ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAIT)

CHEMICAL AND BIO-ENGINEERING

COMBINATION TANNING BASED ON TARA AND SODIUM METASILICATE A NEW CHROME FREE TANNING SYSTEM

By

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Dr. B. Madhan

A thesis submitted to the School of Graduate Studies of Addis Ababa University in partial fulfilment of the Degree of Master of Technology in Chemical Engineering under leather technology stream

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DECLARATION

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

Signature: - …………………………   Date: - …………………….

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List of Acronyms

WS- Wet salted

COD-chemical oxygen demand

BOD- biological oxygen demand

TS- Total solid

TDS-total dissolved solids

TSS- total suspended solids

Ts- Shrinkage Temperature

Uv-vis spec- Ultra violet- visible spectrophotometer

ml- millilitre

mm-milimeter

l-liter

g- Gram

IUP-international union of physical

SATRA-safety and technical rescue association

SLC- Standard Leather Chemical

SLP-Standard leather physical

APHA-America public health Association

IULTCS-international union of leather technology and chemist society

ISO- international organisation of standard

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Abstract

Chrome is the well-established tanning system adopted globally. Consumer awareness and short coming of chrome tanning system calls for a need for the development of chrome free tanning, Hence this research work is focused on, the development of silica and vegetable tanning agent (Tara) combination tanning system as an alternative to chrome tanning. This tanning system eliminates the use of chromium in tanning process thereby environmental impact of chromium can be avoided. Silica remains in solution at a narrow pH range and hence in order to keep the silica in sol at pH of about 3, silica tanning salt was prepared by masking with salts viz., sodium citrate and sodium tartrate. The combination tanning based on silica and tara were optimised for the amount of tara, order of addition and masking salt used for the preparation of silica tanning agent. The order of addition of silica and tara, amount of tara and also the type of masking agent had a significant influence on the shrinkage temperature, physical strength and organoleptic properties of the leathers produced. Tanning system with tara followed masked silica gives resulted in wet white leathers with shrinkage temperature of 80oc. Among the combination system evaluated, leathers obtained by vegetable (Tara) pretannage followed by retannage with masked sodium metasilicate were observed to be stronger, fuller and better general appearance with the durable characteristics. In contrast, pre-tanning with masked sodium metasilicate resulted in leathers with poor organoleptic properties and less hydrothermal stability. In general the characteristics of the leathers obtained by tara- silica combination system provides leathers with good organoleptic properties and comparable physical strength for upper leathers. Physical testing and organoleptic properties of the matched pair leathers of the tara-silica combination tanning system were comparable to that of chrome tanned control leathers. Skins stabilized with tara - silica combination tanning could be adapted to shaving readily; most important is that it would not produce wastes containing chromium means it is zero chrome discharge because chromium is not used in this tanning system. Therefore the tara-silica combination tanning is a good tanning system for the manufacture of upper leathers. The tara-silica combination tanning system also resulted in leathers with good buffeability and hence the leather made from this tanning system is also suitable for the manufacture of suede leathers especially for upper. The cost of the new system is higher but can be compensated with the environmental benefits by eliminating chrome in leather manufacture.

1 Introduction

1.1 back ground

Leather making is a very long process and consists of many different chemical and mechanical process steps. The common raw materials of leather industries are skins/hides, chemicals, water. Other pre-requisites for leather manufacture are energy, machine, and labour. Leather industry has been categorized as one of highly polluting industries and there are concerns that leather making activities can have adverse impact on the environment. Environment includes air, water bodies, and soil. Tanning is the process of making leather, which does not easily decompose, from the skins/hides of animals which are prone for degradation. There are many factors governing the tanning effect: the type of the tanning agent, concentration, pH value, and neutral salt content; the temperature of the tanning bath; and the time of interaction, the previous condition of the skin material is also important. Leather processing involves a series of operations. Many of these factors are interdependent and difficult to consider separately.

The operations involved in leather processing may be classified broadly into four steps: I) pretanning or beam house processed/operations, ii) tanning, iii) post tanning and iv) finishing. Before processing of skins/hides it is better to preserve it. Pretanning process/operations aim at cleaning the hides/skins, tanning stabilizes the skin/hide matrix permanently, the required characteristics of leather is obtained by post tanning and aesthetic values are added during finishing operations.

Preservation is a temporary curing method which prevents putrefaction and keeps skins in good condition until they are processed in tanneries. Being protein in nature, skins are susceptible to attacks by bacteria or mold that leads to putrefaction when conditions favour their growth. There are three different methods of preservation. These are wet salting, dry salting and drying. Those methods of preservation have their own advantages and disadvantages.

Soaking is the first operation carried out in drums, paddles or pits with the addition of required amount of water, wetting agent and bactericides based on the raw material weight to rehydrate and restore the hides/ skins to its natural condition and to remove the adhering dirt, blood, curing agents and some soluble proteins. The method and duration of soaking varies according to the condition of raw stock. Thus, fresh hides/skins require only a few changes of water, preferably cold water, to remove blood, dirt, etc. Wet salted stocks have to be soaked for longer period, depending on the degree of dehydration. In case of prolonged soaking, suitable preservatives are to be used. To reduce the time of soaking, wetting agents are used.

For soaking dry salted stock, soaking aids and preservatives are to be necessarily used. Additives like sodium sulphide, caustic soda, soda ash may be required for proper rehydration. Enzymatic soaking aids have been found to be very useful to reduce the time of soaking. Dried hides require soaking for a period longer than that for dry salted stock, along with suitable wetting agents and preservatives with control drum rpm. Completion of soaking is tested by folding the skins/hides flesh side out, and feeling for uniform softness flexibility. These are taken as evidence of proper soaking.

Liming is the treatment of soaked hides / skins with lime, sharpening agent (sodium sulphide, sulphydrate), surface active agents etc in a drum, pit or paddle. The purpose of liming is to remove hairs, epidermis, natural fats, interfibrillary proteins to swell and split up the fiber bundles into fibers, to soften the collagen fiber matrix and make the final leather non patchy, soft and pliable. In this operation pH is maintained around 12.5- 13. After this stage the hide/ skin is called limed pelt. Liming method depends upon the raw stock as well as the final leather required to be produced. In case of sheep skins where the wool of hair has some value, a paint liming system is to be adopted. In the case of cattle hide and goat skins, hair pulping method is used in paddle/drum. Short liming is necessary to get tighter leather and less looseness in leather. For soft leather where good opening up of structure is required, a slightly longer liming is adopted to increase the swelling and splitting of fibres. Such process is dependent on the type of raw stock. Reliming with the addition of soda ash/caustic soda is done to adjust the desired degree of plumping.

Fleshing is mechanical removal of unwanted loose fleshy portions by hand knife or fleshing machine.

Subsequent to fleshing deliming process is carried out to reduce the alkalinity by washing the pelt in paddle or drum with weak organic acids, acid salts, etc. It is essentially done to reduce the alkaline swelling and to remove physical deposited and chemically bound lime and of capillary lime which is detrimental for subsequent tanning. After deliming thoroughly washing is carried out in order to remove the lime completely from the pelt. The completion of deliming is checked by using phenophtaline indicator.

Bating is the treatment of delimed pelt with enzymatic bate powder to remove non leather making substance such as scud, short hairs and interfibrillary material and to make the grain surface clean, smooth and fine in order to make the leather soft, pliable and stretchy. The efficiency of bating depend on temperature, strength and pH of bate liquor and duration of the process. The completion of bating can be checked by air bubble for skins and thump press for cattle hides.

Pickling is a process of acidification of the scudded pelt in drum with salt solution and pre diluted acids (organic & inorganic) to preserve and to condition the pelt for tanning. The pickling operation is checked by measuring the pH of the cross section of pelt, which should be around 2.8 to 3.0. Pickling is essentially done to bring down the pH in order to condition the pelt for subsequent tanning operation. The salt concentration and pH are most important factor in pickling [1, 2].

Tanning leather involves a process which permanently alters the protein structure of skin with enhanced stability in comparison to raw hides and skins. Often tannin, an acidic chemical compound are used for tanning process. There are different types of tanning. These are mineral tanning agent, vegetable tanning agent (synthetic tanning agents, oil tanning agent) [2, 3].

Today more than 90% of the leathers are produced with chrome tanning agents. Many advantages offered by chrome tanning justify its widespread use for production of almost all types of leather. However traditional chrome tanning process is constantly under pressure to minimize chromium containing effluent discharge and chromium containing trimming, shaving and buffing etc, since chromium salts has negative impact on the environment and health. In some countries there are restrictions on the use of chrome-tanned leathers for certain purposes (Dasgupta2002). Present day research is focused on high exhaustion and eco-friendly products and processes. The research and development must be directed towards studying new products with a low impact on environment, which are easy to handle and can be used for various functions. To overcome the problems associated with chrome tanning researchers throughout the world are looking for alternative tanning systems and many alternative tanning systems for chrome tanning have already been documented. However there is no effective replacement for chrome tanning system is established till date. Significant research has shown that the tanning effects of minerals other than chromium (Al, Zr, Ti, or Fe) are enhanced when they are used in combination with vegetable tannins, aldehydes, or other organic molecules. Leathers produced by the combination of these tanning materials had shrinkage temperature around 100^{o}c and adequate physical-mechanical properties for varieties of application. We will discuss more on tanning in later section.

The process that are performed after tanning but prior to finishing are neutralization, dyeing, retanning and fatliquoring which are referred as post tanning or wet finishing operations. The main objective for this set of unit process/operation are to give a colour to the leather as demanded by the market, impart softness with fatliquor, fullness and uniformity of substances with retanning materials. It is well known that chrome tanning produces empty types of leathers and vegetable tanned leathers produce fuller leathers. Hence in the case of chrome tanned leathers, more efforts are needed to bring about uniformity in fullness and fibre structure. Retanning is the process performed to achieve this objective. Sometimes retanning of chrome tanned leathers or vegetable tanned leathers are carried out to impart special characteristics such as improved dyeing characteristics or improving the affinity for fatliquors by altering the charge characteristics.

Finishing is the last set of process/operation done in leather processing to improve the appearance, aesthetic and sale values of the leathers and protecting the leather surface from damage during usage against rubbing, water, soiling, abrasion, scuff and vagaries of weather. The final colour as demanded by the buyer is adjusted in finishing. In finishing attempt is also made to hide the surface blemishes aiming at the up gradation of the leathers. In finishing, special surface effects and modification of texture are also being done. Therefore the main objective of finishing is to protect the leathers from damage by water, soil, mechanical action, to improve its physical properties such as light fastness, rub fastness, to levelling out patches and grain faults, to apply an artificial grain layer to splits or corrected grain leather, to modify the surface properties. To carry out the above characteristics there are many ingredients used in finishing. The major ingredients used in finishing are colorants, film forming materials and other auxiliaries to modify the feel, flow, flexibility and other surface properties [4].

The broad concern on the negative impact of the leather industries on the environment has forced tanners to pay attention to processes that would reduce the problems related to pollution. Because tannery wastewater contains a complexity of pollutant

Like chromium as indicated earlier, it is vital to dissect the toxic nature of such wastewater both to understand its environmental impacts as well as health and identify potential remediation strategies [5]. Traditionally chrome tanning has been the most predominant method of tannage for commercial leather processing. Looking at the tanning capabilities of the elements present in periodic table many is found to have tanning potency. The success of any tanning system lies in obtaining leathers for different end uses. This is one of the important criteria, which has made chrome tanning to be a dominant tanning system in the tanning industry. Present investigation focuses on the improvement of Tara-silicate (tartrate masked) tanning system, so as to evolve a versatile tanning system, to produce leathers for upper. However, practical criteria like availability, cost and toxicity have to be considered before choosing an appropriate tanning agent. Tanning agents based on vegetable tannins, aluminium, titanium, iron and zirconium have been known for a long time. But all these tanning agents have inherent disadvantages like high cost, less hydrothermal stability, darkening of colour etc. associated with them. Hence, these limitations have forced researchers to look at other alternatives for the purpose of tanning. The present overall status of chromium as a tanning agent is being challenged owing to its toxic nature. Chromium (VI) is a known carcinogen which is converted from chrome (III) [6]. Chromium is known to impart unique properties and produce leathers with very good shrinkage temperature (>120^{o}C). However, in the present scenario, the need to reduce chromium in the effluent is becoming increasingly important. Over the years, several chrome management technologies have emerged [7].

Ecological legislation with reference to the discharge of chromium in many countries become tougher and it is difficult to dispose of chrome containing wastes at economical practise. Therefore procedures have been developed in the last few years in order to reduce or eliminate the large quantities of chrome shavings and thus to avoid their disposal on dumps for hazardous wastes. In general chrome has an impact on environment, human and animal health. The other drawback of chrome tanning is the lack of adequate filling of leathers thereby demanding more usage of retanning syntans. Therefore, different markets require the manufacture of chrome-free leather of course with properties such as feel, fullness, softness, and hydrothermal stability etc compared to chrome tanned leathers [8].

There are different toxicities which are as the result of chromium that used in the leather manufacturing. It has a remarkable complex-forming capacity; the binding of chromium to collagen takes place with carboxyl groups of the amino acid chains. Exhaustion of the tanning bath under normal conditions is far from completion, which is a drawback from the pollution Standpoint; Cr (VI) is a toxic irritant and a carcinogen. In acidic solution some soluble trivalent chromium may be oxidized to Cr (VI). Even trivalent chrome salts are proven to be bio and geno toxic. Exposure to chromium results in skin irritation, pustules, nasal irritation and dryness in the rest of the respiratory tract. It has been found to cause lung, pancreas, colon and vesicle carcinomas. Therefore chrome residues must be precipitated to form sludge and discarded under carefully controlled conditions. Breathing of high-level of Hexavalent chromium can cause irritation to nose, such as nosebleed, ulcers and holes in the nasal septum. Ingesting large amounts of Hexavalent chromium can cause stomach upsets and ulcers, kidney and liver damage and even death [9].

Among the options available to avoid the negative impact substitution (partially/completely) of chromium with an alternative tanning agent is encouraging. The leathers processed not only have the properties imparted by chromium but also have the special properties imparted by the alternative tanning agent. A viable alternative to chrome tanning is of interest to the leather industry mainly to eliminate or reduce the discharge of chromium in any form. Operative processes which enable the production of leathers bearing similar properties to those of conventional chrome tanned requires features, like high hydrothermal stability, good light fastness, low environmental impact, versatility, comparable cost [2, 10, 11].

Silica is the name given to a group of minerals composed of silicon and oxygen, the two most abundant elements which consists of 60% of earth's crust, either in the free form or in the combined form with other silicates in the earth's crust. Silica is found commonly in the crystalline state and rarely in an amorphous state. It is composed of one atom of silicon and two atoms of oxygen resulting in the chemical formula SiO2 Sand consists of small grains or particles of mineral and rock fragments. Sodium metasilicate is produced by the fusion of sodium carbonate with silicon dioxide or silica sand at about 1400 °C. It is commercially available in various grades, differing in sodium silicate concentration in water, in specific gravity, and in viscosity is available and in both the anhydrous and pentahydrate forms from several U.S. companies. Annual capacities range from 50 to 806 million pounds.

Tanning with silicic acid is relatively old invention. In the year1916, Alexander.T. Hough claimed a patent in which the process is clearly defined. The inventor of a process for tanning with silica first perceived the idea in 1911 while perusing the English translation of Poschl's book on colloid chemistry. He read of the classic experiments of Graham, who found that colloidal silicic acid resembles tannins in its property of precipitating gelatin from solution and he marvels that a reaction so definitely established should not have been applied to leather manufacture. The use of sodium metasilicate as it is stated in French patent (1,038,223) allows one to obtain a full tannage. Leathers obtained are very supple, white, fast to light, and of good feel. Unfortunately, they are very weak, until now it has been impossible to establish remedy to this draw back. The advantage of this tanning method is evident, because it is a very cheap raw material which is abundant on the surface of the earth [12].

Tara is the name commonly used for a fairly well known material, which consists of the dried pods of Caesalpinia spinose, a tree or shrub. The pods are similar to divi-divi and algarrobilla and all three belong to the same genus. The tannin content of Tara varies from 30-35%. Tara has been used mainly for tanning light leathers. Although the vegetable tanning system enjoys a few advantages, it suffers from certain drawbacks such as providing fuller and softer leathers and difficulty in making pastel shades. To overcome these constraints, Tara, a hydrolysable tanning agent has been chosen. This tanning agent provides lighter shades and also due to its low astringency and loading nature, can be used in the manufacture of upper and garment leathers. Tara tannin as a solo-tanning agent may not be effective for the manufacture of upper leather. Hence, in this work the use of vegetable based silica combination tanning has been studied.[11]tara tanning agent is known for producing leathers of soft nature. Thus, developing strong leather by using tara is a challenging task and needs proper processing adjustments and appropriate masking agents. In order to improve the properties of leathers, studies on combination tanning of Tara with cotanning agent like sodium metasilicate (masked with tri-sodium citrate and sodium tartrate) has been carried out. Such combination tannages also lead to an increase in hydrothermal stability of the leathers.

The percentages of Tara and silica in the tanning system have been optimized based on the comparisons of hydrothermal stability, grain characteristics (observation) and liquor exhaustion (observation) for each trial. Sodium metasilicate is known to give fuller white leathers with light fastness, suppleness and good feel. Hence, use of silica as a co-tanning agent is expected to improve the properties of Tara leathers.

1.2 Statement of the Problem

Leather industry has been categorized as one of highly polluting industries and there are concerns that leather making activities can have adverse impact on the environment and health. Chrome tanning is the most common type of tanning in the world. The tanning industries, in Ethiopia, are growing fast. Many new tanneries are opened. Chrome tanned leathers are commonly adopted tanning practice due to top handling quality, high hydro-thermal stability and excellent user properties. However, chrome wastes from leather processing poses a significant disposal problem. It occurs in three forms: liquid waste, solid tanned waste and sludge. From the amount of chromium used for tanning only 60-65% of it taken by the leather, the remaining 35%-40% of the chromium salt used is discharged in the tanning effluent.

The environmental impact of chrome waste from tanneries has been a subject of extensive scientific and technical dispute. The present general status of chromium as a tanning agent is being challenged owing to its toxic nature. Recent studies suggest that chromium (III) itself may be toxic at higher levels under certain ligand environments and possibility of conversion (during leather processing) of chrome (III) to chromium (VI) which is a known carcinogen [7].

So to avoid an environmental impact and to maintain human health, we have to find out an alternative leather tanning system, which is eco-friendly and able to produce leathers of comparable quality with that of chrome tanned leather. In this project it is proposed to attempt Tara-silica combination tanning as an alternative chrome free tanning system.

1.3 General and specific objectives

1.3.1 General objective

The overall objective of the study is to develop effective chrome free tanned upper leather based on Tara-Silica combination tanning.

1.3.2 Specific objectives

- To prepare masked silica tanning agent
- To optimize the offer of silica tanning agent
- Optimizing the order of addition of Tara and silica in combination tanning system
- Optimizing the amount of Tara used in the combination tanning system

- Development of effective silica-Tara combination for tanning
- Development of a post tanning process for making upper leather
- Compare the properties (physical, organoleptic, and environmental aspects) of the experimental upper leathers with conventional upper leathers

1.4 Research questions

- What is the optimum amount of sodium metasilicate and tara needed for effective tanning of pickled goat skins?
- How the tanning agents especially sodium metasilicate will be applied in to the tanning system?
- What is the impact of an alternative tanning system on the hydrothermal stability of the pickled goat skins?
- What will be the optimal setting of process parameters in tanning processes to get maximum shrinkage temperature for an alternative tanning system?
- What types of raw materials will be favourable for this alternative tanning system?
- What will be the comparative pollution load generation of the conventional and an alternative system of tanning and post tanning in terms of BOD, COD, TS, TSS and TDS?
- What will be the comparative quality of the leather produced using conventional system of tanning and using an alternative system of tanning in terms of physical test, chemical test and organoleptic properties?
- What will be the cost of this alternative tanning systems?

1.5 Conceptual framework

This study aims to compare the technical, environmental and economic aspects of conventional tanning of pickled pelt with an alternative system of tanning using masked sodium metasilicate and tara. The overall conceptual framework of the thesis work is shown in Figure 1.1; it describes the whole frame of the thesis work.

The technical issues of an alternative system of tanning were compared with the conventional chrome tanning system as control taking the chemical parameters, shrinkage temperature, moisture content, fat content and ash content for tanned as well as post tanned and the physical parameters such as tensile strength, tearing strength and load at grain crack for the leathers made. Then, the environmental issues of an alternative system of tanning were evaluated by comparing the conventional and an alternative tanning system with related to the pollution load parameters such as TS, TSS, TDS, COD, and BOD etc.

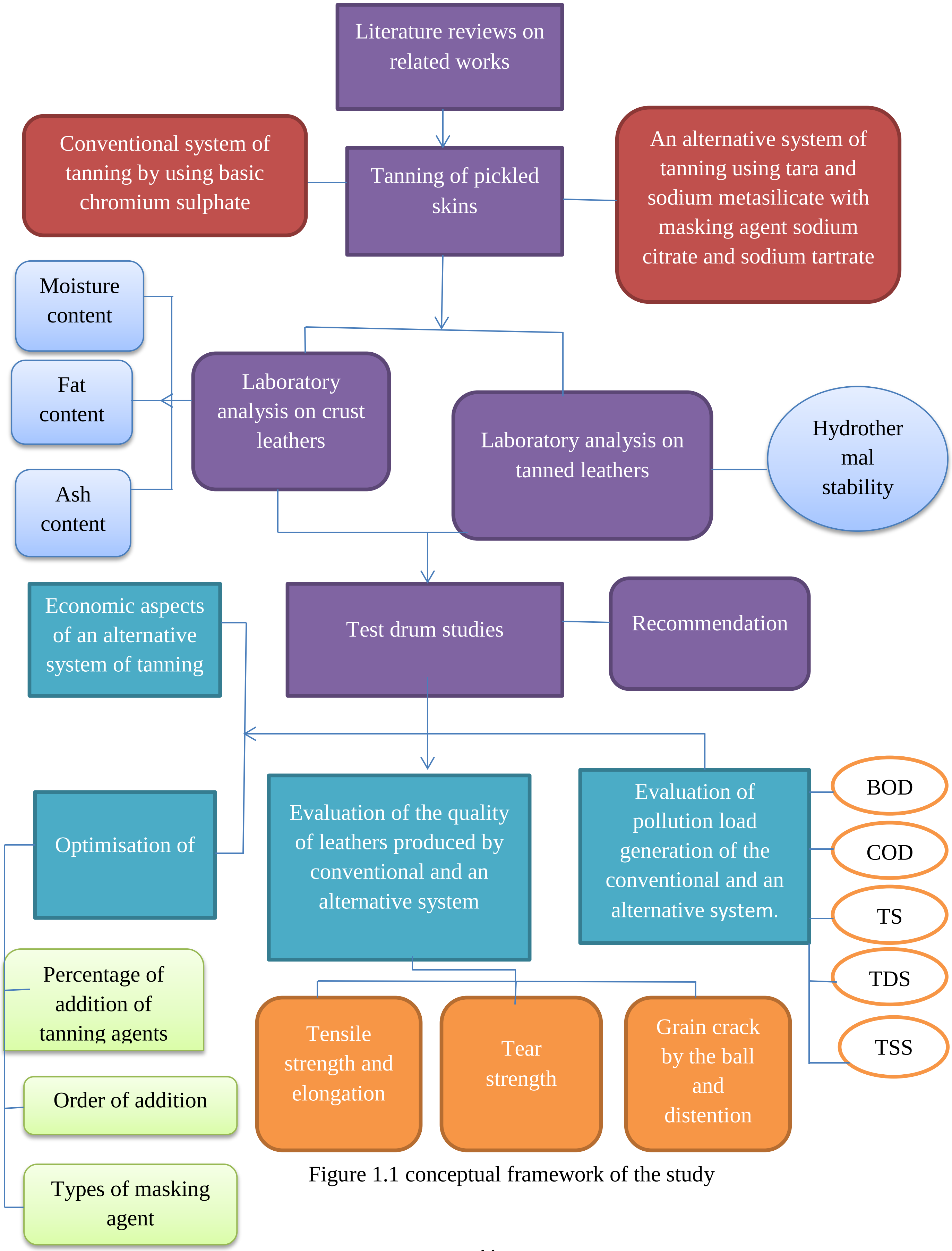


Figure 1.1 conceptual framework of the study

1.6 Significance of the research

- This work enables the development of newer tanning system an alternative to chrome tanning
- This research work will add the knowledge of how the type of tanning agents affects the final leather quality.
- In addition to this, the research work enables us how to outlook the manufacture of leather products from an alternative tanning agent which are technically, economically and environmentally viable.

1.7 Scope of the study

The study covers the development of new tara-silica combination tanning system. The developed tanning system is assessed for environmental, economic and quality aspects in comparison to conventionally adopted tanning process using basic chromium sulphate Processing of the skins into leather and comparing the quality of the leather and effluent produced by these approaches.

2. LITERATURE REVIEW

2.1 Tanning

This is the most chemically complex step. During tanning, the skin structure is stabilised by crosslinking of collagen with complex ions of tanning agent. Depending on the compounds used, the colour and texture of the leather changes. When leather has been tanned it is able to 'breathe' and to withstand boiling water, as well as being much more flexible than an untreated dried skin. Tanning process involves an important consumption of water and generates a complex pollution consisting of a mixture of organic and inorganic substances which are difficult to treat. Large amount of chemicals are used to convert raw cattle hides and goat and sheep skins in to leather; a considerable part of these chemicals is not absorbed in the production process and is discharged in to the environment. The discharged effluent contains both natural substances of the raw hides and skins and chemicals used for the tanning which are not unfixed during the tanning process. Tanning guarantees quality, durability, practicability and the stability of the final leather product by treating the skin with inorganic and organic tannins such as chromium, aluminium, titanium, iron and zirconium basic salts as well as high molecular weight plant polyphenols (vegetable tannins), aldehydes, oils and other substances (Krishnamoorthy, G., Sadulla, S., P.K. and Mandal, A.B. 2012, 173; cassano et al. 2001, 118).

Characteristics of some of the tanning system are presented in table 2.1. Tanning treatment inhibits the biological degradation of the protein containing skin by microorganisms which would result in undesired smell. Furthermore, tanning agents are used in order to prevent the leather from chemical and thermal degradation. The most common tanning agent is chromium sulphate.

The use of leather goes back to the pre-historic time. The principal raw material is the hide or skin of animals' including-to a small extent-that of reptiles, fish and birds. The tannery operation involves converting the raw skin, a highly putrescible material, into leather, a stable material, which can be used in the manufacturing of a wide range of products. The whole process involves a sequence of complex chemical reactions and mechanical processes. Performing various steps of pre-and post-treatment, generates a final product with specific properties: stability, appearance, water resistance, temperature resistance, elasticity and permeability for perspiration and air, etc [13]. Leather is an intermediate industrial product, with numerous applications in down-stream sectors of the consumer products industry. For the latter, leather is often the major material input, and is cut and assembled into shoes, clothing, leather goods, furniture and many other items of daily use. Different applications require different types of leather.

Table 2.1: Characteristics of some different tanning system

Tannage	Collagen-Crosslink liability	Crosslink flexibility	Shrinkage temperature	Eco-toxicology
Mineral				
Aluminum (III)	High	Low	Very low	Moderate
Titanium (IV)	Moderate	Low	Low	Low
Zirconium (IV)	Moderate	Low	High	Low
Chromium (III)	Low	Low	Very high	High
Polyphenol				
Vegetable,__ all	Moderate	High	Low	Moderate
types	Moderate	Low	High	High
Hyd.Veg +Cr	Moderate	Low	Very high	
(III)	Moderate	High	Low	High
Hyd.Veg +Al				
(III)	Moderate	Low	High	High
Cond. Veg +				
Aldehyde	Moderate	High	Low	High
Cond. Veg +	Low	High	Low	High
Oxazolidine,	Moderate	High	Low	High
Syntans				
Syntans, resins,	Moderate	Low	High	Moderate
polymer				
Aldehyde	High	High	Very low	Low
Polymers +	Very high	High	Very low	Low
Aldehyde	Low	**	Very low	Low

2.1.1 Chrome tanning

The use of chromium (III) salts is currently the commonest method of tanning: perhaps 90% of the world's output of leather is tanned in this system.

Chromium salts used in tanning enters the pores of the skin by a diffusion process to react with the collagen carboxyl groups and form inter- and intramolecular cross linking which results in physical, chemical and biological stability. This step is followed by a basification step using weak chemical bases which enhances the anionic character of the carboxylic collagen groups and hence increases the attraction towards the chromium cations Cr3+which results in a final coordinate covalent bond.

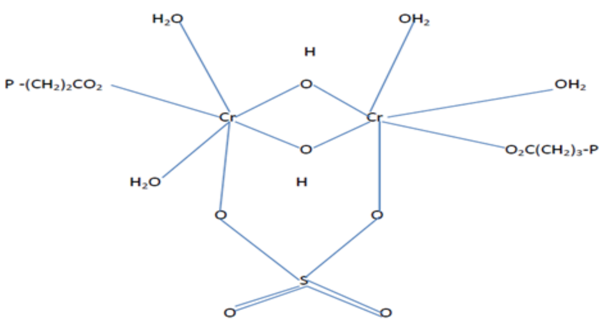


Figure 2.1 Interaction of chromium complex with collagen

The whole tanning process takes about 5 to 6 hours (Sivakumar and Rao 2001, 28). From the chrome salt used, 60-65 % of chrome salt is reacted to the pelt during the tanning step whereas 35-40% of chrome is removed with the tanning effluent (Cassano et al. 2001, 118).

2.1.1.1 Nature of Chrome Tanning and Environmental Concerns

In our country the establishments of industries were only based on their economic benefits to the society. Many of the tanneries are concentrated in Addis Ababa and the establishment of these industries did not consider their harmful effect to the environment and health. As the result the rivers found around these tanneries contain high chromium and has potential harm to the downstream people and animals that uses these water bodies. There are methods of disposal of chrome containing wastes mainly include recycling, burring and incinerating but these are not the only means to avoid chrome waste in tanning industries. Production of wet white leather can be able to produce tannery wastes without chrome, such as shaving, trimming and buffing's etc, which will be so easy to recycle and reuse that can decrease chrome loading [12].

2.1.1.2 Advantages of Chrome Tanning

As has been discussed above, chrome tanning is a proven method of leather processing having its own advantage. These are

• High hydrothermal stability

• Good strength characteristics

• Good affinity and compatibility with dyes, retanning materials, fatliquors and finishing materials

• Good organoleptic properties

2.1.1.3 Disadvantages of Chrome Tanning

Even though chrome tanned leathers have significant advantages, they suffer from the serious disadvantages due to constraints of its discharge norms of 2ppm (Madhan et al 2002). It is well established that hexavalent chromium is carcinogenic and can cause damage to skin, mucous membrane, respiratory tract, kidney etc. It has also been shown that there is a possibility for the formation of chromium (VI) during the various processing conditions.

Recent reports suggest that at higher levels and under certain ligand environments, chromium (III) also in toxic. The problem is aggravated by the fact that the currently practiced chrome tanning procedures results in an uptake of only 60-65 % of the chromium offered to the leather and hence a substantial amount of chrome is discharged into the effluent. Many chrome management measures like addition adjuncts improving the uptake of chromium, reusing/recycling the chrome liquor and recovery and reuse of chromium salts have been attempted. As of now, there is no safe disposal method available for used chrome tanned leather products, which is a major concern. Existing technologies of chrome removal are capital intensive and results in solid wastes that causes disposal problem. Hence to overcome the problems associated with chrome tanning, researches are being conducted on alternative tanning that is effective, economical and environmentally friendly.

2.1.2 Chrome free tanning system

2.1.2.1 Aluminium tanning

This is the oldest inorganic tannage for harness, upper and glove leathers (Procter 1922). Aluminium tannage fulfils separation of the skin fibers to obtain an opaque and supple material after drying. Aluminium salts combine with the skin in a similar fashion to that of chromium salts in that, as they become more basic by addition of alkali. They also become more stringent and they 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.

When compared to the hydrolysis equilibria diagram of chromium sulphate, aluminium salts behave in a similar manner, but the equilibrium constants are different. Aluminium salts do not readily forms such stable ol or oxo complexes as chromium from low basicity salts, but follow simple hydrolysis to give a basic insoluble salts.

Aluminium tanning agents have quite high astringency and one of their outstanding merits is its ability to tighten the fiber structure, either to give a finer grain or a tighter nap on the suede leathers, when used along with chrome tanning salts. It is highly cationic and increases the fixation and reduces the penetration of acid and direct dyes, vegetable tannins and sulphated oils. Thus it is commonly used for getting stronger shade on dyeing or firmer leather by reducing anionic fatliquor penetration. Attention has been drawn already to the interest shown in aluminium tannage as a replacement for chromium salts due to the greater acceptability of alum salts in tannery effluents.

2.1.2.2 Aldehyde tanning

The use of aldehyde in the stabilization of protein fiber has led to a tremendous increase in the volume of research on the aldehyde protein reaction. Aldehyde - protein reaction can be conventionally separated into three types, which are equilibrium, non-equilibrium but chemically reversible type and truly reversible type.

2.1.2.2.1 Formaldehyde

Formaldehyde has several advantages over the other aldehydes both for industrial application and case of analysis. It is not surprising that formaldehyde has been used in most of the studies of the tannage (Pradeep Kumar et al., 2009). Formaldehyde has been known as tanning agent for many years. The fixation of formaldehyde by protein is accompanied by the change in physical properties. Also, the shrinkage temperature was notably increased when the leathers were treated with simple aliphatic-aldehyde such as formaldehyde, gluteraldehyde, acrolien, crotonaldehyde, etc. Acetaldehyde is the most reactive one. The simplest dialdehyde, gluteraldehyde is good tanning agent, which increases the shrinkage temperature by adding more cross linking.

The various factors that are responsible in influencing the formaldehyde fixation are the concentration of formaldehyde, rate of fixation and pH. The functional groups that are involved in this reaction are the amino group, amide group, imidazole group, indole group, sulfydryl group, tyrosyl group and peptide group.

2.1.2.2.2 Glutaraldehyde

Glutaraldehyde is an excellent material, which is capable of crosslinking protein due to its bi functional nature. When used as a tanning agent itself, it can glutaraldehye as a supplementary tannage to chrome tannage has resulted in greater stabilization of the protein fiber, which results in a raise in shrinkage temperature and greater resistance of leather to chemical attack. The glutaraldehyde shearlings have been found to have excellent resistance to urea and are washable, which make it to be used widely.

The application of glutaraldehyde for tanning will result in the increase of perspiration resistance on insole, garment leather and linings and also increases the resistance to acids and burn. Glutaraldehyde has been found to have softening effect on leather and water repellency. Gluteraldehyde is being employed as the retanning agents and supplementary materials to other tannages.

2.1.2.3 Zirconium tanning

A method of producing leather utilizing salts of zirconium, usually under very acid conditions. The high acidity permits the zirconium salts to precipitate basic salts at lower pH values (on the order of 2.0) than either aluminium or chromium, which are also used in the production of leather (Fathima et al., 2003). Zirconium salts tend to be very astringent, and normally produce tight, firm leather; they also cause rapid tannage of the grain of a leather and produce a fine, short nap on suede leathers. By the use of masking salts, such as acetates, their astringency can be reduced, resulting in softer, smooth-grained leather. Zirconium-tanned leather is usually fuller and firmer than that produced by chrome tanning and actually feels more like vegetable-tanned leather. The leather so produced is of a pleasing white colour, has good light fastness, and is superior to alum- tawed skin in that it does not wash out and has a higher (90° C) shrinkage temperature.

2.1.2.4 Iron tanning

Rational studies on iron tannages were from 1856. The ferric ion is pale violet and its solutions are generally collared yellow or brown. The tanning effect of ferric sulfate solution, is a function of basicity, concentration, neutral salts added, duration etc (Thomas & Kelly., 1928). It produces leathers with less Ts, poor lightfastness and dyeability.

2.1.2.5 Vegetable Tanning

Vegetable tanning extract from heterogeneous group of material having common capacity to convert animal skin to leathers (O' Flaherty et al., 1978). The term tanning was introduced by Sequin to denote the substance responsible for the lathering ability of various plant extracts. The recognitions of the complexity have made it more difficult than ever to define a tanning and at the present, it is generally safer to use the term "Tannin extract". The tannin is valuable source of highly reactive polyhydrate phenols, available in large amounts at economical cost level.

Vegetable tannins are in general classified under two categories.

Condensed	Hydrolysable
Quebracho	Chestnut
Wattle	Oak
Mangrove	Tara
Hemlock	myrobalan
Cutch	Sumac

Vegetable tanning extract contain polyphenolic substances. The minimum molecular weight requirement probably varies with nature of the molecule and the number of phenolic group present. It’s lowest can’t be below 400 to 500. Tanning molecule readily broken down by hydrolysis with acids, alkalies or enzymes are termed as ‘hydrolysable tannins’. They commonly possess free acid and carboxyl group in addition to phenolic groups.

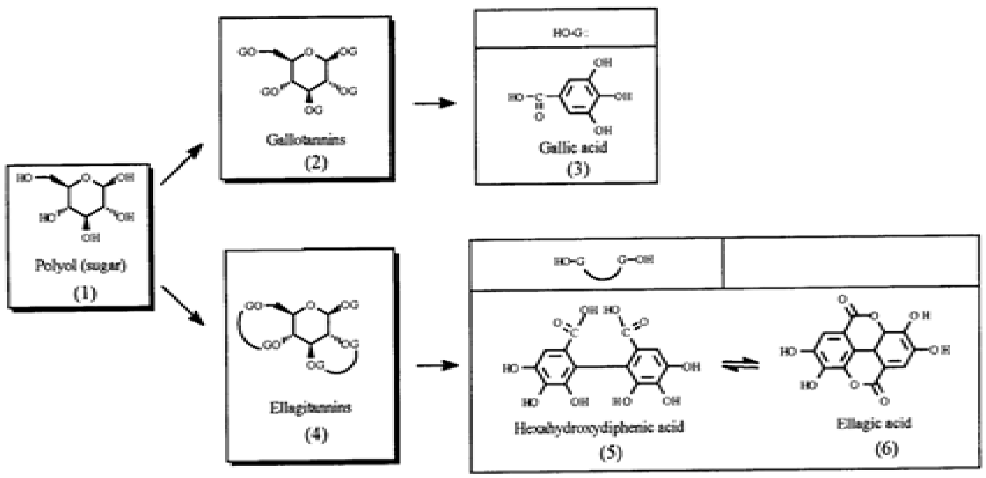


Figure 2.2: Hydrolysable tannin precursors

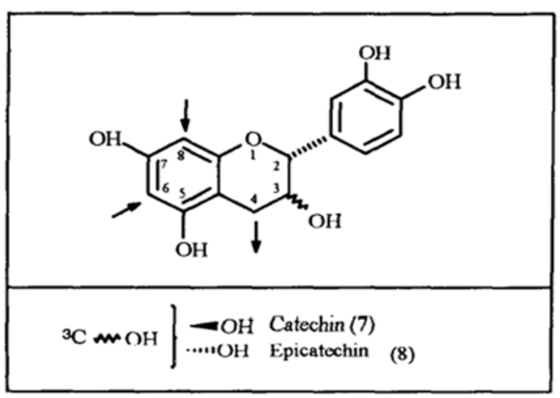


Figure 2.3 Condensed tannins

Other water-extractable polyphenols present in plants contain small amount of carbohydrate, which are not chemically linked to phenolic substances. They contain only traces of gallic and similar substances and fail to give significant yields or simple easily crystalizable phenolic molecules on hydrolysis. These extracts are generally termed as condensed tannins.

2.1.2.5.1 Tanning Mechanism

Vegetable tannins are derivatives of phenol (with several OH groups). Phenols are more acidic than alcohols (pKa~10), but are weak acids therefore form salts only with strong bases. The solubility of vegetable tannin phenolics are approximately around 7% in cold water. Vegetable tannins react with atmospheric oxygen, particularly at high pH values to form quinones (for OH groups that are ortho-para to one another). Vegetable tanning liquors are very complex and continually changing physically, chemically and biologically. They are partly colloidal but easily aggregate and will then sediment. Yeasts moulds and bacteria can grow in the liquors, the main consequence being the fermentation of sugars to acids. Non-tannins are also the constituents of vegetable tanning liquors. The non-tans include, apart from the sugars, acids and their salts, hemicelluloses, pectin and lignin, as well as compounds containing nitrogen and phosphorus. The acids and their salts are the most important for the tanner. Apart from the nature of the tannins themselves, the acids and salts are the principal means of controlling the astringency of liquors and whole process of vegetable tannage. Gallic and other phenolic acids can arise from the breakdown of tannins.

The mechanism of vegetable tanning has been studied by leather chemists for decades; yet there are no clear theories of vegetable tannin fixation. First, the vegetable tannins themselves are such complicated mixtures of components that the materials cannot be defined by relatively simple structures. The second factor is the colloidal behaviour of the vegetable tannin materials. A third complicating factor is the skin protein itself. Its condition, as a result of previous treatment, affects not only its physical structure but also its chemical structure. The degree of opening of the fibres, the availability of reactive sites for vegetable tanning, the degree of hydration, the presence of salts and the extent of swelling of the skin are all-important in practical vegetable tanning. Quite a lot of complex phenomena are involved and there is a further complication of one working against another. There is still no decided conclusion as to what are the groups of protein involved in vegetable tannage and even, whether vegetable tannage is a chemical action or strictly a physical absorption. In all fairness it can be said that both chemical and physical phenomena are occurred in the reactions; it is the combination of these factors and the relationship of the various vegetable tannins to both phenomena, which determine their practical application.

The generally accepted mechanism for vegetable tannage is through hydrogen bonding to the CO-NH peptide backbone of the protein (collagen) through the phenolic hydroxyl group of the vegetable tannin [14]. This type of interaction is concluded from reaction studies with polyamides. Also it is known that polyphenols interact with side chain functional groups; to amino side chains by electrostatic salt links with carboxylate or hydrogen bonding with carboxylic acid groups (depending on pH). It is also now known that condensed tannins have an additional mechanism for reaction, because they are more resistant to removal by hydrogen bond breakers.

Thus the vegetable tannins are essentially unionized through the entire vegetable tanning range, and the ionization of the phenolic hydrogen is not the main factor for fixation. The protein, on the other hand, increases its hydrogen ion fixation with the lowering of the pH; therefore, fixation of the vegetable tannin is dominated by the reaction of the hydrogen ion with the protein, rather than the hydrogen ion on the vegetable tanning material. At the high pH values in the neighborhood of pH 5, the hydroxyl groups on the vegetable tannin material become ionized and the fixation of the vegetable tannin decreases distinctly.

The S-shaped curve near the iso-electric point emphasizes the fact that the reaction is not strictly chemical. The swelling characteristics of the protein are such that hydration of the molecule is least near the isoelectric point but increases both on the acid and the alkaline sides of the isoelectric point. Increase in pH causes an increase in hydration and in the fixation of the vegetable tanning material at pH values just above the isoelectric point. As vegetable tannage proceeds, the fiber is no longer dominated by water of hydration, but rather has changed in character as a result of the fixation of the vegetable tannins. The hydration factor becomes less significant, and the eventual fixation curve is a smoother sweep from the neutral pH range to a high fixation at the strong acid range.

The quantity of vegetable tanning material is important to bring about proper tannage is much greater than one would expect from a chemical point of view. The vegetable tanning aggregate is very large and despite the possibility of multipoint attachment, it cannot reach the available sites in the protein. The physical size i.e. the large size also prevents the attachment of a second molecule to an available site. Vegetable tannage can be considered as being a partial reaction between the protein and the tannin, the reaction being blocked as a result of the physical size of the hide fiber and of the vegetable tanning extract particles. As tannage proceeds, additional vegetable tanning materials are deposited on and between the hide fibers, resulting in eventual coating of the fibers and filling of the voids of the hide with vegetable tanning materials.

2.1.3 New combination tanning as a chrome tanning alternative

2.1.3.1 Silica: An alternate for chrome tanning

Pure sodium metasilicate in addition with tara proved as most preferable option for tanning of pickled pelt which gives effective tanning. Pollution load studies put forward sodium metasilicate as an effective tanning agent for pelts to apply at small industrial scale also.

2.1.3.1.1 Properties of sodium metasilicate

Density is an expression of total solids and is typically determined using a hydrometer. As temperatures increase, density decreases. When the solid content increases, density increases. Weight ratio is the most important silicate variable. Ratio determines the product's solubility, reactivity and physical properties. Ratio is either the weight or molar proportion of silica to alkali.

Total solids are the sum of the silica and the alkali. The tanning salt is white in colour similar to that of other alkaline salts (Figure 2.6).

Figure 2.4 Sodium metasilicate

pH is a function of silicate composition and solids concentration. The pH value of silicates does not truly reflect the alkali content of solution, due to the strong buffering capability of silica. This means the pH of a silicate solution is kept constant until almost complete neutralization. The buffering capacity of silicate solutions increases with increasing ratio of silica to alkali. The pH of the silica used was at alkaline pH (pH=12.5).

2.1.3.1.2 Chemistry of silicate

Sodium Carbonate and sand (SiO_2) are fused at high temperature (1200-14000^{o}c) in a furnace to form sodium silicate with chemical formula Na_2Sio_3 when anhydride.

$$Na_2CO_3 + xSiO_2 \rightarrow Na_2OxSiO_2 + CO_2$$

Soluble silicates are composed of three basic components. Silica-this is the primary constituent of all silicates, alkali-a key component of soluble silicates.

Aqueous sodium silicate solutions appear to contain the low $[SiO_2\ (OH)\ _2]_2$-but, depending on the pH and concentration, polymerized species are also present. Silicates are built up on the basis of sharing oxygen atoms of tetrahedral SiO_4 unites:

Sodium Silicates ($Na_2O.XSiO_2$) are metal oxides of silica. All soluble silicates can be differentiated by their ratio, defined as the weight proportion of silica to alkali (SiO_2/Na_2O) ratio determines the physical and chemical properties of product. Using silicates to tie up metal ions is an inexpensive way to enhance the performance of many processes.

Soluble silica reacts with all multivalent cationic metal ions to form the corresponding insoluble metal silicates. Silicates will precipitate these metals out of solution and render them insoluble or non-reactive. The reactant by-product normally displays long term stability.

2.1.3.1.3 Silica tanning system

The use of silica for tanning dates back to 1914, when Morin obtained the first patent on silica tanning. Later, Hough patented a silica tannage, which was prepared by reacting 30% sodium silicate with 30% hydrochloric acid, ensuring excess acid in the solution so as to neutralize the sodium silicate completely. The problem confronting the tanners is to prepare a very stable solution of silica. A sol of silica purified is much too sensitive for practical use as the silica is precipitated by very small amount of electrolytes, such as would ordinarily be carried by the skins.

Silica tannage is carried out, as we have seen, in silica dispersion in an acid medium, if solutions of strong acid, such as hydrochloric acid, are mixed with sodium silicate solutions either gels (or) sols are obtained. As is well known that silicate is easily soluble in water when a soluble silica monomer $Si(OH)_2$ is formed at concentration greater than about 100-200 ppm as SiO_2 that is greater the solubility of the solid phase of amorphous silica, the monomer polymerizes by condensation to form higher molecular weight species of silicic acid that depend upon the conditions, separate in the form of solution or aggregate in to three dimensional network and form gels. The polymerization behaviour of silica as well as the polymerization degree and the size of the colloidal particles, depend on several factors, the most effective being the pH and the presence of salt. In the presence of salt at every pH value the colloidal particles evolve towards the gel form, while in the absence of salts the colloidal particles assume the state of a stable solution for pH>7. The maximum stability of the solution occurs at pH 1.5-3 while the minimum solution stability occurs at pH 5-6 when salts are absent and at pH 7 when salts are present. To obtain better penetration, it is necessary that the colloidal silica is present in solution as stable solution of small size particles. Since the presence of salt in the tanning solution is necessary to avoid swelling of the skin, silica gelling is inevitable. It is thus necessary to operate in pH ranges in which the gelling time as longer as possible [15]. The sols formed are stable only in a basic or a strongly acid medium. The figure (2.5) given below, taken from Ray and P.B.Ganguly, showing the stability link of these sols a formation of their pH values of their concentration. The solution formed is stable only in a basic or in a strong acidic medium.

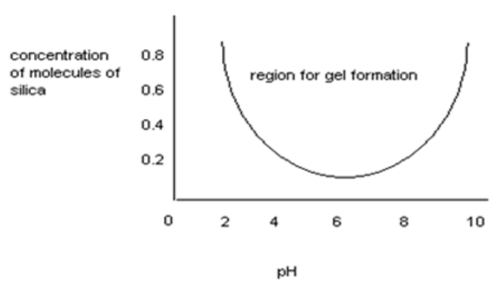


Figure 2.5: The stability link of Silica solution a formation of their pH values of their concentration

One of the best methods to challenge chrome pollution is to avoid chrome itself in tanning system. So research is going on to find out the best eco-friendly system of leather tanning which encounter the requirements what chrome tanned leather have. It has been reported that silicon dioxide and sodium silicate are used for manufacturing wet-white leathers. Silica based tanning produces white leathers hence, the concept of wet-white tanning as a potential alternative to wet blue tanning is appealing. Silica is used for tanning in the form of solution not in the form of powder itself. A study of tanning was carried out with these solutions by a serious of tests with variable amount of silica, tanning times, silicic solution aging and acidities [16]. The ratio of silica absorbed by the skins and the feel of leathers produced were markedly different. From previous studies on silica it is observed that:

1) the silica is absorbed by the skin like any other tanning material, but it can, according to the application conditions, give either leather showing all the characteristics of a full tannage or products keeping the feel of untanned skin, although their silica content is high;
2) The penetration of silica in to the skins is possible only with monomeric or very weakly polymerized products. However those products have no tanning action. To produce tanning it is necessary that polymerization of the solution occurs during the tanning time.
3) To the extent that the fixed silica ratio and the fixation speed are concerned, the silica tannage is situated between inorganic tannage and vegetable tannage.
4) The ratio of silica fixed by deaminized skin is only very slightly lower than that fixed by ordinary skin under the same conditions.
5) Finally tests on mixed tannages give the following results.

a) The chrome tannage after silica tannage is not hindered; the silica tannage after chrome tannage is slightly hindered.
b) The zirconium tannage after silica tannage is partially hindered; the silica tannage after zirconium tannage is not hindered.
c) The vegetable tannage after silica tannage is not hindered; the silica tannage after vegetable tannage is hindered. However there are reports on prior silica tannage hindering the vegetable tannage [16].

Aluminium, tannic acid and silica combination tanning is one of the chrome free tanning system of leather tanning in which silica is involved. The presence of silica in that combination tanning system gives rise to produce supple, soft, smooth, fluffy and fuller leathers because it has an ability to fill the loose portions as well as lubricate due to its inherent gelling nature of the leather [7]. Skins stabilized with silicates could be adapted to shaving readily. In the other studies silica was used in chromium tanning. Since polymeric silica may interact with chromium salts through chelate like coordination bonds, thus improving adsorption of the chrome salt on the silica particles and forming synergism effects to favour the chromium penetration and fixation process [15]. The physical strength and shrinkage temperature of the resultant leather tanned with nano-SiO_2 were all higher than the stipulated Chinese standards of chrome-free leather and were close to the chrome tanned leather control. More importantly chromium was at zero discharge because chrome was not used in this experimental process. At the same time, the values of total solids (TS) of the experiment were lower by 30%, but BOD and COD was slightly greater than with that of control leather.

Biochemical oxygen demand (BOD5), BOD5/COD analysis shown that, the wastewater from experimental treatment was more biodegradable than that of control treatment. Another interesting result was that the nano-SiO_2 shavings produced in this process could be easily reused. High quality gelatin without chromium was obtained and large amount of water and chemical materials was saved in recovery processes, so the secondary pollution caused by the traditional recovery of chrome shaving could be avoided. However, the drawbacks associated with the solo tanning with silica are the lack of desired shrinkage temperature and strength properties in the leathers [17, 18, 19, and 20]. To reduce this drawback of silicate, it is required to use combination tanning and improves the required properties of the leather produced.

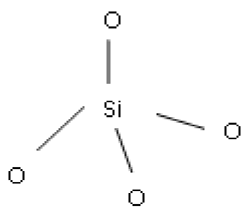
Table 2.2: shrinkage temperature of leathers from tanned with different tanning agents

Chemical modification	Denaturation temperature (ºC)
Raw skins	65
Metal salts: Al(III), Ti(IV), Zr(IV) Fe(III)	75-80
Vegetable tanning agents	70-85
Oil tannage	65-70
Sulfonyl chloride	80
Formaldehyde tanned leather	80-85
Glutaraldehyde tanned leather	75-85
Aldehyde/ aluminium tanned leather	80-90
Chromium sulphate	100

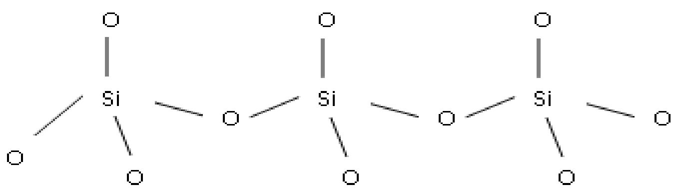
Table 2.2 the distinction of shrinkage temperatures

2.1.3.1.4 Silica fixation on collagen

The first study of this subject was done by Chambard and Favre [19]. These authors studied the stability of silica solutions as the function of acidity and in the presence of several acids. They pointed out that the kind of acid used had little or no influence, and that ionic acidity only must be considered. The maximum stability is obtained at lower pH. This corresponds approximately to the condition of the tanning bath described by Hough. However, chambard and lasserre assumed it was possible in those solutions very rich in silica, that there would be a high state of polymerization and that this condition could influence the solution stability and their penetration power. Thus they were led to use sodium metasilicate ((SiO_2/Na_2O) =1). This product is the only one of the series of commercial silicates which is relatively well defined. It is not a viscous solution, but a solid semi crystalline product [21]. Sodium metasilicate is known to give fuller white leathers with light fastness, suppleness and good feel. Hence, use of silica as a co-tanning agent is expected to improve the properties of Tara tanned leathers.



Monomer



Linear trimer

Figure 2.6: Anionic structures of silicates

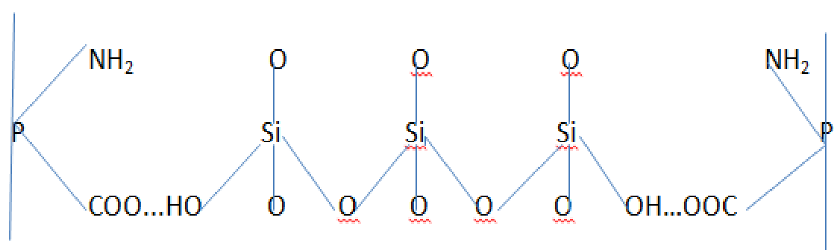


Figure 2.7: Reaction of silica with collagen

Here it is better to understand that the silica solution is reacted to leather collagen with hydrogen bonding. Hence hydrogen bonding is the weak bond results lower shrinkage temperature to leather.

2.1.3.1.5 Advantages of silicate tanning process

Silica has its own advantage in leather tanning. It reduces the pollution load of chrome, Cost wise it is cheaper than Cr and it is easily available, it possesses tanning property and facilitates buff ability in case of suede leather, bright shades could be obtained with sodium silicate tanned leather on dyeing, silicate tanned leather retains soft even on washing, perhaps due to the lubricating nature of silicates, fullness of the leathers is improved considerably, it imparts high tensile strength to the leather [7]. Silica in the form of colloidal silica, silicic acid has applications in leather processing in the context of wet white that it will be useful. The reagent binds to collagen via hydrogen bonding, so it is not unexpected that there is no an increase in shrinkage temperature. The effect cannot be called tanning. However the presence of silica within the fibber structure has the effect of reducing the ability of the fibre structure to slip over itself when subjected to distorting pressure. When the shaving blade applies pressure to untreated pelt, the surface can ripple ahead of the blade, until the pressure gets too much and the blade slips over the surface, generating fractional heat. If the pelt is treated with silica it is stiffened, so the shaving blade cuts rather than distorts the surface. The treated waste/ byproduct can be used as fertilizer, instead of being disposed of to land fill [22].

2.1.3.2: A possible tannin source to make chrome free leathers

Tara is the name commonly given for a fairly well known material, which consists of the dried pots of caesalpinia spinose, a tree or shrub widely distributed in North Western South America. The shrub has been cultivated in Southern Italy, sardhina and in former Indian colonies. In North Africa, it has been found to grow well, especially in morocco. Tara parts are also known in trade as cevalina or carabin, but this name is not in use. The pods are similar to divi-divi and algorabilla, all three being member of the same genus. Tara is one of the hydrolysable vegetable tanning agents. The tannins from Tara are well known in the leather industry and they are appreciated because their light colour and light fastness compared with other traditional vegetable tannins. For this reason, demand of Tara increased during the last decades at the time high performance leather production for automobile upholstery has experienced a growing demand. However, there are no specific promotions and researches for the use of Tara tannins. Its application as tanning agent remains in the technical departments of the chemical suppliers. Tannery technicians obtain very little information from their technical product information-sheets that only specify few recommendations and provide minimum quality values such as concentration of tannins, solids and humidity [23, 24].

Therefore the combination (Tara- silica) tanning of leather could give better fullness, colour etc which is environmental eco-friendly and has no effect on health. Since, Tara and silica produce white leathers, the leathers obtained using these tanning agents are light colour, which are ideal for pastel shade dyeing. Tara is cultivated as a source of high value products from its pods as tannins based on a gallotannic structure used in the leather industry [25].

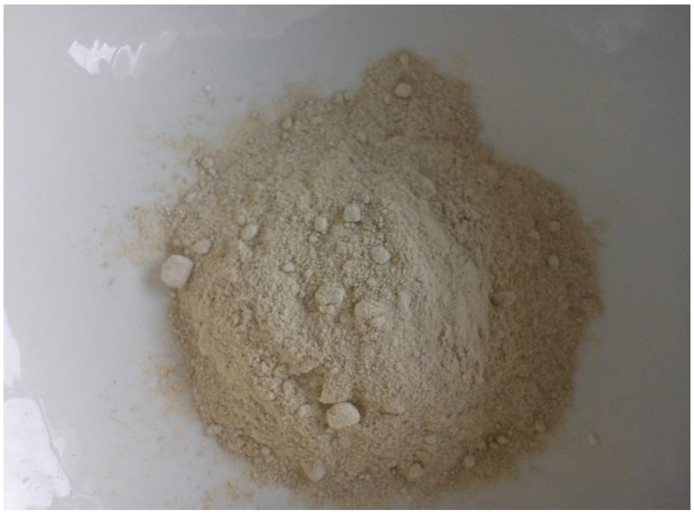


Figure 2.8: Tara powder used for experiment

The pH of the tara powder which used for the experiment was 4.5 at 10% solution in water. There are, however, some drawbacks of the tara tannin when compared with other vegetable tannin extracts:

- High concentration of insoluble solids (tara powder contain high quantities of cellulosic compounds from the tara pods if tannins are not extracted properly)
- Tanning limits when tara tannin is the single compound for tanning. Hydrolyzing vegetable tannins cannot increase the shrinking temperature.
- Easily produces complexes with iron and other metals and form dark spots on the leather when is contaminated. Usually tara mills and several machines used during the leather processing for mechanical operations contain parts made with iron and the risk of such dark spots is quite high[10].

2.2 Properties of upper leather

In the present project work, it is proposed to develop upper leather using the new Tara-Silica combination tanning system. The following are some of the important properties required for a leather to be used as an upper. The following are the important properties required for upper leather

- Grain tightness
- Perspiration resistance
- Air and water vapour permeability
- Resistance to heat
- Fastness to light
- Fastness to wet and dry rubbing
- Grain crack resistance
- Flexural endurance
- Good tear and tensile strength
- Good penetration of dye

2.3 Post tanning

The raw material quality is dependent on several factors viz. breed, origin, region, farming and slaughtering practice, season, transportation and handling system, preservation techniques etc. Moreover, the quality of raw material nowadays is not same. Hence, some quality enhancements are carried out through processing steps after main tanning. Majority of these are done during post tanning/wet end process/operations. Also, the kind of targeted article or final leather is decided at this stage.

Some of the main objectives of post tanning operation are as mentioned below.

- To modify the properties of Wet blue/wet white with characteristic chemicals
- To produce various types of crust/finished/final leather from Wet blue/ wet white
- To achieve properties such as fullness, grain tightness, softness, fat distribution, desired shade through dyeing, fastness, grain fineness, elasticity, buffeability, smoothness etc as desired by the customer

- To prepare good crust leather which is an input material for making full finished leather article through mechanical operations viz. samming/setting, shaving, vacuuming drying, overhead drying, stacking, buffing, dry drumming.

Some operational objectives of each operation are also mentioned as follows

Sammying & Shaving

- The objective of sammying is to reduce the moisture content of the Wet blue/wet white before shaving operation
- The objective of shaving is to get required substance in final leather
- The objective of material segregation in terms of thickness before shaving is to get uniform substance, chemical uptake and desired properties that could be achieved through the retanning, dyeing and fatliquoring processes

Neutralisation & Washing of the wet back leathers helps

At the end of tanning leather is generally at pH around 4.0. With chromium tanning, the pH tends to further decrease since protons are released by hydroxyl bridges of chromium complexes (olation). Since the isoelectric point is higher, the skin protein is in cationic form and is too reactive with regard to the syntans, dyestuffs and fatliquors, all in anionic form, employed in the subsequent steps. The pH value is then raised from 4.5 to 6.5 by using a mild alkaline salt such as sodium formate and sodium bicarbonate. Therefore the aim is:

- To remove the acid liberated after tanning and ageing
- To remove neutral salts and unfixed/soluble/free chromium present in the leather
- To increase the pH for the required product type thereby the affinity is altered to facilitate better penetration of syntans, dyes and fatliquors

Retanning

After the pH is uniformly adjusted along the cross-section, a retanning process is normally performed to correct the properties of the leather, thus defining its ultimate character. Such a transformation is mainly aimed to obtain the desired handle in terms of fullness of the final article and different tanning chemistries can be used here with respect to the main tannage. Although they do not strictly enter the tanning agent definition, hydrogen bondable polymers may be employed for this purpose, often in order to fill up the weaker areas of the hides (flanks) and belly and produce more even leather, or a particular handle. Hence it helps

- To achieve strength properties for crust as per the desired end product
- To fill the loose portions of the chrome tanned or Wet white leather with vegetable or synthetic tannins
- To increase the cutting value or usable area after filling even at belly/flank area
- To achieve less shrinking during drying
- To achieve good tightness, buffeability, embossing and finish properties
- To improve the penetration of anionic type fatliquors, dyestuffs and finish adhesion

Dyeing

The main objective of dyeing with dyestuffs, which are mainly of azoic nature is to impart the colour as desired by the customer or marketing and sales forecast. The introduction of one or more sulphonic functional groups is necessary to make the molecule water soluble and to allow an electrostatic bonding with the cationic amino groups of collagen. For a good penetration the reactivity of the substrate should be minimized by raising the pH value.

- To plan the base colour before finishing for grain based finished articles
- To get uniform shade in case suede and nubuck articles
- To bring aesthetic look for final/finished leather

Fatliquoring

In the fatliquoring process the leather is treated with fatty matters, often sulphonated or sulphated oils that react with the fibrous structure of collagen and prevent them from tough and helps as emulsifying agents for the neutral oil as well as have the ability to wet the leather surface as surfactants. Treatment leathers with fatliquor also prevent the leather fibres from sticking together during drying. This results in giving leather softness, strength and suppleness [22]. Fatliqours are required for all types of leathers.

- To lubricate the leather fibres so as to reduce internal friction while in use and to increase durability
- To form physical or chemical cross links between the fibres, thereby to avoid collapsing or sticking even after drying
- To achieve softness, pliability, stretch, compressibility and tensile strength
- To nullify the effects of temperature changes during summer and winter on finished/final leather

Fixing

Fixing of leathers at the end of post tanning is vital. Fixation is obtained by lowering the pH, typically with formic acid.

- To fix the dyes and fatliquors permanently with the leather
- To avoid bleed even in dry condition and rubbing

Then the leather is Piled and Overnight aged to drain out the water gradually, for proper fixing and distribution of chemicals offered, to avoid folds after unloading and conditioning for next day setting out.

2.4 Wastewater Generation and Characteristics

Volume of wastewater (effluent) and its characteristics vary from tannery to tannery. They may also vary within the same tannery from time to time. The wastewater from beamhouse process viz. soaking, liming, deliming, etc., are highly alkaline, containing decomposing organic matter, hair, lime, sulphide and organic nitrogen with high BOD and COD. The wastewater from tanyard process viz. pickling, chrome tanning are acidic and coloured. Effluent from vegetable tanning contains high organic matter. The chrome tanning wastes contain high amount of chromium mostly in the trivalent form. The pollution load per ton of hides/skins processed for the entire process is shown in Table 2.4

Table 2.3: Pollution Load per ton of Hides/Skins of composite effluent

S.No.	Pollution Parameter	Pollution Load (Kg)
1	Volume of effluent (m3)	30-40
2	BOD	70
3	COD	180
5	Dissolved Solids	600
6	Suspended solids (SS)	4
7	Chromium (Cr)	30

Source: Central Leather research institute (CLRI)

2.5 Colour fastness

In general colour fastness tests are conducted using specific test methods. The extent of fastness that is the extent of colour removal, colour staining on the contact material is assessed with a set of graded scales called Grey scales. Grey scale used to assess the colour change in leather surface is called colour change scale. Grey scale used to assess the colour transfer to the rubbing felt or contact fabric material is called colour transfer scale (SATRA TM8: 1992). The grey scale has five grades from grade one up to five.

3. MATERIALS AND METHODS

3.1 Raw materials, Chemicals and Reagents

3.1.1 Raw materials used

Wet salted goat skins were purchased from Addis Ababa abattoirs and processed following conventional soaking, liming, deliming, bating and pickling. The medium size pickled pelts were taken for preliminary tanning experiments. For optimization one pickled goat skin was cut and used for four trials (one skin cut in to four equal parts). The optimized process is used for matched pair comparison with conventional chrome tanned control. All right side of the skins were used for the experimental trials and corresponding left sides for control. Then the leathers were analysed for the organoleptic properties, chemical and physical tests by comparing chrome tanned leathers after post tanning operation at crust stage using standard procedures for testing as these tests are essential in determining the suitability of the tanning chemicals for upper leather manufacture.

3.1.2 Leather chemicals

The tanning chemicals of sodium metasilicate and tara powder as well as masking agents (citrate and tartrate) were sourced from SRL Ltd Co., India. The leather chemicals used for processing are of commercial grade. These are the chemicals to be consumed during the leather making starting from soaking to pickling and retanning to finishing as in the conventional method of leather manufacture. The tanning chemicals are both commercial and analytical grades.

3.1.3 Reagents used

The reagents used for the chemical analysis are of analytical grade. The chemical analysis those used reagents includes spent liquor determination (COD, BOD), chromic oxide content determination (nitric acid, sulphuric acid and per chloric acid) fat content determination and total ash content determination.

3.2 Laboratory equipment, instruments and Apparatus used for silica solution preparation

- pipette, electronic pH meter
- Burettes, Measuring cylinder, Beakers

- Magnetic stirrer and paddle retriever

3.2.1 Laboratory equipment and instruments used for the preparation of silica solution

- Pipette, electronic pH meter, analytical weighing balance
- Burettes, Measuring cylinder, Beakers
- Magnetic stirrer and paddle retriever

3.2.2 Laboratory equipments, instruments and Apparatus used for chemical analysis

- Standard Measuring Flask, Round bottom flask,
- Soxhlet apparatus, Hot air Oven
- Shrinkage temperature tester
- Thermometer
- UV-Vis Spectrophotometer
- Funnels, Crucible
- Filter paper
- Flasks
- Desiccators

3.2.3 Laboratory Apparatus used for physical testing of leather

- Dynamometer for tensile and tear as well as elongation at break
- Lasto-meter test
- Circular rub fastness tester

3.2.4 Leather processing equipments and apparatus

- Testing drums
- Fleshing machine
- setting machine
- Shaving machine
- Sammying/setting machines
- Vacuum dryer

- Staking machine
- Overhead drier
- Buffing machine
- Thickness gage
- Finishing machines (hand spray, hair cell plate, and plain plate,)

3.3 Methods

3.3.1 Methods Tanning experiments using tara and sodium metasilicate

Combination tanning based on tara and sodium metasilicate were carried out. Two different tanning methods were adopted viz. tanning first with sodium metasilicate followed by tara and tanning first with tara followed by sodium metasilicate.

3.3.1.1 Preparation of masked silica salts for tanning

The silica tanning solution was prepared using 100% water, 10% sodium metasilicate with 1% masking agent/without masking agent and the pH of the silica solution is lowered from basic (12.5) state to acidic (2.8-3) state with the same amount of hydrochloric acid (10%) with that of sodium metasilicate to this pH without forming any precipitate. The amount of hydrochloric acid (10% dilution) required to lower the pH to 2.8-3 is optimized. As mentioned in the previous work, it is excess amount of hydrochloric acid (10% dilution) that brings the silica in solution but in this experiment it was observed that the same percentage amount of hydrochloric acid (1:10) dilution was added to 10% solution of silica (water: silica powder) with gentle stirring to lower the pH from 12.5 to 2.8-3. Stirring is required to avoid formation of precipitate and to form homogenous solution. The quality of the hydrochloric acid determines the percentage amount of it. If the prepared tanning system is not totally solution, it will not penetrate in to the skin matrix and it fixes on the surface of the skins that have an effect on the hydrothermal stability and physical characteristics of the leather. The masking agents that were used in the silica solution preparation for this experiment are tri-sodium citrate and tartrate. These masking agents are used to enhance the stability of the silica tanning salt pH of precipitation point is elevated.

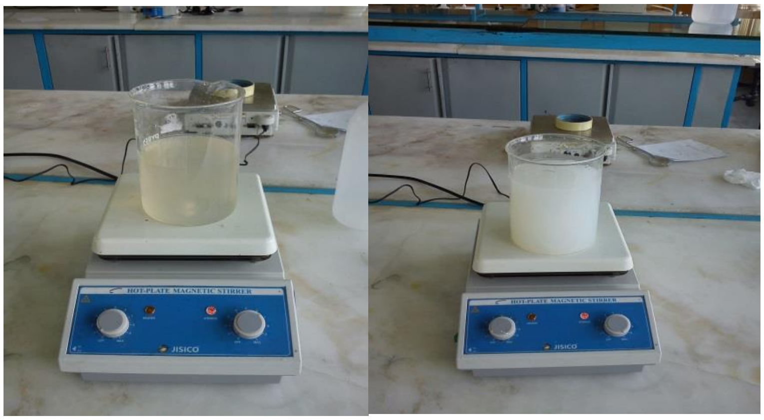


Figure 3.1 a) Unacidified silica b) Acidified silicates

3.3.1.2 Tanning trials using sodium metasilicate followed by tara

Different proportion of silica tanning agents with varied masking were prepared according to the procedure given above followed by tanning with different weight percentage of Tara as 10:1:10 (SCT1), 10:1:10 (STT), 10:1:15 (SCT2) and 10:1:15 (STT2) to optimize the concentration of Tara in the tanning agent. For ex., for SCT1The amounts of sodium metasilicate, tri-sodium citrate (masking agent) and Tara used for tanning are 32.7, 3.27 and 32.7 g based on pickled pelt weight respectively. SC refers to silicate masked with citrate and ST refers to silicate masked with tartrate ligands. T1 refers to 10% tara and T2 refers to 15% tara. Whereas SCT1 refers to the tanning system silica masked with citrate followed by 10% tara tanning. STT1 is silica masked with tartrate tanning followed by 10% tara tanning.

Process: The pickled pelts were taken for further tanning experiments. Add the required amount of prepared silica solution by adjusting the pickle liquor pH 2.8-3 in the drum and run the drum for 2 hours. Then, increase the pH of tanning liquor by adding sodium bicarbonate to 4-4.5 for the fixation of silica and to facilitate the penetration of Tara. Add the required amount of Tara to the liquor and run the drum for four and one half hours. At the end of the process check the penetration of Tara by cutting the butt portion of the pelt and observe the exhaustion of the tanning liquor. The tanning recipe is mentioned in table 3.1

Table 3.1: Recipe for silica followed by tara combination tanning

Study area			LIDI				
TYPE OF LEATHER			Wet white goat leather				
Process			Tanning				
% based on			Pickle wt				
Operation	Water %	T (^{o}c)	chemicals	%	Time	pH	remarks
Depickling	100	30					
			Salt (Nacl)	5	10’		
			Sodium bicarbonate	0.5	3*10’+30’	4.5-4.8	
Repickling			Formic acid	0.5	30’		
			Sulphuric acid	0.1	30’	2.8-3	
Tanning			Masked Silica solution	10	3hrs	2.8-3	
basification			Sodium bicarbonate	1	3*10’+30	4.5-4.8	
			Tara	X (x=10,15)	3hrs+30’	3.5	Check penetration
Again basify			Sodium bicarbonate	0.5	3*10+30’	4	Check exhaustion Drain/W/D
Out/pile for 48 hrs to post tanning							

3.3.1.3 Tanning trials on tara followed by sodium metasilicate

Different tanning trials were designed by varying the Tara percentage, by varying the order of tanning agents and varying the type of masking agent as 10:10:1 (T1SC), 10:10:1 (T1ST), 15:10:1 (T2SC) and 15:10:1 (T2ST) to optimize the concentration of Tara in the tanning system. The amounts of sodium metasilicate, Tara and tri-sodium citrate (masking agent) used to prepare a tanning agent of percentage ratio 10:10:1 (T1: S: T) are 37.5g, 37.5g and 3.75g based on pickled pelt weight respectively. The ligands used in all these experiments were tri-sodium citrate and sodium tartrate. Where T1SC is tara (10%) followed by sodium metasilicate masked with citrate and T1ST is tara (10%) followed by sodium metasilicate masked with tartrate. The tanning process is mentioned here under in table 3.2.

Table 3.2: Recipe for tara followed silica Tanning

Study area			LIDI				
Type of leather			Wet white leather				
Process			Tanning				
% based on			Pickle wt				
Operation	Water %	T(^{o}c)	chemicals	%	Time	pH	remarks
Depickling	100	30					
			Salt (Nacl)	5	10		
			Sodium bicarbonate	1	3*10+30	4.5-4.8	
Tanning			Tara	X (x=10, 15)	3hrs+30'	4	Check penetration
			Masked Silica	10	3hrs	3.5	
Basification			Sodium bicarbonate	0.5	3*10'+30'	4	Check exhaustion and Drain/W/D
Out/pile for 48 hrs for post tanning							

N.B: the above recipe, table 3.1 and table 3.2 was used to find optimal set up of the tanning process, a total of 10 run was made using the following process conditions for optimization

Process 1: one quarter of pickled goat skin (weight= 327gm) was processed with 10% silica (masked with 1% tri-sodium citrate) followed by 10% tara tanning.

Process 2: one quarter of pickled goat skin (weight= 250gm) was processed with 10% silica (masked with 1% sodium tartrate) followed by 10% tara tanning.

Process 3: one quarter of pickled goat skin (weight= 360gm) was processed with 10% tara tanning followed by 10% silica (masked with 1% tri-sodium citrate).

Process 4: one quarter of pickled goat skin (weight= 375gm) was processed with 10% silica, 10% tara tanning followed by 10% silica (masked with 1% sodium tartrate).

Process 5: one quarter of pickled goat skin (weight= 292gm) was processed with 10% silica (masked with 1% sodium tartrate) followed by 15% tara tanning.

Process 6: one quarter of pickled goat skin (weight= 345gm) was processed with with 10% silica (masked with 1% sodium tartrate) followed by 15% tara tanning.

Process 7: one quarter of pickled goat skin (weight= 215gm) was processed with 15% tara tanning followed by 10% silica(masked with 1% tri-sodium citrate).

Process 8: one quarter of pickled goat skin (weight= 249gm) was processed with 15% tara tanning followed by 10% silica(masked with 1% sodium tartrate).

Process 9: one quarter of pickled goat skin (weight= 226gm) was processed 10% silica (without masking), followed by tanning 15% Tara.

Process 10: one quarter of pickled goat skin (weight= 267gm) was processed with 15% tara tanning followed by 10% silica (without masking agent).

The primary objective of the present work is to develop Tara and silica combination tanning system to produce upper leathers with good organoleptic properties. Sodium metasilicate and Tara have been chosen to act as tanning adjuncts to improve the properties of leathers tanned with masking agents. The hydrothermal stability of leathers determined for the combination tanning system is presented in chapter four. In practical it is observed that silica pre-treatment hinders vegetable (Tara) tannage because the hydrothermal stability of silica pretanned leather is lower, whereas silica post-treatment does not hinder Tara tannage because the hydrothermal stability of silica post treated leather is higher and the visual assessment of the tanned leather is better. Hence sodium metasilicate treatment is carried after the treatment of Tara for optimized processes. Theoretically the treatment of leather with silica will not hinder the vegetable tanning agents.

Therefore, it can be concluded that tara pretanning exhibits an increase in the shrinkage temperature when compared sodium metasilicate pre-tanning and have better visual characteristics. This enhanced hydrothermal stability of vegetable (tara) pre-tanning is due to new cross-links formed and consequent changes in the structure of the skin collagen. The tanning trial process was done with small sample drums shown in Fig. 3.2.

Fig 3.2: Sample drum used for tanning trials

3.3.1.4 Tanning experiment with optimized amount of tara

The tanning experiments were carried out on full pickled and partial pickled goat skins for upper leathers. Four full pickled pelts in the range of 3.5 – 4.5 sq. ft were cut in to two parts, the right sides of the pelts were taken for experiment and the left four sides of the pelts were taken for chrome control tanning. The percentage of chemicals used was based on pelt weight. Two partial pickled goat skins were processed to upper leather and from this one half were finished and one half left in crust stage the other leather was used for physical testing.

For full pickled tanning the pH of the liquor adjusted to 4.5-4.8 by the process known as depickling. After pH adjustment, required amount of Tara was added to the liquor in three portions within an interval of one hour and drum was run for one additional hour ; totally four hours to give adequate time for the penetration of tara, then penetration of Tara into the skin matrix was check by cutting at the butt of the skin, if the penetration is ok, add the prepared masked silica solution to the tanning liquor and run the drum for two hours and check the pH of the liquor basify to pH 4 by using bicarbonate for the polymerization and the fixation of silica. Observe the exhaustion of the liquor visually and drain/wash/drain. Then take out the skins and pile for 48 hours by covering with polythene covers. Next to this the sample was taken from the sampling position and the shrinkage temperature was measured. The process recipe presented in table 3.2 is adopted.

For partial pickled goat leathers, the pelt from bating (pH=8.8) step processed in to partial pickled pelt (pH=4.5-4.8) by adding 0.5% (based on wt) formic acid without adding salt as well as sulphuric acid for pickling. This partial pickling methodology avoids pickling and depickling process steps. After that Tara is added to the partial pickled liquor and the drum is run for four hours and penetration of Tara was checked by cutting the butt portion of the skin and the prepared masked (tartrate) silica solution was added and run the drum for three hours. The pH of the liquor was 3-3.5. Then it was basified to increase the pH (pH=4) of the liquor for the fixation of silica on the skin matrix. Next to this drain the liquor and wash the leathers properly and out, pile it for 48 hours by covering it with polyester to keep it safe. Next to this the sample was taken from the sampling position and the shrinkage temperature was measured.

Table 3.3: Recipe for tara followed by silica tanning for partial pickled pelt

Study area			LIDI				
Type of leather			Wet white leather				
Process			Tanning				
% based on			Pickle wt				
operation	Water %	T(^{o}c)	Chemicals	%	Time	pH	remarks
Degreasing		28	Degreasing agent	3	30’		Dry float
	100	28					
			Salt (Nacl)	3	30’		Drain
	100	28					
			Degreasing agent	3			
			Salt (Nacl)	3	30’		D /W/D
pickling	100	28					
			Formic acid	0.5	30’	4.5-4.8	
Tanning			Tara	15	3hrs+30’	4	Check penetration
			silica	10	3	3-3.5	
basification			Sodium bicarbonate	0.5	3*10’+30’	4	Check exhaustion
Out/ pile for 48 hrs							

Control leather: Four left sides of pickled goat skin were taken to process the control leather. Control leathers using conventional process employing 8% BCS were made for comparison for leathers made from partial pickled and full pickled goat skins. Then out/pile and leave it for 48 hours to oxolation. Then the sample was taken from the sampling position and the shrinkage temperature was measured.

N.B: Further with reference to the recipies presented in table 3.2 and table 3.3, conventional chrome, tara alone and silica alone was used to find optimal set up of the tanning process, a total of 5 runs was made using the following process conditions for tanning experiment

Process 1: Four left sides of goat full pickled skins (weight= 1.73kg) was processed with conventional chrome 8% for control.

Process 2: Four right sides of full pickled goat skin (weight=1.77kg) was processed with 15% tara, 10% silica, and 1% tri-sodium tartrate in the order of tara followed silica.

Process 3: Three partial pickled goat skins (weight=4kg) was processed with 15% tara, 10% silica, and 1% tri-sodium tartrate in the order of tara followed silica.

Process 4: One full pickled goat skin (weight=0.74 kg) was processed with only 15% silica.

Process 5: One full pickled goat skin (weight=0.74 kg) was processed with only 15% tara shrinkage temperature was measured by the shrinkage tester.

3.3.2 Post tanning

The post-tanning process of upper involves a variety of operations comprising rehydration, neutralization, washing, retanning, filling, washing, dyeing, fatliquoring, fixing and washing. Post-tanning processes hold a pH range of 4.7-5.2. A large amount of water and chemicals are consumed in post-tanning processes. Usually, only about 60-80% chemical is absorbed in the post-tanning. A common post tanning operation was carried out for all the experimental (tara-silica combination), silica, tara and chrome tanned control leathers in this study. Samming/setting operation was made to reduce the moisture content and shaved at 1.0-1.1 mm to adjust the thickness for upper leather then, takes the weight for post tanning for all the experimental and control leathers. Here the post tanning operation started from neutralization without rechroming for all the experimental and control leathers. The combination of syntans and fatliquors used for the post tanning was chosen to produce fuller, soft and dyed upper Leathers. The chemicals used for post tanning was based on leather shaved weight. The process recipe followed is given in table 3.3:

Table 3.4: Retanning recipe for goat upper leather

STUDY AREA Weight (kg) Thickness (mm)	LIDI … 1.1-1.2	Raw material: sodium metasilicate and Tara tanned goat leathers			
		No of pieces		Date:	Colour: black
		% based on	Shaved wt	Size : medium	Grade:

Operation	Water %	T (^oc)	Chemicals	%	Time	pH	Remarks
neutralization	150	35					
			Neutralizing syntan (donatan nitro A2)	0.5	20’		
			Sodium formate	1	30’		
			Sodium bicarbonate	0.5	3*10’ +30’	4.7-5.2	Drain/wash/drain
Retanning	100	50					
			Acrylic polymer(Novaltan MAP)	3			
			Replacement syntan (donatan F)	6			
			Vegetable tanning(mimosa powder)	4			
			Melamine resin(retanal MD80)	4			
			Black dye (incoflor GTN)	4	45’		Check penetration
			Filler	2	20’		
Fatliquoring	60	60					

			Lecithin (fosfol GR)	3.5			
			Semi-synthetic fatliquor (fosfol AR75)	2			
			Fish oil (nexopol NT)	2			
			Emulsifier (coriline VSN)	0.1	60		
			Steren Mealeaic Resin(tafigal HK)	2	20’		
Fixation			Formic acid	1	3*10’ +30’		Check exhaustion
Out/pile next day setting, vacuum drying, overhead drying, vibratory stacking, buffing to observe the effect of tanning agent to buffeability							

Samming/setting operation is made to remove excess water and to increase its surface area by making flat. Then vacuum drying for further drying and to increase the stand of the leather and to have smooth grain surface with temperature (60^{o}c) for 30 seconds. Then overhead drying for further removal of moisture proceed and then the vibratory staking to bring its softness that it loses during drying. After staking the buffing operation had been carried out on the flesh side to see the effect of tanning material on buffeability of the leathers tanned with tara-silica (masked) combination and compared with chrome control leather. From the buffed skins it was observed that the tara-silica combination tanned was better than chrome tanned. Therefore these tanning agents can be used for suede leather manufacture

3.3.3 Fat Content determination

Fat content was determined via solvent extraction (SLC 8) method. Determination of the fat content plays its role in designing the process recipe for the manufacture of the final product. The fat content of the Tara-silica tanned crust leather and chrome tanned control crust leather for upper was estimated by taking samples (5gm) from the post tanned crust leather. The leather sample is accurately weighed on analytical balance and transferred into a soxhlet thimble and extraction of oils and fats is done with dichloromethane in a soxhlet extraction unit for 5 hrs. It is the Official method of fat extraction, standard soxhlet extraction method with dichloromethane used as the solvent. In the soxhlet the fat was extracted, dried and the solvent was separated and collected in the soxhlet tank to recover. After recovering the solvent from the soxhlet tank, the extract in the round flat bottomed flask was dried at 103±3^{o}c to constant weight at the oven. The fat content was estimated as percentage (w/w) with respect to the input sample.

Calculation

% fat content =weight of extracted fat/weight of sample (5gm)*100

Figure 3.3: Soxhlet extractor

3.3.4 Determination of Ash Content

The known weight of sample was placed in a porcelain crucible. First, the sample was carbonized on a hot plate under a fume cupboard and then placed in a furnace at about 800^{o}C until the constant weight was achieved. If it was difficult to burn off all the carbon, concentrated ammonium nitrate solution was added to the residue and it was heated again. If, even after this step, a complete burning off was not achieved, hot water was added to the residue, the solution was filtered, and the residue, on ashless filter paper, was washed. Then it was placed in the same crucible, and then dried to the constant weight (SLC, 6). The working environmental condition was 21.9^{o}c and 50 % humidity.

Calculations

Ash %= weight of wet sample-weight of dry sample/sample weightX100%

Ash%= M0-M1/M0 X100%

Where M0 is Weight of wet sample (grams)

M1 is Weight of dry sample (grams)

3.3.5 Determination of moisture content

Although often not considered as a true chemical property the moisture content is an important characteristic of leather and its determination is often classified under chemical tests. The moisture content of leather will change depending on the external conditions to which it is exposed and this can often be the cause of changes in the physical properties of leather. Ideal moisture content is often considered as being 12-14 per cent and is determined by drying a sample of leather to constant weight at 105°C (SLC 4), and calculating the weight loss. The loss of small amounts of volatile oils, or solvents may also be included in this weight and so this is often termed as being a determination of volatile matter. In real terms these substances are only a very small part of the total loss and so it is a very good estimation of the moisture present.

The aim is to determine the moisture content of the given sample of crust leather. About 5 gm of leather sample was accurately weighed, dried in an air oven at 105°C for a period of 3 hrs, cooled and weighed, the process of drying, cooling and weighing was repeated until constant weight is obtained. The moisture content of a material is usually expressed in terms of its water content as a percentage of the mass of the dry material. Calculate the moisture content M, expressed as percentage by mass, using the following equation

$\%M = M_0 - M_1 / M_0 X100\%$

Where, M is the percentage of moisture in the sample

M_0 is Weight of wet sample (grams)

M_1 is Weight of dry sample (grams)

3.3.6 Determination of chromic oxide content of chrome control leather

Chrome content of tanned leather as well as the liquor is determined with oxidation method. Wet blue samples from the official butt portion are taken for chromic oxide estimation. A known weight of the wet blue (about 0.5g) was taken and the amount of chromium was estimated as per the standard procedures.

The chrome content of the leather is defined as the amount of chromium compounds found in it, expressed as percent chromic oxide (%Cr_2O_3). Approximately 0.5gm of wet blue leather being cut into smaller pieces was measured and was oxidized by 5ml con. nitric acid and then by 14ml of acid mixture containing conc. sulphuric acid (3.5ml) and per chloric acid (11.5ml) in 250ml conical flask, as well as some glass beads . The flask was equipped with a small funnel to prevent the loss of acid during heating. The content was digested under gently heating in a hood until the color changes to orange. As soon as the orange color was shown stop heating and cooled it. After cooling, 10ml of distilled water was added and re-boiled for 10 minutes to evolve the free chlorine gas. The cooled solution was transferred and made up to 100ml with distilled water. 10ml of the solution was taken and diluted to a known volume of 50ml with distilled water. Sodium Hydroxide pellets were added to the final content till the pH exceeds 10 in the pH paper scale.

The chromic oxide content analysis provides us information regarding the hydrothermal and chemical resistance of the final leather to be produced. This analysis is done by the oxidation of the wet blue leather using acidic mixtures and involves the determination of the absorbance spectrophotometrically at 372nm (ε=4820). The result is expressed as percent of chromic oxide (% Cr_2O_3) content.

3.3.7 Hydrothermal stability of tanned leather

When collagen is wet, the matrix can be degraded by rising temperature, at the same time hydrogen bonds in the triple helix are broken, observed as shrinking, leading to gelatinization. The hydrothermal stability of collagen can be altered by many different chemical reactions, well known in the fields of histology, leather tanning and other industrial applications of collagen. The hydrothermal stability of the wet white (tanned) leather is the measure of the leather to resist against hot water. This analysis is helpful in determining the suitability of the wet white leather for the production of crust as well as finished leathers. This test is conducted using a Theis shrinkage tester. A thermometer is placed together with the sample to read the temperature at which the leather shrinks. The temperature of the water has been gradually increased and the temperature at which the sample shrinks has been measured as the shrinkage temperature of the leathers. The wet white leather hydrothermal stability is compared with chrome tanned leather with its average shrinkage temperature 80 ^{o}c which is less than the shrinkage temperature of that of chrome tanned leather which has a shrinkage temperature 104^{o}c. The temperature at which a skin/hide or leather decreases in dimensions when heated under special conditions, e.g. when heated in water fibres shrunk.

The process of measuring the shrinkage temperature for tanned leathers is as follows. A 2cm sample cut out at the butt area of the tanned leather was clamped between the jaws of the clamp, which in turn was immersed in water with the thermometer to read out the temperature of the water. The temperature of the water was gradually increased and the temperature at which the sample shrinks was noted.

3.3.8 Characterization of Spent Tan Liquor

The tanning liquors collected from both the optimized experiments and control processes. The processes was analysed as per the standard procedure for their BOD, COD, total solids, total dissolved solids and total suspended solids. The term solids is generally used when referring to any material suspended or dissolved in waste water that can be physically isolated either through filtration or evaporation.

Total solids are the term applied to the material residue left in the vessel after evaporation of the sample and its subsequent drying in an oven at a definite temperature. Thus total solids are nothing but summation of total dissolved solids and total suspended solids. Suspended solids are part of solids in wastewater that remain present on filter paper while filtration. Dissolved solids are part of solids present in the filtrate while filtering the sample on filter paper.

The measurement of total solids is by means of the gravimetric procedure. The various forms of solids are determined by weighing after the appropriate handling procedures. The total solids concentration of a sample can be found directly by weighing the sample before and after drying at 103 ± 3^{o}C. However, the remaining forms, TDS and TSS require filtration of the sample. For liquid samples, all these solids levels are reported in mg/L.

To measure total solids take a clean porcelain dish which has been washed and dried in a hot air oven at 105^{o}c for three hour. Weigh the empty evaporating dish in analytical balance and donate (W1). Using pipette transfer 20 ml of sample in the porcelain dish then, dry the sample to get constant mass in an oven by evaporating the moisture for long duration usually 3 hours. After drying cool the container (dish) in a desiccator to avoid loss of mass since it is designed to provide an environment of standard dryness. Then weigh the porcelain dish with dried sample and then repeat it till constant weight obtained then, donate the weight (W2)

Calculation

Amount (in ppm) of total solids present in the sample = {(W2-W1)/V}*1000

Where, W1- weight of dried dish

W2 – weight of dried dish + dried sample

To determine the total suspended solids for waste water it is possible to use the following methods. First take the weight of filter paper (W3) then, add 10ml of waste water sample on the filter paper and filter it then, dry it. After drying take the weight of the filter paper with the dry sample (w4)

Amount of total suspended solids in the sample = (W4-W3)*1000/volume of sample

Where, W3 –weight of filter paper

W4 - weight of suspended solid + filter paper

Total dissolved solid (TDS) is determined from total solid (TS) and (TSS) by subtracting TSS from (TS).

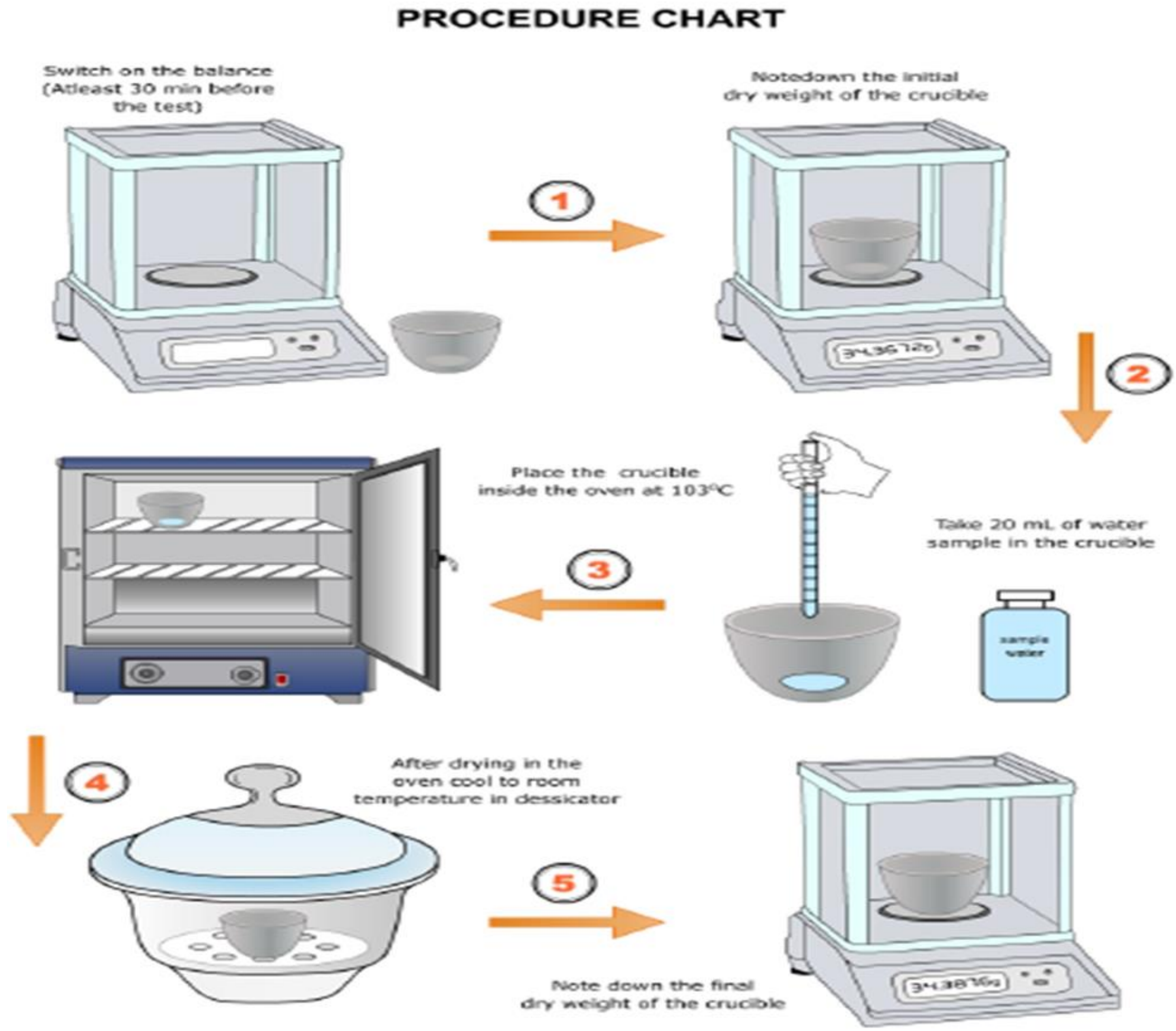


Fig 3.4: procedures chart for total solids

Table 3.5: Total solids and total suspended solid determination data sheet

Description of TS		Weight (g)	Description of TSS		Weight (g)
Initial weight of the crucible	W1		Initial weight of the filter paper	W3	
Final weight of the crucible + sample (gm)	W2		Final weight of the filter paper + sample (gm)	W4	

Weight of residue (gm)	W		Weight of residue (gm)	W	
Volume of the sample (ml)	V		Volume of the sample (ml)	V	
Total solids (mg/l)	TS		Total suspended solids (mg/l)	TSS	

Chemical oxygen demand (COD)

The aim of the test is to measure the pollution potential of wastewaters in terms of organic matter present in it. Samples of the liquor from various experiments and control process was taken and tested with the APHA 5220B-COD standard test methods.

The chemical oxygen demand (COD) test measures the oxygen required to oxidize organic matter in experimental and chrome control wastewater samples by the action of strong oxidizing agents under acid conditions in milligram per litre (mg o_2/l) . Then the COD content is determined based on the standard test procedure.

By take 15 ml COD digestion tubes (pre-washed with dilute H_2SO4) to carried out the test analysis and add the required amount things in sequence. Transfer 0.50 ml wastewater sample (Inlet) or 1.00 ml treated sample. Then add 2.5 ml standard potassium dichromate digestion reagent slowly and mix. Next add 3.5 ml sulphuric acid reagent through sides of the tubes and let it go to the bottom. Cap and mix the contents (wear gloves as contents are very hot) and cool. Transfer tubes to the pre-heated COD digester at 150 C and digest for 2 hrs. After that run 3 blanks by substituting DW for sample and proceed exactly as sample.

Titration

Transfer the contents of the COD digestion tube in 100 ml beaker. Add distilled water to make the volume to 50 ml. add 1-2 drops of Ferroin indicator and titrate against 0.05 M Ferrous Ammonium Sulfate solution.

Calculation:

COD as mg O2/L= (A-B) X M X 8000 ml sample

Where: A. ml FAS used for blank, B. ml FAS used for sample, M. molarity of FAS

Biological oxygen demand (BOD)

It is the amount of dissolved oxygen needed by aerobic organisms in a water body to break the organic materials present in the given waste water at certain temperature over a specific period of time.

The sample is filled in airtight bottle and incubated at specific temperature for 5 days. The dissolved oxygen (DO) content of the sample is determined before and after five days of incubation at 20^{o}c and the BOD is calculated from the difference between initial and final DO. Samples of the liquor from various experiments and control process was taken and tested with standard test method 6.

3.3.9 Organoleptic properties of crust leathers

The control and experimental upper Crust leathers were assessed for softness, grain tightness, grain smoothness, fullness, dyeability, roundness and general appearance by standard tangible evaluation technique. Experienced tanners rated the leathers in a scale of 0-10 points for each functional property.

The comparative ratings for each property are given in Fig III. The ratings are averaged values from two different tanners. Fullness, softness, grain smoothness, grain tightness, roundness and dyeability of experimental leathers (EI and EII) are better than from that of the control leathers treated with 8% BCS (CI), tara tanned and silica tanned leathers. The grain smoothness, roundness and dye uniformity of the leathers tanned with masked silica and Tara tanning agent from partial pickled skin has been found to be significantly better than the control leathers. When comparing the area of the full pickled experiment leather with that of the chrome control leather which was medium size, the full pickled experimental leather is better (6.25% increase) than chrome control leather significantly (i.e the area of the experimental leather is increased by 0.25 square feet from that of chrome control leather) from full skins (4 sq.ft). Experimental tara-silica combination tanning have been found to result in leathers with good uniformity in color. No differential dyeing (between grain and flesh) has been observed for the experimental tara-silica combination tanned leather. It is clear that the use of tara-silica combination for tanning did not affect the dyeing characteristics of the leather. Post tanned with sodium metasilicate produced fuller leathers compared to pretanned with sodium metasilicate and chrome control leathers.

On the whole the leathers tanned with tara-silica combination had been found to be better than chrome tanned leather. Hence use of tara-silica combination for tanning appears to be an effective option for making leathers with good organoleptic properties. Hence 10% sodium metasilicate post tanned leathers have been optimized for the tanning experiments.

3.3.10 Physical Testing of Leather

Conditioning of leather sample or leather cut test specimen is very important step in physical testing of leather. The moisture present in the leather matrix varies according the moisture (relative humidity) present in the working place. Temperature is also a well-known factor to influence the properties of matter. Hence it is an accepted procedure to conduct the test at a predefined test environment. Hence samples for various physical tests were obtained as per IULTCS methods (ISO 2418:2005) from experimental and control crust leathers. The material is to be kept in a standard atmosphere (temperature 20±2 ^{0}C, humidity 60±5% RH) for 48 hours prior to testing to bring it to natural condition. Tensile strength, % elongation at break, tear strength, distension at grain crack and load at grain crack were examined as per the standard procedure [25].

3.3.10.1 Measurement of tensile strength

The samples were cut parallel and perpendicular to the backbone using a dumbbell shape. The thickness and width of the specimen were measured in the same position using a standard thickness gauge and vernier calipers, respectively, i.e. one measured at the midpoint and the other two at midway. Then the mean thickness (mm) is calculated. The specimens were cut as a rectangle 50 mm long and 10 mm wide using a press knife which cuts out the specimen. The area of cross section of each specimen was calculated by multiplying its width by its thickness (SLTP 6, IUP/6: BS3144). The jaws of the tensile machine were set 50 mm apart, and then the sample was clamped in the jaws, so that the edges of the jaws lay along the midline. The machine was run until the specimen was broken and the highest load reached was taken as the breaking load. The tensile strength load is in Newtons and the unit of the tensile strength is newton per millimetre square (n/mm^2) (SLP6, IUP/6: BS3144).

Calculation

Tensile strength =maximum breaking load (N)/cross sectional area (mm^2)

3.3.10.2 Percentage of elongation at break

The initial free length between the clamps before the load is applied was measured and the final free length between the clamps at the instant of break was measured. The initial free length was set at 5 cm and the elongation calculated from the readout from the machine (SLP6, IUP/6: BS3144) standard method. The percentage of elongation is calculated as following.

Calculation

Elongation, %= final free length-initial length/initial free length

3.3.10.3 Measurement of tear strength

There are two types of tear strength tests are followed for leather material.

1. Double edge tear strength – Baumann Tear strength

2. Single edge tear strength - Tongue/trouser tear strength

From the above two double edge tear strength (baumann tear strength) method was used. Tear strength test method is intended for use with any types of leather. The official method (SLP 2: IUP/2) measures the tear load on a specimen in which a slot has been cut and which is slipped over the turned-up ends of a pair of holders attached to the jaws of a tensile strength machine. The forces exerted during separation of the holders are recorded and the highest force is taken as the tearing load and expressed in newton. Tearing load can be expressed as the quotient of the load by the thickness of the sample. Cut six test specimen (three test specimen from along direction and three test specimen from across directions) using a cutting knife as a rectangle 50 mm long and 25 mm wide using a press knife which cuts out the specimen having a central slot in 1 operation (Template machine). Conduct the test by operating the tensile tester at the rate of 100 ± 10 mm/ minute speed until the test specimen is torn apart and the highest load reached during tearing was recorded as the tearing load. Continue the test for remaining test specimen. The readings of the load fell into that part of the scale which has been shown by calibration to be correct within 1%. The tearing load is in Newtons or kilograms (SLP2, IUP2).

Tear strength = maximum tear force (N)/thickness (mm)

3.3.10.4 Grain burst by the ball

The ball burst test is intended particularly for use with shoe upper leather where it gives an evaluation of the grain resistance for cracking during top lasting of the shoe uppers. The grain of the leather is subjected to more stain in shoe making process. Therefore the grain is liable to exhibit grain cracks on the shoe surface especially at toe area. This may be due to filling of more retanning materials into the leather matrix to give sufficient substance. Rapid tanning practices over loads the grain side instead of allowing the tanning chemicals, fatliquors and dyes to move into the entire thickness of leather. This is also a reason for exhibiting grain cracks in shoe making process. This grain crack failure cannot be visualized by simple folding and flexing. Therefore selection of leather for shoe making has to be made after testing the leather for grain crack load and distension properties using standard test equipment called lastometer. In the shoe manufacturing places "instant lastometers: are used before cutting the components from the leather for making shoe upper. Three specimens cut in the circular size with diameter 50mm. The load and distension at grain crack is read out from the testing machine. The unit of the load is expressed as N/mm [26].

3.3.11 Colour fastness to circular rubbing for finished upper leathers

The object of finishing is to give a treatment of coatings to the grain surface to protect it against dirt, staining, wetting, mechanical stresses like rubbing, scuffing, flexing etc., levelling or evening out the colour of the grain surface, hiding grain blemishes and upgrading its quality, improving the aesthetic appeal and the sales value of the product. By the finishing process, the grain surface of the leather is coated with various substances and is then submitted to different mechanical operations, depending upon the purpose intended whereby the appearance of leather can be highly influenced to make it more useful, attractive and appealing to users. Finishing may be employed to impart colours, a uniform shade, special patterns, a smooth or grained or printed/embossed surface, lustre (Matt or glossy) as well as opaque (covered) or transparent (aniline/semi-aniline) appearance to the leather surface. Hence in my case semi-aniline protein finish type of finish is used and the process recipe of finishing is given in table 3.2.

Table 3.6: Finishing recipe

Coats	Chemicals	Amount (gm/l)	
Clearing coat	IPA	100	
	Ammonia	100	
	water	800	2x, wait to dry
Season coat	Acrylic binder (medium soft)	125	
	Resin binder (PU)	75	
	Casein binder	100	
	Wax	50	
	Pigment	150	
	Dye solution	10	3x coat, hair cell at 70^{o}c, then 3x dry
Top coat	Liquor	100	
	Water	100	2x coat, Plain plate at 70 ^{o}c

The rub fastness test is the method intended to assess the degree of damage and transfer of a material's surface colour or finish onto the rubbing felt during mild dry and wet rubbing. Hence the samples for various physical tests were obtained as per SATRA TM 8:1992 test methods

Dry rub fastness

Generally this test is conducted for the following order of cycles, 8,16,32,64,128,256,512 and 1026.The number of cycles and grade of colour change and colour transfer are depend up to the type of leather and customer's requirement.

Cut one test specimen about 75 mm square from the finished leather. Place the test specimen on the horizontal plat form. Secure a felt pad on to the spindle and bring in contact with the test specimen. Adjust the weight to24.5±0.5N, operate the machine for specific number of revolutions. Stop the machine in between for a few seconds to avoid thermal damage caused to the finish of the leather. Continue the test until specified number of cycles (512 cycles). Remove the leather and felt pad from the machine. Place the test specimen and felt pad inside the light cabinet to view the materials at 45^{o}angle. Assess for change in colour (marring) grade for leather and transfer of colour (degree of staining) with the help of respective grey scales.

Wet rub fastness

Immerse a felt pad in cold water; boil for 1 minute for complete wetting of the felt pad. Cool, remove excess water from the wet felt by slight squeezing, attach to the spindle, adjust the weight to 7.1 N forces, bring the spindle into contact with leather specimen, weight for 60 seconds, and operate the machine to the desired number of cycles (256 cycles). Assess for colour change and colour transfer after complete drying of the sample

4. Results and Discussions

Tanning is a chemical process by which new cross-links are introduced into collagen, binding the active groups of tanning agents to the functional groups of protein (Bienkiewicz, 1983). The tanning effect mainly depends on the extent of cross-linking between the collagen molecules and the thermodynamic stability of the cross-linking bonds.

A new combination tanning system based on Silica and Tara combination has been prepared as an attempt to widen the options for alternative tanning system, to combat chrome pollution. In the present investigation, the addition of silica to Tara is expected to improve the leather properties as well as abate chrome pollution.

4.1 Various Experiments for Optimization of Percentage of Tara

The shrinkage temperature on the application of different percentage amount of Tara and Silica with and without masking agents (tri-sodium citrate and sodium tartrate) in silica-Tara combination is mentioned in Table 4.1

Table 4.1: Effect of masking on silica (10%) followed by Tara (10%) combination tanning for optimization

Experimental trials	Order of addition of tanning	Masking agent used for silica solution preparation	Shrinkage temperature(^{o}c)
ST1	Silica-Tara	NIL	65
ST1C	Silica-Tara	citrate	76
ST1T	Silica-Tara	tartrate	70

4.2 Effect of masking agent on Tara followed by silica tanning system

In order to determine the effect of masking on the silica tanning in the tara followed by silica tanning system, the leathers processed without and with masking agent (citrate and tartrate) are determined for shrinkage temperature and presented in Table 4.2.

Table 4.2: Shrinkage temperature of leather with and without masking agent Tara (10%) followed by silica (10%) tanning order

Experimental trials	Order of addition of tanning	Masking agent used for silica solution preparation	Shrinkage temperature(^{o}c)
T1S	Tara-silica	NIL	75
T1SC	Tara-silica	Citrate	79
T1ST	Tara-silica	Tartrate	80

From the above table 4.1 and table 4.2 it is evident that the shrinkage temperature of Tara - sodium metasilicate order is significantly higher than that of sodium metasilicate-tara tanning system.

4.3 Silica followed by Tara and Tara followed by Tara tanning for upper leather

Previous section reported the effectiveness of masking in silica tanning in the silica and tara combination tanning system and the order of addition for tara and sodium metasilicate in combination tanning system. However the amount of Tara used were only 10%. It is hypothesised that the amount of Tara required for tanning particularly making upper leather is higher. Hence experimental trials increasing the amount of Tara to 15% were attempted. The shrinkage temperature of experimental leathers processed at different conditions (order of addition and masking agents) with higher amount of Tara is presented in Table 4.3. The leathers produced by increasing the amount of Tara gave the improved shrinkage temperature is comparison to leathers processed with only 15%. Hence the hypothesised amount of 15% Tara is taken as adequate amount that gives the maximum shrinkage temperature with the order Tara followed by Silica tanning masked with sodium tartrate.

Table 4.3: Shrinkage temperature of leather tanned with Tara (15%) and masked silica (10%) tanning

Experimental trials	Order of addition of tanning	Masking agent used for silica solution preparation	Shrinkage temperature(^{o}c)
ST2C	Silica-Tara	citrate	77
ST2T	Silica-Tara	tartrate	78
T2SC	Tara-silica	citrate	80
T2ST	Tara-silica	tartrate	80

4.4 Optimized Combination tanning using Silica and Tara compared with chrome tanned leathers

Based on previous section it is clearly established leathers with adequate thermal stability and organoleptic properties can be made silica and Tara combination tanning. Further it is established that masking in silica tanning enhanced the thermal stability of leather greater than 5^{o}c. there was no significant difference in leathers obtained from citrate and tartrate masking. However tartrate masking is chosen for further studies in view of its less grain harshest characteristics. The order of addition with tara followed by silica resulted in thermally stable leather compared to silica followed by tara tanning as explained in table 4.1 and table 4.2 in the above. This could be possibly due to the decrease in the availability of the sites in the skin matrix for the interaction of tara after pretreatment with silica (can be masked/ unmasked) as the tara is big molecule and known to form cyclic polymeric networks. Where silica can manage to find sites for interaction even after tara treatment as tara binds with collagen through non covalent interactions. 10% of silica and 10% of Tara appears to be sufficient for tanning. However use of tara to 15% enhances the thermal stability of leather by 1^{o}c and fullness of the leather. Hence 15% tara and 10% silica tanning can suit for upper leather manufacture. Further experimental trials were carried out to see the efficiency of the Tara followed by silica tartrate masking tanning suit for the manufacture of upper leather in comparison to conventional chrome tanned leather and leathers tanned with 15% of tara and 15% of sodium metasilicate as controls. Increase in the mount of Tara usage will result in higher pollution load in effluent and also affects the cost of the leather. Hence 15% of tara and 10% of sodium metasilicate are the optimum % for the manufacture of upper leather. Therefore the shrinkage temperature of experiments and all the controls are given in table 4.

Table 4.4: Shrinkage Temperature of the optimized combination tanning and Controls of upper leather

Experiments	Shrinkage temperature (^{o}c)
CI	55±2
CII	59±1
CIII	104±1
EI	78±2
EII	76±2.5
Where, CI-silica tanned control ; CII- tara tanned control; CIII-chrome tanned control; EI- full pickled combination tanned experiment and EII-partial pickled combination tanned experiment	

The hydrothermal stability of chrome tanned leather is better than that of experiments as well as tara tanned and silica tanned controls as shown in Table 4.4 in the above, which is because of the crosslinking capability of chromium with that of collagen carboxylic groups with covalent coordinate bond. But tara and silica can only make weak hydrogen bonds with collagen as it is stated in chapter two rather they have the capacity to fill the leather and give fullness since they are bigger size molecules as compared to chromium.

4.5 Organoleptic properties of crust upper leather

Experimental and control upper crust leathers were assessed for softness, fullness, grain smoothness, grain tightness, general appearance and dye uniformity by hand and visual examination. Two experienced tanners rated the leathers on a scale of 0-10 points for each functional property, where higher points indicate better property and lower points indicates lesser properties. Based on the indicated evidence dyeability, grain smoothness, grain tightness, roundness, softness and fullness of leathers tanned by tara-silica combination is comparable to chrome tanned crust leathers. General appearance, dyeability and roundness of the leathers processed from tara-silica combination tanned leathers are found to be better than from that of chrome, silica and tara tanned controls. But all the organoleptic properties of experimental leathers are better than those of the silica tanned and tara tanned control leathers. Tara tanned leather is the lower grade from all of the experimental and control leathers in its properties especially for softness which has bony feel for hand touch. The tara tanned leather needs more amount of fatliquor or needs especial kind of fatliquors to be comparable with chrome tanned leather softness. It is clear that the use of silica and tara did not affect the dyeing characteristics of the leather compared to control. No differential dyeing (between grain and flesh) has been observed for all tara followed by silica combination tanned leathers and chrome tanned leather. Leathers pretanned with tara and post tanned with silica solution (EI) shows good grain smoothness, however, the partial pickled (EII) shows better grain tightness, roundness and overall appearance for the upper leather compared to control leathers as well as full pickled experiment(EI). Hence use of tara followed sodium metasilicate combination for tanning appears to be an effective option for making leathers with good organoleptic properties. The value of the organoleptic properties for upper leathers are given below in table 4.5

Table 4.5: Visual Assessment of the organoleptic properties of control and experimental Post Tanned upper Leathers

Parameters	EI	EII	CI	CII	CIII
Fullness	9.0	9.5	9.0	8.0	8.5
Softness	8.5	9.0	8.0	6.0	9.0
Grain tightness	8.5	9.5	8.0	8.0	8.5
Grain smoothness	9.5	9.0	8.5	7.5	9.0
Dye ability	9.0	9.5	9.0	8.5	8.5
Roundness	9.0	9.5	8.5	8.5	8.0
General appearance	9.0	9.5	8.5	7.5	8.5
Where EI-full pickled combination tanned experiment , EII-partial pickled combination tanned experiment, CI-silica tanned control, CII-tara tanned control and CIII- chrome tanned control					

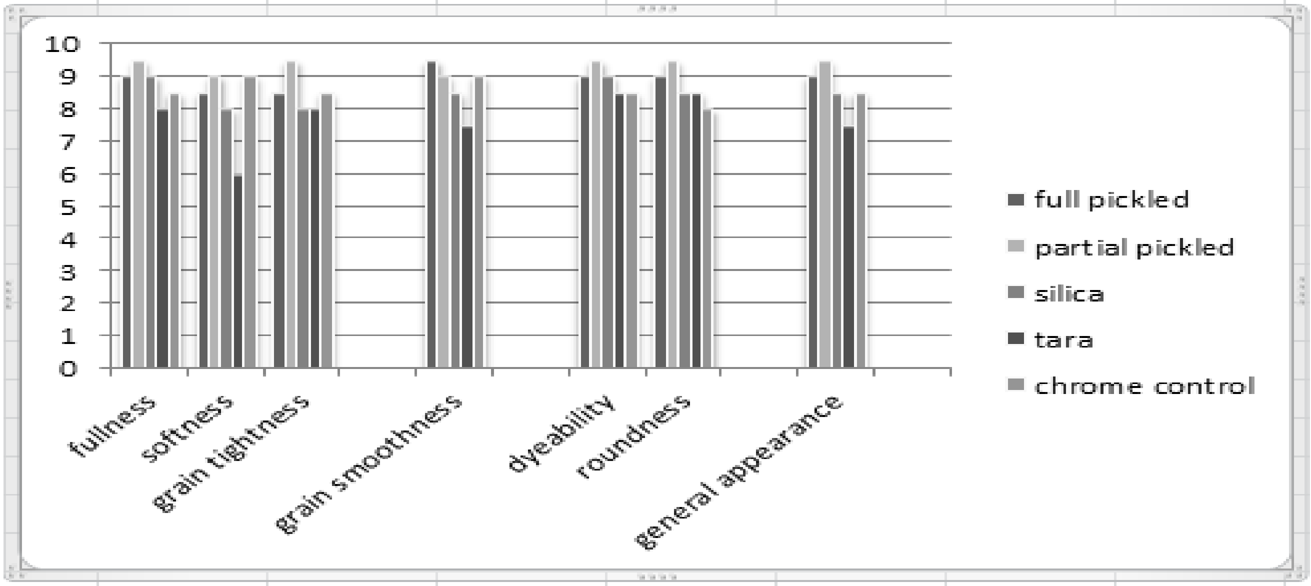


Fig 4.1 Visual assessment of upper leathers made from different experiments and controls

A) Silica tanned b) Tara tanned

C Tara followed Silica tanned D Chrome tanned

Fig 4.2: Leathers tanned with different tanning agents

As observed from the above fig the leather tanned with silica is white compared with others, next to silica, tara-silica combination tanned leathers are whiter than the other tara and chrome tanned leathers.

4.6 Spent Liquor Analysis

Based on the standard procedures for the total solid and COD content of both the control and experiment test results for tanning and post tanning liquors are explained as follows.

Table 4.6 Tanning liquor test results for goat upper leather

parameters	EI	EII	CI	CII	CIII
TS	67000	69000	45000	81000	88000
TDS	51000	38340	30800	30000	76000
TSS	16000	30660	14200	51000	12000
COD	3598.6	5398.6	2002.0	18649.8	3258.7
BOD	2560	3360	1280	7520	1200
Where, CI-silica tanned control; CII- tara tanned control; CIII-chrome tanned control; EI- full pickled combination tanned experiment and EII- partial pickled combination tanned experiment, all in mg/l					

Table 4.7 Post tanning liquor test results for goat upper leather

parameters	EI	EII	CI	CII	CIII
TS	39000	32000	43000	48000	44000
TDS	24000	27000	34500	38900	32000
TSS	15000	5000	8500	9100	12000
COD	9598.6	11503	22946.3	22673.2	5923.8

From the table 4.6 & 4.7, it is observed that the spent liquor results processed using both the experimental (full pickled and partial pickled) and all the controls in tanning and post tanning liquors. The spent tan liquor analysis from tara-sodium metasilicate combination tanning was carried out to evaluate the impact of the same on environmental pollution load. The chemical oxygen demand (COD), BOD and total solids (TS) values for tara-sodium metasilicate and control chrome tanning system are shown in Table 4.6 for tanning and table 4.7 for post tanning. It is seen from the table that total solids load is less than from that of the chrome control tanning system, whereas the COD and BOD values are slightly higher. The increase in COD is due to the presence of tara, which is known to increase the COD content of the liquor. Biochemical oxygen demand (BOD5), BOD5/COD analysis revealed that the wastewater from experimental treatment was more biodegradable than that of chrome control and silica treatment but it is less biodegradable than that of tara tanning liquor control. This proves the presence of vegetable tanning agent in tanning liquor increases the amount of BOD value. Even though the BOD and COD are higher, the wastewater can be easily treated employing simple treatment methods such as aeration, ozonization or aerobic biological treatment methods and the total solids content can be reduced by simple sedimentation or settling techniques. In the other side silica is the very nice tanning agent that doesn’t load the COD and TS compared to chrome and tara which indicates silica was exhaustively penetrated and fixed with the skin and it also shows that the exhaustion of any tanning liquor (chrome, veg etc) can be improved in the presence of silica. Though the BOD and COD load of the Tara – Silica tanned leather is higher compared to chrome tanned control leather they are treatable. It is should noted that the chrome is completely eliminated from the wastewater.

4.7 Chemical Analysis of Crust Upper Leather

The chemical analysis data for the experimental leathers is compared with that of control leathers.

Table 4.8: Chemical analysis of both experiment and control upper crust leathers

Parameters	EI	EII	CI	CII	CIII
Moisture content (%)	12	11	10.6	12.9	14.8
Fat content (%)	6.6	10.8	17.1	7	7.0
Ash content (%)	6.8	6.7	9.6	9.5	10.9
Chrome oxide content (%)	-	-	-	-	~2.6
Where, CI-silica tanned control; CII- tara tanned control; CIII-chrome tanned control; EI- full pickled combination tanned experiment and EII- partial pickled combination tanned experiment					

The chemical analysis values of full pickled and partial pickled combination tanned experimental crust leathers and control chrome, tara and sodium metasilicate leathers are given in table 4.8. The chemical analysis data for the experimental leathers is comparable to that of control leathers. However, the ash and moisture content for the control leathers is more compared to the experimental leathers. The fat content of both the experimental and control leathers were comparable except silica tanned leather which has higher fat content compared from others. This high content of fat could be due to the use of the recovered dichloromethane for the extraction of silica tanned sample, or due to weighing problem of fatliquors. The amount of fat content extracted indicated that, the amount of fatliquors which is fixed as well as the natural fat and causes to formation of fat spue. The percentage of chrome content (Cr_2O_3) from the result shows the amount of chromium oxide fixed to the leather that gives strength to the leather by crosslinking with the carboxyl groups of the collagen.

4.8 Physical strength characteristics of crust upper leathers

It is crucial to study the influence of the tanning system on the strength properties of leathers. The physical strength measurements includes tensile strength, elongation at break, tear strength, load at grain crack and distension at grain crack were carried out for the control and experimental upper crust leathers. The data is given in table 4.9 and the standard is given in annex 2. As we can see from test results all test results of strength properties are greater than the test standards except tear strength which is slightly less compared to the standards. The tear strength can be improved by adding some special fatliquors and by increase the amount of fatliquors used because the vegetable tanned leather required little more amounts of fatliquors. However E-II resulted in leathers with strength properties comparable to chrome tanned control leathers

Table 4.9: physical analysis of both experiment and control upper crust leathers

Expt	EI	EII	CI	CII	CIII
Tensile strength (N/mm2)	21.4	23.6	22.1	30.7	26.9
Elongation at crack (%)	34.5	51.5	37.4	35.2	74.3
Tear strength (N/mm)	30.3	34.0	34.4	50.1	36.7
Load at grain crack (N/mm)	323.0	395.3	297	370	460.0
Distension at grain crack (mm)	9.8	12.2	9.4	11.6	13.0
Where, CI-silica tanned control; CII- tara tanned control; CIII-chrome tanned control; EI- full pickled combination tanned experiment and EII- partial pickled combination tanned experiment					

The experimental and control leathers tanned from goat skins have been post tanned for upper leathers. The strength characteristics of upper leathers from different tanning trials are shown in Table 4.9. From the upper leathers made by Tara (15%) and silica (10%) combination tanning system and other control leathers, partial pickling combination tanned leather (E II) exhibit higher tensile strength of 23.6N/mm^2 compared to full pickled combination tanned leather but slightly less than from that of tara and chrome control leathers. But all have higher tensile strength from the physical test standard. They exhibit tear strength comparative to the standard Grain crack strength is also found to be more than the standard for all experimental leathers and controls, which exhibits resistance to crack until 395.3 N/mm for partial pickled combination tanned, 323 for full pickled combination tanned leather and the distension at grain crack for all experiments and control leathers maintain higher values from the minimum standard distension. All the physical test (strength properties) except tear load for both the experimental and control leathers were higher than the standard values for normal goat upper leather. But the tear load is comparably lower to the standard; it may be due to the process parameters, chemicals used.

4.9 Colour fastness to circular rubbing for finished upper leather

Fastness can be judged by the effect on the sample material or the transfer of colour to the rubbing pad. The change in appearance of the finish and the colour transferred to the rubbing pad was assessed by reference to the standard grey scales and are presented in table 4.10. From the table we can observe that the wet rub test have better result compared to dry rub test for all the samples tested. All the tests maintain greater results from the minimum grey scale standards. This indicates both the tanning materials do not affect the finishing process and finishing result. Matched pair comparison has also been performed to study the finishing characteristics of the developed tara-sodium metasilicate combination tanned crusts with that of the chrome tanned crusts as well as tara and sodium metasilicate crust leathers. The wet and dry rub fastness measured for both control and experimental finished leathers process using same composition and quantity of finishing components per unit area are shown in Table 4.10. From the table, it is observed that the fastness properties of both chrome control and experimental leathers are very much comparable. The rub test results of tara and silica tanned control leathers have slightly less rubbed fast. This indicates that the tara-sodium metasilicate combination tanning system does not affect the finishing, which indicates that the tara-silica combination tanning system results in leathers with finishing characteristics similar to that of chrome tanned leathers.

Table 4.10: rub fastness for experiments and control upper crust leathers

Tests	Dry rub test		Wet rub test	
	Test piece	Felt pad	Test piece	Felt pad
EI	4/5	4/5	4/5	4/5
EII	4/5	4/5	4/5	4/5
CI	4	4/5	4/5	4/5
CII	3/4	4	4/5	4/5
CIII	4/5	4/5	4/5	4/5
Where, CI-silica tanned control; CII- tara tanned control; CIII-chrome tanned control; EI-full pickled combination tanned experiment and EII- partial pickled combination tanned experiment				

5 Conclusion and recommendation

5.1 Conclusions

Almost all tanneries uses chrome tanning process to make good quality leather. These chromium salts and its derivatives are very perilous to human health and to the environment. The detailed research study has been made on the development of a new tara – silica combination tanning system. The outcome of the research work clearly suggests that chrome tanning system can be replaced by Tara-Silicate combination tanning system so that the perilous environmental impacts caused by the chromium compounds can be eliminated.

In this study, we have shown that a combination tannage involving a vegetable tanning agent (tara) and sodium metasilicate uniquely cross-links collagens, producing leather with shrinkage temperature around 80◦C. The order of addition of the tanning agents was shown to be important with best results from samples tanned first with vegetable tanning agents then re-tanned with sodium metasilicate. Previous studies indicated that vegetable tannins are able to penetrate the collagen inter-fibrillar space making the collagen peptide groups more accessible to sodium metasilicate tannins. In contrast, pretanning with silicate possibly fills the collagen fiber network, preventing high molecular weight vegetable tannins from interacting with collagen fibres. The other possibility is that the free amino acid side chains of collagens are exhausted on pretanning with sodium metasilicate (combined by acid with coordination), reducing the number of collagen–silicate –vegetable tannin cross-links when vegetable tannins are introduced. Optimal results were obtained when 15% (w/w) vegetable tannins (tara) and 10% (w/w) sodium metasilicate was used. In conclusion, the evidence has been presented for the possible chemical modifications of collagen brought about by vegetable tan (tara) -sodium metasilicate combination tanning [13].

The organoleptic properties of Tara- silicate combination tanned leathers are better than that of all control leathers. But the physical strength properties of the Tara-Silica combination tanned leathers especially partially pickled system had comparable physical properties with that of chrome tanned leather. Hence Tara-silica combination tanning system is a highly viable option as a replacement for chrome tanning. This tanning system presents the tanners the option of producing chrome free eco-friendly leathers. The major advantage of the tanning system using Tara and silica combination is the ability to produce white leathers, which is difficult in the case of other dominant tanning system existing at present. Both chromium and vegetable tanning systems induce a base color to the leathers, which leads to difficulty in producing pastel/light shades. Through the addition of suitable adjuncts and by the involvement of proper process control, leathers with good characteristics are obtained from the Tara-silica combination tanning system. The tara-silica combination tanned leathers, post tanned for making upper, produced fuller, smooth grain and fluffy leathers comparable to chrome tanned leather. These fuller, softer, good napp and fluffy properties of Tara-silica combination tanned leather led us to conclude as these tanning agents are also used to produce suede leathers. Since, tara and silica produce white leathers, the leathers obtained using this tanning agent are light colored, which are ideal for pastel shade dyeing.

5.2 Recommendations

Based on the results and conclusions of this study, the following recommendations are formulated

- As indicated from the shrinkage temperature and physical measurements results it should be clear that leather can be made from the combination tanning system but it needs careful control of the pH during the preparation of masked silica solution
- There is scope to improve the strength properties of leathers tanned with tara-silica combination tanning system
- The leathers tanned with tara-silica combination system careful control to each parameters is significant to reduce process defects
- To see the practical applicability of an alternative system of tanning, Awareness creation for leather industries and societies should be done so as to use sodium metasilicate and tara combination instead of basic chromium sulphate to reduce the environmental impact due to chromium.
- Substitution of conventional tanning agent by sodium metasilicate and tara combination is one option by which we can remove chromium discharge from tanning effluent. Other tanning agents (particularly plant extracts and minerals) can be researched as a partial or whole substitute for Basic chromium sulphate that could efficiently tann the pelt and reduces the chromium and TDS discharge from tanning effluent.

6 References

1. Preparation of Eco-Friendly Leather by Process Modifications to Make Pollution Free Tanneries, Volume 2, No.5, May 2013

2. Mahdi, haroun1, palmina, k. gurshi, a. covington, d, potential of vegetable tanning materials and basic aluminum sulphate in Sudanese leather industry (part II), Vol. 4(1), March 2009

3. A.E. Musa a and G.A. Gasmelseeda, Development of Eco-friendly Combination Tanning System for the Manufacture of Upper Leathers, March 2013, Vol.1

4. Virgilijus Valeika1, Justa Širvaityte2, Kęstutis Belska, Estimation of Chrome-free Tanning Method Suitability in Conformity with Physical and Chemical Properties of Leather, Vol. 16, No. 4. 2010

5. M.winyikione Mwinyihija , Essentials of ecotoxicology in the tanning industry, JECE, Vol. 3(13), pp. 323-331, 22 November, 2011

6. Jennette, K.W.; 'Chromate metabolism in liver microsomes', Boilogical Trace Element. Res. 1, 55

7. N. Nishad fathima, B.Madhan, J. Raghava Rao, B.U Nair, mixed metal tanning using chrome-zinc-silica: a new chrome sever approach, JALCA, VOL. 98, 2003

8. Virgilijus Valeika1, Justa Širvaityte2, Kęstutis Belska, Estimation of Chrome-free Tanning Method Suitability in Conformity with Physical and Chemical Properties of Leather, Vol. 16, No. 4. 2010

9. Leonard, A., Lauwery, R.R.; 'Carcinogenic & mutangenitic of chromium', Mutation research 76, 227, 1980.

10. Joan Carles Castell Escuer, The sustainable source of tannins for innovative tanning processes (2012)

11. A.E. Musa a and G.A. Gasmelseeda, Development of Eco-friendly Combination Tanning System for the Manufacture of Upper Leathers, Vol.1, March 2013

12. A. Sundrrajan, B. Madhan, J. Raghava Rao AND B. Unni Nair, studies on tanning with zirconium oxychloride: part II development of a versatile tanning system, JALCA, VOL. 98, 2003

13. Ministry of Environment and Forest Government of India. (2009). Technical EIA guidance manual for Leather/skin/hide processing industry. Hyderabad: IL and FS ecosmart limited.

14. Anthony D Covington, tanning chemistry, the science of leather,2009

15. LifenHao, XilongWang, Wei Xu, High Exhaustion Chrome Tanning Process Aided by Sodium Silicate

16. Fred O Flaherty volume III

17. B. Madhan, R. Aravindhan, N. Ranjithakumar, V. Venkiah, J.Raghava Rao, B.Unni Nair, combination tanning based on Tara: an attempt to make chrome free garment leathers, JALCA, VOL. 102, 2007

18.Yan Lu, Yi Chen, HaoJun Fan, BiYu Peng, Bi Shi, A Novel Nano-SiO2 Tannage for Making Chrome-Free Leather

19. J.M. Garro Galvez1, B. Riedl1 and A. H. Conner, Analytical Studies on Tara Tannins

20. Potential of vegetable tanning materials and basic aluminium sulphate in Sudanese leather industry

21. Eco-leather: Chromium-free Leather Production Using Titanium, Oligomeric Melamine-Formaldehyde Resin and Resorcinol Tanning Agents and the Properties of the Resulting Leathers

22. K.T. Sarkar, theory and practise of leather manufacturing, 4th edition 1991

23. B. Madhan, R. Aravindhan, N. Ranjithakumar, V. Venkiah, J.Raghava Rao, B.Unni Nair, combination tanning based on Tara: an attempt to make chrome free garment leathers, JALCA, VOL. 102, 2007

24. N. Nishad fathima, B.Madhan, J. Raghava Rao, B.U Nair, A new chromium-zinc tanning agent : available option for less technology JALCA, VOL. 97, 2002

25. Potential of vegetable tanning materials and basic aluminium sulphate in Sudanese leather industry (part ii)

26. Society of leather technologists and chemists (SLC), official methods of analysis, 1996

Annexes

Annex 1: Physical test standard for upper leather

S.N	Parameters	Values
1	Tensile strength for normal shoe upper	15 N/mm^2 (min)
2	Percentage elongation for shoe upper	40-60 %
3	Tear load for shoe upper leathers	40 N/mm
4	Load at Grain crack for shoe upper leather	200N/mm (mim)
5	Distention at grain crack for upper leather	7mm (min)
6	Dry rub fastness	Min 3
7	Wet rub fastness	Min 3

Source: central leather research institute

Annex 2: Provisional standards for discharge of effluent by leather tanning and finishing industries

Table 1: Emission Limit Values for Discharges to Water

Constituent Parameter	Emission Limit Value (mg/L)
Temperature	40^{o}c
pH	6 – 9 pH units
BOD5 at 20^{o}C	>90% Removal or 200 mg/l
COD	500
Suspended Solids	50
Mineral Oil (Interceptor)	20
Chromium (as total Cr)	2
Chromium (as Cr VI)	0.1
Oils, Fats, and Grease	15

Annex 3: Photos of Equipments used in the study

a) Digital weighing balance

b) Desiccators

c) Hood

d) Air dry oven

e) Electrophotometric spectroscopy (UVI-Visible)

f) Dynamometer

g) Lastometer

h) Circular rub fastness tester

I) Shrinkage tester