CHAPTER ONE

INTRODCTION

1.1 Background

Leather tanning without a doubt is one of the oldest human activities. In the beginning, skins obtained from hunting and livestock breeding could be used for clothing or tents, but they became stiff at low temperatures, while they rotted with heat. It was probably then that attempts were made to render them more flexible and stronger by rubbing in animal fats; the first rudimental tanning process is mentioned in Assyrian texts and in Homers Iliad. Another process was smoking, which almost certainly started by accident, and which later became formaldehyde tanning, as this substance is found in the vapors produced by burning green leaves and branches. It was soon discovered that the rotting process could also be stopped by drying, carried out by exposure to the sun or by the dehydrating action of salt. Vegetable tanning was also known in very ancient times although it is not clear how the tanning action of the tannin contained in the bark of some plants (especially oak) was discovered. Another method known since the earliest times is tanning, based on the use of alum, a mineral which is fairly widespread in nature, particularly in volcanic area (Leather Resource, 2008).

These methods, which gradually became more refined and efficient, allowed skins to be used in the ancient world and continued to do so for century after century up to the present day. That the use of these techniques was widespread is witnessed by numerous written documents and paintings as well as archaeological finds. In Mesopotamia between the fifth and the third millennium B.C., for example, the Sumerians used skins for long dresses and diadems for ladies. The Assyrians used leather for footwear but also for liquid containers and as inflated floats for rafts. The ancient Indian civilization first processed the type of leather known as the "Morocco" today (Leather Resource, 2008).

The Egyptians also achieved considerable skill in processing leather, which they used for clothing (even for gloves), tools, and arms or simply for ornament. The historian, Strabo, tells of an interesting use developed by Phoenicians who made water pipes from it. During Roman times, leather was widely used in all the provinces of the empire, and more efficient tanning techniques were introduced where they had not been developed locally. the Egyptian wall paintings, prove that leather is a material which is as old as humanity and consequently leather tanning represents one of the eldest human activities (Leather Resource, 2008).

The Romans used leather both for footwear and clothing and for making shields and harnesses. A tannery was uncovered amid the ruins of Pompeii and the same equipment of the kind still in use for centuries thereafter was found in it. (Leather Resource, 2008)

Skipping forward to the 8th century of Spain (then under the dominion of the Moors) we have the development of the production of "Cordovan", thanks to important progress in tanning, a type of leather famous throughout Europe for centuries. That skill in leather tanning was not a prerogative of the western world as recounted by Marco Polo. In his "Travels" he tells us that the Mongols used leather flasks, covers, masks, and caps, decorated artistically, and it was him who coined the expression "Russia Leather" to indicate a type with a characteristic fragrance (Leather Resource, 2008).

A considerable improvement in processing techniques occurred in the 12th century with the result being that between then and the last century; there were no substantial changes to tanning systems. Even oil tanning was used to produce protective garments while tawing was widespread although the results were not always satisfactory. Often, finishing operations were carried out to improve the malleability of the leather and improve its appearance, especially by dyeing. The products, though essentially practical, also met decorative requirements (Leather Resource, 2008).

In the fourteenth century, for instance, leather was being used in combination with wood in chairs, arm-chairs, and settles with craftsmanship that reached the levels of an art-form. This was also the case later on with tapestries (especially in Venice in the fifteenth and sixteenth centuries) with chests and cases, and of course, with book bindings, perhaps the most lasting and refined use of the material. Going back to tanning techniques, it is more or less in the Middle Ages that the depilating action of quick lime was discovered, a technique which is still valid and normally used today (Leather Resource, 2008).

A radical shake-up was provided in the middle of the last century with the discovery of the tanning power of chrome salts which led to a drastic improvement in production and was applied in practice in industrial production towards the end of the century. Another revolutionary element was the substitution of the tanning pit with the rotating drum, along with the discovery of new types of tannins (Leather Resource, 2008).

Our world is full of vegetable tanning materials like (Wood, Barks, Leaves, Fruits, Roots and growth) containing usable tannin. Plants in the tropical and sub-tropical regions of the world have mostly high content of tannin which is more important in the production of leather. Some of the barks used most commonly worldwide are Mangrove, Mimosa, Garad and Pine). Whereas woods of (Chestnut, oak and Quebracho) are also famous for their use (G.Reich, 1996).

Leaves found in Asian and African countries like sumac and gambir have also good tanning effect, fruits like Valonea and Myrobalans also show similar effect like leaves tannin.

The re-tanning process is a very important step in the leather manufacturing because it overcomes some of the disadvantages of chrome tannage. Re-tanning may not only modify the properties of the leather, but will typically also modify the reactivity of the pelt towards other reagents. Even if the processes do not include specific reactions to assist uniform coloring, it is possible to achieve such a side effect as a bonus. Alternatively, if the re-tannage includes mineral reagents, they may also have a mordanting effect on the dyeing step, to achieve modified colour or better fixation. (G Reich, 1996).

1.2 History of Leather Manufacturing in Sudan

Leather production is one of the oldest industry in Sudan and at its beginning plants and herbs were used in tanning and it evolved over the centuries with the increasing needs of man and development, and access to modern techniques of leather production (Fikriya AbaYazid, 2010).

Production of leather is one of the oldest craft in Sudan where processed leather exports from the country, including soft tanned and pickled pelt, constitute about 50% of the exports of cattle’s rawhide and more than 95% of sheep and goats’ rawskin. The leather manufacture also contributes to the provision of shoes, leather products and other popular products for various businesses. The modern sector began in 1945 with the establishment of a machine tannery next to a shoe factory and then the government set up three large tanneries during the sixties and seventies, followed by a number of small tanneries established by the private sector. The tanning industry expanded after privatization in the early nineties and raw hides exporting was closed in 1993. There are 24 tanneries to date beside wide rural craftsmen sector in many cities of western Sudan, Sennar, Medani, Kosti, Gedaref, Kassala and Omdurman with about 30 conventional tanning complex associated with broad artisan sector for the making of the popular shoe product of footwear (Almarkob) and other products. In the early sixties International Bata Shoes Company has established a big plant in Khartoum North, a model for Africa and the Middle East, which was nationalized in 1971. Shoemaking expanded during the seventies by the establishment of medium factories and workshops of various sizes whose number estimated at more than 600 workshops. By the beginning of removing the export ban of rawhides, the capacities started to fall down and factories, tanneries, workshops closed and this coincided with the market dumping of cheap and low quality leather and artificial products from East Asia(FikriyaAbaYazid, 2010).

This traditional artisan sector remained playing its role as many of the artisans moved from Darfur to Omdurman engaged in the making of ‘Almarkob’ and other popular products in the area west of Omdurman. (FikriyaAbaYazid, 2010).

Sudan has one of the large livestock population. It consists of about 28 million Bovine, 56.163 million sheep and lambs, 43.441 million goats and kids (FAO, 2013) (**Table 1.1**).

Table 1.1 Estimate of animal population plus annual growth rate (2002-2013)

Year	**Bovine**		**sheep and lambs**		**Goats and kids**	
	thousand heads					
	SUDAN	**WORLD**	**SUDAN**	**WORLD**	**SUDAN**	**WORLD**
2002	38,183	1,494,113	48,136	1,028,503	41,485	775,756
2003	39,760	1,510,414	48,440	1,037,709	42,030	791,586
2004	39,760	1,527,027	48,910	1,068,223	42,179	815,735
2005	40,468	1,545,000	49,797	1,099,716	42,526	839,498
2006	40,994	1,564,486	50,390	1,106,268	42,756	844,399
2007	41,000	1,573,401	50,944	1,108,427	42,987	855,225
2008	40,000	1,593,409	51,100	1,096,695	43,100	877,227
2009	39,563	1,605,163	51,555	1,076,609	43,270	899,201
2010	40,761	1,619,348	52,079	1,078,255	43,441	909,969
2011	30,043	1,625,266	52,079	1,095,729	43,441	919,096
2012	28,000	1,632,921	56,163	1,088,866	43,441	913,999

(FAO, 2013)

Table1.2. Hides and skins production in million (2002- 2012).

Year	**million pieces**		
	SUDAN	**AFRICA**	**WORLD**
2002	3.3	22.4	319.6
2003	4.0	22.9	325.9
2004	4.7	23.0	330.1
2005	5.5	24.2	334.3
2006	7.4	25.0	342.6
2007	7.5	25.6	368.6
2008	7.9	26.6	349.6
2009	8.3	26.9	353.2
2010	8.4	27.6	354.6
2011	8.4	28.2	352.3
2012	8.4	28.1	355.2

(FAO, 2013)

1.3 SCOPE OF THE WORK

Tannins occur extensively in the vegetable kingdom, in barks, leaves, pods and fruits. Aqueous extracts from tannin bearing plants such as, mimosa, garad, hraz, quebracho, chestnut, myrobalan, sumac, divi-divi, ect. , have been used in converting row skin or hide to stable material. Vegetable tannins are water soluble plant polyphenolic molecules having molecular weight between 500-3000D. Vegetable tannins are divided chemically into two groups namely pyrogallol (hydrolysable tannins) and catechol or (condensed tannins). The natural Vegetable tanning materials and their extracts are heterogeneous i.e., they contain tannins and non-tannins. To determine the character of the tannin extract it is necessary to know the proportion of tannins to non-tannins in the mixture.

Garad (*Acacia nilotica)* is a member of the family Mimosaceae. It is found in the Sahel and the adjoining Sudan savannah from the Atlantic Coast to East Africa and across the Arabian Peninsula to India. Garad extract contains a mixture of several polyphenolic compounds with varied molecular weight.

1.4 The objectives of this study

1. Analysis and identification of components of *Acacia nilotica* (Garad) bark.
2. Application *Acacia nilotica* (Garad) bark in tannage, combination tanning and retanning.
3. Economical evaluation of its application.
4. To Protection of environment from chromium use

CHAPTER TWO

LITERATURE REVIEW

2.1 Hides and skins reception and storage

2.1.1 Sorting

Sorting may be carried out in the slaughterhouse, by dealers, and/or in the tannery. On receipt, hides and skins may be sorted into several grades by size, weight, or quality. Hides are also sorted by sex. Materials unsuitable for the particular type of leather manufactured may be sold to other tanners (BAT, 2013).

2.1.2 Trimming

Trimming is generally carried out during the sorting process. Some of the edges (legs, tails, face, udders, etc.) of the raw hides and skins can be cut off.

This process step may be carried out in the slaughterhouse, but it can also be carried out in tanneries. It produces a waste which is subject to control under the Animal By-Products Regulation (BAT, 2013).

2.1.3 Curing and storage

Curing is a process that prevents the degradation of hides and skins from the time they are flayed in the slaughterhouse until the processes in the beam house are started (Ms. Catherine Scally 1996, Frendrup 1999, BAT, 2013).

Curing is carried out at the slaughterhouse, at the hide dealer's premises, at the hide market, or at the tannery. In certain cases, it might be necessary to repeat the step at the tannery, e.g. if chilled hides are slated for longer storage or if the initial salting was not sufficient to dry the hides.
The methods for curing for long-term preservation (up to six months) are: salting, brining, drying and salt drying. Long-term preservation methods are used when hides and skins are drying and salt drying. Long-term preservation methods are used when hides and skins are traded, particularly for inter-continental trading. For example, much of the raw material for the leather industry in Italy is imported in salted or dried form.

Methods for short-term preservation (2 – 5 days) are cooling, using crushed ice or refrigerated storage, and biocides.

Hides and skins are generally stored as they are received by the tannery on pallets in ventilated or air conditioned and/or cooled areas, depending on the method of curing chosen. From storage, the hides and skins are taken to the beam-house.

2.2 Beam-house processing

Incoming hides are soaked in water for 16-24 hours to remove blood, dirt and salt, and to hydrate dried bides. The hides may be soaked in pits or rotating drums in which the water is changed frequently. During the next stage, the hides are immersed in a lime and sodium sulphide solution for 12-18 hours to loosen and remove the hair. The hair may either be removed mechanically or by pulping in a drum. During the next step, the hides are treated with lime to open up the collagen structure by removing interstitial material. After liming, the hides are scraped mechanically to strip excess flesh from the underside(UNEF, 1996).

2.2.1 Soaking

Soaking is carried out to allow hides and skins to reabsorb any water which may have been lost after flaying, in the curing process, or during transport. Soaking also cleans the hides and skins (removal of dung, blood, dirt, etc.) and removes interfibrillary material. The soaking methods used depend on the state of the hides. The process is mostly carried out in two steps: a dirt soak to remove the salt and dirt, and a main soak. The duration of soaking can range from several hours to a few days. Putrefying bacteria can thrive during soaking and biocides may be added to curtail their activity.

Depending on the type of raw materials being soaked, other additives may be used, such as surfactants and enzyme preparations (BAT, 2013).

2.2.2 Unhairing and liming of bovine hides

The aim of unhairing and liming is to remove the hair, epidermis, and to some degree, the interfibrillary proteins, and to prepare the hide or skin for the removal of adhering flesh and fat by the fleshing process. Hair removal is performed by chemical and mechanical means. The keratinous material (hair, hair roots, epidermis) and fat are traditionally eliminated from the pelts mainly with sulphides (NaHS or Na_2S) and lime. Alternatives to inorganic sulphides include organic sulphur compounds such as thioles or sodium thioglycolate in combination with strong alkali. Enzymatic preparations are sometimes added to improve the performance of the process (BAT, 2013).

2.2.3 Painting and liming of sheepskins

The aim of painting is to bring about the breakdown of the wool root within the skin, so that as much undamaged wool fibre as possible can be pulled easily from the pelt. Paint, a solution of sodium sulphide at concentrations between 5 and 20 % thickened with an equal amount of hydrated lime, is applied to the flesh side of the skin and then left for several hours. The soluble chemicals in the paint penetrate the skin from the flesh side and dissolve the basal young epidermal cells of the epidermis and the wool or hair root, thus loosening the hair or wool which should be easily removed by wiping or light pulling. Paint can be applied either manually or by spraying machines. Several hours after the application, the wool can be 'pulled' from the skin, either manually or mechanically. After pulling, the skins are limed in process vessels, with the same purpose as the liming of bovine hides (BAT, 2013).

2.2.4 Fleshing

Fleshing is a mechanical scraping off of the excessive organic material from the hide (connective tissue, fat, etc.). The pelts are carried through rollers and across rotating spiral blades by the fleshing machine.

Fleshing can be carried out prior to soaking, after soaking, after liming or after pickling. The process of fleshing is called green fleshing if the removal is done prior to liming and unhairing.

If fleshing is performed after liming and unhairing, it is called lime fleshing. Sheepskins may be fleshed in the pickled state. Fleshing operations give rise to an effluent containing fatty and fleshy matter in suspension (BAT, 2013).

2.2.5 Splitting

The aim of the splitting operation is to produce hides or skins of a set thickness. They are split horizontally into a grain layer and, if the hide is thick enough, a flesh layer. Splitting is carried out on splitting machines, fitted with a band knife. Splitting can be done in the limed condition or in the tanned condition (BAT, 2013).

2.2.6 Deliming

After the liming process, the lime or other alkali in the skin is no longer required, and, in most cases, it has a detrimental effect on subsequent tannage. The deliming process involves a gradual lowering of the pH (by means of washing in fresh water or by weak acidic solutions or by salts such as ammonium chloride or sulphate or boric acid), an increase in temperature and the removal of residual chemicals and degraded skin components (BAT, 2013).

The extent of deliming to be achieved depends on the type of final leather; a thorough deliming results in a softer leather, whilst partial deliming gives a firmer leather. At this stage, the hides and skins are ready for vegetable tanning but, for chrome tanning, the delimed hides and skins have to be further processed by bating and pickling. Delimed skins must be taken to the next process immediately, as once the alkali has been removed, putrefying bacteria can thrive. The acidification of liquids which still contain sulphide may generate hydrogen sulphide gas. With prior treatment using hydrogen peroxide or sodium hydrogen sulphite to oxidise the sulphide, this problem can be avoided.

The use of CO_2 instead of ammonium salts reduces the release of ammonia in the effluents (BAT, 2013).

2.2.7 Bating

The unhairing process leaves the surface of the skin or hide clean, however, some hair roots and pigments are still not removed during unhairing, which is not desirable for certain types of leather. The removal of these hair roots and pigments is achieved by the bating process. Bating uses commercially available proteolytic enzymes (BAT, 2013).

2.3 Tanyard processing

The first steps in the tanyard are deliming and bating. The hides are typically treated with ammonium sulphate or ammonium chloride to remove the lime. Following this, hides may be bated using a protein-digesting enzyme solution to break down any unwanted protein. Two tanning processes may be used for hides, and skins (UNEF, 1996).

A wide range of alternative tanning materials is available for the primary tan or for complementary tanning. These include Vegetable tans synthetic tans, Chromium, aluminum, titanium and zirconium, salts and aldehydes ;cod oil is used in the production of chamois leather. Aluminum is unsuitable as a primary tan since it is not sufficiently resistant to water and perspiration (UNEF, 1996).

Titanium and zirconium tanned leathers would not be suitable for modern shoemaking processes (UNEF, 1996).

2.3.1 Degreasing

Degreasing is most relevant in processing sheepskins, where the natural fat content is about 10 –20 % of dry weight. Degreasing as a separate process step is not usual for bovine hides. The nature of this fat makes it difficult to remove because of the presence of glycosides and a high melting temperature. Excessive amounts of grease in the skin may interfere with uniform penetration of tan or dye, causing difficulties in the finishing processes and creating dark and greasy patches on the finished leather. Degreasing of greasy skins is particularly important before chrome tannage as the chromium salts can react with the greases and form insoluble chromium soaps, which are very difficult to remove subsequently (Sharp house 1983).

The three different methods commonly used for degreasing are:

1. Degreasing in an aqueous medium with an organic solvent and a non-ionic surfactant.
2. Degreasing in an aqueous medium with a non-ionic surfactant
3. Degreasing in a solvent medium (BAT, 2013).

2.3.2 Pickling

Pickling is carried out to reduce the pH of the pelt prior to mineral tanning and some organic tannages (e.g. chrome tanning, glutaraldehyde tanning, and vegetable tanning), thereby sterilizing the skin, ending the bating action, and improving the penetration of the subsequent tanning material. The choice of the exact pickling parameters depends on the subsequent tanning step. Pickling involves treating the bated stock with a solution of sulphuric acid and common salt. The process not only serves to prepare the stock for subsequent tanning, but also if necessary in the preservation of the stock for quite long periods. The pH of the medium is kept at around 3.5.

Tanning can be carried out in the pickle liquor, where both operations are undertaken at the same location (BAT, 2013).

2.3.3 Tanning

In the tanning process, the collagen fiber is stabilised by the tanning agents, such that the hide is no longer susceptible to putrefaction or rotting. In this process, the collagen fibers are stabilised by the cross-linking action of the tanning agents. After tanning, the hides or skins are not subject to putrefaction, their dimensional stability, resistance to mechanical action, and heat resistance increase, (Andres, 1995) (HMI, 1995).

There is a wide variety of tanning methods and materials and the choice depends chiefly on the properties required in the finished leather, the cost of the materials, the plant available, and the type of raw material.

The majority of tanning agents fall into one of the following groups:

- mineral tannages
- vegetable tannins
- syntans

- aldehydes
- oil tannage.

The most commonly used tanning agent is basic chromium sulphate(Cr (OH) SO_4). A high proportion (80 – 90 %) of all the leather produced today is tanned using chromium (III) salts.

Hexavalent chromium (chromium (VI)), in contrast, is not used in the tanning process and has no tanning effect. The possible formation of chromate in leather during its manufacture depends on synergetic effects of several components. The raising of the pH during the neutralisation of wet blue facilitates the oxidation of chromium (III) to chromium(VI)). The drying of leather and its intermediate products may also create favourable conditions for the formation of chromium (VI). Fatty acids in the fatliquor may have an especially important influence (unsaturated fats may promote chromium oxidation).

In order to avoid the formation of chromium (VI), the precautions given below can be taken.

- The use of a reducing agent as an auxiliary during the neutralization of wet blue.
- Avoidance of the use of ammonia as a wetting back agent for crust leather before dyeing.
- The use of vegetable retanning agents for chromium-tanned leather or the addition of a small proportion of a vegetable tanning agent (e.g.

0.25 – 4 % depending on the agent) in the retanning process step. Vegetable tannins derived from Tara are particularly effective in this role.

- Choosing a fatliquoring agent that does not contain simple or multiple unsaturated free or esterified fatty acids.
- The use of fatliquors with antioxidants.
- Degreasing skins with a high content of natural grease (sheep and pig skins) before tanning (Hauber and Knödler, 2008) (Rydin, 2002)**.**

There are several types of vegetable tanning systems, and the types of leathers produced with each system do not have characteristics comparable to chrome tanned leathers, e.g. resistance to high temperature and flexibility. Conversely some of the qualities of vegetable tanned leathers, e.g. tooling, burnishing can only be found in this type of leather (BAT, 2013).

2.3.4 Draining, horsing, samming, and setting

After tanning, the leathers are drained, rinsed and either horsed up (piled onto a 'horse') to 'age'(allow further fixation of the tan and setting out of the fibers to occur), or unloaded in boxes and subsequently 'sammed' (squeezed between rollers) to reduce the moisture content, prior to further mechanical action, such as splitting and shaving. The setting-out operation can be carried out to stretch out the leather. Machines have dual functions which combine the samming and setting action. After samming and the setting out, hides and skins can be sorted into different grades after which they are processed further or sold on the market (BAT, 2013).

2.3.5 Shaving

The shaving process is carried out to reduce and/or even out the thickness throughout the hide or skin. The hides and skins are put through a machine with a rapidly revolving cylinder cutting fine, thin fragments from the flesh side. Shaving can be carried out on tanned or crusted leather.

The small pieces of leather which are shaved off are called shavings (BAT, 2013).

2.4 Post-tan processing

To produce finished leather, the tanned leather is pass through a series of post-tan processes, which treated with preparations of natural and/or may include retanning, dyeing and fat-liquoring. Synthetic oils used to replace the natural oils lost and Retanning agents modifies the characteristics of the leather during processing.

After post-tan processing, the hides are dried and pressed; to create the correct shape and surface texture; they may also be trimmed, split, shaved and buffed. A decorative and protective surface coating may also be applied (the 'finishing' process)(UNEF, 1996).

2.4.1 Neutralisation

Neutralisation is the process by which the tanned hides are brought to a pH level suitable for the process steps of retanning, dyeing and fatliquoring (BAT, 2013).

2.4.2 Bleaching

Vegetable tanned skins and leathers with wool or hair may need to be bleached in order to remove stains, or to reduce the colouring in the hair, wool, or leather prior to retanning and dyeing (BAT, 2013).

2.4.3 Retanning

The retanning process can be carried out with the following objectives:

- To improve the feel and handle of the leathers;
- To fill the looser and softer parts of the leather in order to produce leathers of more uniform physical properties and with more economical cutting value to the customer;
- To assist in the production of corrected grain leathers;
- To improve the resistance to alkali and perspiration;
- To improve the 'wetting back' property (susceptibility to rehydration) of the hides which will help the dyeing process.

A wide variety of chemicals can be used for the retannage of leather. They can generally be divided into the following categories: vegetable tanning extracts, syntans, aldehydes, mineral tanning agents and resins (BAT, 2013).

2.4.4 Dyeing

The dyeing process is carried out to produce consistent coloring over the whole surface of each hide and skin, and for exact matching between hides in a commercial pack. Typical dyestuffs are water-based acid dyes. Basic and reactive dyes are less commonly used by the leather industry (BAT, 2013).

2.4.5 Fatliquoring

Leathers must be lubricated to achieve product-specific characteristics and to re-establish the fat content lost in the previous procedures. The oils used may be of animal or vegetable origin, or may be synthetics based on mineral oils.

Stuffing is an old technique used mainly for heavier vegetable-tanned leather. The sammed leather is treated in a drum with a mixture of molten fat (Heidemann 2000). The retanned, dyed, and fatliquored leather is usually washed before being piled onto a horse to age allowing the fat migrate from the surface to the interior of the material) (BAT, 2013).

2.4.6 Drying

The objective of drying is to dry the leather whilst optimising the quality and area yield. There is a wide range of drying techniques and some may be used in combination. Each technique has a specific influence on the characteristics of the leather. Drying techniques include samming, setting; hang drying, vacuum drying, toggle drying and paste drying. Generally samming and setting are used to reduce the moisture content mechanically before another drying technique is used to dry the leather further. After drying, the leather may be referred to as crust. Crust is a tradable intermediate product (BAT, 2013).

2.5 Dry finishing operations

The overall objective of finishing is to enhance the appearance of the leather and to provide the performance characteristics expected of the finished leather with respect to:

- colour
- gloss
- handle
- flex
- adhesion
- rub fastness,
- as well as other properties as required for the end use, including:
    - ➢ extensibility

- break
- light and perspiration fastness
- water vapour permeability, and
- Water resistance.

Generally, finishing operations can be divided into mechanical finishing processes and coating (BAT, 2013).

a) Mechanical finishing processes

A wide range of mechanical finishing processes may be carried out to improve the appearance and the feel of the leather. The following list of operations includes commonly used mechanical finishing processes:

- conditioning (optimising the moisture content in leather for subsequent operations);
- staking (softening and stretching of leather);
- buffing/dedusting (abrading of the leather surface and removing the resulting dust from the leather surface);
- dry milling (mechanical softening);
- polishing;
- plating (flattening);
- embossing a pattern into the leather surface.

These operations may be carried out before or after applying a coat, or between the applications of coatings. The list is not exhaustive and many other processes exist for special leathers such as sole leathers, wool-on skins, and special effects leathers (BAT, 2013).

b) Applying a surface coat

The purpose of applying a surface coat is:

- To provide protection from contaminants (water, oil, soiling);
- To provide colour;
- To provide modifications to handle and gloss performance;
- To provide attractive fashion or fancy effects;
- To meet other customer requirements.

There is a wide range of application methods, each of which has its advantages and disadvantages. A combination of methods can be used to achieve the desired effect on the finished product. In principle, the following types of application methods can be distinguished:

- padding or brushing the finishing mixture onto the leather surface;
- spray coating;
- curtain coating, which is passing the leather through a curtain of finishing material;
- roller coating, which is the application of finishing mixture by a roller;

transfer coating, which is the transfer of a film/foil onto leather previously treated with an adhesive(BAT, 2013).

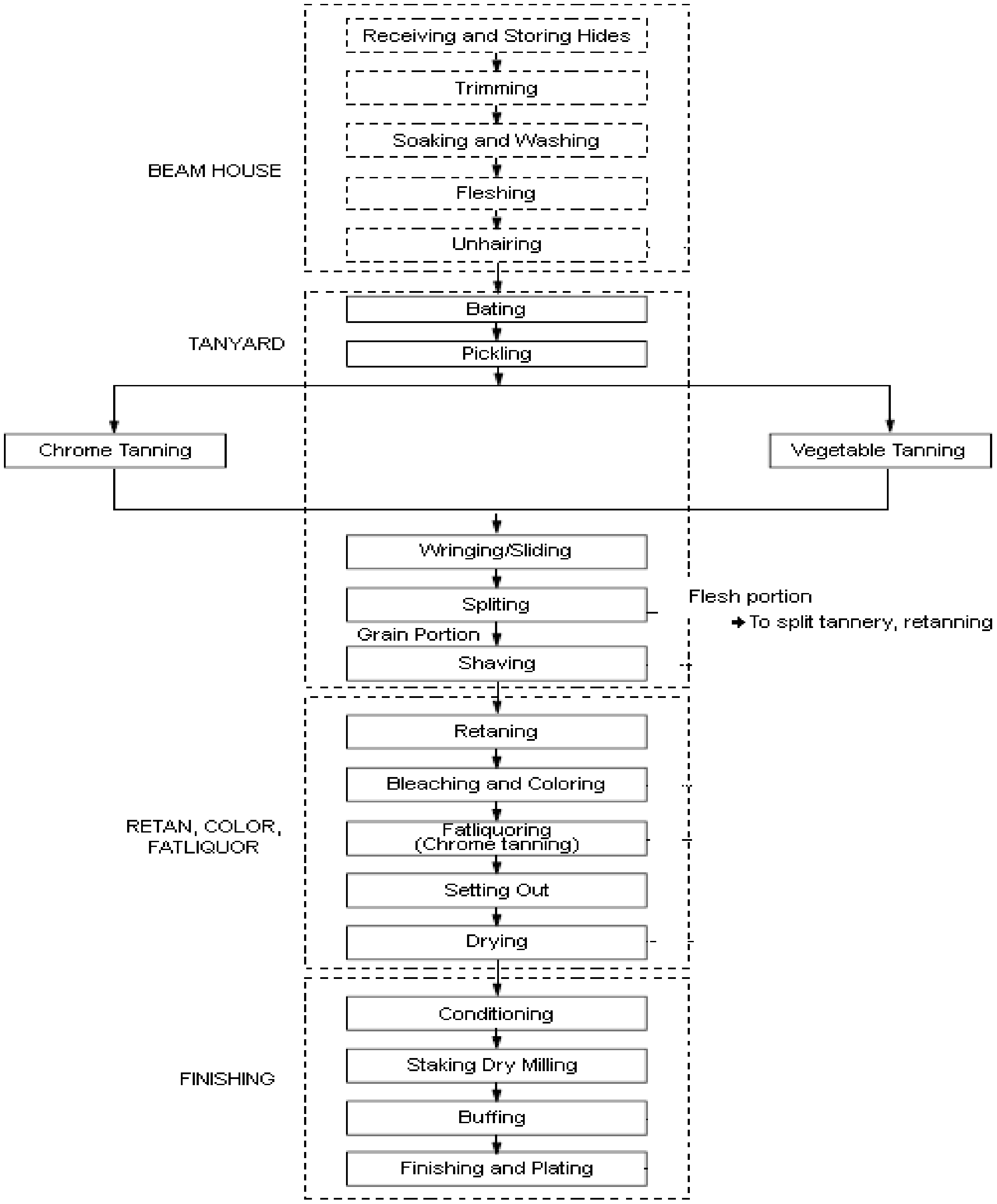


Figure 2.1 Process flow sheet for conventional leather processing

2.6 Tannage

The tannage is converts the protein of the rawhide or skin into a stable material, which will not putrefy and is suitable for a wide variety of purposes.

There are many different tannages are use today (Harold 1993), but the most important are still vegetable and chrome tannage (Musa, 2009).

2.6.1 Vegetable tannage

Many plant materials contain polyphones that can be used in tanning. To be effective, the molecular mass must be 500 – 3000; lower molecular mass frictions in the tannin are referred to as non- tans and higher molecular mass species are gums (Covington, 1997; Mahdi, 2001). Tanning products may be powdered plant parts or aqueous extracts of those parts; the properties they confer to the leather are as varied as the many sources from which they are obtained (Covington, 1997 ; Mahdi, 2001).

As the result of the very slow penetration of these large molecules, the saturation of the hide with these large amounts of tannin takes much more time than with other tannages that are performed with much smaller tanning molecules (Heidemann, 1993 ; Mahdi, 2001).

Tannin solutions are naturally weakly acidic, with pH values of between 3 and 6, due to a number of acidic carboxyl groups on the molecules. Pelt does not swell in natural tan solution. Swollen pelts from the alkaline regain their natural unswollen state in these solutions very slowly. Hide proteins on the surface of the hide react rapidly with fresh vegetable tannins, causing a constriction of protein structure. This superficial reaction slows the diffusion of the tannin in to the center of the hide and results in the first tanning stage in uneven tanning of the inside and outside. Astringency is special term used in the evolution of taste or palatability of beverages or foods containing natural tannins, like tea. Tannins are often used in herbal remedies and food just for this effect (Heidemann 1993).

The reaction between hide protein and natural polyphenols is dependent on the acidity. The principal attraction between protein and tannin is based on hydrogen bonding and dipole interaction. The speed of binding is rapid and is quite firm under acidic conditions of pH between 3 to 4. It slows down at pH values above 6 and the tan solutions themselves became darker (Heidemann, 1993).

O'Flaherty et al. (1974) prepared a summary description of the properties of vegetable tannins from many plants; factors influencing their penetration in to hide; interrelationships between penetration into and fixation onto the hide; the importance of such factors as pH, temperature, and tannin solution concentration on tannin fixation. Optimizing the vegetable tanning processes clearly remains a complicated art of balancing opposing responses to process variables. For example, the amount of tannin fixed increases but penetration rate decreases significantly as the tannin solution pH is decreased from 5 to 3.

The presence of non- tans and salts such sodium chloride or particularly sodium chloride can increase the penetration rate, but decrease the extent of fixation (Gazave, el al .1975).

Gustavson (1966) concluded that a hydrogen bonding is responsible for the fixation of the vegetable tannin to the protein. Most vegetable tannagre occurs on the acid side of the iso-electric point of collagen; hence, protein carries a positive charge. On the other hand, the tanning materials being phenolic substances, are substances, are unlikely to be negatively charged at these acid pH levels. It is especially improbable that increased acidity, that is lower pH, would increase the fixation, if electrovalent forces were involved; yet this is experimentally true. Further, both the vegetable tannin and collagen contain a high frequency of hydroxyl groups as well as unshared electron pairs.

The shrinkage temperature of collagen is the temperature at which collagen spontaneously contracts when heated in water (Meyer and Mark 1950). At the isoelectric point, collagen shrinks at 60- 64°c, when tested under specified experimental condition. Vegetable tannage customarily increases the shrinkage temperature to 80-85°C (condensed tannin) under the same experimental conditions.

Gustavson (1965) provides a very interesting account of the use of the vegetable tannin in Italy and compares the processes used there with those in the United States. The Italian industry used blends of chestnut, quebracho, and wattle tannins in the manufacture of shoe sole leather . Quebracho tannin is particularly useful because of the fast diffusion in to the skin and good capacity to fix to the fibre. The wattle tannin also has a fast diffusion rate, but its main advantage is the light colour of leather that can be obtained. The chestnut tannin is the major component used in Italian practice. Chestnut tannin has a particularly high fixation level and good colour characteristics that are relatively stable to light. The chestnut tannin is also considered to improve substantially on the tanning properties of the quebracho and wattle tannins. In Italy skins are first treated with a light syntan pretannage followed by a pit tannage in which the tannin blend is composes of 50% Chestnut tannin, 15% of a sweetened (treated with sulphite) Chestnut tannin, 18% cold water- soluble quebracho extract, and 17% of wattle tannin. The pit tanning is followed by a drum tannage with a blend of 60% Chestnut extract, 30% sweetened Chestnut extract,and 10% cold water- soluble quebracho extract. Hergret(1989) also describes a tanning blend used in an ultra- rapid drum tanning process which is made up of 45% Chestnut extract, 25% cold - soluble quebracho extract, 15% sweetened chestnut extract, and 15% wattle tannin.

Wattle and quebracho tannin are the predominant vegetable tannin used in the United States. Only a few cottage industry- scale tanneries use vegetable tannins obtained from domestic sources, such as oak (Quercus spp.) or hemlock (Tsuga spp) extracts. Because the United States leather industry uses a significant proportion of the chromium imported to the United States and because of environment concerns with its use present as well, there is a glimmer of renewed interest in the use vegetable tannin from indigenous plants of North America. Vegetable tannins are often used as a retannage of chromium tanned leather for the production of shoe uppers. Williams- Wynn (1970) has summarized the results of a series of studies made on this type of tanning process at the leather industry research institute in South Africa.

Chromium pre-tannage increase the reactivity of vegetable tannins, apparently by increasing the availability of amino groups as well as by formation of co-ordination complexes of both the tannin and non-tan with the chromium. When this leather are dried and aged, further reaction takes place resulting in an increase in free sulphate and high acidity. The low pH causes hydrolytic degradation of the collagen with loss of strength of the leather. Williams-Wynn, (1970) offered suggestions of ways to modify this tanning process to improve the properties of chromium–vegetable tanned leather. They included the degree of chromium tannage and/or use of anionic syntans prior to the vegetable retannage. Format making was very effective in reducing the loss of chromium in the retannage, in reducing the amount of vegetable tannin fixed in the retannage and in reducing the acidity of the resulting leathers.

Retannage with condensed tannins (wattle or quebracho) was much better than with the hydrolysable tannins (myrobalans) or chestnut tannin. Wattle tannin reacted more slowly than quebracho tannin. Use of a wattle retannage neutralization gave the most stable leather. The wattle tannins were also superior, because of the lower level of non-tan, as they also reacted with the chromium and increased the amounts of chromium striped off vegetable retannage (Atkinson, 1978).

2.6.2 Mineral Tannage

` Four elements play a significant role in the modern leather tanning industry, i.e. chromium(III), aluminium (III), titanium(IV) and zirconium(IV) (Covington,1997), of which chromium(III)is the most important. Nowadays more than 90%of the world’s leather is tanned with chromium, which is 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 is also has considerable potential for environmental pollution. The interactions of collagen with chrome have been extensively investigated since the end of nineteenth century. The fundamental reaction is the formation of complex bonds with the ionized carboxyl groups of aspartic and glutamic acid residues on collagen fibers. Others 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. The maximum shrinkage temperatures of leather tanned with Al(III),Ti(IV), and Zr(IV) salt are 79,90,and 97C respectively(Heidemann,1993).

2.6.2.1 Chrome tannage

Chrome tanning occupies an outstanding position in the tanning industry since its introduction in 1884 by Knapp. 90% of tanning processes use basic chromium sulphate for tanning. Basic chromium sulphate as tanning material is frequently criticized by the researchers as it causes pollution and suffers with toxicological problems (Karthikeyan , 2008).

Chrome-tanned leather tends to be softer and more pliable than vegetable-tanned leather, has higher thermal stability, is very stable in water, and takes less time to produce than vegetable-tanned leather. Almost all leather made from lighter-weight cattle hides and from the skin of sheep, lambs, goats, and pigs is chrome tanned (Sarkar. , 2005).

Chrome tan is still the major tanning agent, and widely used over the world. Chrome tanned leathers are characterized by their light weight and high tensile strength.

Chrome tan cross-links with polypeptide chains by principle valences through coordination bonds with the acidic amino acid side chains of the collagen. The cross-links induce physical and mechanical properties that give the chrome tanned leathers its high quality. Although, there are some disadvantages of chrome tanned leather such as lack of fullness and course nap especially in suede leather. Chrome tannage is still the most widely used method in the tanning industry (ElShahat, et al. 2010).

Now a day the use of chromium has accelerated in the leather industry as it is enables faster and cheaper production of highly resistance and durable leathers. Today more than 80% of finished goods are tanned using basic chromium sulphate. However high pH value, temperature, UV lights, unsuitable storage conditions and the effect of using lubricants with double bonds in the molecule during production possibly run up the oxidation of the trivalent chromium into the hexavalent form (Bahry,et al. 2008).

After pickling, when the pH value is low, chromium (III) salts are added. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross- linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant to bacteria and high temperature.

In the following paragraph, the formation of the highly stable chromium leather waste will be explained. GRAPH 1A illustrates the reaction of the used tanning agent chromium with the collagen of the skin resulting in a stabilization of the triple helical structure of collagen matrix. Chromium is cross linked with the carboxylic groups of the polypeptidic chain of the skin collagen resulting in the formation of a chromium collagen complex (Malek, et al. 2009).

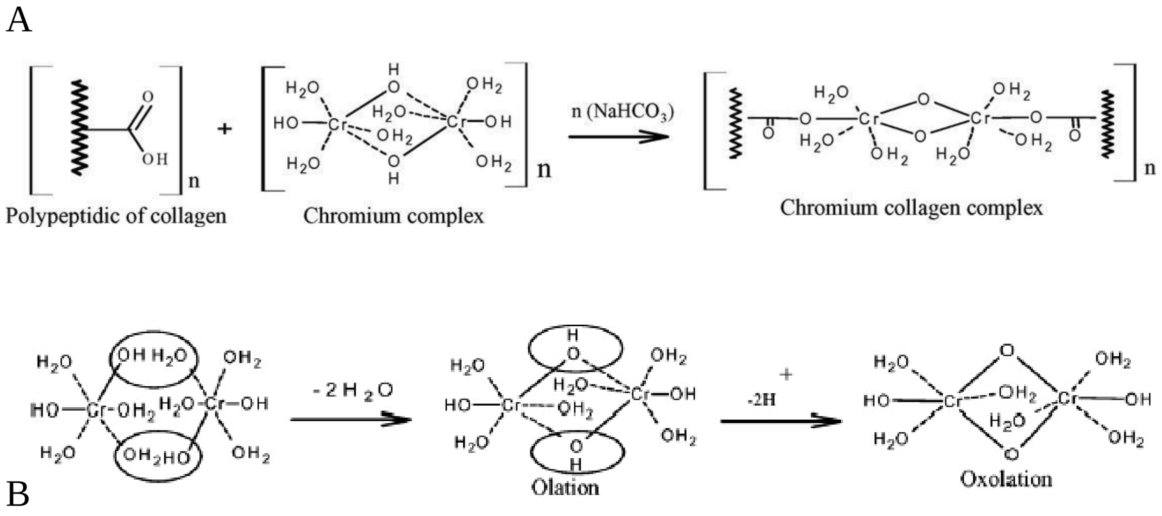


Figure 2.2 GRAPH A: Coordinate covalent linkage of chromium complex with the polypeptidic chain of the skin collagen;GRAPH B: Olation and oxolation process .

The following chemical reactions which take place are called “olation and oxolation”. Olation appears as the alkaline milieu of the tanning solution increases resulting in dehydration. This is followed by a dehydrogenation step and the discharge of two hydrogen atoms occur resulting in the covalent linkage of the oxygen-chrome as it is depicted in GRAPH 1B (Martinetti 1995). The obtained oxolation bridges result in high stability of the chromium – collagen complex which causes the adverse environmental impact due to the non-degradable toxic material (Robert, 1983). The tanning waste contains about 4.3 % of chromium and 14 % of nitrogen (Malek et al. 2009).

Yet, there is no suitable technique that exists which describes an efficient way to recover chromium. The traditional method is alkaline hydrolysis by precipitating the chromium as chromium hydroxide ($Cr(OH)_3$) using sodium hydroxide solution followed by the dissolution in sulfuric acid (Cassano, et. al.2001). Another treatment to recover the chromium is acidic hydrolysis (Wojciech, et al. 1998) and enzymatic hydrolysis (Taylor,M.M,,et.al. 1997). However, those treatments generate new waste products of low quality, for example the chrome cake which is a chromium – protein mixture (Malek et al. 2009).

2.6.2.2 Aluminium tannage

This is the oldest inorganic tannage for harness, upper and glove leather. Aluminium tannage fulfills separation of the skin fibers to obtain supple material after drying. Aluminium salt combine with the skin in a similar fashion to that of chromium salt in that, as they become more basic by addition of alkali, also they become more stringent and fix more firmly to the fibers. Aluminium salts differ from chrome leathers, where they give white leathers, in which they are not firmly fixed to the fibers. They can be simply washed out with water to give untanned skin, unless they have been for a longer period. (getaneh2014).

Aluminum salts in dilute solution, hydrolyses in water with the formation of colloidal precipitate of basic aluminum salts as aluminum chloride or aluminum sulphate (salts containing Al). In solution, has an acid reaction due to hydrolysis:

$AlCl_3 + H_2O$ ==== $Al(OH)Cl_2 + HCl$

(Basic aluminium chloride)

Or $Al^{+3} + H_2O$ ==== $Al(OH)^{+2} + H^+$

Similarly, $Al_2(SO_4)_3 + 2H_2O$ ==== $2Al(OH)SO_4 + H_2SO_4$

(Basic aluminiumsulphate)

Or $2Al^{+3} + 2H_2O$ ==== $2Al(OH)^{+2} + 2H^{+2}$

The hydrolysis of aluminum chloride or sulphate can be further assisted in the presence of a pelt (skin protein) which will absorb the hydrogen ions formed in the hydrolysis. This makes the pelt more positively charged, producing essentially a pickling affect, and exerts some swelling action on it. The subsequent absorption of the basic aluminum salt by the pelt can only be favoured provided that there is some salt in the bath to suppress the swelling caused by the absorption of acid ions and also when the tanning bath is highly concentrated (Sarkar,1981).

Instead of adding salt to the solution leather can be produced by gradual additions of a little soda which will neutralize the liberate acid and convert the normal aluminum sulphate to basic aluminum sulphate. The pelt, being spared of acid swelling, absorbs the basic salt and become, satisfactorily' tanned. Addition of alkali to aluminum salt increases the take–up of aluminum by skin (Miller, 1962).

2.6.2.3 Zirconium tannage

Zirconium sulphate and/or its basification are the most commonly used tanning agents. The chemical behavior is much more similar to that of aluminium tanning agents. The treatment of leather with this tanning agent results in leather with a pure white cross-section and neutral white surface with excellent light-fastness as like aluminium tannage. In this tannage, tanning is more compact and fuller improving the density of fiber texture which points out the special character of this tanning more suitable to treat loose and spongy raw hides. Additionally, it is also possesses better hydrolysis properties compared to aluminium and chrome tannage (Gerhard, 1996).

2.6.2.4 Titanium tannage

Titanium was first considered as a possible tanning agent in 1930, as its properties allow it to react with collagen carboxyl groups present in leather. Titanium used as a tanning agent has been proven to produce leather with a level of quality suitable for commercial use. What is more, it is a non-toxic metal and gives additional advantages in that it is biocompatible, inert and avoids possible allergic reactions derived from contact with the skin.

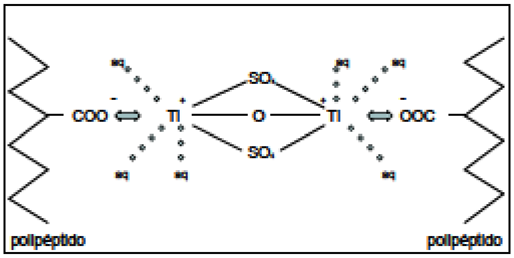


Figure 2.3 Titanium and skin collagen bone

Titanium has some advantages with regard to conventional chrome tanning, i.e. it is a non-toxic, inert and non-allergenic element. Besides, titanium tanning avoids chrome contamination in tannery effluents and in wastewater treatment sludge, which improves the overall environmental impact of the process (JoaquinFerrer, et al. 2012).

2.6.2.5 Sulphur tannage

Sulphur tannage has no real tanning effect and is not correct term; however, the name is commonly used. This method is used rarely in special cases to make special technical leathers such as belt, picker bands and lace leathers, mostly in combination with other tanning agents like vegetable tanning agents, chrome tanning agents and fat tanning agents. This tannage has the advantage of producing excellent firmness, elasticity and high pliability in the skin (Narayan, 2013).

2.6.2.6 Iron tannage

Iron tannage is the recent discovery in the tanning industry to compensate the economy and fulfill the place/shortage of chromium, due to environmental legislation. Recent findings and trends point out iron tannage to be more suitable in the production of wet brown/wet iron leathers for preliminary tannage. These leathers produced by iron (II) tannage show similar handle properties of chrome tanned leathers. But these leathers have low resistance to boiling. Therefore, to fix this defect, they should be retanned using synthetic, vegetable or chrome tanning agents.(Narayan, 2013).

Joseph R, et al(1943) have suggested lactic, citric, hydroxyacetic, and gluconic acids were found satisfactory for stabilizing iron solutions to be used for tanning leather. The influence of pH and concentration on the combination of iron (Fe_2O_3) with standard hide powder was investigated.

The maximum fixation of 23 to 25 percent of ferric oxide occurs in the pH range 3.5 to 4.0.

Practical tanning experiments were made with goat- and calf-skins. The shrinkage temperatures of the iron-tanned leathers are lower than those of well-tanned chrome leathers. The results of accelerated aging tests indicate that all of the iron-tanned leathers tested had at least fair aging qualities except where gluconic acid was used. The use of iron salts for replacing those of chromium in the tanning of leather shows most promise where citric acid is used for stabilizing the solution.(Narayan, 2013).

2.6.3 Aldehyde tannage

Aldehyde tannage is rarely used as tanning methods in its all. But it is used greatly for pretanning and retanning treatments. Aldehydes like glutaraldehyde and some of its modifications have proved to be more competent than others (Narayan 2013).

2.6.3.1 Formaldehyde tannage

Formaldehyde is not that popular but it is also used in aldehyde tannage (Wojdasiewicz, et al. 1992). When the pH ranges 6.5 to 8.5, formaldehyde gives its best tanning effect. Excessive amount of formaldehyde should not be used to avoid callouses on the grain. Leathers seem to absorb more water in this process giving pure white color of leather with a fine closed appearance of grain (Gerhard, 2005).

2.6.3.2 Glutaraldehyde tannage

Glutaraldehyde and its modifications are more popular in use than formaldehyde as it gives more soft leather with greater fullness and increased fastness to heat, perspiration and washing. The effect of tanning starts at low pH around 2.5 giving the finer appearance of grain. However, this has also some disadvantages like line shrinking effect due to alkaline liquor and bad odours along with slight tinge of yellow which appears occasionally (Narayan, 2013).

2.6.4 Polymers tannage

The use of polymers as a tanning agent has also been more popular for a decade but polymers are not yet recognized as a self tanning agent because they do not have adequate self tanning effect. Polymers are used as pretanning and retanning agents. Some of the examples are polymers of acrylic acid, methacrylic acid, ethyl esters or methyl esters of acrylic or methacrylic acid, copolymers of different monomers, styrene maleic acid and oligomers (Narayan Kumar Sah 2013). All of these polymers have ecological advantages as well as different molecular size with different degree of polymerization (Magerkurth, 1987).

According to their ionic properties, they are classified as anionic products and amphoteric products.

2.6.5 Fatty substances tannage

One of the oldest methods of tanning is tanning with fatty substances (Narayan , 2013). The oil of different marine fish and animals has reactive double bonds which makes the real tanning possible with fatty substances. This tanning is further divided into three groups which are:

2.6.5.1 Chamois tannage

This tannage process treats the skin of lamb, sheep, red deer, chamois, reindeer and elks to make garment leathers, mostly leather for Tyrol trousers. Fish oil is used under controlled temperature not exceeding 45 ºC in a hot air drum. Formaldehyde and/or glutaraldehyde can be used as a pretanning agent to get more softness in the leather (Gerhard, 1996).

2.6.5.2 Fatty alcohol sulphates tannage

This tannage has pretanning and retanning effect. It does not have self tanning effect. This method is still in use because it gives very soft and elastic leathers in conjunction with mineral tanning agents. But this process has disadvantage of increasing wettability (Gerhard, 1996).

2.6.5.3 Sulphochlorides tannage

In this tannage, paraffin sulphochlorides are used. The tanning effect is gained by attachment to the amino group of the collagen. This tannage gives pure white leathers, properties similar to the chamois leather as this tannage is mainly combined with aluminium tanning agents (Gerhard, 1996).

2.6.6 Synthetic tannage

The term syntan means synthetic tanning agent. This class of tanning agents was introduced early in the last century, with the purpose of aiding vegetable tanning, although the range of reactivates currently available means that they may serve several different functions. They are classified into three types, according to their primary properties (Marion Kite and Roy Thomson, 2006).

4.6.6.1 Auxiliary syntans

These compounds are frequently based on naphthalene and are synthesized by the ‘Nerodol’ method (Figure 2.4), i.e. the base material is sulphonated to a high degree and then polymerized, typically by formaldehyde the products are usually relatively simple chemical compounds.

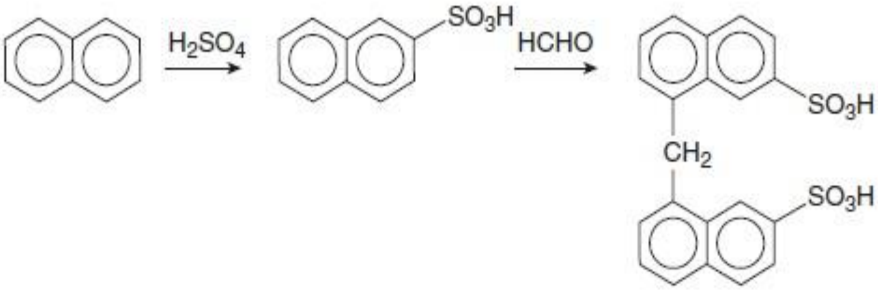


Figure 2.4: The Nerodol synthesis of syntans

The presence of the sulphonate groups means that these compounds can interact strongly with the amino side chains of collagen at pH < 6:

Collagen—NH_3^+---_$^{-}O_3S$—Syntan

In this way, reaction sites for vegetable tannins can be blocked promoting penetration, through the hide cross-section. At the same time they serve to solubilize the aggregated phlobaphenes of condensed tannins, thereby reducing reaction with the hide surfaces. Tanning power, these syntans work best as retanning agents; they are applied after main chrome tannage, to modify the handling properties of the leather (Marion Kite and Roy Thomson, 2006).

4.6.6.2 Combination or retanning syntans

These syntans are usually based on simple phenolic compounds, they are synthesized by the 'Novolac' method (figure 2.5), i.e. the base material is polymerized, typically with formaldehyde, and then the product may be partially sulphonated.

The products are more complex than the auxiliary syntans, having higher molecular masses, and may be crosslinked in two dimensions. Their enhanced tanning functionality means that they can confer means that they can have a filling effect. Because they are relatively small polymers, with consequently weak tanning power, these syntans work best as retanning agents; they are applied after main chrome tannage, to modify the handling properties of the leather (Marion and Roy, 2006).

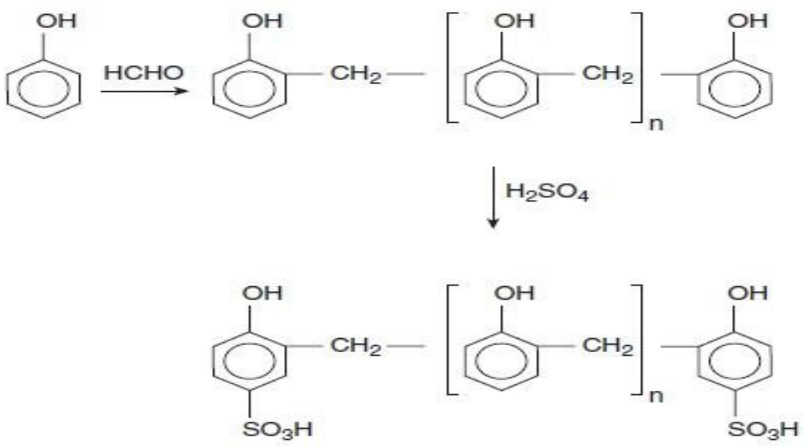


Figure 2.5: The Novolac synthesis of syntans

4.6.6.3 Replacement syntans

By increasing the tanning power of syntans, the agents may be classified as replacement syntans, by which it is meant that they could replace vegetable tannins. These syntans can be used for solo tanning, because their properties of tanning are comparable with plant polyphenols. Again, there is no clear distinction between the retanning syntans and the replacement syntans, the difference lies in the degree of the effects. Base materials for syntans can range from the simple to the relative complicated. In addition, the bridging groups may be more diverse, including dimethyl methylene, ether, and urea. They rely less on sulphonate groups for their reactivity, but synthesis by the Novolac method may incorporate some sulphonic acid functionality. The replacement syntans vary in their effects on leather, but can produce properties similar to vegetable tannins, including raising the shrinkage temperature to 80 – 85°C. They are still used to prepare hide to receive vegetable tannins, though they can be used in their own right, to make leather that is more lightfast than vegetable-tanned leather; a common use is for making white leather (Marion and Roy, 2006).

2.7 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: (Madhan, B.et al. 2001) 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 (Madhan, B.et al. 2001).

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. 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 (Lampard, G. S. and Covington, A. D. 2004).

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. 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 T_s, so blocking of carboxyl groups by methylation did not affect the final shrinkage temperature (Kallenberger, W. E. and Hernandez, J. F. 1984).

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 (Kallenberger, W. E.

and Hernandez, J. F. 1983). 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 2.6) is based on complexation of metal ion by the metal-polyphenol. The chelated complexation of the metal centre creates cross links 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 (Covington, A. D. 2008).

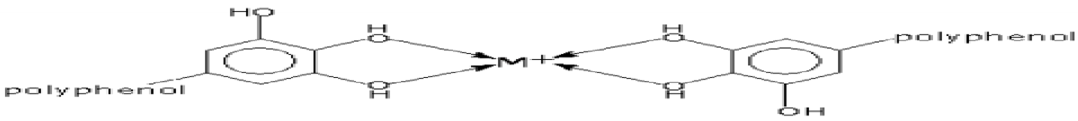


Figure 2.6 Schematic model of the semi-metal tanning interaction

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 trihydroxybenzoate) 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 (Brewer, G. J. and Prasad, A. S.; Eds. 1977).

In the past, zinc as a tanning agent has attracted very little attention. Zinc (II) being a $3d^{10}$ system can form tetrahedral complexes. Reports exist on the usage of zinc salts for preservation of raw hides/skins (Hausam, W.; Boll. 1941).

Vegetable-zinc combination tannage has been shown to provide higher shrinkage temperature (Morera, et al. 1996). Procter (1922), 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 (JALCA. 1962). Tanning agents based on aluminum-zinc combination have been shown to increase the shrinkage temperature of leather above 90^{o} C. 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.

2.8 Tannins

2.8.1 Nature of tannins

Tannins are one of the natural products which are widely distributed in plant kingdom, they are composed of different phenolic compounds (A. S. Hussein, 2011).

Tannin is a biochemical with established markets and many end uses. We all consume some tannin in our daily diet, as it is present in many fruits, berries, legumes, nuts and beverages such as wine, cider, fruit juices and tea (reviewed by Serrano,*et al.* 2009). Tannins have been shown to possess e.g. bactericidal, molluscicidal, antihepatoxic and antitumor activities (reviewed by Haslam, 1996). Industrially produced tannins of plant origin are called vegetable tannins. Hydrolysable tannin is produced from the galls of Chinese nutgall tree (*Rhussemialata*) and Aleppo oak (*Quercusinfectoria*), the leaves and bark of Sicilian sumac (*Rhuscoriaria*), tara fruit pods (*Caesalpinaspinosa*), myrobalan nuts (*Terminaliachebula*) and the wood of the chestnut tree (*Castanea sativa*) (Bhat*et al.*, 1998). Condensed tannin is produced from the bark of wattle (*Acasiamollissima*and*A. mearnsii*) and the wood of quebracho (*Schinopsislorentzii*and*S. balansae*) (Bhat, *et al.* 1998). These two species produce extracts with a naturally high tannin and a low non-tannin content (Roffael,*et al.* 2000). The total production of tannins is in the range of 160 000 – 200 000 tons per year (Pizzi, 2006).

Tannins are an amorphous yellowish or light brown powder, flakes or sponge. Tannins are soluble in water and alcohol but insoluble in organic solvents. Extracts usually have three fractions (Covington, 2011): non tannins characterized by low molecular weight <500, tannins that have medium molecular weight i.e. 500 – 3000 and gums of high molecular weight >3000. They are used to convert hides and skins into leather. They come from plant sources, and they are called vegetable tannins. They have origins, however, and they differ in strength and in character, color, concentration and quality. Thus they produce leathers of different types- hard, soft, light colored, dark colored, heavy or light. These tannins can be used singly or in various combinations to produce different effects (Ebtesam, 2015).

Tannins are complex heteropolymers conveniently divisible into major type, hydrolysable and condensed tannin, according to their structure and origin (Mahdi 2001) (Table 2.1), the former contains ester and/or glycosidic linkages, and on hydrolysis yields acids, sugars, and/or alcohol. Gallic acid, ellagic acid, and glucose are common hydrolysis products. Tannins of this class occur in galls and leaves but are not very common in woods (Browning 1963, Mahdi 2001). The condensed tannins (phlobaphenes) on treatment with acid are polymerized further, rather than being hydrolysed in to simple substances. Freudenberg (1920) suggested that they are built up of catechin units, and that the tannins from different sources chiefly in the hydroxylation pattern. The main components of the codenesed tannin are the catechins (flavan-3-ols) and the leucoanthocyanidins (flavan-3, 4-diols).

Table 2.1 Classification of plant tannins (Mahdi 2001)

Nomenclature	**Structure**	**Molecular weight**
Condensed tannin		
Proanthocyanidin	(oligomers of catechin and flavan-3,4-diols flavanes)	1000-3000
Hydrolysable tannin		
Gallotannins	Esters ofgallic acid and glucose	1000-1500
Ellagitannins	esters of hexahydroxydiphenic acid and glucose	1000-3000
Prototannins		
Tannin precursors	Catechin and gallocatechin,flavan-3,4-diols	200-600

2.8.2 Tannin types

2.8.2.1 Hydrolysable tannins

Hydrolysable tannins are esters of sugar with single or mixture of polyphenolic carboxylic acid. The sugars are usually glucose but in few cases, polysaccharides or branched chain sugars are known to occur. The esters in these are readily hydrolyzed by the action of acids, alkalis or enzymes such as tannase. The hydrolysable tannins are further classified into a- gallotannins, which give Gallic acid figure 2.7

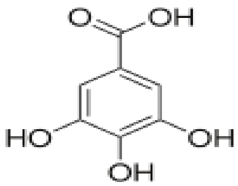


Figure 2.7 Gallic acid

b- ellagitannins, which give hexahydroxydiphenic acid normally isolated as a stable lactone from ellagic acid on hydrolysis. The hydrolysable tannins give clear well defined spot when chromatographed in dilute acetic acid (5-10) in the first direction and n-butanol- acetic acid- water (4: 1:5 v/v upper layer) in the second direction. Various combination of the second solvent system e.g. sec-butanol- acetic acid- water (14: 1: 5) (white et al. 1958), n-butanol- acetic acid- water (6: 1: 2) (Hill and Carle 1960), benzyle alcohol-tert. Butyl alcohol- iso constituents are readily located on chromatograms spraying with ammoniacal silver nitaate (Partridge 1948) ferric chloride and potassium ferriccyanide, potassium iodate solution and Gibbs reagent (Haslam 1966).

Studies on the chemistry of galltannins started with isolation of tannin by Macquer and Monnet (1778) and Schele (1787). Later Freudenberg (1933) and Karrer (1923) did pioneering work on the chemistry of gallotannins. The simplest hydrolysable tannins (Haslam 1989) are simple polygalloyl esters of glucose. The prototypical gallotannins is pentagalloyl is glucose (β- 1,2 ,3 4, 6- pentagalloy- O- D glucopyranose) is shown in Figure 2.8. pentagalloyl glucose (PGG) has given identical ester linkages that involve aliphatic hydroxyl groups of core sugar. The number of ester links in a tannin molecule in central core.

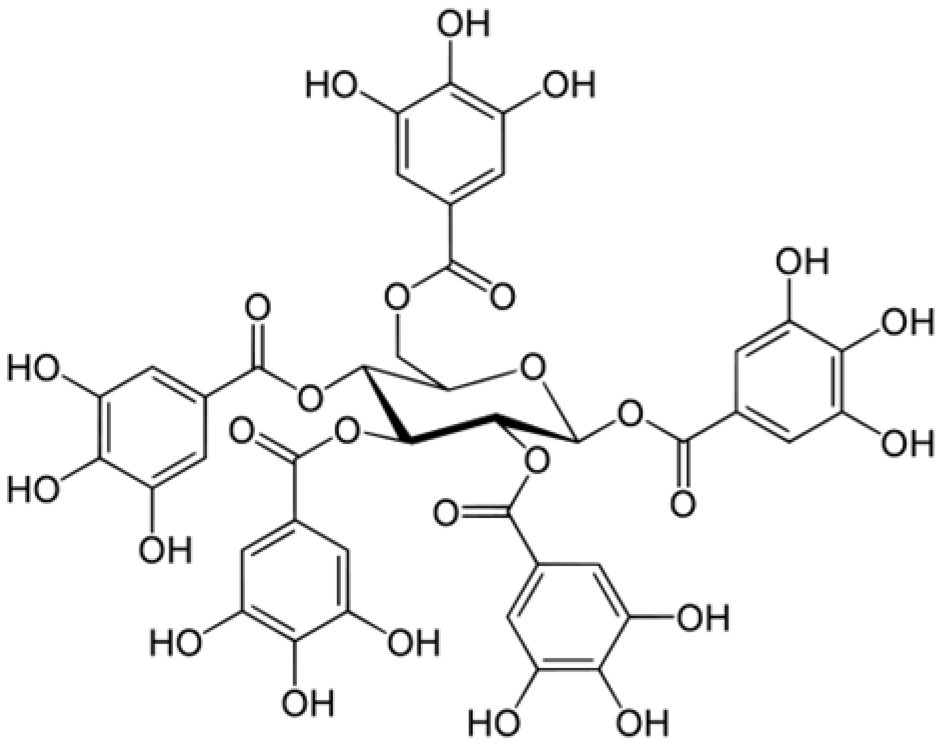


Figure 2.8 β- 1,2 ,3 4, 6- pentagalloy- O- D glucopyranose

The tannic acid extracted from Chinese tannins (*Rhussemialata*) (Hagerman et al 1997) is simplest of gallotannins available and structure is similar to the pentagalloyl glucose with few more galloyl groups attached to them. Otherwise gallotannins are more complex in nature. Gallotannins occur in Acer,Quercus, Rhus and Pelargonium species (Haslam. 1986). Simple gallotannins with up to 12 esterified galloyl groups and core glucose are routinely found in tannins from sumac or oak galls (Okuda et al 1995).

The ellagitannins are differentiated from gallotannins by the formation of ellagic acid hydrolysis. Ellagitannins occur widely in woody dicotyledon plants with esters of gallic acid. Schmidt (1954) showed that ellagic acid dose not occur as such in the structure of tannin but will produced by lactonization of hexahydroxydiphenic acid as indicated by alkaline hydrolysis of methylated ellagitannins and further showed that the optical activity of hexahydroxydiphenic acid observed is due to restricted rotation in diphenyl nucleus. Oxidative coupling of galloyl groups convert gallotannins. The simple ellagitannins are esters of hexahydroxydiphenicacid (HHDP). HHDP spontaneously lactonize to ellagic acid in aqueous solution i.e. HHDP spontaneously dehydrated to the lactone form, ellagic acid (Feldman. 2000).

The insoluble deposits, which settle out in ellagitannin liquor are known to tanners as bloom. Bloom contain ellagic acid and large molecules containing glucose and gallic acid and its derivatives e.g.chebulinic acid. Oak bark, valonia, chestnut and myrobalans are examples of ellagitannins. Corilagin was the first ellagitannin to be isolated from *Caesalpiniacoriaria,Terminaliachebula*(King and White 1957). Chebulagic acid occurs in myrobalans and divi-divi extracts. On complete hydrolysis with dilute sulphuric acid, it yields equimolar proportions of gallic acid, gallic acid chebulic acid and glucose, while the addition of on mole of water gives neochebulagic acid (Schmidt et al 1954).

2.8.2.2. Condensed tannins (Proanthocyaidins)

Proanthocyanidins (PAs) are more widely distributed than hydrolysable tannins (HTs). They are oligomers or polymers of flavonid units (i.e flavan-3- ol)linked by carbon- carbon not susceptible to cleavage by cleavage by hydrolysis. Proanthocyanidins are often called condensed tannins due to their condensed structure. Their multiple phenolic hydroxyl groups lead to the formation of complexes with proteins (Harborne.

1998)and metal ions (Foo et al 1997). The term ,proanthocynidins, is deived from the acid catalized oxidation reaction that produces red anthocyandins upon heating PAs in acidic alcohol solution (Giner 1996). The most common anthocyandins produced are cyanidin (flavan- 3- ol, from procyanidin) and delphinidin (from prodelphinidin). Proanthocyanidins may contain from 2 to 50 or greater flavonoid units. PAs polymers have complex structures because the flavonoid units can differ for some substituents and because of the variable sites for interflavan bonds (Hemingway and Karchesy 1989).

Anthocyanidin pigments are responsible for wide array of pink, scarlet, red, mauve and blue colors in flowers, leaves and fruits. They are also responsible for a stringent taste of fruits. Proanthocyanidins carbon- carbon bonds are not cleaved or hydrolysis. Condensed or flavonoid tannins being structurally related to flavonoid group of compounds, form insoluble “phlobaphenes”or tannins reds on the treatment on mineral acid in aqueous media. The typical structure of flavonoid is shown in Figure 2.9

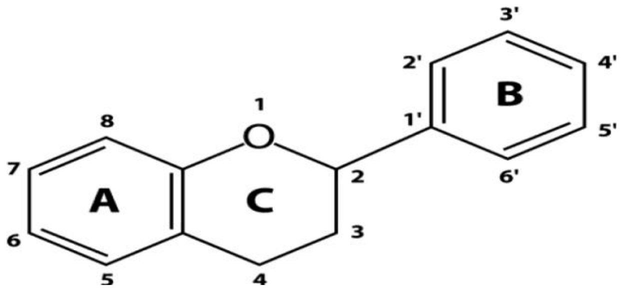
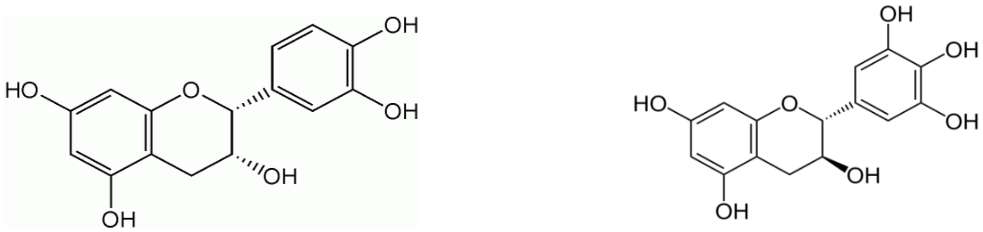


Figure 2.9 Structure of flavonoids

They are widely distributed in nature, in particular among certain families such as Fagaceae (chestnut, oak), Anacardiaceae (quebracho), rhizophoraceae (Mangrove) and Myrtaceae (eucalyputs). The condensed tannins are studies by two – dimensional paper chromatography using the solvent systems 6% acetic acid in the first direction and n-butanol: acetic acid: water (4:1: 5 v/v upper layer) (Harborne 1959) in the second direction. From time to time different solvents systems were used on different absorbents (Haslam 1975) for separating individual constituents of condensed tannin extracts. The chromatograms are sprayed generally with

a) Ferric chloride
b) Ferric chloride and potassium ferricynide
c) Ethanolic vanillin and hydrochloric acid
d) p-toluenesulphonic acid etc.(Roux 1957).

The catechins (flavan-3-ols) have been considered to be the phenolic precursors of condensed tannin (Freudenbergs 1920). Hatchway (1957) classified condensed tannins into different groups consists of condensed tannins where flavan- 3- ols are principal accompanying polyphenols. Whereas the second group consists of flavan- 3, 4-diol as important accompanying polyphenols. Weinges et al (1969) proposed that these two group of substance should be named as leucoanthocyanidins and proanthocyanidins on acid treatment. Proanthocyanidins (condensed tannins) are polymeric flavonoids. The flavonoids are diverse group of metabolites based on heterocyclic ring system derived from phenylalanine (B) and polyketide biosynthesis (A). The most widely studied condensed tannins are based on the flavan- 3- ols (-) epicatechin and (+) catechin Figure 2.10



Epicatechin catechin

Figure 2.10 Structure of epicatechin and catechin (Flavan- 3- ols)

Addition of a third phenolic group on the B-ring yields epigallocatechin and gallocatechin (Hagerman 1992). The best condensed tannins are linked via a carbon- carbon between C8 of terminal unit and C4 of the extender. The four common modes of coupling are illustrated by the dimmers isolated by Haslam (1989), and originally named B-1, B-2, B-3 and B-4. The more complete names specify the position and stereochemistry of the interflavan bond completely. In addition to these dimmers, linked by C6 of the terminal unit and C4 of the extender have been isolated. The products of the acid butanol reaction are unmodified terminal unit and the colored anthocyanidins produced by extender unit (Porter et al 1986) and epicatechin- based polymers produce cyanidin and thus are know as procyanidins. Gallocatechin and epigallocatechin- based polymers yield delphinidin, and raremono- 3ol based polymers yield pelagronidin.

Important group of condensed tannins are 5- deoxy- flavan- 3 ols polymers. Branching is common on these tannins, because of the reactivity of the 5-deoxy A ring. Profisetinidins and Profisetinidins comprise the major tannins found in quebracho and acacia tannin preparations. Acid butanol reaction yields the 5- deoxy anthocyanidins fisetinidin and robinetinidin. Flavan-3, 4-diols are monomeric flavonoids that yield the anthocyanidins upon treatment with heat and acid. Flavon- 3, 4- diols when heated with acid, yield varying amount of coloured amorphous polymers in addition to the corresponding anthocyanidins. This behavior closely resembles that of the condensed tannins, which under similar conditions also give amorphous phlobaphenes. Bate- Smith and Swain (1992) suggested that both flavan-3, 4- diols and flavan-3-ols acted in nature as precursors of these tannins. Freudenberg (1956) indicated that flavan- 3- ols constitute the terminal unit in most condensed tannins.

2.9 Commonly used vegetable tanning materials

Different vegetable tanning materials have been used around the world to process hides and skins into leathers depending on their availability and percentage of tannin concentration. Some of important plants used in tanning and their tannin concentration are chest nut 10.7%, quebracho 20%, cutch 35%, sumack leaves 25%, avaram bark 18%, babul bark 12%, konam bark 11-14%, goran bark 26-36%, myrobalam 30-40% , wattle tree 30-40%, kahra 16%, ashan bark 12%, dividivi 35-45% tannin, sandri bark 11%, dhundri bark 28-31%, gurjan bark 35%, gorra bark and behra nuts (Wamegah, 2014; Musa and Gesmelseed, 2012;Alex, 2015).

2.10 Garad (Acacia *nilotica)*

2.10.1 Description of garad(Acacia *nilotica)*

Synonyms:

Mimosa nilotica L.

M. scorpioides L.

M. arabica Lam.,

Acacia Arabica (Lam.) Willd.

1st. Scorpioides (L).

Arabic name: Sunt (tree); garad (fruit).

Family: Mimosaceae.

Description: tree 4-25 m high and 10- 60 cm in diameter. Bark dark grey, dark brown or black (especially on var. *tomentosa)*, rough, deeply fissured longitudindinally, flaking off in large irregular patches. Blaze 1- 1.5 cm thick; slash red – brown with blackish streaks, hard (Elamin 1990).

Four sub species occur in Sudan:

- *ssp. nilotica* with glabrous pods strongly constricted between the seeds.
- *ssp. pubescens* (Benth) Brenan (*Syn, A. arabica*)(Lam Willd). With pubescent pods, strongly constricted between the seeds.
- *ssp. Adansonii* (Guill, and per.) Brenan – with the pods only slightly constricted between the seeds.

- ssp tomentosa (Benth). Brenan – pods necklace – like narrowly and regularly constricted between seeds, tomentose.

Flowering time: July-September.

Fruiting time: March-May.

Distribution: It is found in the Sahel and the adjoining Sudan savannah from the Atlantic Coast to East Africa and across the Arabian Peninsula to India. Subspecies *adansonii* is confined to flooded areas, it is also found on sand under rainfall of as low as 300 mm, in general is confined to the region west of El Obied. Subspecies *subalata* is found in the Southeast Sudan from Torit eastwards. Sub species *tomentosa* prefers clay, alluvial soils and tolerates long, periodical inundation. It is a tree that prospers on depressions and rivers beds, on the banks of seasonal ponds especially along Blue Nile. Subspecies *nilotica* is more common along the White Nile, and in Western Sudan.

2.10.2 Uses of garad (Acacia nilotica): The wood is dark in colour , very hard and heavy and very durable. Its main use in the Sudan is for railway sleepers, but sawn timber is also used for native beds, and building construction of native boats. The firewood is of excellent quality, but the charcoal is liable to emit sparks when burning. Roasted seeds serve as a spice. In some regions, young pods are eaten as a vegetable; they serve, as well as the leaves and shoots, as forage for goats, sheep and camel, occasionally also for cattle. In some parts of India, A. *nilotica*is said to be the most important forage tree. One tree can produce up to 80 kg of pods per year (Von Maydell 1986; Mahdi 2001). Tannin, which is of great importance in the Sahel, has its highest quality when produced from green pods. They contain about 30% of tannin (not more than about 15% when mature; the bark has over 20%). Seeds must be removed from the pods for manufacture of high quality leather (Von Maydell 1986; Mahdi 2001). The pods, know in the Sudan garad , are valuable tanning materials and are widely used by local tanners. Black, red or yellow dyes are produced from the pods as well as from the gum. Ink is made from the pods too.

Tannin content: Deseeded sun pods from both eastern and western Sudan generally contain from 30-40% of tannin. Ripe pods contain much less. The proportion of the tannin in the husk may be up to 45%. The presence of seeds causes de facts in the tannin due to mucilage. The bark of smaller branches and roots contain 18-20% of tannin, and that of the trunk 18-23%. In the ssp.*adansonii* these parts are even richer, the root bark containing up to 36.4% smaller branches up to 25.6% and inner bark of the trunk also has a large amount (Broun and Massey, 1929)

2.10.3 Chemical composition and nutritional value of *Acacia Nilotica*

The mean content of trace and essential mineral elements (g/100g DW) in the mature dry seed of *Acacia Nilotica* samples is shown in table 1. The samples were analyzed by wet digestion method and standardized international protocols were followed for the preparation of material and analysis of mineral contents and analyzed by Atomic Absorption Spectrophotometer (KarimAbbasian, et al. 2015).

Table 2.2 The Mean content (g/100g DW) composition of the mature dry seeds of A. *Nilotica* from Hormozgan Province, Iran

Minerals	Mean content ± SD* (g/100 g)	Minerals	Mean content ± SD* (g/100 g)
Sodium	0.0421 ± 0.0001	Manganese	1.0911± 0.0111
Potassium	2.1006 ± 0.0036	Phosphor	8.6778 ± 0.2719
Calcium	0.6340 ± 0.0091	Iodine	0.9871 ± 0.1206
Magnesium	0.4602 ± 0.0026	Cobalt	0.1208 ± 0.0021
Iron	203.11 ± 25.067	Sulphur	2.4350 ± 0.1111
Copper	322.73 ± 20.56	Fluorine	0.0052± 0.0052
Selenium	0.003 ± 0.001	Lithium	0.002 ± 0.0005
Zinc	108.703 ± 23.778	Molybdenum	0.001± 0.0

*SD = Standard Deviation

Proximate composition and physicochemical characteristics of the samples has shown in table 2 , based on the fresh weight. (Karim Abbasianet al 2015).

Table 2.3 Proximate analysis of A. *Nilotica* from Hormozgan Province, Iran

Nutrient	Percentage (%)
Dry Matter(DM)	91.3
Crude Protein (CP)	25.3
Crude Fiber (CF)	28.4
Ash	13.1
Fat	3.4

2.11 Vegetable Tannin Extracts Manufacture

Traditionally the tannins are extracted with water as solvent in open vats at moderate temperature. However, water used for extraction (leaching) should not contain iron and should be soft (Sundararao 2001). The commercial vegetable tannin extracts or tan liquors as they are popularly known in the leather industry are mixtures of polyphenolic compound with a definite T/NT ratio, astringency etc, along with other plant products.

The manufacture of the vegetable tannin extract is essentially based on the extraction of tannins from the tanning material using a suitable solvent, usually water, followed by concentration and spray drying to get powder or solidification to get solid (block) extract Figure 2.11**.** The following steps are involved in the process (Sundararao,2001): (i) Selection of raw materials (ii) Size reduction – crushing and grinding (iii) Leaching (extraction of tannins)

(iv) Settling (v) Filtration (vi) Concentration (evaporation) (vii) Bleaching (viii) Drying-solid (Block) extracts, Spray dried powder (ix) Packing.

2.11.1 Selection of raw materials

Selection of raw material is made on basis of different criteria like tan/non-tan content, and good colour, ect. The raw materials should be free from fungal/insect attack of rotting and should be fresh.

2.11.2 Size reduction-crushing and grinding

Bark of wattle and babul are disintegrated into small size (5-15mm log) and nuts like myrobalans are crushed 1:10mm. The size reduction helps better leaching of soluble materials. Technically, there is several advantage of employing small particle size for achieving high extraction.

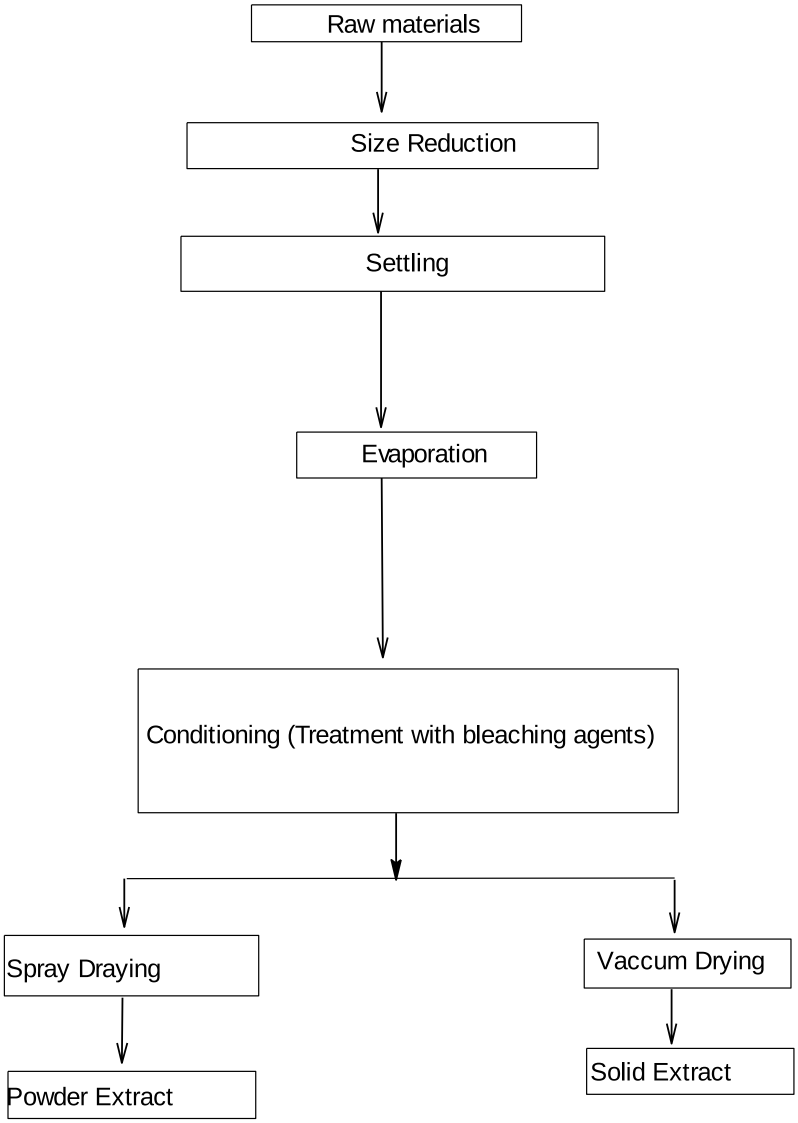


Figure 2.11 Process block diagram for the manufacture of vegetable tannin extracts

2.11.3 Leaching (Extraction of tannins)

The extraction of tannins from the physically disintegrated plant material is by solid-liquid extraction, generally by the following processes (Purushotham, et al. 1992):

1) Open vat extraction
2) Rotary system
3) Pressure autoclaves
4) Vacuum extraction (Nanceprocess).
5) Gases lift agitation method.

2.11.4 Settling and filtration

The liquor withdrawn from the leaching battery is collected in a settling tank and is allowed to settle down for about 4-6 hours to separate the insoluble matter and any foreign matter and sent for filtration. Gravity filter is more ideal to filter the leach liquor, which is filtered using a filter cloth of 10 micron (Purushotham 1992).

2.11.5 Concentration (Evaporation)

The filtered liquor, which contains generally 9-10% solids is further concentrated to 35-40% in a suitable evaporator is recommended for commercial use because of steam economy and suitability of carrying evaporation under vacuum as the tannins are heat sensitive.

2.11.6 Bleaching

The manufacture of tannin extract is basically a physical process involving unit operations like leaching (extraction), evaporation (concentration) and drying. The only unit process involved is the bleaching of extracted tannin liquor to get a lighter colored product. Bleaching is generally carried out by treating the concentrated liquor sodium bisulfate, sodium sulphite and sodium hydrosulfite for 4hr followed by oxalic acid for 1hr (in case the liquors are to be left overnight for more than 10 hours, addition of suitable PCP-free preservative is suggested) (Purushotham 1992).

2.11.7 Solid extract

Solid extract is produced from the concentrated liquor (35-40%solid) by further evaporating it in a vacuum pan with continuous stirring until a very viscous liquid containing about 85% solid is obtained. The slurry so obtained is run into wooden blocks and left as such for settling into solid extract with about 15% moisture (purushotham 1992).

2.11.8 Powder extract

The liquor containing 35-40% solids is spray dried to get the powder extract with 4-6%. Recently granulated powders are introduced to avoid dust pollution and occupational health hazards due to the fine nature of spray dried powders.

2.11.9 Packaging

As most of tanning extracts are hygroscopic and light sensitive, they are packed in bituminized polythene lined gunny bags in 25kilo packs. The bags will bear markings such as batch number and lot number, date of manufacture, and warnings like use no hooks and keep in cool and dry place etc. it is very essential to note that iron hooks will produce darker colour extracts (Sundararao 2001).

2.12 Occupational Health and Safety from tannery

Tanning and leather finishing processes involve the use of a variety of hazardous chemicals. Guidance on the management of hazardous materials, including handling, storage, and transportation, is provided in the General EHS Guidelines.

Occupational health and safety issues associated with the construction and decommissioning of tanning and leather finishing facilities are common to those of most large facilities and are addressed in the General EHS Guidelines. Specific occupational health and safety issues associated with the operation of tanning and leather finishing facilities primarily include the following:

- Exposure to chemicals;
- Exposure to biological hazards (Environmental, Health, and Safety Guidelines for Tanning and Leather Finishing.2007).

2.12.1 Chemical Hazards

Tannery workers may be exposed to chemical hazards during loading, unloading, handling, and mixing of chemicals; during the washing, and disposing of chemical containers; and during the management and disposal of chemical waste and effluent. Hazardous chemicals should be managed according to the guidance in the General EHS Guidelines. Additional recommendations applicable to tanning and leather finishing facilities include the following:

- Replace organic solvent-based chemicals with water-based chemicals in degreasing and finishing processes;
- Limit exposure to hazardous chemicals by promoting chemical handling procedures, and dosing and transferring chemicals in fully or partly closed systems using automated systems;
- Implement management procedures and controls for discharge of floats from paddles and drums;
- Use equipment and techniques (e.g. roller coating) to minimize indoor air pollution (e.g. during spraying and general application of finishing treatments);
- Use air extraction systems and ventilation in areas / machines for dry shaving, buffing, dedusting, spraying, and weighing (e.g. chemicals);
- Use of personal protection equipment (e.g. gloves, glasses boots, aprons, masks, hoods, respirators), particularly in the wet activity areas of the tannery. Respirators / masks with particulate filters and glasses should be used when handling powder and liquid chemicals (Environmental, Health, and Safety Guidelines for Tanning and Leather Finishing.2007)

2.12.2 Chemical Storage and Handling

The following measures should be employed for tanning and leather finishing facilities:

- Chemicals that will react should be segregated. Specifically, acids should be stored away from sodium sulfide, and alkalis away from ammonium salts, to prevent accidental mixing and release of dangerous gases (e.g. H_2S, NH_3);
- Pipes, valves, and other equipment should be designed to prevent incorrect addition or mixing of incompatible chemicals (e.g. from a tanker into the wrong storage tank, particularly for acid into a sulfide solution);
- Small containers (e.g. dyes and fatliquors samples) should be safely stored on racks and shelves. Heavier chemical containers (particularly those containing liquid chemicals, such as acids) should be stored on wooden or plastic pallets at the floor level;
- Chemicals should be distributed from a gangway located over the beamhouse, and the tanning / post-tanning drums. The gangway should be equipped with adapted tanks connected to the drum axle.

2.12.3 Biological Hazards

Workers may be exposed to disease-agents such as bacteria, fungi, mites, and parasites which may be present in the hides or as part of the manufacturing process. Management measures that can be taken to avoid the negative consequences of worker exposure to biological hazards include the following:

- Inform workers of potential risks of exposure to biological agents and provide training in recognizing and mitigating those risks;
- Provide personal protective equipment to reduce contact with materials potentially containing pathogens;
- Ensure that those who have developed allergic reactions to biological agents are not working with these substances.
- Table 3. Presents effluent guidelines for this sector. Guideline values for process emissions and effluents in this sector are indicative of good international industry practice as reflected in relevant standards of countries with recognized regulatory frameworks (Environmental, Health, and Safety Guidelines for Tanning and Leather Finishing.2007).

Table 2.4 Effluent levels for tanning and leather finishing

Pollutant	Units	Guideline values
PH	S.U	6.9
BOD5	mg/L	50
COD	mg/L	250
Total suspended solid	mg/L	50
Sulfide	mg/L	1.0
Chromium (hexavalent)	mg/L	0.1
Chromium (total)	mg/L	0.5
Chloride	mg/L	1000
Sulfate	mg/L	300
Ammonia	mg/L	10

Oil and grease	mg/L	10
total nitrogen	mg/L	10
Total phosphorous	mg/L	2
Phenols	mg/L	0.5
Total coliformbacteria	MPN^a/100ml	400
Temperature increase	$_o$c	< 3^b
Notes: a MPN = Most Probable Number b At the edge of a scientifically established mixing zone which takes into account ambient water quality, receiving water use, potential receptors and assimilative capacity		

CHAPTER THREE

MATERIAL AND METHODS

3.1 Raw materials

Acacia nilotica **(garad) bark was** collected from City of El Geneina (West Darfur State) El Jaili (Khartoum State).

The samples were air-dried and reduced to powder with a star mill. The fractions passing through 40-mesh and retained on 85- mesh sieves were collected, thoroughly mixed and kept in tightly closed containers.

3.2 Analysis of Tannin

3.2.1 Preparation of Sample for Analysis

Garad bark was quantitatively analysis in order to determine their tannin and non tannin contents. Many quantitative methods have been suggested but only the gravimetric method (SLC 112 1996) based on the absorption of tannins by hide powder is of practical importance.

A known quantity of the resulting fine powder that would give, as nearly as possible, 4 gm per liter of tanning matter absorbable by hide powder was always taken for extraction using Procter extractor. Two liter of the extract of the required analytical strength was normally collected per sample.

The material was first soaked, in cold distilled water overlying a layer of sea- sand in the extractor overlying before commencing the extraction. Next morning draw off the infusion obtained, and continue the extraction at such uniform speed that 2 liter will be obtained in 4 hours.

After collected the first 150 ml at room temperature, the temperature was raised to 50ºC and the next 750 ml was collected. The temperature was again raised, as rapidly as possible, to boiling point, when the remainder (to make 2 liter) was extracted. A clear solution of the extract could be ensured because apart from its passing through a fine layer of sea sand, the delivery tube inserted in to the sand-bed always had a wide funnel- shaped end, which was tied to a piece of finely woven filter cloth.

By the time the two liter of the required tannin extract would have been obtained, the sample must have been wholly leached of its tannins. The extract used to cool to room temperature under running tap and then made up to the mark with distilled water.

3.2.2 Determination of moisture

2 gm of the finely ground material was dried to a constant weight at 98.5- 100° C in a vacuum oven (SLC 113 1996). (The constant weight was recorded when the last two weightings differ only by less 2 mg). If say x gm of moisture content been driven off, then percentage moisture content is calculated by:

$$\% \text{ moisture content} = \frac{x}{2} \times 100$$

3.2.3 Determination of total solid

50 ml of the unfiltered tannin extract was evaporated to dryness on water bath and dried to a constant weight in a vacuum oven at 98.5- 100° C in a vacuum oven (SLC 114 1996).

y = the amount of solids in 50 ml of the extract

z = the original weight of test material (crushed) extracted, then

$$\% \text{ total solids} = \frac{2000 \times y}{50 \times z} \times 100$$

3.2.4 Determination of total soluble

50 ml of the filtered tannin extract was evaporated to dryness over a water bath and dried to a constant weight in a vacuum oven 98.5- 100° C in a vacuum oven (SLC 115 1996).

If a = the amount of total soluble found tobe present in 50 ml of the filtered extract, then.

$$\% \text{ total soluble} = \frac{2000 \times a}{50 \times z} \times 100$$

3.2.5 Determination of insoluble

Insoluble was calculated by subtracting % total soluble and % moisture from 100 (SLC 118 1996)

3.2.6 Determination of non- tans

In this determination it is necessary to first prepare chrome tanned hide powder (SLC 116 1996). 6.25 gm of the dry hide powder was diluted ten time its weight with distilled water and shacked for about one hour. 1 ml of 3% chrome alum solution per gram of the dry hide powder was taken. The mixture was stirred continuously for several hours and left to stand overnight. The chrome treated hide powder was transferred to a filter cloth, allowed to drain and was then squeezed to remove excess water. A quantity of water, 15 times the weight of dry powder taken, was poured on to the powder in the filter cloth, and mixture thoroughly stirred for 15 minutes. The cloth containing the powder was then lifted out, allowed to drain, and then squeezed to about 75% moisture content. To the powder was added water, and again stirred as above. This process was repeated three times. Finally, the powder was squeezed to about 75% moisture content it was then broken up mixed uniformly, before it was weighted.

A quantity of wet chromed powder, containing 6.25 gm of dry hide powder was added to a suitable shaker bottle containing 100 ml of unfiltered tannin extract. The bottle was then violently shaken by hand for 15 seconds before

It was transferred to mechanical rotator y shaker at an average sped of 60.r.p.m. for 10 minutes, after which the content of the bottle was wholly transferred onto a filter cloth supported by a funnel. When the powder had drained off water it was squeezed with hand and 1 gm of kaolin was added to the filtrate.

After allowing the kaolin to mix thoroughly, the mixture was filtered repeatedly until the solution the solution was clear. At this stage it was tested with gelatin salt to confirm whether or not the whole of the tannins had been absorbed by the hide powder.

50 ml of this filtrate was then evaporated to dryness and kept in the vacuum oven at 98.5- 100°C until a constant weight was obtained.

When the calculation for the non- tan was carried out, the residue weight was multiplied by a factor 1.2, because of the dilution of 20 ml of the water introduced into 100 ml of tannin solution by the wet hide powder.

If c = the amount of non- tan in 50 ml of the soluble fraction of the extract then

$$\% \text{ non-tan} = \frac{2000 \times c \times 1.2}{50 \times z} \times 100$$

3.2.7 Determination of tannin matter absorbable by hid powder

The tannin matter absorbed by the hide powder was the difference between the percentage of total soluble and non-tans (SLC 117 1996).

3.2.8 Determination of pH

The filtered tannin solution was employed and the pH was determined by using a pH paper, after it had been standardized using a buffer solution (SLC 120 1996).

3.3 Preparation of 70% Methanol garad bark Extract

Ground garad bark of known quantity have been soaked in 70% aqueous Methanol (1:10) and the mixture was kept at room temperature for 24 hrs. The methanol solution was removed and fresh lot of 70% aqueous methanol was added, the process continued till the extraction was complete. The combined 70% aqueous methanol extract filtered was evaporated to small volume by rotary evaporator and filtered off from the chlorophyll and viscous matter.

3.3.1 Fractionation of 70% Methanol garad bark Extract

70% methanol garad bark Extract was taken and extracted successively with hexane, diethyl ether and ethyl acetate using separating funnel and the solution were separately evaporated to dryness through rotary evaporator to give hexane soluble (Fraction I), diethyl ether soluble (Fraction II) and ethyl acetate soluble (Fraction III) and residue.

3.4 Garad bark Combination Tanning

3.4.1 Materials

Conventional processed pickled goat skins were taken for two combination tanning trials. Garad barks sourced from Sudan were used for the study. Preparation of Basic Aluminum Sulphate Solution and zinc Sulphate Chemicals used for retanning trials include mimosa and phenolic syntan. Chemicals used for post tanning processes were of commercial grade. Chemicals used for the analysis of spent liquor have been of analysis reagent.

3.4.2 Aqueous Extraction of Tannin from Garad barks

Ground Grade barks of known quantity were soaked in water (1: 10 w/v) at a temperature of 80±2°C in water bath for one hour, filtered through a piece of Cotton cloth and concentrated and used in combination tanning.

3.4.3 Preparation of Basic Aluminum Sulphate Solution

A known amount of aluminum sulphate was taken in a beaker and 150% of water (% based on the weight of aluminum sulphate) was added and the Solution stirred for 15-20 minutes, subsequently required amount of ligand (sodium citrate and sodium tartrate) was added and stirring continued for 45 min followed by slow addition of sodium carbonate until the pH raised to 3.5.For 0.5 M of aluminum sulphate, 0. 1M of ligand was added.

3.4.4 Garad bark Based Combination Tanning Trials

Pickled goat skins have been used for two combination tanning trials: The first trial, Al-Garad bark and Garad bark -Al tanning are given in table 3.1 and 3.2 respectively. The amount of Aluminum sulphate used for the combination tanning trial has been 2% Al_2O_3 in the experimental process. A control process for all trials has been carried out using Garad bark only as given in table 3.3. The second trial zinc- garad bark process mentioned in table 3.4 and garad bark- zinc process mentioned in table 3.5. The post tanning process as mentioned in table 3.6 has been followed for experimental and control leathers.

Table 3.1 Formulation of Garad bark−Aluminum combination tanning system for pickled goat skin to produce Upper Leather

Process	**%**	**Product**	**Duration (min)**	**Remarks**
Pickling pelt	50	Water	10	
	10	Salt	10	
	1.2	Sulphuric acid	3× 15	pH 2.8-3.0
Adjustment of the pH	100	Water		
	1	Sodium bicarbonate	3*15	pH 4.5-4.7
Tanning	2	Phenolic syntan	30	
	10	Garadbark	120	
	10	Garad bark	120	
	2	Al_2O_3 (prepared Aluminium Sulphate solution)	90	
Basification	1	Sodium bicarbonate	3*15	Check the pH to be 4.Drain the bath and pile over night .Next day sammed and shaved to 1.2mm .The shaved weight noted

Table 3.2 Formulation of Aluminum−Garad bark tanning system for pickled goat skin Upper Leather

Process	%	Product	Duration (min)	Remarks
Pickling pelt	50	Water	10	pH 2.8-3.0
Aluminium tanning	2	Al_2O_3 (prepared Aluminium Sulphate solution)	120	
Adjustment of the pH	1	Sodium bicarbonate	3*15	pH 4.5-4.7
Tanning	2	Phenolic syntan	30	
	10	Garad bark	90	
	10	Garad bark	90	
Fixing	0.5	Formic acid	3*10+30	Check the pH to be 3.5.Drain the bath and pile overnight. Next day sammed and shaved to 1.2mm .The shaved weight noted

Table 3.3 Formulation of control Garad bark tanning system Upper Leather

Process	**%**	**Product**	**Duration (min)**	**Remarks**
Pickling	100	Water	10	
	10	Salt	10	
	1.2	Sulphuric acid	3× 15	pH 2.8-3.0
Adjustment of the pH	100 0.75	Water Sodium bicarbonate	3*15	pH 4.5-4.7
Tanning	2	Phenolic syntan	30	
	10	Garad bark	120	
	10	Garad bark	120	
Fixing	0.25	Formic acid	3*10+30	Check the pH to be 3.5.Drain the bath and pile over night. Next day sammed and shaved to 1.2mm .The shaved weight noted

Table 3.4 Formulation of Garad bark−Zinc combination tanning system for pickled goat skin to produce Upper Leather

Process	**%**	**Product**	**Duration (min)**	**Remarks**
Pickling pelt	50	Water	10	
	10	Salt	10	
	1.2	Sulphuric acid	3× 15	pH 2.8-3.0
Adjustment of the pH	100	Water		
	0.75	Sodium bicarbonate	3*15	pH 4.5-4.7
Tanning	2	Phenolic syntan	30	
	10	Grade bark	120	
	10	Grade bark	120	
	0.25	Formic acid	3×15+30	pH 2.8-3
	9	$ZnSO_4.7H_2O$	90	
Basification	0.75	Sodium bicarbonate	3×15+30	Check the pH to be 4.Drain the bath and pile over night .Next ,day sammed and shaved to 1.2mm .The shaved weight noted

Table 3.5 Formulation of Zinc−Garad bark tanning system for pickled goat skin to produce upper lleather

Process	%	Product	Duration (min)	Remarks
pickling	100	Water	10	
	10	Salt	10	
	1.2	Sulphuric acid	3× 15	pH 2.8-3.0
Z tanning	9	$ZnSO_4.7H_2O$	90	
Adjustment of the pH	1	Sodium bicarbonate	3×15+30	pH 4.5-4.7
Tanning	2	Phenolic syntan	30	
	10	Garad bark	120	
	10	Garad bark	120	Check penetration
Fixing	0.5	Formic acid	3*10+30	Check the pH to be 3.5.Drain the bath and pile over night .Next day sammed and shaved to 1.2mm .The shaved weight noted

Table 3.6 Formulation of Post-tanning process for control and experimental leathers

Process	**%**	**Product**	**Duration (min)**	**Remarks**
Washing	200	Water	10	Drain
Neutralization	100	Water		
	1.5	Sodium formate	30	
	1	Sodium bicarbonate	3× 15	pH 5-5.5
Retannig	100 8	Water Synthetic tannin	90	
Fatliquoring	9	Synthetic fatliquor	40	
Dyeing	3	Acid dye brown	30	
Fixing	1.5	Formic acid	3 x 10 +30 min	pH 3.5
Washing	200	Water	10 min	Leathers were piled overnight; Next day set, hooked to dry, staked, trimmed and buffed

3.4.5 Determination of Shrinkage Temperature

The shrinkage temperature of control and experimental leathers was determined using this shrinkage tester (McLaughlin and Thesis 1945). 2x 0.5 cm^2 piece of tanned leather 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.

3.4.6 Analysis of Spent Liquor

The spent liquor from control and experimental tanning processing were collected, filtered and analyzed for chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), and total dissolved solids (TDS) as per standard procedures (Clesceri 1989).

3.4.6.1Chemical oxygen demand (COD)

Chemical oxygen demand is defined as the amount of a specified oxidant that reacts with the sample under controlled condition. The quantity of oxidant consume is expressed in term of its oxygen equivalence. COD often is used as a measurement of pollutant in waste water and natural water. Reagents used for determination of the COD include, standard potassium dichromate 0.25N, COD acid, standard ferrous ammonium sulphate (FAS) 0.1N, ferroin indicator, mercuric sulphate. Take sample of the spent liquor and made up to 100 ml distilted water and from that take 2.5 ml and transferred to clean COD tube, add 1.5 ml potassium dichromate and 3.5 ml of COD acid. Add spatulaof mercuric sulphate. Also the blank was prepared in the same way with 2.5 ml distilled water; 1.5 ml potassium dichromate and 3.5 ml of COD acid and mercuric sulphate .All tubes were kept in the COD incubator at 150°C for two hrs. After incubation samples were titrated against ferrous ammonium sulphate in burette for the COD value using few drops of ferroin indicator and the point of the reaction is the persistence of reddish brown color.

$$\text{COD (mg/l)} = (A - B) \times N \times 800 / \text{volume of sample}$$

A = volume of FAS used for titration of the blank (ml)

B = volume of FAS used for titration of the sample (ml)

8000 =Milliequivalent weight of oxygen × 1000 ml/l

N = Normality of FAS

3.4.6.2 Biochemical oxygen demand (BOD)

The biochemical oxygen demand determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirement of waste- water effluents and polluted waters. Apparatus and reagents used for determination of the BOD include, incubation bottles (300 ml capacity with ground glass stoppers), air incubator thermostatically controlled at 20°C, phosphate buffer solution, magnesium sulfate solution, calcium chloride solution, ferric chloride solution, manganese sulphate and alkali iodide- azide.

Procedure: Pipette suitable volumes of sample into bottles known capacity and the bottles were filled with sufficient dilution water to permit insertion of stopper without leaving air bubbles and keep blank using dilution water alone. Incubate the blank and diluted samples for 5 days in the dark at 20°C. After 5 days remove the bottle from incubator. Add 2 ml manganese sulphate solution, followed by 2 ml alkali iodide- azide reagent. After 2 min add 2 ml Con.H_2SO_4. Take 200 ml from the bottle for titration. Titration with sodium thiosulphate using starch as indicator. End point is disappearance of the blue color.

BOD (mg/l) = (Blank value–titrated volume of sample) × 300/ volume of sample

3.4.6.3 Total dissolved solids (TDS)

A well mixed sample was filtered through filter paper No 1 and the filtrate was evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solid.

Total dissolved solid (mg/l) = (A –B) × 1000/ sample volume

Where

A = weigh of dried residue + dish in mg

B = weigh of dish in mg

3.4.7 Visual Assessment of the Crust Leather

Experimental and control crust leathers were assessed for softness, fullness, grain smoothness grain tightness (break), 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 points indicate better property. The tanners evaluated the dyeing characteristics viz., uniformity of dye, shade intensity and differential dyeing for both experimental and control crust leathers.

3.4.8 Physical Testing

Samples for various physical tests from experimental and control crust leathers were obtained as per IULTCS methods. Specimens were conditioned at 20±2°C and *65±2%* R.H over a period of 48 hrs. Physical properties such as tensile strength, and tear strength were measured as per standard procedures. Each value reported is an average of two samples (2 value along the backbone and 2 value across the back bone).

3.4.8.1 Preparation for Physical Testing (Conditioning)

The specimens for physical testing were kept in a standard atmosphere of temperature 20±2^{o}C and relative humidity 65±2% over a period of 48 hrs.

3.4.8.2 Tensile strength

Tensile strength is the load per unit area of cross section required to pull apart or break a strip of leather material. The tensile strength of control and experimental leather were measured as per procedure given in (IUP 6, 2000).A dumb-bell shape leather sample parallel to the direction of backbone of the animal was punched out using a steel press knife of standard dimensions. The samples were of 9 cm total length and of 5 cm in the experimental region. After condition for 48 hrs at temperature 20±2°C and 65±2 % R.H., The thickness of the sample at the middle point and at two points midway between the middle and ends were measured as per procedure given in(IUP 4, 2000).The samples were tested in an Instron Universal Testing Machine. First the jaws were set 5cm apart. The sample was clamped such that 2 cm on both ends were clamped in the grips and 5 cm of the sample underwent elongation. In this way the Specimen was placed in the Instron Universal Testing Machine such that its long dimension was parallel to the direction of application of the force. The tension was distributed uniformly and symmetrically throughout the cross-section of the sample. The jaws were run at a speed of 10 cm/min. slowly the sample was elongated and was ruptured after reaching the maximum bearable tension. The load elongation curve at every moment was plotted by a strip chart recorder. From the plot the breaking load was noted and tensile strength was calculated buy sing the formula:

Tensile Strength (kg / cm^2) = (Breaking load (kg))/ (thickness x width (cm^2)).

3.4.8.3 Percent elongation at break

The Percent elongation at break was measured simultaneously while the Tensile strength was being determined. The separation of the jaws was noted from the automatic strop chart recorder in the Instron Universal Testing Machine corresponding to the belong point.

Percent elongation at break = (Increase in length at break/original length)

3.4.8.4 Tear strength

The Tear strength of control and experimental leather were measured as per procedure given in (IUP 8, 2000).A sample of the size *7.5 x2.5* cm was slit at rights angles to the grain and flesh sides for about half the length. One end of the piece formed by the slit was clamped in the upper jaw of the Instron Universal Testing Machine and the other end was fixed to lower jaw. When the Instron Machine was run, the sample teared. The average load corresponding to the tearing of the tongue was calculated from strip chart recorder. This load divided by the average thickness of the sample was taken to be the tearing strength of the samples in kg/cm. Control and experimental samples were tested for the determination of tearing strength parallel to the direction of the backbone, similar procedure was repeated for equal number of samples taken from direction perpendicular to the direction of backbone.

Tear strength (kg/cm) = Load (kg)/ Thickness (cm)

3.4.8.5 Grain crack strength and distension at grain crack

This method was intended to assess how much a material can stretched simultaneously in two directions without damaged (IUP 9, 2000). Principle of method: a circular specimen of the sample was clamped round its edge and gradually distended by forcing a small metal attached to a plunger through specimen. The distended crack appears on the Surface. Test specimen 44.5 mm diameter, test cut from testing area of leather. Test conditioned at 20±2ºC and 65±2% RH for 48 hours. Procedure: Tightly clamp the test specimen in the machine. Start the machine forcing plunger at rate of 0.2 + 0.05 mm/s. The load in kg and distension in mm at grain crack were noted.

3.4.9 Chemical Analysis of Leather

The chemical constituents such as %moisture, Cr_2O_3 content, total ash content, %oils and fats, % water soluble, hide substance; % insoluble ash and degree of tannage were carried out for control and experimental leathers according to standard procedures (Official Methods, 1965).

3.4.9.1 Preparation of Sample

The leather was cut into small pieces, to pass through a screen with circular perforations of 4 mm. The pieces were thoroughly mixed and brought to a state of homogeneity by keeping them in a closed container for at least one night. After determining their moisture content, they were stored in a jar for further analysis (ALCA, 1957).

3.4.9.2 Moisture content

A piece of tanned leather was taken and vas cut into small pieces in crucible. Initial weight of crucible and weight of crucible and leather were noted. The crucible was covered with a filter paper to prevent it from other contaminants and was dried in air oven at 100-105°C for a period of 5 hours, cooled and weighed. The process of drying, cooling and weighing was repeated until constant weight was obtained. Percentage of moisture was calculated from the difference in weights.

Weight of empty crucible = a gm

Weight of crucible + leather = b gm

Weight of crucible + leather after drying = c gm

Calculation:

$$\%\ \text{moisture content} = \frac{b-c}{b-a} \times 100$$

3.4.9.3 Determination of oils and fats

Oil and fats were determined as per procedure given in (SLC 4). 10 gm of leather sample was weighed accurately and put into soxhlet apparatus by means of thimble which was attached a previously weighed round bottomed flask. Oils and fats were extracted with petroleum ether (B.P 40-60°C) in a soxhlet extraction unit for not less than 4 hrs. The round flat bottomed flask was dried and weighed till a constant weight was obtained. After distilling the petroleum ether, the oils and fats in the flask were dried at 98-100°C for 3 hours, cooled and weighed. The process of drying, cooling and weighing was repeated until constant weight was obtained. The amount of oils and fats expressed as % of the weight of the sample.

Weight of leather sample = w_1

Weight of empty round bottomed flask = w_2

. Weight of round bottomed flask after extraction and drying = w_3

% oil and fat content $= \frac{w3 - w2}{w1} \times 100$

3.4.9.4 Determination of water soluble

The water soluble in control and experimental leather were determined as per procedure given in (SLC 4) (Official Methods, 1965). After the soxhlet extraction as described previously in section 3.4.9.4, leather was allowed to dry by spreading down on a clean surface and leaving it exposed to air but no heat. The oil free leather is transferred to a wide necked bottle of suitable capacity (usually 500 ml) and fitted with a rubber cork and 250 ml of distilled water was added to it. The contents were shaken in a shaker running at 55 to 60 rpm for 2hrs, the liquid is separated from the residual leather by filtration, using a Whatman No. 1 or 4 filter paper. The first 50 ml of the filtrate was rejected. To determine the water soluble, 25 ml of the clear filtrate was evaporated to dryness in an evaporating basin over water bath the residue was dried at 98.5-100°C for 3 hours. Then cooled in desiccators before weighing. The process of heating and weighing was repeated for constant weight.

Weight of leather sample = w_1

Weight of empty basin = w_2

Weight of basin and filtrate after drying = w_3

Weight of water soluble = $w_3 - w_2$

% water soluble = $\frac{(w3-w2)\times 250}{w1\times 25}\times 100$

3.4.9.5 Hide substance

Nitrogn in the leather is converted to ammonium sulphate by disgesting conc. H_2SO_4 in presence of a catalyst mixture. The ammonia liberated by the addition of excess caustic soda is distilled by titration. Reagents used for determination of the hide substance include. Standardized 0.2 N standard HCl, pure concentrated sulphuric acid (sp.gr.1.84), 40% NaOH solution, 4%boric acid solution, catalyst mixture ($CuSO_4$: k_2SO_4 1 : 10), mixed indicator (methyl red 1part + bromocresol green 5 parts each 0.1 solution in ethanol) . The hide substance was determined as per procedure given in (SLC 7). 0.5 gm of the leather was weighed accurately and transferred to a clean – dry Kieldahl flask.10 ml of concentrated sulphuric acid was added to the leather. The flask was placed in an inclined position and heated.5 gm catalyst mixture was added to the content of the flask. The temperature was raised and solution boiled until the liquid becomes quite clear and colourless. A small funnel was kept in the neck of the flask to prevent under loss of acid during the digestion. The content of the flask are allowed to cool.

After cooling, 200 ml of water is added to dilute the contents and one or two porous chips, 1 ml of 1% indicator solution were added . An excess of 40% NaOH are poured into the flask carefully through sides of flask and then connected in the distillation assembly. The contents are distilled for a minimum period of 45 min. The distillate was collected in 4% boric acid solution containing a few drops of mixture indicator. When the evolution of ammonia was completed the receiver was removed and the distillate with the 0.2 N HCl, the end point in the color change from green to faint red. Hide substance contain 17.8 gm of nitrogen per 100 gm of collagen. Therefore, the percentage of hide substance was calculated by multiplying the percentage of nitrogen by 5.62 provided no other nitrogen compound other than hide substance is present.

Nitrogen content = (ml HCl× 0.2 N× 1.4)/ leather weight in g

% Hide substance = 5.62 × nitrogen content = 5.62 ×(ml 2.4 N× 1.4)/ leather weight in g

3.4.9.6 Determination of total ash content of leather

A small piece of leather was cut and made into small pieces. A crucible was taken , dried and weighed, weighted was done after placing the leather pieces in the crucible . It was heated gently first and when the leather is completely in a muffle furnace at 800°C until all the carbon was consumed. Then it was cooled in a desiccator and weighted till constant weight was obtained.

Calculation:

Weight of leather sample taken = w_1

Weight of crucible + sample = w_2

Weight of crucible + sample after incineration = w_3

% total ash content =$\frac{w_2 - w_3}{w_1} \times 100$

3.4.9.7 Determination of the degree of tannage

the degree of tannage was determined as per procedure given in (SLC 12)(Official Methods, 1965) the difference between 100 and sum of percentages of moisture, oils and fats, water soluble, hide substance and insoluble ash given the fixed tannin in the material. The degree of tannage calculated.

Bound organic substance = % moisture +% oils and fats + % water soluble + %hide substance + % insoluble ash

Degree of tannage = (Fixed tannin$\times$ 100)/ Hide substance

Degree of tannage = (100-bound organic substance)×100/ Hide substance

3.5 Investigation of Garad bark as A Retanning Agent

3.5.1 Materials

Conventionally processed wet blue goat skins were taken for the re-tanning trials. Garad (Acacia nilotica) barks were sourced from Sudan. Chemicals used for post tanning were of commercial Garad; while the chemicals used for the analysis of leather and spent liquors were of analytical grade. The required amount of ground Garad (Acacia nilotica) bark powder was used in re-tanning.

3.5.2 Aqueous Extraction of Tannin from Garad barks

The procedure adopted was same as described as outlined in the section 3.4.2.

3.5.3 Garad bark Based Retanning Trials

Two wet blue goat skins were taken for experimental and control retanning trials using Garad bark extracts and wattle. The post tanning process mentioned in table 3.7 is followed for both experimental and control leathers.

Table 3.7 Formulation of Post-tanning process of wet blue

Process	%	Product	Duration (min)	Remarks
Washing	200		10	Drain
Neutralization	100	Water		
	1	Sodium formate		
	0.75	Sodium bicarbonate	3× 15	pH 5-5.5
Retanning	20	Garad bark (Experimental)/ Wattle (Control)	60	
Fatliquoring	5	Synthetic fatliquor	45	
Dyeing	3	Acid brown dye	45	Penetration of dye was checked
Fatliquoring	5	Synthetic fatliquor	45	
Fixing	1.5	Formic acid	3x10 +30	pH 3.5
Washing	200	Water	10	Leathers were pile over night; Next day set, hooked to dry, staked, trimmed and buffed

3.5.4 Determination of Shrinkage Temperature

The procedure adopted for estimation of shrinkage temperature of leather was same as described as outlined in the section 3.4.5

3.5.5 Analysis of Spent Liquor

The procedure adopted for estimation and analysis of Spent Liquor was same as described as outlined in the section 3.4.6.

3.5.6 Visual Assessment of the Crust Leather

The procedure adopted for estimation of visual assessment of the crust leather was same as described as outlined in the section 3.4.7

3.5.7 Physical Testing

The procedure adopted for estimation of various physical tests of leather was same as described as outlined in the section 3.4.8.

3.5.8 Chemical Analysis of Leather

The procedure adopted for estimation of chemical analysis of the crust leather was same as described as outlined in the section 3.4.9.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Garad Bark Analysis

4.1.1 Analysis of tannin and non-tannin of Garad bark

The barks of Garad were collected and estimated: for tannins by official method of analysis and the results are given in Table 4.1. Qualitative analysis of Garad extract has been performed to investigate the type of tannin. It is seen from the iron alum solution test that the Garad bark gave green color, which clearly indicates of the presence of condensed tannin. Also forma1dehyde-hydrochloric acid test gave precipitate with Garad bark extract, which clearly indicates the presence of condensed tannin.

Table 4.1 shows the percentages of tannin, non-tannin, total soluble, total solids, insoluble and the moisture of the Garad bark. The Garad bark extract gave pH 5.5.

Table 4.1 Tannin analysis of Garad bark

Characteristic	Percentage,%
Tannin	23
Non – tannin	14
total soluble	37
Total solid	41.45
Insoluble	54.35
Moisture	8.65
pH	5.5

4.2 Combination Tanning Systems Using Garad bark

4.2.1 Garad bark -Aluminum Combination Tanning

4.2.1.1 Optimization of combination tanning system using garad bark and Aluminum

Combination tanning using garad bark powder – Aluminum oxide with a Al_2O_3 offer of 2%, keeping the garad bark offer of garad bark constant at 20%, and changing the order of addition was carried out. Though, the tanning system using garad bark and Al_2O_3 are eco friendlier, it is essential to study the properties of the leathers whether it is comparable to that of chrome tanning system. The thermal stability of chrome tanned leathers is well known to be greater than 100°C. The shrinkage temperature data for various combinations are given in Table 4.2**.** It is seen from the table that just by the use of 2% of Al_2O_3 in combination with garad bark powder exhibited more than 10°C increase in shrinkage temperature compared to garad bark powder control leathers. The garad bark –aluminum oxide combination tanning provides shrinkage temperature of 100°C compared to 84°C for control.

Table 4.2 Shrinkage temperature of control and experimental tanning processes

Sample	**Shrinkage temperature, Ts (ºC)**
AL-Garad bark (2%$A1_2O_3$)	96±0.5
Garad bark –AL (2%$A1_2O_3$)	100±1
Garad bark (control)	84±0.5

The shrinkage temperature of leathers obtained from combination tanning of Garad bark -Al is slightly higher than Al-Garad bark combination tanning systems. Both the combination tanning systems Garad bark -Al and Al-Garad bark resulted in leathers with shrinkage temperature above *95°C*, whereas control tanning using Garad bark alone resulted in a shrinkage temperature of 84°C. From Table 4.2, it can be observed that Garad bark -Al combination tanning system resulted in enhancement of shrinkage temperature similar to that of wattle-Aluminum combination tanning System.

Gustavson (1956) proposed a mechanism for the increase instability of alum-tanned leathers retanned with vegetable tannins. Interaction of tannins and non-tannins with aluminum complexes results in increased fixation of vegetable tannins. However, tanning with the same combination but reversing the order (vegetable- tanned leather retained with Aluminum), results in increasing the amount of irreversibly fixed tannins due to mordanting effect of the basic aluminum salts on the uncombined tannins and non-tannins in leather (official methods 1965*)*. It is observed that there is an increase in the amount of Garad bark fixed in the presence of aluminum and this lead to increase in shrinkage temperature of combination tanning systems of Garad bark. As the shrinkage temperature has been better for the experimental leathers processed with 2% A1$_2$O$_3$ accordingly Al-Garad bark with 2% A1$_2$O$_3$ and 20% Garad bark combination tanning optimized. system has been

4.2.1.2Analysis of spent liquor

The COD, BOD and TDS of the spent liquor for both experimental and control trials were determined and are given in Table 4.5. From the table it is observed that the COD, BOD$_5$ and TDS of the spent liquor processed using Garad bark-Al and Al-Garad bark tanning system (experimental) is lower than the spent liquor from Garad bark (control).However the COD, BOD$_5$ and TDS of the spent liquor processed using Al-Garad bark tanning (experimental) has been observed to be higher than the spent liquor from Al-Garad bark tanning (experimental).

4.3 Characteristic of spent liquor for control and experimental

Experiment	COD(mg\l)	% reduction in COD	BOD5(mg\l)	% reduction in BOD	TDS(mg\l)	% reduction in TDS
Garad bark (Control)	49400±295	-	25000±900	-	39500±1550	-
Al- Garad bark	44400±300	10	16500±1100	34	20200±1050	49
Garad bark -Al	43600±280	13.8	12500±600	50.8	19200±1000	51.4

4.2.1.3 Organoleptic properties of experimental and control leather

The organoleptic properties (visual assessment) of upper crust leathers for experimental and control are shown in Fig 4.1. From the figure, it is observed that crust leathers processed by experimental combination tanning system exhibited good softness, fullness, smoothness, general appearance and dye uniformity compared to control leathers from garad bark tannage. The organoleptic properties of the Garad (Sunt) bark -Al crust leathers are slightly better compared to Al- Garad (Sunt) bark crust leathers..

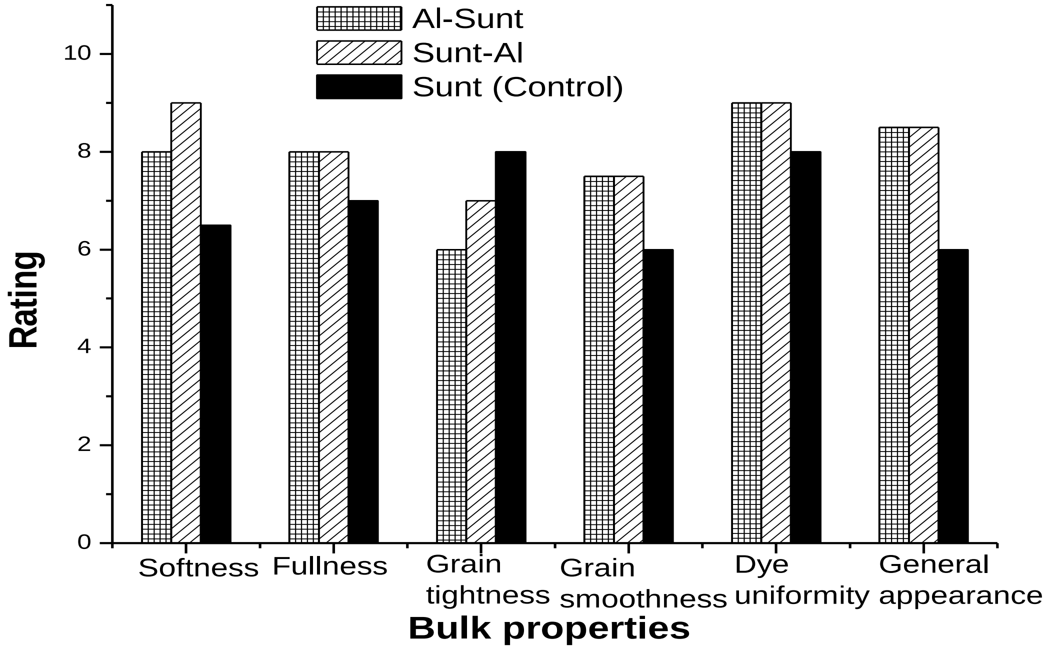


Figure 4.1 Graphical representations of organoleptic properties of experimental and control leather

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

4.2.1.4 Strength characteristics of 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 crack and distension at grain crack were carried out for the control and experimental crust leathers and the data is given in Table 4.4. It is observed that the tensile strength characteristics like tensile strength, elongation, tear strength of Garad bark -Al tanned crust leathers is found to be higher compared to that of the control and Garad bark tanned crust leathers, whereas load at grain crack and distension at grain crack of both control and Garad bark tanned leathers are found to be marginally lower.

Table 4.4 Physical strength characteristics of experimental and control crust leathers

Parameter	Garad bark-AL	AL - Garad bark	(control) Garad bark
Tensile strength (Kg/cm^2)	246±2	222±2	210±3
Elongation at break (%)	58±1.6	56±0.6	42±1.6
Tear strength (Kg/cm)	60±1.7	51±1.7	48±0.7
Load at grain crack (kg)	25±1.5	22±1.5	24±1.5
Distention at grain crack (mm)	12±0.5	10±1.5	10±07
Flexibility (after 100,000 flexes)	No crack	No crack	No crack

4.2.1.5 Chemical analysis of the crust leather

The chemical analysis of crust leathers from control and experimental tanning trials are given in Table 4.5. The chemical analysis data for the experimental leathers is comparable to the control leathers. However, the moisture for the control leathers is more than the experimental leathers.

Table 4.5 Chemical Analysis of crust leather of experimental and control

Parameter	Garad bark (control)	AL - Garad bark	Garad bark-AL
Moisture %	14.2	12.3	12.0
Total ash content %	2.8	2.4	2.2
Fats and oils %	3.3	2.7	3.2
Water soluble matter %	4.8	3.4	3.5
Hide substance %	51	53	52
Insoluble ash %	1.3	1.2	1.6
Degree of tannage %	49.8	51.7	53.3

4.2.2 Garad bark Zinc Combination Tanning (Zinc oxide)

4.2.2.1 The shrinkage temperature of leathers

The shrinkage temperature of leathers obtained from combination tanning of Garad bark -Zn is slightly higher than Zn- Garad bark combination tanning systems. Both the combination tanning systems Garad bark –Zn and Zn- Garad bark resulted in leathers with shrinkage temperature above 90°C, whereas control tanning using Garad bark alone resulted in a shrinkage temperature of 84°C. From Table 4.6, it can be observed that Garad bark -znic combination tanning system resulted in enhancement of shrinkage temperature.

Table 4.6 Shrinkage temperature of control and experimental tanning processes

Sample	**Shrinkage temperature, Ts (ºC)**
Zn-Garad bark (9%ZnO)	95±1
Garad bark –Zn(9%ZnO)	99±2
Garad bark (control)	84±0.5

4.2.2.2 Analysis of spent liquor

The COD, BOD and TDS of the spent liquor for both experimental and control trials were determined and are given in Table 4.7. From the table it is observed that the COD, BOD_5 and TDS of the spent liquor processed using Garad bark-Zn and Zn-Garad bark tanning system (experimental) is lower than the spent liquor from Garad bark (control).However the COD,

BOD_5 and TDS of the spent liquor processed using Zn-Garad bark tanning (experimental) has been observed to be higher than the spent liquor from Zn-Garad bark tanning (experimental).

Table 4.7 Characteristic of spent liquor for control and experimental

Experiment	COD (mg\l)	BOD_5(mg\l)	TDS(mg\l)
Garad (control)	114800±2660	27800±1200	99850±1250
Zinc- Garad	101500±1250	18500±1200	78500±1200
Garad-Zinc	95500±1650	15450±850	65650±1350

4.2.2.3 Organoleptic properties of experimental and control leather

The organoleptic properties (visual assessment) of upper crust leathers for experimental and control are shown in Fig 4.2. From the figure, it is observed that crust leathers processed by experimental combination tanning system exhibited good softness, fullness, smoothness, general appearance and dye uniformity compared to control leathers from garad bark tannage. The organoleptic properties of the Garad bark -Zn crust leathers are slightly better compared to Zn- Garad bark crust leathers.

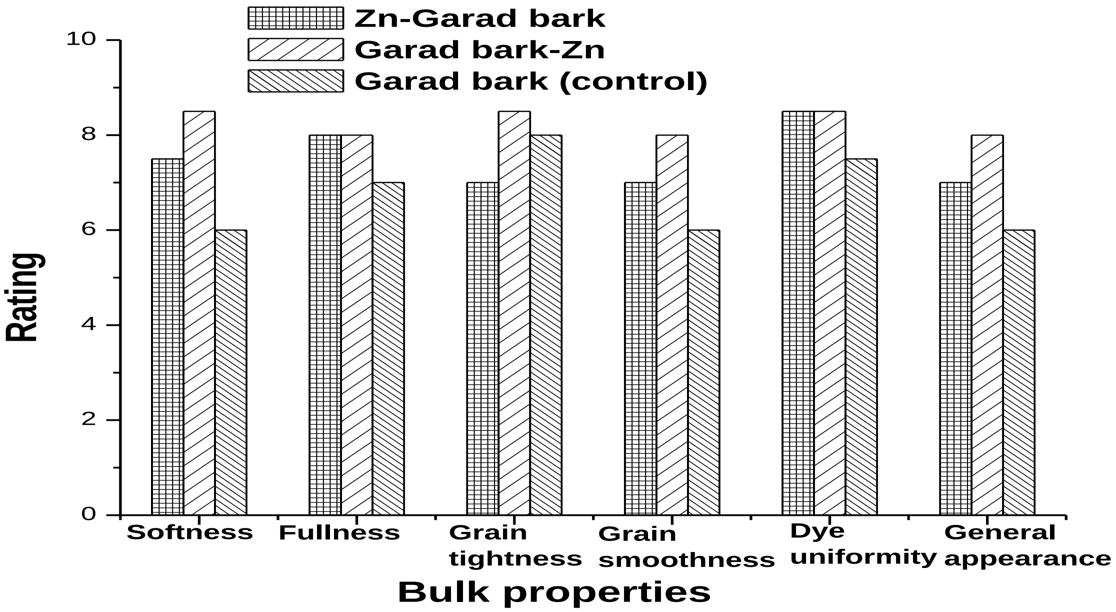


Figure 4.2 Graphical representations of organoleptic properties of experimental and control leather

4.2.2.4 Strength characteristics of 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 crack and distension at grain crack were carried out for the control and experimental crust leathers and the data is given in Table 4.8. It is observed that the physical strength characteristics like tensile strength, elongation, tear strength of Garad bark -Zinc tanned crust leathers are found to be higher compared to that of the control Garad bark tanned crust leathers, whereas load at grain crack and distension at grain crack of both control and Garad bark tanned leathers are found to be comparable.

Table 4.8 Physical strength characteristics of experimental and control crust leathers

Parameter	**Zinc-** Garad	Garad **-** **Zinc**	Garad **(control)**
Tensile strength (Kg/cm^2)	225±2	248±2	212±2
Elongation at break (%)	52±1.40	57±1.50	42±1.6
Tear strength (Kg/cm)	51±1.50	62±1.50	48±0.70
Load at grain crack (kg)	25±0.52	28±0.52	24±0.52
Distention at grain crack (mm)	11±1.28	12±1.35	10±0.7

4.2.2.5 Chemical analysis of the crust leather

The chemical analysis of crust leathers from control and experimental tanning trials are given in Table 4.9. The chemical analysis data for the experimental leathers is comparable to the control leathers. However, the moisture for the control leathers is more than the experimental leathers.

Table 4.9 Chemical Analysis of crust leather of experimental and control

Parameter	Garad bark (control)	Zinc – Garad bark	Garad bark - Zinc
Moisture %	14.2	12.55	13.10
Total ash content %	2.8	2.35	2.65
Fats and oils %	3.3	2.95	3.20
Water soluble matter %	4.8	3.55	3.30
Hide substance %	51	52.50	51.40
Insoluble ash %	1.3	1.25	1.35
Degree of tannage %	49.8	51.81	53.79

4.3 Investigation of Garad bark as Retanning Agent

4.3.1 Shrinkage Temperature

Shrinkage is a phenomenon, associated with dimensional changes of hide, skin or leather when subjected to heating. The temperature at which the material shrinks is termed as “shrinkage temperatur” (Ts); an this varies when the hide or skin is tanned. Shrinkage temperature value (Ts ^{o}C) of a specimen in water as the heating medium, is taken as measure of hydrothermal stability and the boil test (viz, test for curling of leather in boiling water) is used even today, to assess the completion of chrome tanning (Kedlaya 1987). The shrinkage temperature of wet blue crust leathers retanned using sunt (Garad bark) powder and wattle is given in Table 4.10. The wet blue leathers resulted in shrinkage temperature of 109˚C; however the retanning with wattle and sunt bark powder resulted in increase of shrinkage temperature to 116˚C and 113˚C respectively. It is obvious that the treatment of sunt (Garad bark) improves the shrinkage temperature significantly similar to the case of wattle; hence retanning with sunt bark appears to be a promising option in terms of its reactivity with the leather matrix.

Table 4.10 Shrinkage temperature of crust leathers retanned with Garad bark and wattle

Sample	**Shrinkage temperature, Ts (ºC)**
Wattle (Control)	116±2
Garad bark (Experimental)	113±2

Note- Shrinkage temperature of wet blue leathers were 109±2˚C

4.3.2 Analysis of spent liquor

The COD, BOD5 and TS of the spent liquor for both experimental and control trials were determined and are given in **Table 4.11**. From the table it is observed that the COD and BOD of the spent liquor processed using garad (sunt) retanning is lesser than the spent liquor from wattle retanning. However the solid content of garad retan liquor has been observed to be higher than the wattle retan liquor. Even though the solid content of the garad retan liquor is higher, the degradability of the same is easier than the wattle retan liquor.

4.11Characteristic of spent liquor for control and experimental post tanning trials

Parameter	**Wattle (Control)**	**Sunt (Garad bark) (Experimental)**
COD (mg/l)	89980±3000	71780±1100
BOD5 (mg/l)	30450±850	27500±750
Total solid (mg/l))	23550±800	32480±850

4.3.3 Tactile properties of sunt (garad bark) retanned leathers

Control and experimental crust leathers were evaluated for various organoleptic properties by hand evaluation. The organoleptic properties of leathers retanned using sunt bark and control wattle is given in Fig 4.3. From the figure it is observed that retanning with sunt bark resulted in leathers with good grain tightness and roundness compared to wattle retanned leathers. The fullness of leathers with wattle retanning is found to be better than that of sunt bark. However, the softness of leathers with sunt bark retanning is found to be better than that of wattle. The grain smoothness of sunt bark retanned leathers has been found to be similar to that of wattle retanning. On the whole the leathers retanned with sunt bark had been found to be better than wattle retannng. The results show that the sunt bark powder has a retanning filling ability and can markedly improve the organoleptic properties of the leather.

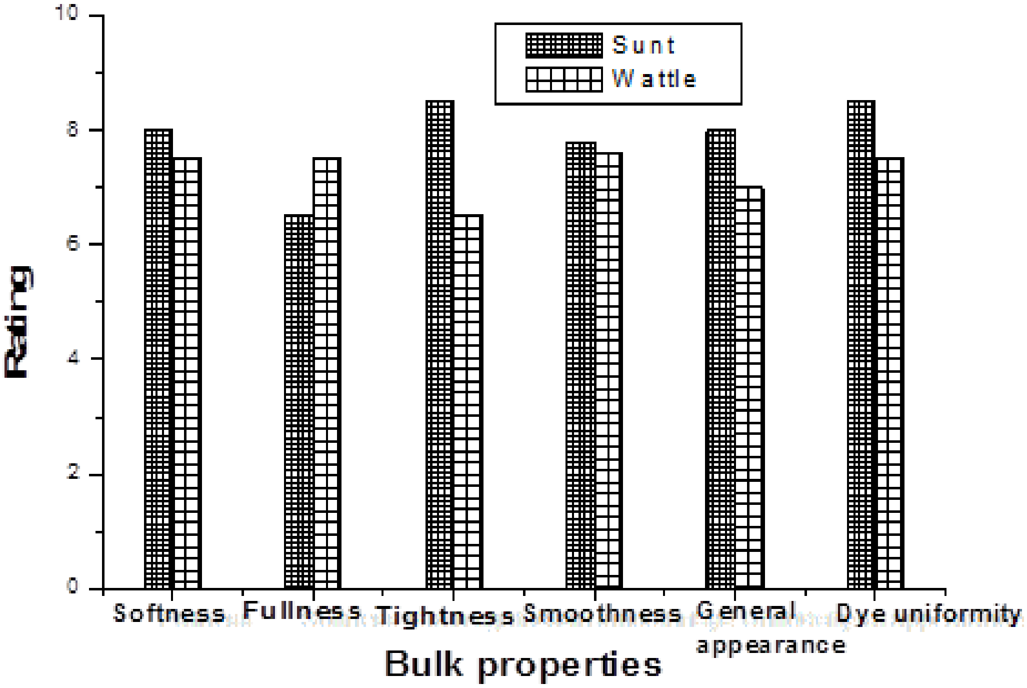


Figure 4.3 Graphical representations of organoleptic properties of experimental and control leather

4.3.4 Dyeing Characteristics of Sunt Bark Retanned Leathers

The dyeing characteristics of sunt bark and wattle retanned leathers have been evaluated by experienced tanners and the results are given in

Table **4.12.** The uniformity of dye of the sunt bark retanned leathers has been found to be better than the wattle retanned leathers. The shade intensity of the sunt bark retanned leathers has been found to be better than the wattle retanned leathers. No differential dyeing (between grain and flesh) has been observed for both sunt bark and wattle retanned leathers.

Table 4.12 Visual evaluation of the general characteristics of crust leathers retanned with Garad bark and wattle

Property	**Sunt (Garad bark) (Experimental)**	**Wattle (Control)**
Uniformity of dye	V.Good	Good
Shade intensity	V.good	Good
Differential Dyeing	Nil	Nil

4.3.5 Physical Strength Characteristics of Garad bark **Retanned Leathers**

The physical strength measurements of matched pair garad bark retanned experimental and wattle retanned control leathers are given in **Table 4.13** The physical strength measurements viz., tensile strength, % elongation, tear strength, load at grain crack and distension at grain crack been found to be comparable. The strength values of Garad bark retanned leathers have been found to meet the norms for chrome retanned leathers. (BIS, 1964)

Table 4.13 Physical strength characteristics of crust leathers retanned using Garad bark and wattle

Parameter	Garad bark	Wattle	BIS norms*
Tensile strength (Kg/cm2)	254.55±17.8	252±19.8	250
Elongation at break (%)	61. 30± 10.42	64. 40 ±3.70	60-70
Tear strength (Kg/cm thickness)	38.98±8.546	42.43±4.56	30
Load at grain crack (kg)	25±5	27±7	20
Distention at grain crack (mm)	10.33±0.66	11.50±0.50	Min 7

*Bureau of Indian standards (BIS) specification for chrome retanned upper leathers

4.3.6 Chemical Analysis of the Crust Leather

The chemical analysis of crust leathers from control and experimental tanning trials are given in Table 4.14**.** The chemical analysis data for the experimental leathers is comparable to the control leathers. However, the fats for the control leathers is more than the experimental leathers.

4.14 Chemical characteristics of the Crust Leathers retanning using Sunt (Garad bark) and wattle

Parameter	**Garad bark Experimental)**	**Wattle (Control)**
Moisture %	14.20	15.00
Total ash content %	4	4.3
Fats and oils %	5.7	6.2
Water soluble matter %	5.2	6.0
Insoluble ash %	1.70	1.55

4.4 Evaluation cost of garad bark

For 1 kg Garad bark extract it will cost 0.48$ and for 1 kg mimosa it will cost 3 $. Mimosa extract powder cost more than 2.8$ increase in cost of garad bark powder. that mean Garad bark it is better than mimosa.

For any development of a new innovative process requires commercial feasibility, followed by cost effectiveness. Total soluble of garad bark 37%. Hence cost per kg of garad bark extract will be around **0.48** US$, where as the cost of per kg of wattle extract used for leather making is around **3 US$.** Therefore the use of garad bark for retanning certainly has commercial advantage.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

In the present study, investigation of Garad bark (Acacia nilotica***)*** bark widely distributed in Sudan gave a number of conclusions. The analysis of dried Garad bark bark powder gave the following values: Tannin 23%, Non-tannin 14%, Total soluble 37*%*, Total solid 41.45, Moisture 8.65**,** pH 5.5 The phytochemical investigation of the bark of *acacia* nilotica show that the type of tannin was condensed.

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 Garad bark and Aluminum it is seen that combination tanning using Garad bark (20%) followed by Aluminum (2% Al_2O_3) resulted in leathers with shrinkage temperature of 100^{o}C, which is 15^{o}C more than the control (Garad bark tanned) leathers. Aluminum followed by Garad bark tanning resulted in leathers with shrinkage temperature 96^{o}C. The physical and chemical characteristics of experimental leathers are comparable to control leathers. The experimental leathers are softer than the control leathers.

Tanning using Garad bark (20%) followed by Zinc (9% Zn Sulphate) resulted in leathers with shrinkage temperature of 99^{o}C, which is 14^{o}C more than the control (Garad bark tanned) leathers. Zinc followed by Garad bark tanning resulted in leathers with shrinkage temperature 95^{o}C. 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 Garad bark and Aluminum, and using Garad bark and Zinc appears to be an eco-friendlier option and results in leathers with good thermal stability and organoleptic properties that is important for commercial viability of the tanning system.

The retanning may be a single chemical process or may be a combination of reactions applied together or more usually consecutively. The purpose is to modify the properties and performance of the leather. These changes include the handle, the chemical and hydrothermal stability or the appearance of the leather. The effects are dependent on both the primary tanning chemistry and there tanning reactions. Most organoleptic properties of the experimental leathers produced from Garad bark extract are better than control leathers produced from wattle. However softness property is better in the case of wattle retanned leather and the physical strength properties are comparable with the matched pair control leathers. Retanning with Garad also facilitates in intense dyeing. Hence using Garad bark appears to be a good alternative for the retanning processes. Further exploration is required to find effective utilization of Garad bark extract in leather processing.

5.2 RECOMMENDATIONS

- Feather Analysis and identification of phenolic compounds of Acacia nilotica (Garad) bark.
- May be used garad bark extract to produce crust leather for export instead of export in wet blue.
- More studies to compare economic effectiveness between this study and tannage by using minerals tanning agents.

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