (Mangrove) | Rhizophora mangle | Bark | 20-30 |
| Fagaceae (Oak) | Quercus robur | Bark | 12-16 |
| Pinaceae | Picea abies | Bark | 5-20 |
| | Pinus sylvestris | Bark | 16 |
| | Larix decidua | Bark | 5-20 |
| Rubiaceae | Uncaria gambler | Leaves, twigs | - |

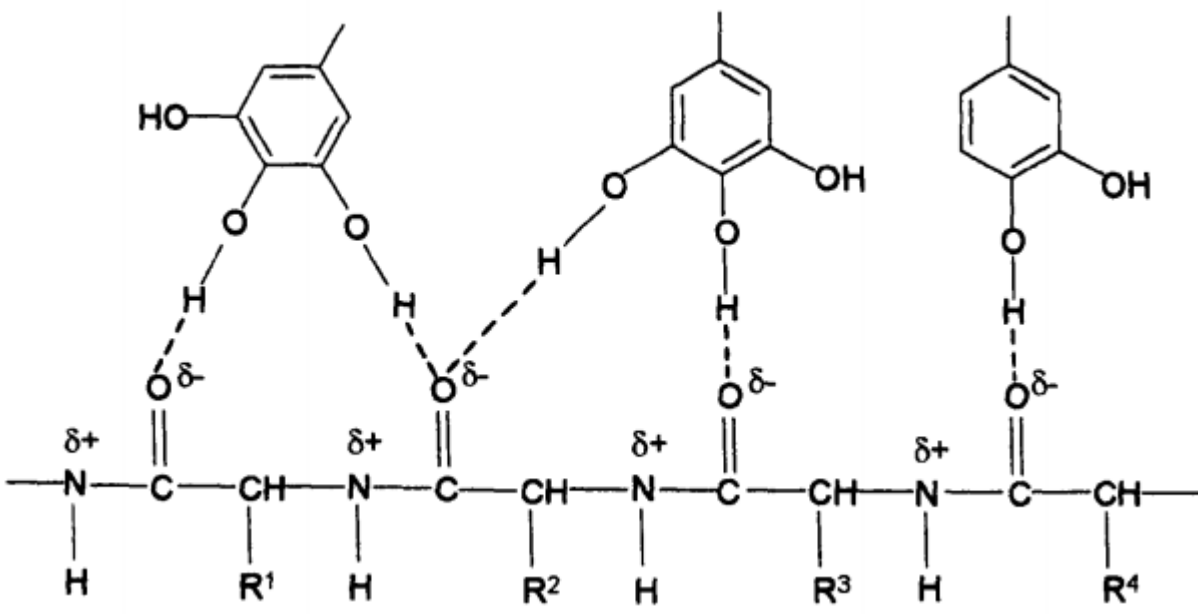



Figure 2.7 Model of hydrogen bonding collagen''' between plant polyphenols and collagen[34]

### 2.4.3 Aldehyde tanning

Several aldehydes have reactivity towards collagen and prevent putrefaction of the skins and hides. Among the aldehydes, formaldehyde (HCHO) has been known as a tanning agent. The fixation of formaldehyde by proteins is accompanied by changes in the physical properties: thermal stability and resistance to tryptic enzyme digestion are increased. The hydrothermal stability of formaldehyde tanned collagen is increased with increase in concentration, temperature, and time: shrinkage temperature (Ts) is increased with pH and fixed amount of formaldehyde up to pH 8.0, but at higher pH values there is no further increase in shrinkage temperature[41]. The shrinkage temperature of formaldehyde tanned leather is 80-85°C, although its use in industry is effectively banned due to its toxicity.

A rise in shrinkage temperature has been reported when collagen was treated by other simple aliphatic aldehydes, such as acetaldehyde, glyoxal, acrolein, and crotonaldehyde, Glyoxal, which is the simplest dialdehyde, is a good tanning agent[41].

Although the cross-linking reaction of collagen with aldehyde, especially formaldehyde, has been studied for a long time, the mechanism is still not completely clear[35, 42, 43]. Most researchers accept that aldehydic compounds react with the free amino groups of lysine and form cross-links

$$\text{Collagen-NH}_2 + \text{HCHO} \longrightarrow \text{Collagen-NH-CH}_2\text{OH}$$

The N-hydroxymethyl group is highly reactive and cross-linking may occur at a second amino group:

$$\text{Collagen-NH-CH}_2\text{OH} + \text{H}_2\text{N-Collagen} \longrightarrow \text{Collagen-NH-CH}_2\text{-NH-Collagen}$$

Note, formaldehyde will react as a polymerise species, depending on the conditions.

Glutaraldehyde (OCH-$(CH_2)_3$-CHO) is a dialdehyde that can be used as tanning agent. It forms semiacetal bonds with the hydroxyls of hydroxyproline, hydroxylysine, and serine. With phenols, it produces insoluble compounds, so it cannot be used with vegetable tannins. Glutaraldehyde gives leather with the characteristics of perspiration resistance, washing resistance, better fullness and density[34]. As with formaldehyde, glutaraldehyde is polymerised in solution (Figure 2.8); the terminal hydroxyl groups of the polymer are active and capable of reacting with amino groups. With regard to health and safety implications, formaldehyde and glutaraldehyde are unlikely to be suitable for the leather industry of the future. Besides

that, the hydrothermal stability of the aldehydes tanned leather is not high, i.e. 85°C maximum[35].

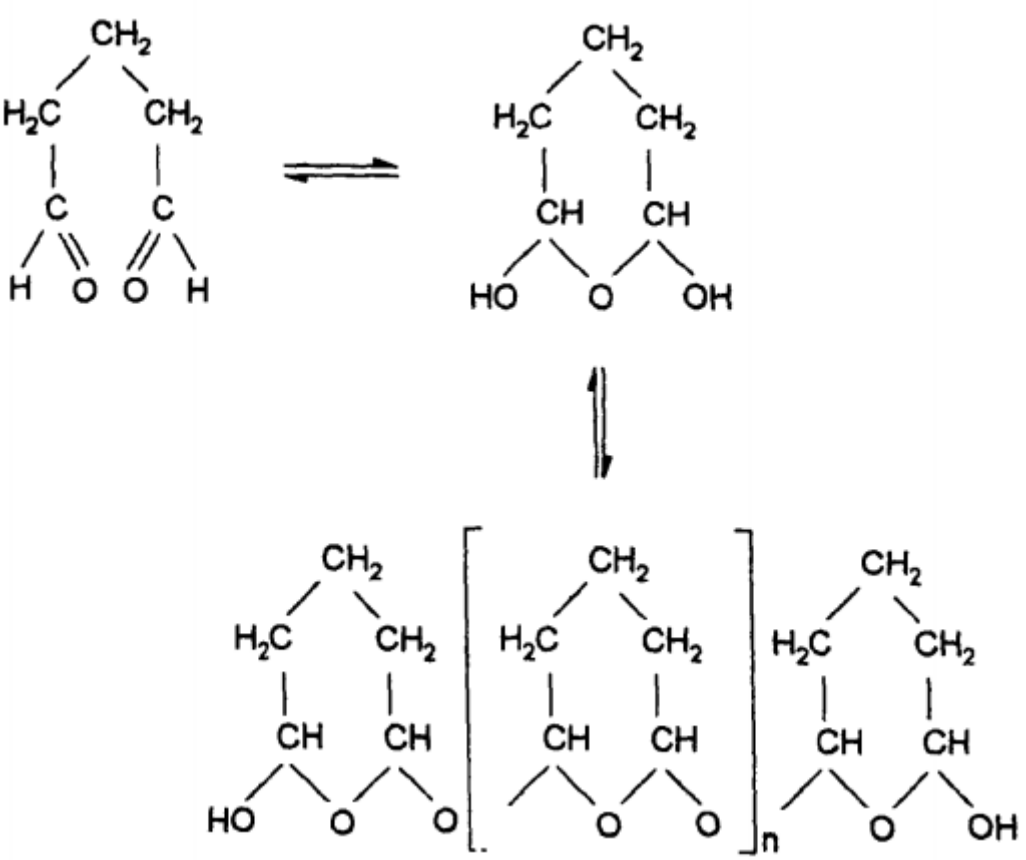
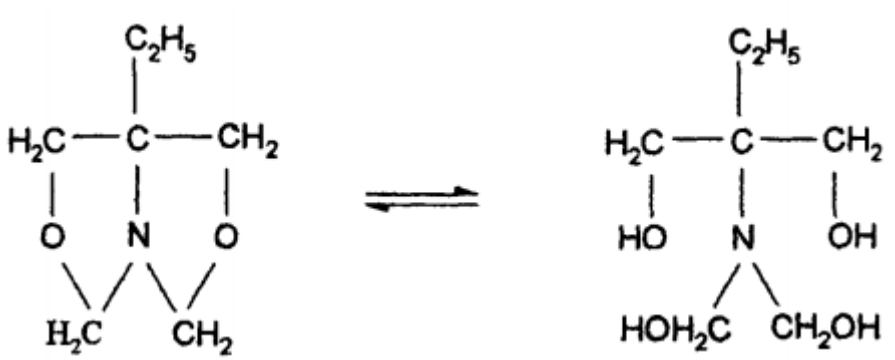


Figure 2.8 The reactivity of glutaraldehyde[35]

Oxazolidines, heterocyclic derivatives obtained by the reaction of aminohydroxy compounds with formaldehyde[44, 45] are an alternative to aldehyde tannage. Under hydrolytic conditions, the rings open to form an N-hydroxymethyl compound, which can react with one or more amino groups to produce effective cross-linking (Figure 2.9)[44]. However, the reaction mechanism of oxazolidine with collagen and its toxicity needs further investigation.

Oxazolidines have been shown to possess high reactivity and good tanning ability. Leather tanned by oxazolidine (Figure 2.9) has similar shrinkage temperature to glutaraldehyde tanned leather[44] but is less full and less hydrophilic, because the molecular weight of monomeric oxazolidine is smaller than that of polymerised glutaraldehyde.



5-(ethyl or hydrozymethyt)-1-azapropane 1, 3-dihydroxy-2-(ethyl or hydroxymethyo-

3, 7-diozabicyclo(3,3,0)-octan 2 N)V-bis (hydroiymethyl) propane

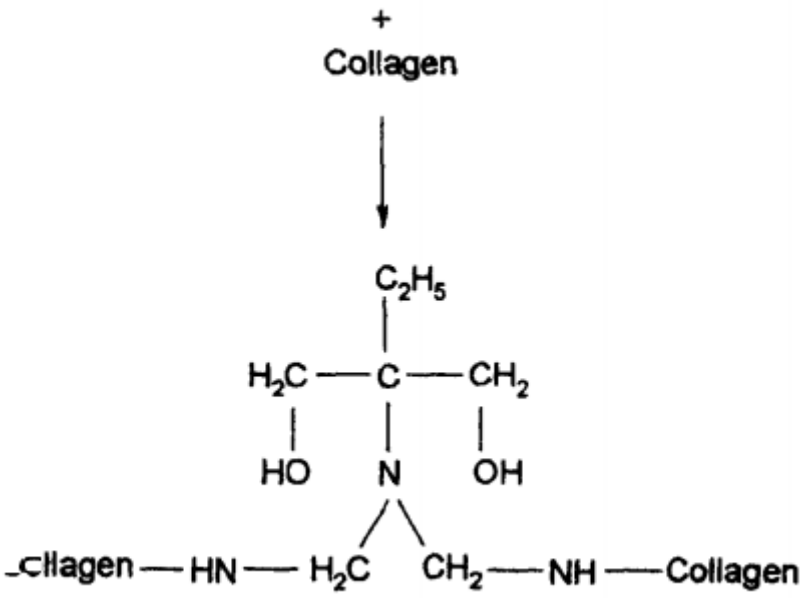



Figure 2.9 Ring opening of oxazotidine and cross-linking of collagen with oxazolidine[45]

### 2.4.4 Quinone tanning

Quinone tanning is usually separately discussed as a specific tanning process. The tanning agent involved is a compound of small molecular size, containing a functional group of one kind only. In the time of chromium shortage (e. g. in France during World War (II), quinone was used in the pretanning process[34].

Quinones react with the collagen amino groups to form aminohydroquinone or 2, 4-aminoquinone[46] as shown in Figure 2.10[30,47]. As a result of nucleophilic attack on quinone, ring aromatisation occurs: the redox potential of quinone decreases by about 250 mV, so the

compound obtained is easily oxidised by another quinone molecule; hence two hydroquinone molecules may react, so a cross-linking quinone is formed. Products of this type can be separated from the reaction mixture. The reaction kinetics are pH-dependent; in acidic or alkaline (pH 10) medium, the Ts. increases rapidly, and then it maintains the level reached or drops slightly. In neutral solution, the Ts. initially rises quickly, but the reaction remains incomplete for a long time.

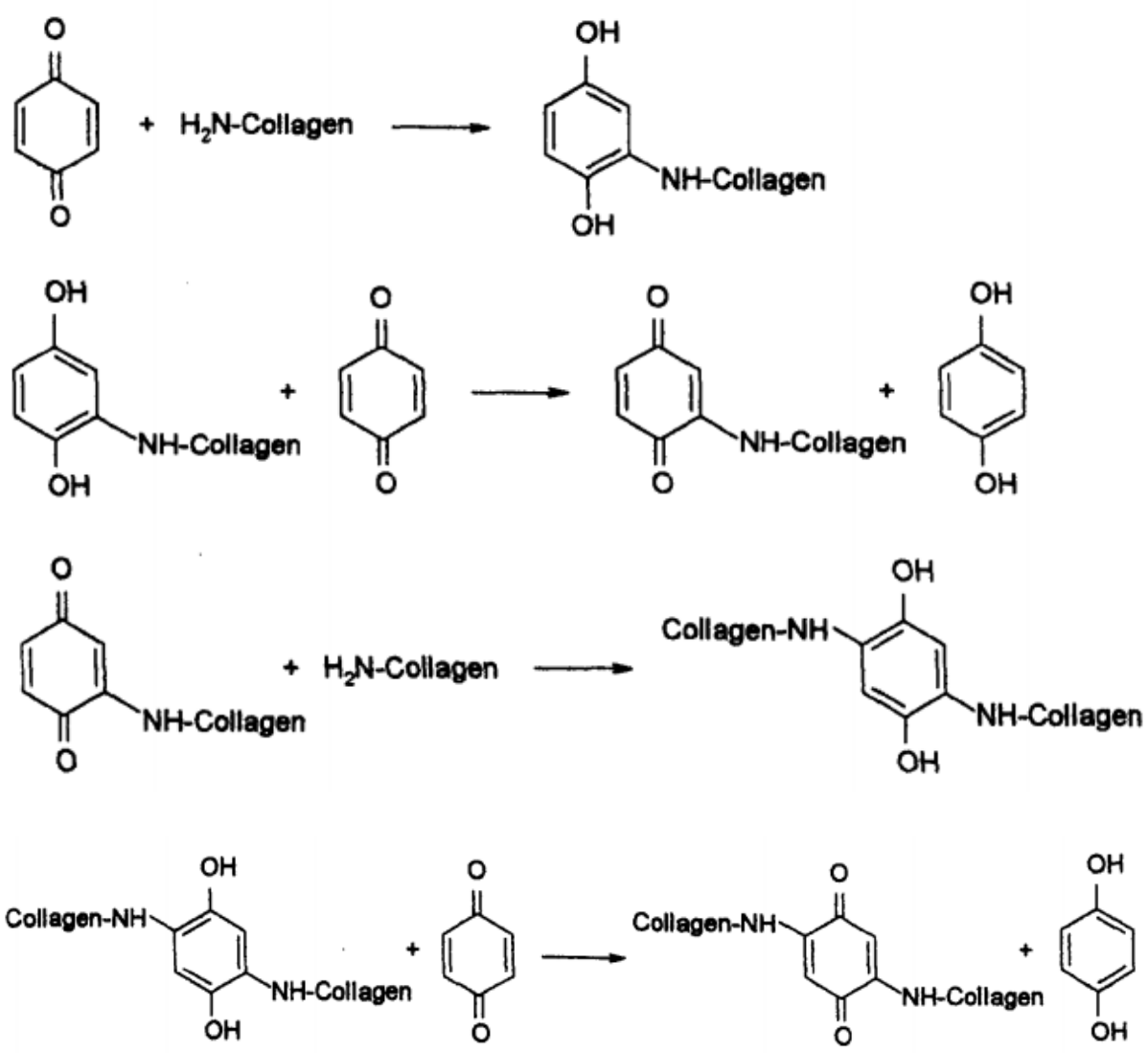



Figure 2.10 Reaction of quinone with collagen[30, 47]

Quinone tanning is conducted in buffer solution, because with pH increase, quinone solutions become dark and so does the leather. The properties of the anion of the buffering compound affect the value of pH at which quinone-collagen binding occurs. For borate buffer, the optimal binding pH is about 5, for phosphate it is pH 7-8. The tanning process takes 24-48 hours. The shrinkage temperature (Ts) of quinone tanned leathers may be as high as 90°C.

The amount of quinone bound is high, 20% or more, pardcularly at optimal pH. The proteolytic resistance of quinone-tanned leather is very high[46].

### 2.4.5 Synthetic tanning materials

Synthetic tanning materials (syntans) are organic compounds capable of converting skins or hides into imputrescible leather. Syntans are produced with the aim of aiding or substituting vegetable tanning, with the incentive of decreasing cost and providing unlimited supply. Syntans can be classified into three types, according to their primary properties, i.e. auxiliary syntans, replacement syntans, and combination or retanning syntans [2,3,35].

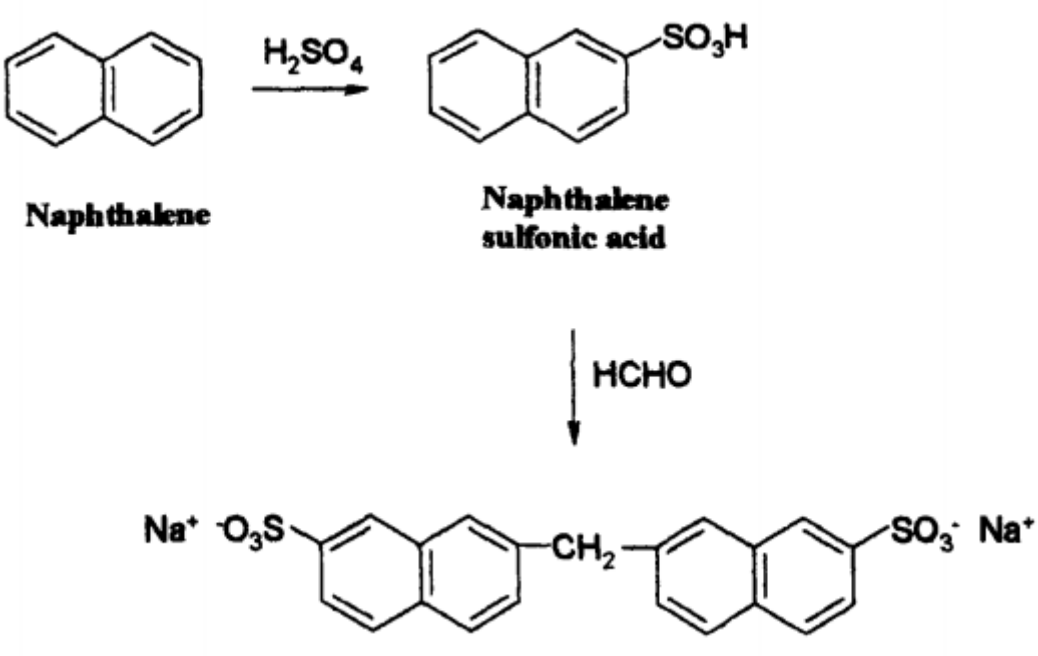



Figure 2.11 The Nerodol syntheses of syntans[2, 3, 45]

Auxiliary syntans are frequently based on naphthalene and are synthesised by the ‘Nerodol' method, i.e. the base is sulfonated to high degree and then may be polymerised by formaldehyde (Figure 2.11)[3,45]. The presence of the sulfonate groups means that these compounds can interact with the amino sidechains of collagen:

$$\text{Collagen-}NH_3^+ \longrightarrow O_3S\text{-Syntan}$$

The auxiliary syntans have low tanning power; they are poor tanning agents, if used alone. They are mainly used to bleach the surface, level dyes, disperse tannins, and fatliquors[35].

Replacement syntans or exchange syntans are used to replace vegetable tannins, so they can be used as solo tanning agents. They vary in their effects on leather, but they can produce

properties similar to vegetable tannins, including raising the shrinkage temperature to 75-80°C[35].

Combination syntans are usually based on simple phenolic compounds: they are synthesised by the `Novolac' method, i.e. the base material is polymerised with formaldehyde and then the product is partially sulfonated (Figure 2.12)[2, 3, 35]. They are relatively small polymers, with consequently weak tanning power[35]. These syntans are used in mixture with vegetable tanning material to give a better degree of tannage, yield, and fullness. This type can tan on its own, but not to the same degree as replacement syntans, so they are usually used as retanning agents.

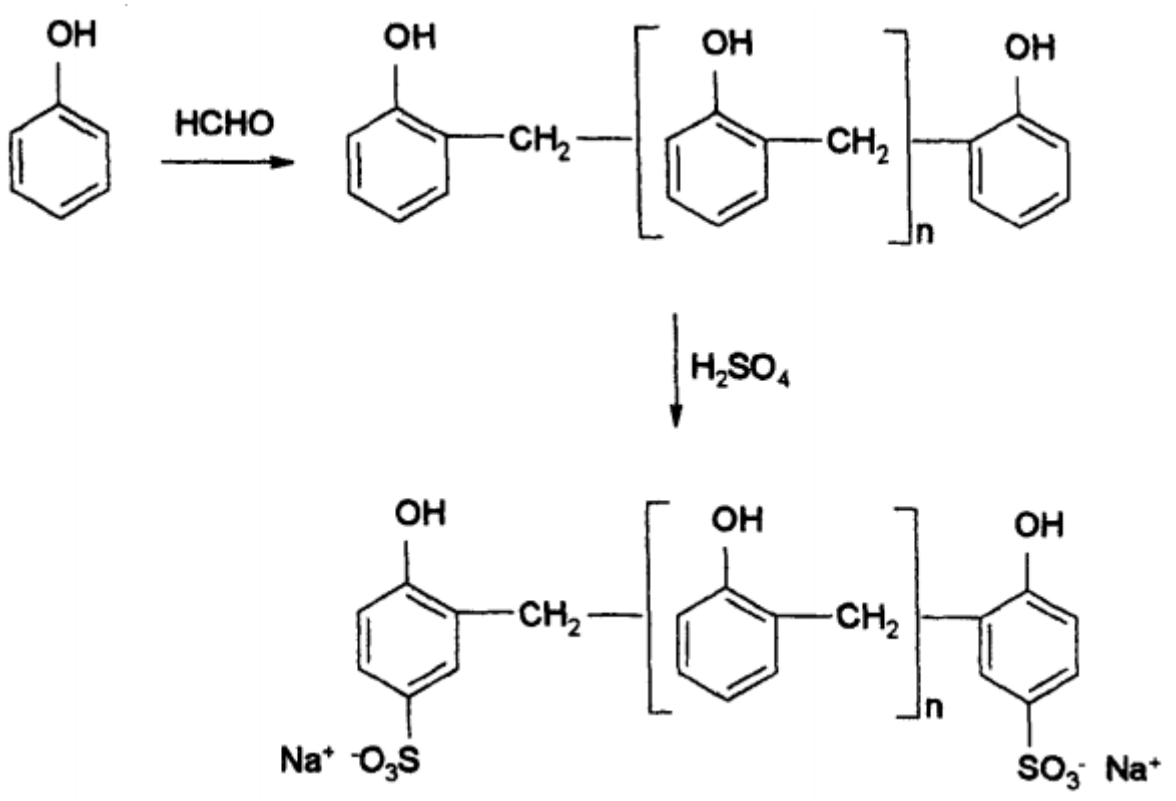



Figure 2.12 The Novolac syntheses of syntans[2, 3, 35]

The use of lignosulfonic acid in auxiliary syntans was reported by Kraft and Rodziewicz[48]. Lignosulfonic acid is the main solid component of sulfite liquor, which is produced in great amount by the pulp and paper industries. The structures of the main components of the sulfite liquor are similar to those of condensed vegetable tannins, but they do not have good tanning properties.

## 2.5 Combination tanning

Today 90% of all leathers are manufactured with chrome tanning agents. So far chrome salt is used widely in leather-making because of its excellent features; no any other single tanning agent can displace it completely. However, tanners are finding it increasingly difficult to comply with emerging regulations with respect to the chrome content of effluent as well as the disposal of chrome containing solid wastes such as sludge, shavings, leather trimmings and buffing dust. In some countries there are restrictions on the use of chrome-tanned leathers for certain purposes. On the other hand, its toxicity on organism and environment is the disputed talking for people. Consequently, many researchers in this field have explored alternatives to the traditional chrome tanning system. The ideal tanning agent to rival chrome should incorporate the following features [52, 53]: high hydrothermal stability, lower metal salts, white or pale coloured, lightfast and low environment impact.

The alternative-tanning agents could be organic or inorganic based. Vegetable tanning, an organic tanning, does not produce leathers with high hydrothermal stability. Further vegetable tanning systems induce some base colour to the leather. Recently, it has been shown that the use of acrylics in vegetable tanning improved the hydrothermal stability and other properties of leather[54].

In vegetable tanned leathers, tannin molecules form multiple hydrogen bonds with collagen and create a polyphenolic tanning matrix. The shrinkage temperature (Ts) of vegetable tanned leather is in the range of 70-85$^{o}$C[63]. By retanning with metals such as aluminium the Ts of vegetable tanned leather can be elevated considerably in a process that is commonly known as semi-alum tanning. Similarly, retanning of vegetable tanned leather with metal salts has been referred to as semi-metal tanning[64].

In combination tanning using metals and vegetable tanning agents, the order of tanning is important with respect to hydrothermal stability of the leather. Retanning of metal- tanned leather with vegetable tannin confers lower shrinkage temperature, while retanning of vegetable tanned leather with metal salt results in a synergistically increased shrinkage temperature[65]. In regards to the mechanism of semi-metal tanning, Slabbert (1981) suggested that metal ions form complexes with the already bound tannin molecules and form covalent links with the carboxyl groups of collagen. However, another study later showed that semi-aluminium tanned samples of normal and methylated hide powders have similar Ts, so blocking of carboxyl groups by

methylation did not affect the final shrinkage temperature[65]. Furthermore it was demonstrated that even metals that are known to have weak interaction with carboxyl groups of collagen can significantly increase the shrinkage temperature of vegetable tanned leathers[66]. The results indicated that the collagen-metal interactions are not critical with regards to the creation of the high hydrothermal stability.

The accepted model of the principal interaction in semi-metal tanning (illustrated in Figure 2.13) is based on complexation of metal ion by the metal-polyphenol. The chelated complexation of the metal centre creates crosslinks in the polyphenolic tanning matrix resulting in the formation of an extended supramolecular tanning matrix around the collagen. Subsequently, the shrinkage temperature is increased considerably[67].

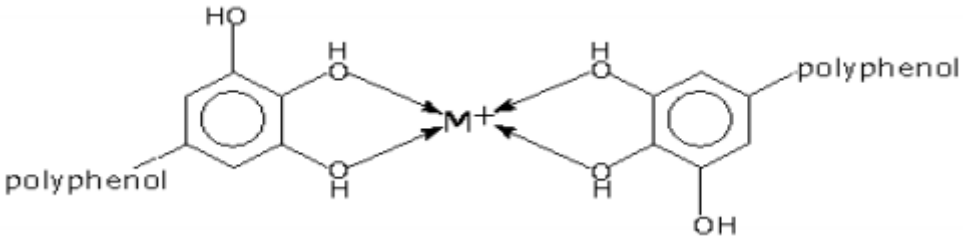



Figure.2.13 Schematic model of the semi-metal tanning interaction[63]

Sykes and Hancock et al. (1980) showed that phenolic compounds having one or more pyrogallol (3,4,5-trihydroxybenzene) or galloyl groups (3,4,5 trihydroxy benzoate) in their structure are more reactive towards metal salts compared to catechol (1,2-dihydroxybenzene) derivatives. The presence of the third hydroxyl group in the pyrogallol/galloyl groups increases deprotonation of the adjacent ortho-dihydroxyl group because by its inductive effect.

The approach of chrome saver technologies has a combined advantage of totally remove chrome pollution together with the advantages of unique properties imparted to leather by usage of vegetable and the alternative tanning agent partly substituted for chromium. The tanning agent chosen for substitution of chromium should not only satisfy environmental requirements but also should not induce any color to the leather. Accepted from the ecological viewpoint and being non-expensive, zinc can be used in combination with quebracho for tannage, with the aim of diminishing chrome pollution. Zinc is essential to the proper functioning of plants and animals. Zinc as sulphate and oxide is used as a feed supplement [55]. In the past, zinc as a tanning agent has attracted very little attention. Zinc (II) being a $3d^{10}$ system can form tetrahedral complexes[56]. Reports exist on the usage of zinc salts

for preservation of raw hides/skins[57]. Vegetable-zinc combination tannage has been shown to provide higher shrinkage temperature[58]. It was Procter[59] who first noticed the tanning property of zinc salts when he used them as deliming agents, shown by a characteristic increase in shrinkage temperature, and later patents on zinc tanning have been registered[60, 61]. Tanning agents based on aluminum-zinc combination have been shown to increase the shrinkage temperature of leather above $90^{o}$ C[62]. Zinc tannage produces white leathers. Hence, leathers obtained from the quebracho-zinc combination tannage will have the lighter shades ideal for the production of pastel colors. While retanning of quebracho tanned leather with zinc salt results in a synergistically increased shrinkage temperature and quebracho exhaustion.

# CHAPTER THREE

## EXPERIMENTAL METHODS AND MATERIALS

### 3.1 Materials

**Materials required for the experiment**

Sheep skins were collected from slaughtering house / from LIDI

Shrinkage tester, testing drum and glassware's were used to conduct the experiment.

**Chemicals and Reagents**

Chemicals and reagents required for the experiment were analytical grade chemicals and commercial grade chemicals and Beamhouse chemicals, Retanning chemicals, Tanning chemicals, zinc sulphate heptahydrated and laboratory chemicals were purchased from chemical agents.

### 3.2 Processing methods

**Quebracho and Zinc sulfate Combination Tannage**

Sheep skins were employed for combination tanning trial; quebracho-zinc tanning processes was given in Table 3. Four Sheep skins were used for process optimization. One skin was sided into quarters and tanning trials were done with different offers of quebracho and zinc sulphate. The amount of a zinc sulfate used for the tanning trials 2, 4, 6, and 8% and 5, 6, 12 and 15 % of quebracho was employed for all sixteen experimental processes. A control tanning process was carried out using quebracho and zinc tanning system only as given in Table 4 and 5, respectively. The post tanning process as mentioned in Table 6 was followed for experimental and control leathers. All the tanning and post tanning experiments were carried out using smaller drums. Sixteen trials were done to optimize quebrachi-zinc sulffate combination tanning system depending on response parameter shrinkage temperature and the process which gives maximum shrinkage temperature was selected as optimized process recipe and used for main experiment.

Table 3. Formulation of zinc sulphate-quobracho combination tanning system for pickled sheep skins

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 8 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 6 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |
| Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness. | | | | |

Table 4. Formulation of quobracho tanning system for pickled sheep skins

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depicling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| | | | | wash/drain/wash |
| pickling | 80 | water | | |
| | 8 | salt | 10 | |
| Add pelt | | | | |
| | 0 .5 | formic acid | 30 | |

| | | | | |
|---|---|---|---|---|
| | 0.25 | sulfuric acid | 3X10+30 | pH= 4.5 |
| | | | | Drain half float |
| Tanning | 20 | quebraco | 120 | check penetration |
| Fixing | 1 | formic acid | 30 | |
| Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness. | | | | |

Table 5. Formulation of zinc sulphate tanning system for pickled sheep skins

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| | | | | Wash/drain/wash |
| Pickling | 80 | water | | |
| | 8 | salt | 10 | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulfuric acid | 3X10+30 | pH= 2.8/3.0 |
| | | | | Drain half drain |
| Tanning | 8 | zinc sulphate | 60 | |
| Fixing | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | |
| Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness. | | | | |

Table 6. Formulation of post tanning system for control and experimental leathers

| Process | % | chemical | duration (min) | remark |
|---|---|---|---|---|
| Washing | 200 | water | | |
| | 0.5 | wetting agent | 10 | |
| Neutralization | 100 | water | | |
| | 1 | sodium formate | 10 | |

| | | | | |
|---|---|---|---|---|
| | 1 .5 | sodium bicarbonate | 3x10+ 30 | pH= 4.5 |
| | | | | Drain/wash/drain |
| | 100 | water | | |
| Re-tanning | 4 | quebraco | | |
| | 4 | mimosa | | |
| | 2 | acrylic syntan | | |
| | 3 | dicyanideamide | | |
| | 4 | protein filler | 60 | |
| | 50 | water | | |
| Fatliqouring | 4 | synthetic fatliqour | | |
| | 4 | semi synthetic fatliqour | 60 | |
| | 1 | formic acid | 30 | |
| | 1 | Cationic fatliqour | 20 | |
| Fixing | 1 | formic acid | 30 | |

### 3.2.1 Analysis Methods

Proximate chemical analysis, spent liquor analysis and strength properties of the leather, hydrothermal stability and colour and bulk properties of quebracho-zinc sulphate combination tanned leather was performed according to official standard methods.

**Measurement of hydrothermal stability of leathers**

The shrinkage temperature of control and experimental leathers has been determined using shrinkage tester. 2X0.5 cm pieces of tanned leather were cut from the official sampling position was clamped between the jaws of the clamp and was immersed in solution containing 3:1 glycerol: water mixture.

The solution was continuously stirred using mechanical stirrer attached to the shrinkage tester. The temperature of the solution was gradually increased and the temperature at which the sample shrinks was measured as the shrinkage temperature of the leathers.

**Measurement of Grain crack crust shoe upper leather**

Three test specimens 44.5 mm diameter of control and experiment were cut using a circular cutting knife. The test specimens were conditioned at 20 ± 2$^{o}$C and 65 ± 2% RH for 48 hours. One test specimen was tightly clamped between the circular rings facing grain side

upwards in the machine. The machine was started by forcing the plunger at the rate of 0.2 ± 0.05mm/s. The surface of the specimen was continuously observed at the center for initial crack on the grain. The maximum distance and force were recorded at this point. The test for the remaining two test specimens was repeated. The mean values of the test results were calculated for the following

a. Grain crack load in Kgs or N

b. Distension at grain crack, min

**Measurements of Double edge tear strength of crust leather**

Six test specimens of control and experiment were Cut (three test specimen from along direction and three test specimen from across directions) using a cutting knife 50 mm x 25 mm size having a central slot, the test specimen were Condition for 48 hours and measured the thickness. One of the test specimens was inserted through the slit into the sample holding "L" clamps that were fixed to the tensile tester. The test was conducted by operating the tensile tester at the rate of 250 ± 10 mm/ minute speed until the test piece was torn apart.

The maximum force was recorded.

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

**Measurement of Tensile strength and elongation at break of crust leather**

Six test specimens of control and experiment were Cut (three test specimen from along direction and three test specimen from across directions) using a cutting knife and conditioned at 20 ± 2$^{o}$C and 65 ± 2% RH for 48 hours. The thickness of each test piece was measured to the nearest 0.01 mm using thickness gauge at three places on grain side of the leather test specimen and the average thickness was recorded. The area of cross-section on the test specimen was calculated by multiplying its width and thickness. the distance between the grips of the tensile tester was set of 50 mm for standard test specimen. The test specimen was inserted between the grips, taut the grips with sufficient pressure. The tensile testing machine was operated at a speed of 100±2 mm/minute until the leather sample breaks. The machine was stopped immediately, measured the distance between the two grips and the maximum force found at leather break was recorded.

Calculation

$$\text{Tensil strenght} = \frac{\text{Force (N)}}{\text{Area (width in mm x thickness in mm)}}$$

$$\%\ \text{Elongation at break} = \frac{b - a}{a}$$

Where b =initial distance between the jaw in mm

a = final distance between the jaw in mm

**Comfort properties of crust leather**

- **Water penetration resistance (WPR)**

Rectangular pieces of leather 75 mm x 60mm were taken (two from each direction) from the sampling location and the test pieces was conditioned. The finish on the grain surface was slightly scoured using 180 grade emery paper using the following procedure. The leather with finish was placed side up on a table. A piece of 180 grit paper was placed on it, gently scoured the finish with 1 kgf force in to and fro direction for 20 strokes to break the surface coat.

The water resistance testing machine (Penetrometer) was set to give a required amplitude after determining amplitude of crank motion as per procedure mentioned above. The test specimen ($W_1$) was weighed. The trough like test assembly between two cylinders was made keeping the grain side of the leather facing outward and the distance between the cylinders was 40 mm. the ends covering was tighten with metal ring clamps so as to avoid entry of water through the clamping ends. The outer surface of the trough was grain layer or the layer that would form the outer part of the shoe. This assembly was transferred into the holders of testing machine. The brass or copper turnings was inserted inside the trough and lowered the electrode plate to make contact with tunings. The water tank was raised and made sure that the level lies 1 cm below the top of the cylinders. The motor was started and measured the time required for first sign of penetration of water through leather specimen which is indicated by appearance of light on indicator lamp or partial counters. If sign of water penetration was noticed before 60 minutes period, the test was continued until 60 minutes, 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 taken the weight ($W_2$). If water there was no sign of water penetration for 60 minutes also, the test specimen was removed and taken the weight ($W_2$).

Calculation

1. Time for water penetration in minutes

2. Water absorption, percent for 60 minutes

$$\text{water absorption}, \% = \frac{w_2 - w_1}{w_1} * 100$$

- **Water Vapour Permeability (WVP)**

a square piece of leather with at least 50mm side length was cut from the sampling location and broken the surface coating of the leather using 180 grit papers under 0.2 kgf pressure. the leather sample was placed on a table with grain upwards, pressed with 180 grade emery paper against the leather under a load of 200gm and drawn the emery paper across 10 times in various directions. three test specimens were cut from this grain buffed leather using a circular cutting knife with 34 mm diameter. A jar of half its capacity was filled with freshly dried desiccant silica gel (dried in an oven at 125 ± 5oC for at least 16hrs and cooled for at least 8 hrs in a closed bottle). The circular cut test specimen was inserted into the open end of the top screw type bottle cover facing the grain side inward for upper leather (flesh side inward for lining leather). This test piece holder was screwed on the mouth of the bottle. This test jar was fixed in the holder of water vapour permeability testing machine. Two more jars were prepared and secured into the testing machine. The experiment was started and run for not less than 16 hours. This operation was done for making the continuous permeation and absorption process between the leather and desiccant. After 16hrs, these three leather samples were replaced into three fresh jars filled with dry desiccant silica gel and taken weight individually. these bottles were fixed into the holders of the test machine and run the machine for not less than 8 hrs. The bottle was removed and weighed for increase in weight. The time between these two weighings was noted in minutes.

Calculation

$$\text{water vapour permeablity}, \frac{\text{mg}}{\text{cm}^2} = \frac{7639 \text{ x m}}{\text{D}^2 \text{ x t}}$$

Weight, m = Gain in weight in mg

Weight, D = Mean internal diameter in mm of the neck of the bottle

Time, t = Time in minutes between the two weighings

- **Water Vapour Absorption, (WVA)**

About four square test specimens were cut with 150 mm side length. The test specimen (150 mm x150 mm) was inserted between the stationary clamp and moving clamp so as to form a trough without creasing in the middle of leather. The clamp ends were tightening so that water cannot enter through the ends of the test piece. The other three test specimens were secured into the remaining test stations. The trough area was filled with steel balls. The water tank was filled with water and raised it to make contact with the test specimen maintained the level of water is about 1 cm below the edges of leather. Connect the machine with electronic digital counters and start the motor. The oscillations of the movable clamp part make a flexing effect to the leather at 30o angle. Once water penetrated, the counter was stop to function. That is an indication of water penetration cycles. The machine was stopped after all four samples have registered water penetration cycles. Number of cycles was reported for water penetration.

**Assessment and hand evaluation of bulk properties leathers**

Experimental and control crust leathers have also been assessed for softness, fullness, grain smoothness, grain tightness (break) and general appearance by hand and visual examination. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property, where higher values indicate better property of leathers.

**Fat content of crust leather**

The evaporating dish was washed and dried in the oven at 104±1$^{o}$C for 1hr and cooled in the desiccator then weight of dried dish was taken. The leather samples were chopped into small pieces and extracted using soxhlet extraction method with sufficient amount of diethyl ether until fat totally leached out. The filtrate was transferred to the evaporating dish and

evaporated till the solvent totally get evaporated. The dish was put in the desiccator and cooled and the final weight of the dish was taken.

Calculation

$$\text{Fat content} = \frac{W_2 - W_1}{W_1}$$

Where $W_2$= weight of dish plus sample

$W_1$= weight of evaporating dish

**Analysis of spent liquors from tanning trials**

The spent tannin liquor from control and experimental tanning processes was collected, filtered and analyzed for chemical oxygen demand (COD), biochemical oxygen demand ($BOD_5$), and total dissolved solids (TDS) as per the following procedures.

- **Determination of BOD of tanning liquor**

Required volumes of diluted samples was prepared and bring the diluted samples temperature to 27$^o$C and saturated with air by shaking in partially filled bottles by bubbling with organic free filter air or by storing in cotton plugged bottles for a day and measure DO and after five days incubation measure the DO of the sample. Dilution water, find the DO consumption of unseeded dilution water by determining initial and final DO.

Calculation

$$\text{BOD, Mg/l} = \frac{Do - DT}{P}$$

Where Do = DO of diluted sample, mg/l

$D_T$ = DO of diluted sample after 5 days incubation at 27$^o$C, mg/l

P = decimal volumetric fraction of sample used

❖ **Determination of COD of tanning liquor**

About 50 ml of sample was diluted with distilled water in 500ml refluxing flask and 1g of $HgSO_4$ and 5ml $H_2SO_4$ reagents were added, mixed and cooled. 25ml of 0.0417M $K_2Cr_2O_7$ solution was added, mixed and connected to the flask to the condenser and turn on cooling water, additional 70ml of $H_2SO_4$ reagent was added through open end of condenser with swirling and mixing. The solution was refluxed for 2hrs cooled and then washed down condenser with distilled water to double the volume of contents, cool. About 2 drops of ferroin indicator were added and titrated with ferrous ammonium sulphate (FAS) the remaining potassium dichromate until a color change from bluish green to reddish brown. A distilled water blank also was refluxed and titrated with reagents

Calculation

$$\text{COD, mg } O_2/\text{l} = \frac{(\text{A}-\text{B})*\text{M}*8000}{\text{ml sample}}$$

Where, A = FAS used for blank, ml

B = FAS used for sample, ml

M = molarity of FAS

❖ **Determination of Total Solids of tanning liquor**

The evaporating dish was washed and dried at 104±1$^{o}$C for 1hr, cooled and stored in a desiccator. The dried evaporating dish was weigh immediately before use. Specific volume of sample was taken and transferred to evaporating dish with washing to a weighed evaporating dish and evaporated to dryness in an oven at 104±1$^{o}$C after evaporation for 1hr cooled in desiccator and weighed.

Calculation

$$\text{mg dissolved solids} = \frac{(\text{A}-\text{B})*1000}{\text{ml sample}}$$

Where A= weight of residue plus dish. mg

B = weigh of dish, mg

❖ **Determination of ZnO from tanning liquor**

Known amount of chopped leather/approximately 0.5-1.0 ml zinc effluent liquor was taken accurately in different conical flasks and digested using nitric and sulphuric acid mixtures (in the ratio of 6:4). The contents were then made up to a known volume. Atomic absorption spectrophotometer was used for the analysis. The maximum absorption wavelength chosen for zinc is 213.9 nm, where the interference of one metal over the other was not observed.

Standard solutions of zinc were prepared and the linearity for the intensity Vs concentration curve was sketched. Then the made up sample was analysed for zinc after suitable dilutions and the % ZnO was calculated.

Calculation

$$A = \varepsilon cl$$

Where A= absorbance at 213.9 mm wavelength

c= concentration

l= cell length

ε = molar absorption coefficient

# CHAPTER FOUR

## RESULTS AND DISCUSSION

### 4.1 Processing methods

The optimized combination tanning experiment using quebracho and Zinc sulphate were carried out with a concentration of 8% and 6% offer respectively. The shrinkage temperature data of leathers tanned with Quebracho-zinc combination along with Quebracho and zinc controls are given in Table 7.

Table 7. Shrinkage temperature of quebracho-zinc sulphate combination tanned and control leather (zinc and quebracho tanned leathers)

| Trails No. | Percentage offer of zinc | Percentage offer of quebracho | Shrinkage temperature($^{o}$C) |
|---|---|---|---|
| 1 | 2 | 5 | 71 |
| 2 | 4 | 5 | 70 |
| 3 | 2 | 8 | 72 |
| 4 | 4 | 8 | 72 |
| 5 | 6 | 5 | 70 |
| 6 | 8 | 5 | 75 |
| 7 | 6 | 8 | 87 |
| 8 | 8 | 8 | 85.5 |
| 9 | 2 | 12 | 80 |
| 10 | 4 | 12 | 81 |
| 11 | 2 | 15 | 82 |
| 12 | 4 | 15 | 83 |
| 13 | 6 | 12 | 80 |
| 14 | 8 | 12 | 84 |
| 15 | 6 | 15 | 85 |
| 16 | 8 | 15 | 85 |
| Controls | Quebracho | 20 | 81 |
| | 8 | Zinc sulfate | 72 |

From the table it is seen that both the combinations resulted in leathers with better shrinkage temperature than control leathers (Quebracho and Zinc tanned leathers). The shrinkage temperature of leathers obtained from Quebrach-Zinc combination tanning is higher than quebracho and zinc tanned leathers and this experiment resulted in leathers with maximum shrinkage temperature of 87$^{o}$C, which is much better than controls of Quebracho tanned leather of Ts 81$^{o}$C and Zinc tanned leather of Ts 72$^{o}$C. From table 6, it can be observed that Quebracho-Zinc combination tanning system resulted in enhancement of shrinkage temperature of individual tanning system.

**Comfort properties of crust leather**

The hygienic data of leathers tanned with Quebracho-zinc combination along with Quebracho and zinc controls are given in Table 8. The performance of leathers can be affected by the tanning system followed during leather making. The comfort property such as WVP, WVA and WPR values for the experiment excels the control. These results indicate that the combination tannage (quebracho-Zn combination) brought excellent hygienic properties to the final leather. This could be due to the tanning system followed.

Table 8. Hygiene properties of control and experimental leather

| Parameters | Sample type/code | | |
|---|---|---|---|
| | E (zv) | Control 2 (Vc) | Control 1 (Zc) |
| WVP | 1.5 | 0.9 | 0.85 |
| WVA | 20, 700 | 20, 100 | 17, 800 |
| WPR | 23.25 | 27.3 | 29.75 |

These results further tell us the single tannage (Zn tannage and Quebracho tannage) are less hygienic as compared to experimental leathers.

**Bulk properties of leathers - hand and visual assessment of leathers**

Crust leather from both control and experimental processes has been evaluated for various bulk properties by hand and visual evaluation. The average of the rating for the leathers corresponding to experiment has been calculated for each functional property and is given in Fig 4.1. Higher numbers indicate better property. From the figure, it is observed that quebracho-zinc sulphate combination tanned experimental crust leathers

exhibited comparable fullness compared to quebracho tanned control leathers and good fullness compared to zinc tanned control leathers**.**

The organoleptic properties of the quebracho-zinc crust leathers are better compared to quebracho crust leathers. This is primarily due to improved penetration and fixation of quebracho and zinc in the experimental process, compared to control process. Other properties such as softness, grain tightness, smoothness and general appearance are comparable to that of conventionally processed leathers. The overall appearance of optimized experimental leathers is better than that of control leathers.

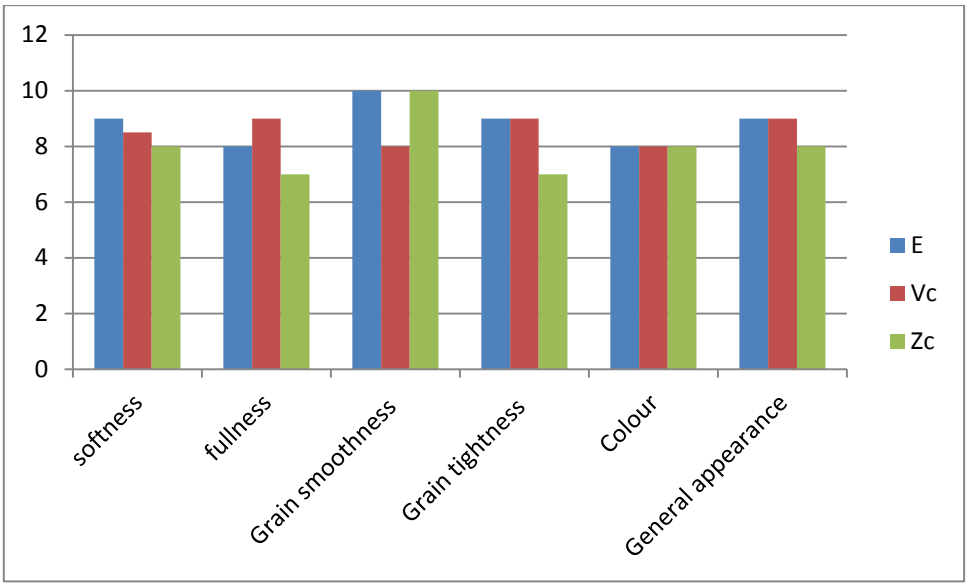



Figure 4.1 Bulk properties of crust leather

**Physical testing of experimental and control crust leathers**

It is essential to study the influence of the tanning system on the strength properties of leathers. The physical strength measurements viz., tensile strength, elongation, tear strength, load at grain burst and distension at grain burst were carried out for the control and experimental crust leathers and the data is given in Table 9.

Table 9. Physical strength characteristics of experimental and control crust leathers

| Parameter | Experiment | Control 1 (Zc) | Control 2 (Vc) |
|---|---|---|---|
| Tensile strength ($N/mm^2$) | 25.08 | 20.35 | 22.41 |
| Elongation at break (mm) | 57.57 | 21.6 | 55.13 |
| Tear strength (N/mm) | 27.35 | 22.25 | 25.47 |

| | | | |
|---|---|---|---|
| Load at grain burst (N) | 242.5 | 160.5 | 475 |
| Distention at grain burst (mm) | 12.6 | 8.45 | 10.15 |

The performance of leathers can be affected by the tanning system followed during leather making. The strength properties such as tensile, tear, load at grain burst values for the experiment excels the control. These results indicate that the combination tannage (quebracho-Zn combination) brought excellent performance properties to the final leather. This could be due to the higher degree of crosslinking that occur b/n the fibers and the tanning system followed here. These results further tell us the single tannage (Zn tannage and Quebracho tannage) are not recommended for the leathers to possess higher performance properties to meet the requirements.

**Fat content of crust leather**

Table 10. Fat content of crust leather

| Parameter | Sample type/code | | |
|---|---|---|---|
| | E (Zv | (Vc) | (Zc) |
| Fat content (%) | 7 | 6.7 | 6.5 |

The fat content of the leathers produced by the single tannage (Zn tanning system and quebracho tanning system) and those produced with the combination tannage are almost similar. This tells us that the tanning system followed has no effect on the fat distribution of the leathers.

**Spent liquor analysis**

Table 11. Spent liquor analysis

| Parameter | Sample type/code | | |
|---|---|---|---|
| | E (Zv) | (Vc) | (Zc) |
| BOD, mg/l | 112 | 208 | 150 |
| COD, mg/l | 4560 | 12,200 | 5080 |
| TDS, mg/l | 14 | 17.6 | 20.4 |
| Zn, mg/l | 22.78 | - | 43.93 |

It is well known that the wastewater from tanning industries is polluting the environment. Therefore, the waste water discharged from tanning industries must be analysed for different parameters such as BOD, COD, TDS and Zn content before discharge. As we can see from the results, the BOD, COD and TDS values were very less for the experiment (Quebracho-Zn combination) tanning system. Doing all these parameters will enable us to evaluate the efficiency of the processing system. Accordingly, the combination tannage is far better in its effect on the environment compared to the individual tanning system.

# CHAPTER FIVE

## CONCLUSION

The selection of tanning agents for combination tanning should be carried out judiciously to avoid competitive fixing. In the present study, an attempt has been made to produce upper leathers using a new eco-friendlier combination tanning process based on quebracho and zinc. It is seen that combination tanning using quebracho (8%) followed by zinc (6% $ZnSO_4.7H_2O$) resulted in leathers with shrinkage temperature of $87^oC$, which is $6^oC$ and $15^oC$ more than the controls (quebracho tanned and zinc tanned) leathers. The physical and chemical characteristics of experimental leathers are comparable to control leathers. The experimental leathers are softer than the control leathers. The combination tanning using quebracho and zinc appears to be an eco-friendlier option and results in leathers with good thermal stability and mechanical properties that is important for commercial viability of the tanning system.

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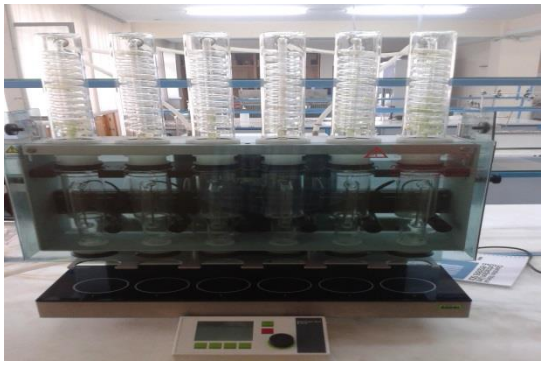
# APPENDICES

Appendix-I Photos of tanning chemicals and laboratory equipments used

a) Zinc sulphate heptahydrate

b) Quebracho



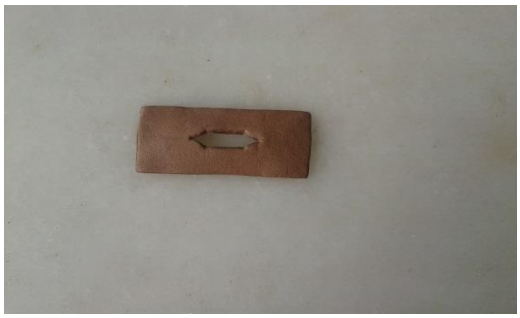
c) Soxhlet

d) colorimeter

e) lastometer

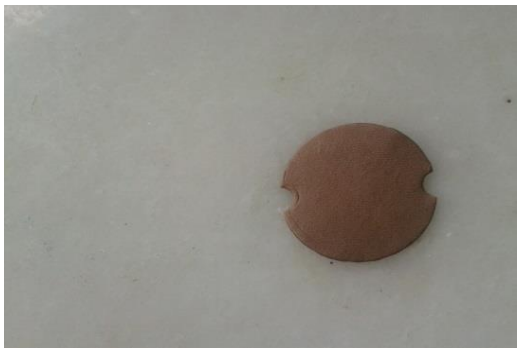
f) dynamometer

Appendices II Quebracho-Zinc combination tanned leather samples



g) Tear test sample

h) tensile test sample



i) Grain crack test sample

Appendix-III Quebracho-Zn Combination tanning system recipe used (from trial 1 to 16) for process optimization

Trail number 1

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |

| | | | | |
|---|---|---|---|---|
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 5 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 2 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |
| Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness. | | | | |

Trial number 2

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 5 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 4 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |
| Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness. | | | | |

Trial number 3

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 8 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 2 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |
| Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness. | | | | |

Trial number 4

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |

| | | | | |
|---|---|---|---|---|
| | | | | Drain half float |
| Tanning | 8 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 4 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |

Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness.

Trial number 5

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 5 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 6 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |

Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness.

Trial number 6

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 5 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 8 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |
| Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness. | | | | |

Trial number 8

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |

| | | | | |
|---|---|---|---|---|
| | | | | Drain half float |
| Tanning | 8 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 8 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |

Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness.

Trial number 9

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 12 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 2 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |

Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness.

Trial number 10

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 12 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 4 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |
| Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness. | | | | |

Trial number 11

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |

| | | | | |
|---|---|---|---|---|
| | | | | Drain half float |
| Tanning | 15 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 2 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |

Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness.

Trial number 12

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 15 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 4 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |

Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness.

Trial number 13

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 12 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 6 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |
| Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness. | | | | |

Trial number 14

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |

| | | | | |
|---|---|---|---|---|
| | | | | Drain half float |
| Tanning | 12 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 8 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |

Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness.

Trial number 15

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 15 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 6 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |

Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness.

Trial number 16

| Process | % | product | duration (min) | remark |
|---|---|---|---|---|
| Depickling | 100 | water | | |
| | 1 | sodium formate | 15 | |
| | 1.5 | sodium bicarbonate | 3X10+30 | pH=5.6 |
| Pickling | | | | drain/ wash/ drain |
| | 50 | water | | |
| | 8 | salt | | |
| Add pelt | | | | |
| | 0.5 | formic acid | 30 | |
| | 0.25 | sulphuric acid | 3X10+30 | pH=4.5 |
| | | | | Drain half float |
| Tanning | 15 | quebracho | 120 | check penetration |
| | 50 | water | | |
| | 0.25 | formic acid | 10 | pH= 2.8/3.0 |
| | 8 | $ZnSO_4.H_2O$ | 60 | |
| | 1 | sodium formate | 15 | |
| fixing | 1.5 | sodium bicarbonate | 3X10+30 | |
| Check the pH to be 5.0. Drain/wash/drain and pile overnight. Next day sammed and shaved to the require thickness. | | | | |