ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING

Standardization of Post tanning for waterless Chrome Tanning: Upper Leather

A Thesis Submitted to Addis Ababa University, Addis Ababa Institute of Technology, the School of Chemical and Bio Engineering in Partial Fulfillment of the Requirements for the Attainment of the Degree of Masters of Science in Chemical Engineering (Leather Technology Stream)

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Abstract

Waterless Chrome Tanning Technology (WCTT) is a new technology in which the chrome tanning part of leather processing is carried out without water and with simple chemicals that insure excellent absorption of chromium by the hide thus avoiding the chrome waste water. but to bring the consumers (tanneries) to use this new technology in large scale we need to remove their fear and build their confidence in this new technology; one way of doing this is to have or show them a standardized process (post tanning). This research focuses on standardizing the post tanning operation for WCTT upper leather; different recipes were experimented with trial and error, but first to find if there is even a need to have a new post tanning recipe for the WCTT both conventional chrome tanned and WCTT were processed with the same conventional post tanning recipe, after that both the conventional chrome tanned and WCTT final crust leather were evaluated with organoleptic method and physical testing. The WCTT final crust made with conventional post tanning shows some lower organoleptic values, so to correct this, different post tanning trials were done, some of the trials were avoiding re chroming and checking the chrome oxide content, adjusting the neutralization by using different percentages of sodium bicarbonate and checking the pH of the leather, using different re tanning recipes, using neutralizing syntan in neutralization stage, on the dye part different percentage of dye is used and the best percentage is chosen based on the organoleptic result of the final leather and the final liquor color; also a trial of adding the dye in two batches to shorten the dye penetration time. The final leathers were assessed for fullness, roundness, grain smoothness, looseness, grain tightness, colour uniformity. Organoleptic properties or Functional properties of leathers in a scale of 0 – 10 points were rated by three experienced CLRI staff and average values were taken. Higher values indicate better properties. The physical properties such as tensile strength, water vapour permeability, water penetration, colour fastness, elongation at break were also done.

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List of Abbreviations

WCTT	Waterless Chrome Tanning Technology
FAO	Food and Agriculture Organization
FDI	Foreign Direct Investment
WT	Waterless Tanning
NF	No Float Tannage
CSIR	Council of Scientific & Industrial Research
WVP	Water Vapour Permeability
WVA	Water Vapour Absorption
BCS	Basic Chrome Sulphate
ISO	International Organisation for Standardisation
IUP	International Union for Physical Test
DE	Double Edge Tear Strength
IULTCS	International Union of Leather Technologist and Chemists Societies
ASTM	American Society for Testing and Materials
BASF	Badische Anilin und Soda Fabrik (Chemical Manufacturing Company Name)

1. Introduction

1.1 Background

Ethiopia has the biggest livestock population in Africa. There is more than 50 million cattle population. Out of the 50 plus million cattle population around 98% is local breed while the rest is hybrid or exotic breeds. (2) The potential for development of the leather sector is substantial, most of hides and skins (about 80%) arriving in the formal market come from rural areas where they are collected by private traders. The remaining 20% are derived from slaughter houses found in major town and cities. 1.2 million Pieces of cattle hides are supplied to the tanneries per annum. The annual off take rate of cattle is around 7% and from this the potential production is estimated at 2.38 million cattle hides.(3) Ethiopia uses different ways for producing hides some of them are individual households, rural slaughter slabs, municipal slaughter houses and mechanized, modern abattoirs. Around 78% of cattle are slaughtered in abattoirs. Then these hides are collected and sent to tanneries so that the tanning processing starts. Tanning is the process of transforming the raw hides and skin which is a biological material into a non-biological material called leather. (4,1)

Upper leather is leather used for making the upper part of shoe. Leather made from hide is best suitable for making upper leather; this is due to the coarseness of the corium fibers and the compactness of their weave. The outer layer consisting of the grain layer and part of the underlying corium, the grain split, is used for shoe uppers or upholstery or case leather. This outer layer can be split to 1.3 to 2 mm for shoe uppers. Chrome tanning is most widely used type of tanning in which it is a result of side chain carboxylic groups on the protein molecule co-coordinating with the multinuclear chromium complexes present in chrome tanning liquors.(5) Waterless chrome tanning technology (WCTT) is a process developed in India, it is carried out without water during the chrome tanning stage, it is similar to the conventional chrome tanning except in WCTT there is no pickling, no basification and no final waste water thus it is a very useful technology in helping to avoid chromium contaminated wastewater. Tanneries are a type of industry that has a lot and different kinds of waste that pollutes water bodies and soil, highly toxic chromium contaminated water is one of the

wastes that is released by tanneries. This waste can be removed by using expensive waste treatment systems but small tanneries can't afford this so they simply release the waste to the environment. Hence a cost-effective solution such as WCTT may have a big impact in avoiding the problem associated with chromium contaminated wastewater.(6)

After chrome tanning the next operation is Post tanning which involves retanning, dyeing, and fatliquoring. It is a transition process between tanning and finishing. bulk and special properties are added in this operation.(8) Post tanning operation represents a very important phase in order to obtain specific characteristics, such as fullness, roundness, colour, etc on the finished product. Retanning is one of the operations and the main chemicals used are acrylic resins, dicyandiamidic resins, melaminic resins, syntans and so on and the fatliquor can be carried out using fatliquores such as lectin, synthetic, semi synthetic, neatsfoot etc. (7) Retanning gives the leather fullness with selective filling of the structure and to provide a tight and uniform grain surface for leather finishing. Most of the time synthetic retanning agents are widely used such as acrylic types this is due to acrylics having many side carboxylic acid groups that can give tanning property both reacting with multiple chrome centers on the leather and having a chemical bound to groups of collagen. (8) Fat liquoring is another operation in post tanning. The main purpose of fat liquoring is to prevent the final product from having a thin and dry handle and to minimize fibril adhesion during drying. Fatliquoring works in such a way that the oils enter the leather so that the fibers are uniformly coated and the fibers will be easy to slide on each other easily without breaking or being dry, the property of the final leather is extremely affected by the way the oil is distributed throughout the leather.(10)

The potential advantage of WCTT in a country like Ethiopia with largest no of livestock is huge, for this advantage to be possible the tanneries must have confidence in this technology and having a standardized post tanning that produces a quality final product is one way of building the confidence of tanneries and so this research focuses on having a post tanning that can produce a final leather that meets standard requirements.

1.2 Statement of the problem

Conventional chromium tanning was first patented by an American chemist and become very popular in short time interval; the reasons for chrome tanning to become very popular are quick and easy to produce usually taking up to a day, soft and supple final leather, water resistant, high thermal stability etc…conventional Chrome tanning with chromium (III) salts accounts for around 85% of global leather production (as per 2014). 95% of shoe upper leather,70% of leather upholstery. Even though there are a lot of advantages in conventional chrome tanning the Chrome waste has strong impact on the environment due to the negative effects on ecosystems and public health, and the high cost involved in treatment process especially in developing countries like Ethiopia the toxic wastewater can seep into the ground and affect soil and groundwater supplies.(1) The current chrome management options like high exhaustion tannage, chrome recycling and recovery–reuse methods, though offer improvements, do not provide comprehensive solutions.(2)

WCTT is a new technology developed in India; it is carried out without water and with simple chemicals that insure excellent absorption of chromium by the hide thus avoiding the chrome waste water. But with every new technology there is resistance and one of the ways of avoiding these problem is having a standardized process that shows tanneries the new technology can be done. So to fully bear the fruits of WCTT such as its lack of chrome waste and lower chrome use we have to have a standardized post tanning operation that produces similar or better final crust leather. So in this thesis it is attempted to standardize the post tanning operation of the WCTT for upper leather.

1.3 Objective

1.3.1. General objective

The general objective of this study was to develop a standardized post tanning for WCTT so that the final upper leather meets international standard.

1.3.2. Specific objectives

- To characterize the physical properties of WCTT and Conventional chrome tanned crust processed by using different post tanning formulations
- To determine the suitable re-tanning formulation for WCTT
- To study the effect of neutralization time on pH for WCTT
- To study the effect of different dye percentage on WCTT

1.4 Significance of Study

- Help in showing tanneries that waterless chrome tanning can produce a good final upper leather
- Used as a secondary data for further research work
- Can be used as a reference for tanneries if a problem occurs in the final leather

1.5 Scope of the Study

This research focus on standardization of post tanning for WCTT that produces final crust leather that meets specified standard requirements, by having a standardized post tanning tanneries will have more assurance in using this new technology and also by using this technology all the environmental and cost saving benefits will be fully possible.

2. Literature review

2.1 Raw material in the world and Ethiopia

"The total livestock population of world is estimated to be more than 1.67 billion for bovine animals, 1.08 billion for sheep and lambs, and 0.91 billion for goat and kids" (2).as it can be seen from table 2.1 peak of the global share of the livestock population is found in developing countries, 80.7% for bovine, 70.4% for sheep and lambs and 95.3% for goat and kids are found in developing countries. From developing country, Africa shared 13.6% for bovine, 19.7%sheep and lambs and 28.2% for goat and kids. Out of this, 3.23% for bovine, 2.35% for sheep and lambs and 2.44% for goat and kids are found in Ethiopia. (14)

Table 2.1 Livestock population of the world: Average 2009-2011 (14)

Livestock Population	Bovine animals (in million)
World	1616.6
Developed Countries	311.3
Developing Countries	1303.3
Africa	220.6
World	1616.6
Developed Countries	311.3
Developing Countries	1303.3
Africa	220.6

The farmers and animal herders in Ethiopia are categorized in small scale cattle animal; large scale ranches are small or negligible in Ethiopia. More than half of the population lives in the rural area and their livelihood fully or partially depend on cattle. (2) Ethiopia has the largest livestock population in the world. Ethiopia is 6^{th} in world with over 60 million cattle population and the largest in Africa.(13) The national annual off take for Ethiopian cattle is 14 % based on this the number of hide that should be produced annually is expected to be 8,442,000 hide. Off take is usually defined as a percentage of sale or slaughter at the end or during a production cycle to the initial stock. In general Ethiopia has one of the lowest off take rate in the world especially

for cattle. (12) The hides and skins of animals are the source of leather. The skins of large animals such as cattle and horses are referred to as hides The actual number of hides collected in the country is 26% hide, which reach the different tanneries; the rest being either consumed locally or sold illegally through cross border illicit markets. Even though Ethiopian hides are preferable in the world, the hides reaching tanneries have low quality due to different preventable problems this leads to having low grade or rejected hide that couldn't reach the world market. (13) Hides are turned in to leather by tanning there are many ways of tanning but all of them cause the following changes in the raw hide. A tanned hide when put outside will not cause smell or putrefy and when drying the tanned hide it will not be hard, it will have the same property as it was first tanned. Different kinds of tanning are there, the type of tanning is chosen based on what kind final leather is needed. (15)

2.2 Background of Ethiopian leather sector

The Derg was a militaristic regime in Ethiopia which ruled from 1974-1991 one of the distinct characteristic of the regime was nationalizing big private companies, from the leather sector eight tanneries and six shoe factories were nationalized which means the government is now managing them this caused a downfall of the leather sector that was producing value added products, since it was not viable to make the leather sector produce value added product the raw hide and skin exports re dominated during the Imperial and Derg periods, until being banned in the 1980s to secure input for the increasing capacity of nationalized state-owned Leather Production firms.(17) Ethiopia has largest no of cattle, low labor cost, duty free access to key markets and having internationally valued sheep & goat skin but with all this advantages Ethiopia is not able to produce value added product that can be exported, so now raw hides are just exported with low price, one of the ways of solving this problem is integration into regional market and reducing the problem associated with quality.(2) The Ethiopian Leather and leather product value chain can be roughly divided into four key segments: (i) the livestock sector (ii) collectors and local traders (iii) tanneries (iv) local leather product manufacturers may export to global buyers or supply the domestic market.(16) There are 30 tanneries with 7516 employees in Ethiopia with a capacity of 275 million square feet per year, before the 2000s most of the tanneries were locally owned but after the millennium there was a lot of FDI and 10 out of the tanneries were FDI. The main reason for the increasing of the FDI is due to low salaries for

employees, raw material potential, attractive market network and small strict in environment. Most of the FDI tanneries either bought old locally owned tanneries, upgraded them or they dislocated the tanneries to other places. (16)

The main objective of the government in the leather sector is to increase the export earning, one of the ways of increasing the export earning is by value addition meaning having a final product that passed through all the leather processing, which goes from hide to wet blue to crust leather and exporting in short run and exporting finished leather in the long run. So to have this export capability possible there is a lot of work that needs to be done such as increasing FDI in the leather sector, upgrading the current tanneries, human resource development etc (18)

2.3 Fundamentals of leather processing

Leather processing is a process that changes putrefy able hide in to leather, when an animal skin is to be processed, the animal is slayed and skinned before the body heat leaves the tissues. This can be done by the tanner, or by obtaining a skin at a slaughterhouse, farm, or local fur trader. The animal hide is usually preserved by using mainly salt. This is a temporary preservation that lasts for short period. This preservation is necessary until the hide reaches to the tannery. The main processes in the leather processing are Flaying, curing, washing, liming, unhairing, fleshing, deliming, bating, pickling, tanning, ageing, splitting, shaving, washing, (rechroming) neutralizing, retanning dyeing, fatliquore, fixing, ageing, setting out, drying, staking, finishing.

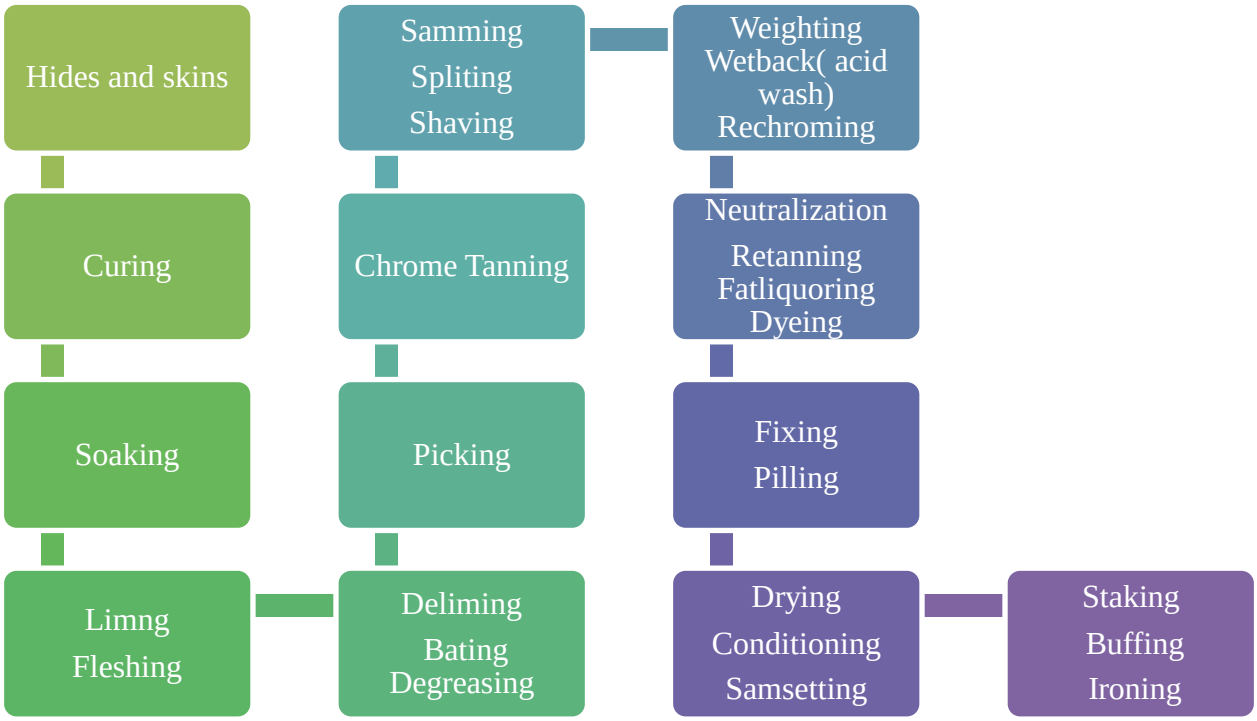

Fig 2.1 Conventional Leather process (15)

2.3.1 Curing

Raw hides and skins are first preserved to stop them from deteriorating before it goes to the leather processing, before the raw hides and skins are tanned; they can be attacked by bacteria, etc and become putrefied. So to avoid this damage we use different methods of preservation including salting, chilling, freezing and the use of biocides. (15)

2.3.2 Soaking

Soaking is the first operation of leather processing; it is used to clean hides and skins by removing various unwanted contaminants such as dirt, blood, flesh, grease and dung. It is carried out in alkaline conditions of a pH of 5.5-10. Soaking furthermore rehydrates the skins and hides, in this operation some enzymes are used such as proteases and carbohydrases. Proteases work by dissolving inter fibrillary proteins that compact fibres together while carbohydrases break up carbohydrates within the hide and as a result increase water uptake. Wet salted hides are soaked by laying in drum with water around 10 ^{o}c -16^{o}c. Satisfactory soaking is judged by feel, cleanliness and absence of salt. Temperature, chemical additions, mechanical action and time must be carefully controlled to have a good soaking without damage.(35)

2.3.3 Liming & fleshing

Liming removes the epidermis, hair and also slightly breaks the chemical cross links of the collagen due to alkaline swelling which is also called fibre opening; liming is carried out in basic condition by using milk of lime and sharpening agent such as sodium sulphide, cyanides, amines, etc…Fleshing is also done after liming and as the name indicates it simply means removing the flesh part of the hide this is usually done by using mechanical fleshing machines.(9)

2.3.4 Deliming, Bating & Degreasing

The residual alkalis left by the previous stage are not needed so to remove the alkalis the pH is brought down to around 8 and the chemical used are called deliming agents these are chemicals that are either weak acids or salts some of them are ammonium sulphate, ammonium chloride, boric acid, lactic acid, formic acid ,acetic acid, sulphuric acid & hydrochloric acid. After deliming the hides goes to bating process in this process the hides are treated with enzyme so that the hides become softer, here the time of bating is important factor as such more time means softer final product (15) the next process in called degreasing which simply removes the natural fat found in hide but this operation is most relevant for skins since skins have huge fat content. Bovine hides don't usually have a separate degreasing step since the type of fat in hides is challenging to remove and there is relatively small amount of fat. Degreasing is important for fatty skins before chrome tanning because if the chromium salts react with the grease they will produce insoluble chromium soaps that is difficult to remove subsequently.(19)

2.3.5 Pickling

Pickling operation is usually termed as preparatory operation before chrome tanning because in this operation the pH is adjusted to about 2.8-3 so that the hide will have ideal pH condition for the penetration of chrome salt in the skin matrix so as to form coordination covalent bond with the COO- group of collagen during basification. The conventional recipe for pickling based on limed pelt weight is 100% Float, 10% salt, 1% Sulphuric acid. In this operation salt is also added to prevent fibre swelling (9)

2.3.6 Tanning

Tanning operation is the main step in leather processing here the protein of the hide is converted in to a stable material So that the hide doesn't putrefy and also become suitable for a wide

variety of purposes. The biggest difference between tanned hide and raw hide is the latter dries out to be horny material and if rewets it putrefies while the tanned hide doesn't putrefy. As it can be seen from Fig 2.2 There are different types of tanning and the main ones are mineral tanning such as chrome tanning, aluminium tanning,… and vegetable tanning which uses tanning material extracted from plans leaves, barks, etc…(19,15)

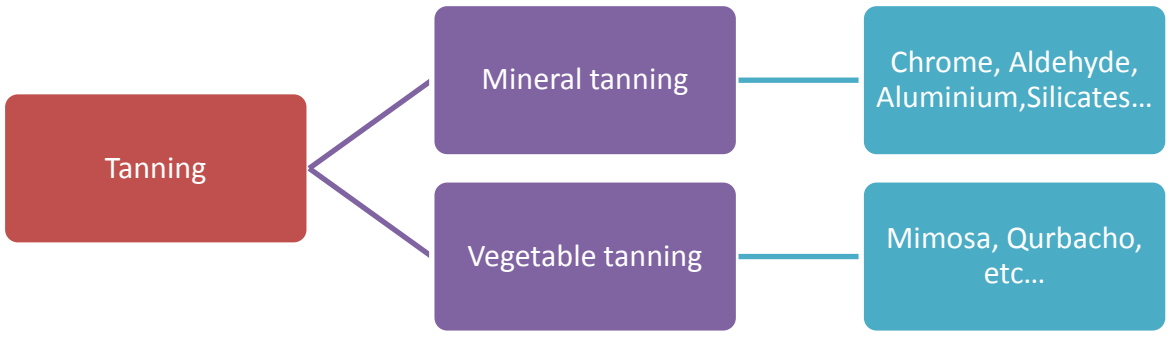

Fig 2.2 Types of Tanning (9)

2.3.7 Chrome Tanning

Chrome ores are compounds with iron which occur naturally in many parts of the world. The chromium salts are separated by first heating them with alkali to form yellow sodium chromate and sodium ferrate. Chrome tanning is done by using chromium sulphate (Cr_2SO_4) a green salt produced by reduction of the dichromate. One of the important properties of chromium salts is that chromium salts when dissolved in water hydrolyse until equilibrium is reached between the salt, the water, the hydrolysed salt (the basic salt) and the acid produced by hydrolysis. Such equilibrium depends upon the concentrations of the components present, the dilution, the temperature, etc.

$Cr_2(SO_4)_3 + H_2O$ ---------- $2Cr(OH)SO_4+H_2SO_4$

During the beginning of chrome tanning there was two bath chrome tanning in which at first the leather is processed with dichromate solution and then finally it is processed in molasses,

glucose, etc which act as a reducing agents. But nowadays chrome tanning is processed in one bath using basic chrome sulphate with 33% basicity.(21)

Chrome tanning is the most commonly used tanning process in leather industry. As it can be seen from Fig 2.3 88.8% of the global leather production is processed by chrome tanning this signifies the importance of chromium-tanning salts in the leather industry. In chrome tanning the chrome fixes on the acid groups of the protein of the collagen where they will displace the bound water but they are liable to form complexes of two or more metal atoms which might then form cross links between adjacent acid groups on the skin collagen molecule.(19)

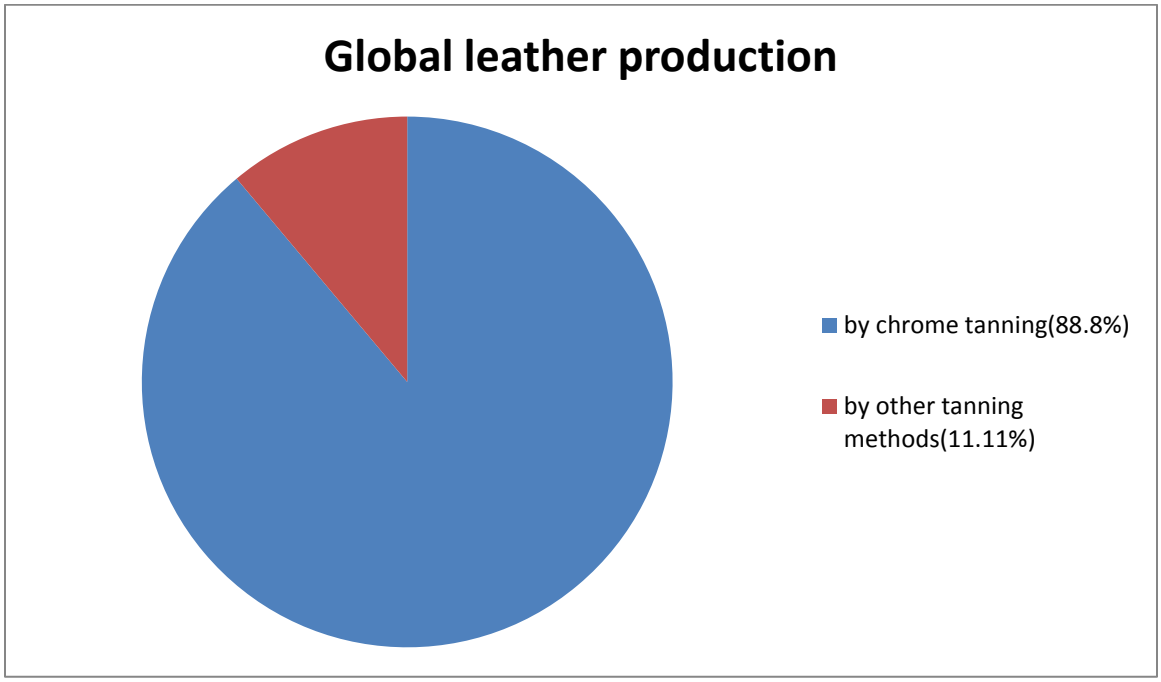

Fig 2.3 Global leather production (19)

Conventional chrome tanning consists of the treatment of de haired hide with sulphuric acid and sodium chloride around the pH of 2.8-3. This operation is called pickling this treatment usually takes 24 hr. after that the hide is treated with basic chromium sulphate 6-8% using 100-150% of water as a medium. After checking the penetration of chromium by inspecting the cross-section, the pH of the tanning bath is raised to 3.8–4.0 using 10% alkali solution. The duration of chrome

tanning varies from 5–6 h.(21) Conventional chrome tanning system brings excessive discharge of chromium into effluents as well as abundant chrome shavings. 40-70% of chromium is absorbed in to the hide and the rest goes to wastewater. The amount of absorption is directly affected by the amount of reactive sites of the collagen and due to low affinity tanning material.(20) If the effluent is not treated and chromium is released to the environment there is a chance that the chrome (III) might oxidize in to chrome (VI). Chromium in its +6 oxidation state is referred to as Hexavalent chromium which is a carcinogenic and if people get exposed for a prolonged time, It has been reported to cause lung cancer, nasal cancer, eye damage, eye irritation, skin allergies, dryness, fissured skin, skin ulcers and swelling. Other effects of chromium include dizziness, growth problems, reproductive disorders, discoloration and erosion of teeth.(25)

The post tanning operation is one of the main operations in leather processing. It gives the tanned leather different properties such as aesthetic, physical, colour etc… to meet the end use requirement. These properties are imparted on the wet blue following a series of mechanical and chemical process giving us useable leather called crust leather.(27) Re tanning, dyeing and fat liquoring are the three main operations in the post tanning operations, in post tanning we can divide the individual operations in to two i.e mechanical and chemical, the mechanical operations are samming, shaving, staking, buffing, ironing. The chemical operations are rechroming, neutralization, re tanning, dyeing, fat liquoring, fixing.(15,27) Washing, samming, splitting, shaving, neutralization can be taken as preparatory steps these operations as the name indicates are preparing the wet blue for retanning, dying and fat liquoring operations. Retanning ,dyeing and fatliquoring are also called wet finishing operations and drying, conditioning, staking, buffing, drying, dry drumming etc are the final operations which are mainly focused on texture refinement. (26) The different chemicals and mechanical operations are chosen according to the properties required for the final leather. For example the choice of retanning and fatliquoring chemicals depends on the desired properties (softness, touch, fullness, grain firmness or looseness, smell, adhesion properties, water uptake or release, and water repellence) of the final leather.(27)

2.3.8 Samming

This operation is done simply to remove the excess water from the tanned leather usually by a hydraulic machine. A hydraulic machine puts pressure on the wet blue and the water is squeezed out.

2.3.9 Splitting

This is a mechanical operation that splits the thick hide skin in to two finally we get the grain side which is made into upper leather and other types, the flesh side is the bottom split which is mainly used for making suede leathers. Splitting is also useful for reducing the thickness of thick hides.

2.3.10 Shaving

This is another mechanical operation that is used to reduce the thickness of the hide according to the requirement of the final product. For example for upper leather the thickness requirement is 1-1.2 mm thickness.

2.3.11 Weighting

Now after adjusting the thickness the next post tanning processes are done in a drum and different chemicals are used and the amount of the chemicals used are known by percentage of the shaved weight so taking the weight is important and the weight is called shaved weight.(28)

2.3.12 Wet back/acid wash

This is the first operation done in a drum. it is performed to wash away any unfixed/loosely held chrome and also adjust the pH for re-chroming. The chemicals used include an acid, mostly acetic acid and chrome dispersing agent (an amphoteric agent most of the times). Sometimes, oxalic acid is also used to scavenge hexavalent chromium if any in the leather or in the case of white or pastel coloured leathers.

2.3.13 Re Chroming

The purpose of re-chroming for chrome tanned leather is to get more uniform chromium content in a pack of leathers obtained from different sources and/or to get uniform layer-wise distribution of chrome in thicker bovine leathers or to get the required amount of chrome as required by the type of leathers or as demanded by the buyers. Another reason for re-chroming is to get fresh

cationic charge in the aged wet blue leathers to improve affinity for dyes and fat-liquors. It is necessary to basify the chrome in re-chroming to a pH of about 4.0 to increase the fixation and allow the re-chromed leathers to age overnight before the leathers are taken for further processing. This is to ensure completion of olation process. If the re-chromed leathers are taken for neutralization process without aging, there is a possibility of stripping out chrome in the bath and the more serious issue with respect to production of free mineral acid in the leather due to continuing olation process resulting in poor strength properties of the leathers. (35,29)

2.3.14 Neutralization

This is one of the main operations of post tanning, here as the name indicates neutralizes the free acid present/liberated from the chrome complexes due to oxolation during aging in the chrome tanned leathers. If post tanning operations are performed without neutralization, the following problems will occur.

- The dyes will get fixed only to the surface without penetration, patchy and non-uniform surface dyeing will occur and the cross section will not be dyed
- The fat liquore will not go through the cross section and this causes surface greasiness, hard bony leather with no internal softness
- The re tanning materials will not penetrate through the cross section but it will only load on the surface which will produce empty leather with coarse grain and if there is too much surface loading the grain might crack

The extent of neutralization required for different types of leathers are as follows:-

Corrected grain upper leather (pH -4.8-5), Softy upper (pH-5.0-5.2), Suede leathers (pH -5.2-5.5) Nappa garment leather (pH 5.5-6.0), Glove leather (pH-6.0-6.2). The chemicals commonly used in neutralization are mild alkalis in combination with basic buffering salts. Sodium bicarbonate in combination with sodium formate is commonly employed for neutralization. Sodium formate is a buffering salt with slight alkalinity and performs the role of not allowing the pH to shoot up suddenly. Care must be taken so that the pH don’t shoot suddenly this is done by adding the chemicals in batches in small amounts with a small distance of time in between adding the chemicals to avoid formation of coarse grains, chrome patches and color un uniformity . Care also must be taken to finish the neutralization with short period of time as

much as possible to avoid looseness. For example for upper leathers grain tightness is one of the important properties so we need to have short neutralization as much as possible. Finally after achieving the required pH the leathers must be washed to remove the salts and leftover alkalis.(27)

2.3.15 Re tanning

Hides have different fiber structure due to different reasons such as difference in breeds, sex, age and nutritional status of the animals during their life time and also based on the climatic conditions in which they are breed, also a hide or skin will have different fiber structures from different parts on the same hide/skin for example butt and bell regions have different fiber arrangement and properties, to have relatively similar properties for the final leather we use re tanning. Re-tanning is a process performed to achieve uniformity in fullness and fiber structure of the leather and is especially important for chrome tanned leathers since empty types of leathers are produced by chrome tanning.(15) Sometimes, re-tanning of chrome tanned leathers are carried out to impart special characteristics such as improved dyeing characteristics or improving the affinity for fat-liquors by altering the charge characteristics or bleaching or bringing about whiteness etc. The choice of retanning chemicals depends on the desired properties (fullness, grain firmness or looseness) of the final leather.(9,29)

There are different kinds of retanning agents:

- Inorganic example chrome, aluminium, zirconium salts (Inorganic retanning agents are usually used in rechroming stage for chrome tanning.)
- Organic example vegetable, mimosa, synthetic, etc…

The most widely used re tanning agents are found from organic materials especially the synthetic retanning organic agents. Some of them are phenol based, melamine based, acrylic based. Synthetic retanning organic agents can be divided into three main groups:

1) Syntans these are condensation products of aromatic compounds like phenol, naphthalene sulphonic acid with formaldehyde or urea

2) Resins these are condensation products from formaldehyde with amino and amido compounds like urea, melamine, and dicyandiamide

3) polymers, mainly acrylic (polymerization products from acrylic acid derivatives).

Syntans are widely used in retanning operations, it have pros and cons one of the advantages is it takes short time to penetrate due to fast water solubility, small size, easily fixes to the leather material and also help to modify the physical properties of leather with respect to its strength, softness, fullness, weather resistance, dye penetration, levelness and brilliance of dye shades, grain characteristics, etc. The disadvantage is there is a small chance it can react with chrome 3 and gives off the caricigonic Cr 6. Resin are useful to produce leathers with good fullness, soft handle and smooth grain characteristics, since resin syntans are bigger size they are blended with dispersing agents for easier penetration into the hide. They are used to fill loose areas of the hide, melamin and dicyandiaminde are preferred, usually used with auxillary syntans to help the resin syntan to penetrate easily. Resin syntans give tighter fiber structure and fine grain break. Acrylic are another type of rettaning chemicals theses are polymeric in nature, they are useful in achieving round full firm handle and good grain characteristics with softness, they are anionic in nature can be used with other anionic syntans. Vegetable tans are from the group organic materials theses are produced from different plant parts such as roots, barks etc. vegetable tanning materials give good fullness to the final product, can reduce or prevent the formation of harmful Cr(VI), promote antioxidation properties, improve burnishability and glazing, fix cationic dyes.(9) To produce upper leather it is required around 25% of retanning agents on shaved leather weight and generally it's constituted of inorganic retanning agents (≅5%), vegetable tannins and syntans (≅8%) and resins (≅12%).(8)

The main objectives of the re-tanning are:

- To improve the fullness and uniformity of substance
- To fill the looser areas in order to get uniform substance and fiber compaction in all parts of the skins
- To impart body and round feel
- To avoid grain looseness and improve ''break'' properties and grain tightness by filling the void spaces between grain and corium by selective filling
- To improve the overall cutting value by bringing about uniformity of substance and fiber compaction(27,29)

Table 2.2 The individual effect of each re tanning agents (33)

Re-tanning chemicals	Purpose	
Melamin based	Improves grain tightness & flatness, predominantly affecting the belly region	Both improve roundness
Phenol based	Improves fullness	

2.3.16 Fatliquoring

A raw hide has natural fat, this fat is removed so that problems such as grease stains, uneven tanning, uneven colouring, soaps and fat spew are prevented; but by removing the fat we are left with thin and dry final leather which is useless; to avoid this we add different kinds of oil in water emulsions in a process called fat liquoring. Sulphated, sulphonated, sulphited and phosphated fat as well as mixtures of neutral fat with different emulsifiers are used to obtain fat liquoring emulsions to lubricate the leather. This operation is usually carried out in a drum at the highest temperature practical for the type of leather, or about 45°C for vegetable tanned leather and 60 to 65° C for full chrome tanned leather. The leathers are run in a drum for 30 to 40 minutes. (15,29,10) The main purpose of fat liquoring is to prevent the final product from having a thin and dry handle and to minimize fibril adhesion during drying and this in turn imparts softness, flexability, feel, drape, run, etc…The minimization of fibril adhesion results in reduction in the internal friction resulting in an improved strength properties. (29)

fat liquoring is also important to waterproof the final leather, since the collagen fibres have many polar functional group such as –OH, -COOH, -NH_2 and –CONH we can add different kinds of fat liquoring chemicals which are mostly hydrophobic to make the leather water proof. Here what we have to know is waterproofness of leather is not only due to chemical substances used in leather manufacture (tanning agents, re tanning agents, dyestuffs, fat liquoring agents and finishing agents). The initial quality of skin or hide and operation of each process of the skin/hide conversion to the finished leather have significant influence on the waterproofness degree of finished leather.(27) Fat liquors are classified based on their charge characteristics as

follows; anionic, cationic, non-ionic and multi charged depending on the nature of functional emulsifying group. Fat liquors are also classified based on the origin of oils such as vegetable, animal and synthetic.

Table 2.3 classification of fat liquors (27)

	Animal based	Vegetable based	Synthetic based
Viscosity	Good	Average	Average
Lubrication	Very good	Good	Fair
Roundness	Very good	Good	Fair
Penetration	low	Fairly Good	good
Fastness	poor	Average	Very good
Reactivity	high	Less reactive	poor

As it can be seen from Table 2.3 Fatliquors are classified based on their origin, animal based is a fatliquor made using animal fats such as neatsfoot oil, Vegitable based fatliquor is made using plant based raw materials and synthetic based fatliquors are made using synthetic chemicals. Fat liquors are also classified based on their preparation such as sulphated, bisulphate, sulpho chlorinated fat liquors. Each of them has different properties which are used for different kinds of final leather

2.3.17 Dyeing

Dyeing is another post tanning operation. As the name suggests, it is used to impart colour on the leather, for upper leather a good through and through dyeing is necessary. Commonly used dyes are acid, direct and metal complex dyes. Fastness rating for dyes types is Basic < Direct < Acid <1:1 Metal complex < 1:2 Metal complex. The dyes should be carefully dissolved following the procedure as follows: step 1 the anionic dyes are first dissolved in cold water and step 2 boiling hot water is added to the dye solution with stirring, step 3 the stirring is continued until all the dyes are completely dissolved. Step 4 the dye solution is filtered through a filter paper to remove the insoluble matter before addition into the drums. Finally we fix all the post tanning chemicals by adding acid such as formic acid.(10)

2.4 Waterless tanning (WT), Waterless chrome tanning (WCTT) and No float tannage (NF)

In the future as the world population grows and resources get scarce engineers will face demanding challenges so due to this they will have to think about sustainability aspects, including the economic, environmental, social and multi-generational dimensions. Engineers of the past were relatively focused on the technical and economic feasibilities of system design. Waterless tanning (WT) and WCTT can be taken as a product from "engineers of the future" due to its ability to address problems associated with sustainability, economy and the environment. It can be one of the tools used in bringing a paradigm shift in production and consumption pattern in the leather sector.(23)

WCTT is crucial to address present challenges faced by humanity such as global warming and depletion of water resources. Global warming in return brings challenges such as environmental pollution, resource depletion and threats to food. Hence we can say waterless tanning can be one of the tools used in bringing a paradigm shift in production and consumption pattern. Before WCTT was discovered there were old technologies which tried to either conserve water or change the water with other recyclable solvents. Such as no float tannage and waterless tanning: chrome tanning in ethanol and its derivatives.

2.4.1 No float tannage

The amount of float does not affect the chemistry of processing but it will affect the rates of both the penetration and reaction. The shorter the float the more concentrated is the reagent and the faster that reagent will penetrate and react. But if the rate of fixation is faster than the rate of penetration the cross section might not be sufficiently tanned.

Some of the mechanisms of no float tannage

- There will be low concentration of liquor these conditions cause vigorous mechanical action due to absence of water
- High chrome salt concentration causes rapid diffusion into the interior of the skin.
- High chrome salt concentration results in high sulphate concentration

- High sulphate concentration causes sulphate ions to co-ordinate to the chromium tan molecule
- Co-ordinate of sulphate ion to chromium tan causes masking of chromium salt
- Well masked chrome salt will have less astringency
- After 30-60 min sulphate ions leave chrome complex resulting in less masking (15)

2.4.2 Waterless tanning: chrome tanning in ethanol and its derivatives

This is another technology that tried to find alternatives for water based chrome tanning by replacing the water medium by three solvents namely ethanol, ethyl lactate and ethyl acetate. Out of the three solvents ethanol medium enables good chrome tanned leathers in terms of colour, chrome content and organoleptic properties.(24)

2.4.3 Waterless chrome tanning technology (with no water liquor during tanning operation) WCTT

This is a new process that avoids the use of water for chrome tanning process, which is carried out without pickling and basification. WCTT is a new technology discovered by by Council of Scientific & Industrial Research (CSIR), this new technology works in such a way that the water absorbed by the hide is enough for chrome tanning operation so that it means there will be no chrome waste water. As it can be seen from Fig 2.4 This tanning process involve the use of pre-treatment chemical that eliminates pickling operation but the operations soaking, liming, deliming, bating, degreasing are similar to the conventional process.(22)

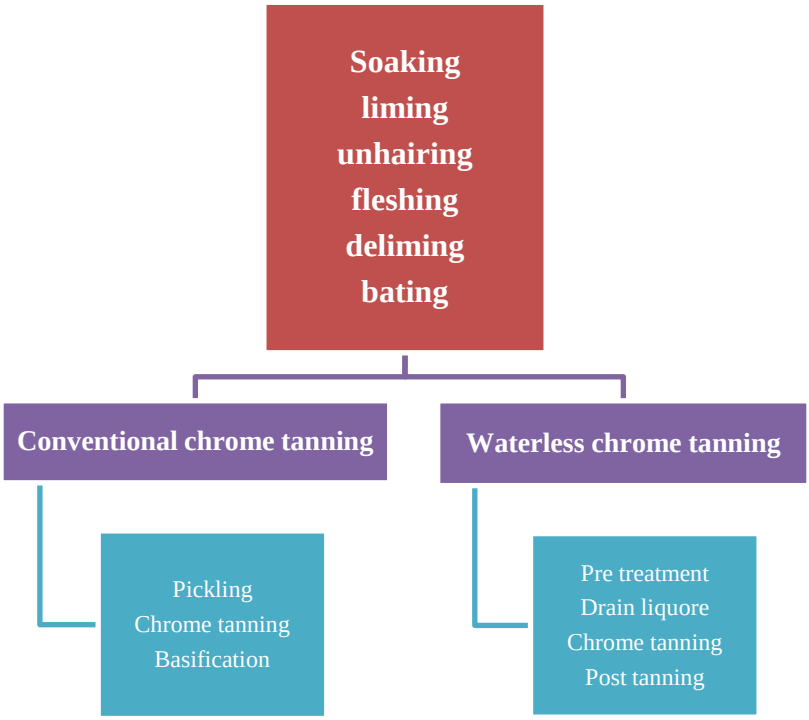

Fig 2.4 Conventional vs Waterless chrome tanning (22)

Unique Features of Waterless Chrome Tanning Technology

- Complete elimination of water input for chrome tanning
- No discharge of wastewater from chrome tanning
- Total elimination of pickling and basification
- High shrinkage temperature to that of conventionally tanned leathers
- High chrome content in leather
- Cost savings due to:-
- Reduction in BCS offer by 1 to 2%
- Reduction in water usage
- Reduction in wastewater volume
- Elimination of chrome recovery
- Enhanced productivity due to the elimination of intermediate unit processes like pickling and basification
- Simple process and does not demand additional infrastructure or new chemical

- Suitable for all type of product varieties from hides and skins
- Crucial to address present challenges faced by humanity such as global warming and depletion of water resources.

2.5 Important Qualities for upper leather

The leather used for making of upper components of shoe is known as shoe upper leather. the best tanning type for shoe upper is chrome tanning and even better tanning for shoe upper is combination tanning in which chrome is used with vegetable, synthetic or other types so that the fullness firmness and other important desired properties are improved. As it can be seen from table 2.4 the desire properties are color fastness, tensile strength, water vapour permeability, tear strength, percentage of Elongation at break, grain crack and etc (30)

Table 2.4 important qualities required for shoe upper leather (30)

No	Test	Requirements
1	Flexing endurance in the cold	50000dry, 10000 wet min. 30000 flexing
3	Rub fastness	Min. 50 rub cycles
5	Split tear force	Min.18 N (with lining) Min. 25 N (without lining
6	Tensile strength	Min. 150 N
7	Elongation at break	Not less than 40%
9	Fastness to migration	Max. Rating 3 (blue scale)
10	Water vapor permeability(WVP)	1.0mg/h.cm2
11	Water vapor absorption(WVA)	10mg/cm2 (after 8 hrs)
12	Water proofing	Penetrate water min.60min Absorption of water max 35%
13	Water spotting test	Drying without staining

2.6 Standardization of new Technology

Standardization is the processes of making something conform to a standard. By developing standards to specify acceptable product or service performance through dimensions like functional level, performance variation, service life time, efficiency, safety and environmental impact. Standards increase compatibility of final products to the consumer needs and also standard allows information to be shared within a larger network and attracting more consumers to use the new technology. Other benefits of standardization to consumers are reduced uncertainty, because consumers can be more certain that they are not choosing the wrong product. Consumers may also get the benefit of being able to mix and match components of a system to align with their specific preferences.(31) The Potential negative impact of standardization is that negative economic effects can occur. They typically result from three problems 1. Multiple standards for the same technology,2. Poorly designed standards, and 3. Poorly timed standards.

Sometimes when innovating firms are so eager to achieve market penetration they develop multiple standards this usually happens during the early stages of technology development.. At this point, the market is often not large enough to warrant investment in technologies such as sophisticated test methods. Poorly designed standards can be resolved by additional research to develop better technologies, which can then be adopted as single industry standards. The timing of interface standards is very important, thus, poorly designed or delayed interface standards can have decidedly negative effects on market structure. (31)

2.7 Adoption of new technology

The invention of new technology happens in a single event or jump, but for that technology to be diffused it will be a slow process. The economic growth and rate of change of productivity is highly affected by the diffusion of new technology so invention or innovation without diffusion is useless. Until this new technology is broadly accepted and used, the advantage associated it will not be possible. So it is important to focus on how to make this newly discovered technology diffuse or be adapted faster. There are different factors for the speed of diffusion of new technology some of them are Skill level of workers, Customer commitment and relationships, Market structure and firm size, Government and regulation etc…

Skill level of workers:- if the new technology needs complex new skills and if this skill development is time consuming and expensive then the adoption of the new technology will take more time. So all the available skills in the company and as well as the manner in which the necessary skills are attained are vital factors of diffusion. Customer commitment and relationships:- A steady and safe customer base is a vital factor for technology adoption in some industries. Since changing to new technology and adopting needs investments and companies want an assurance that their investment in the new technology can be payable by the income it generates. Market structure and firm size:- new technology in big firms have huge benefits due to that they are more likely to undertake innovation. Government and regulation:- governments develop different kinds of regulation and this forces firms to use new technologies because regulations will either prohibit or require the use of certain technology or production methods. Sponsoring is a vital factor for technology adoption and this sponsor is usually given by government, so government plays great role. These are some of the factors for having quicker diffusion of new technology however we must also not forget the importance that the makers of new technologies to offer numerous training courses in their use. (32)

3. Materials and Methods

3.1 Materials and Equipment

The raw material is wet salted cow hide and the Equipment's are analytical weighing balance, small and medium size tannery drums, pH meter, pH paper, hide fleshing machine, hide shaving machine, hide staking machine, hand spray, iron plating and different laboratory equipment for testing the final leather such as Dynamometer, gray scales, Double edge tear strength. The chemical used in leather processing are commercial leather processing chemicals (see the recipe on annex), for laboratory analysis analytical grade chemicals were used such as nitric acid, acid mix, sodium thiosulfate and potassium iodide.

3.2 Methods

Similar grade wet salted cow hide were collected from storage room, hides were split along the backbone and processed with the same process from soaking to degreasing, after degreasing the hides were separately processed so that half side was processed in conventional chrome tanning which includes pickling and chrome tanning, the other side was processed by WCTT which includes chemical treatment and chrome tanning without float. After reaching wet blue stage the samples were piled for 24hr sammed and shaved to a thickness of 1.2mm and their weight was measured. Then using two medium sized drums such that in one drum the conventional chrome tanned and in the second drum the waterless chrome tanned sides were put and processed.(33)

3.2.1 Process design and standardization

After discovering the different problems encountered by using the conventional post tanning in the WCTT, such as inappropriate neutralization, reduced organoleptic properties, inadequate dye penetration, a method was developed to address the problem. To achieve a good neutralization the time and amount of neutralizing chemicals was targeted. To improve the organoleptic properties the amount of tanning chemicals was targeted and to have a good dye penetration the time and stage of addition of dye chemicals was targeted. Since the properties associated with fat liquor such as softness, water vapor permeability etc… were good enough for upper leather the fat liquor is made constant.

Table 3.1 Sample Codes

No	Sample CODE	Type of leather	Type of chrome tanning	Type of post tanning	Side of hide
1	IZ	Hide	conventional	conventional	Left side
2	IXZ	Hide	Waterless	conventional	Right side
3	IZi	Hide	conventional	conventional	Left side
4	IXZi	Hide	Waterless	conventional	Right side
5	IY	Hide	conventional	Experiment	Left side
6	IXY	Hide	Waterless	Experiment	Right side
7	IIY	Hide	conventional	Experiment	Left side
8	IIXY	Hide	Waterless	Experiment	Right side
9	IIIX1	Hide	Waterless	Experiment	Left side
10	IIIX2	Hide	Waterless	Experiment	Right Side
11	IIIX3	Hide	Waterless	Experiment	Right Side

The above table shows the different type trial's sample code, type of leather, type of chrome tanning, type of post tanning and side of hide. It can be seen that all the waterless chrome tanned have X in their sample code, there are two types of chrome tanning; conventional chrome tanning is the current type tanning done in tanneries, waterless chrome tanning is new technology discovered by Indian scientists, there are also two types of post tanning; the conventional post tanning is the one used in tanneries, the experiment type post tanning is the

different trials done in this research. The side of hide indicates the full hide is split along the backbone and labeled as left and right side. The type of leather specified in the table indicates the raw material for making the final leather and in this research all the raw material is cow hide.

3.2.2 Re tannning trials

Table 3.2 Retanning trials *(% is based on shaved weight)*

Chemicals	Conventional (IZ)(IXZ) (IZi)(IXZi)	Trial 1 (IY) (IXY)	Trial 2 (IIY) (IIXY)	Trial 3 (IIIX1)	Trial 4 (IIIX2)	Trial5 (neutralization syntan) (IIIX3)
Acrylic %	5.0	4.0	3.0	3.0	3.5	3.5
Melamin %	5.0	6.0	6.0	6.0	6.0	6.0
Phenolic %	6.0	6.0	7.0	7.0	7.0	7.0
Mimosa %	5.0	5.0	5.0	3.5	3.5	3.5
Synthetic fatliquore %	4.0	4.0	4.0	4.0	4.0	4.0
Semi-Synthetic fatliquore %	4.0	4.0	4.0	4.0	4.0	4.0
Neatsfoot oil %	2.0	2.0	2.0	2.0	2.0	2.0
Lectin %	2.0	2.0	2.0	2.0	2.0	2.0

Conventional post tanning (Sample code IZ and IXZ)

Sample IZ and IXZ these are the first samples as seen from the table, sample IZ is the conventional chrome tanned and sample IXZ is the waterless chrome tanned these two samples are processed with a standard conventional post tanning recipe so that the difference between conventional (IZ) and the waterless (IXZ) is determined to find out what kind of adjustment are needed for the waterless.

The wet back is properly checked by feeling the samples with hand then after washing the re chroming is done which was left overnight then basification next followed by neutralization with sodium formate 0.5% and sodium bicarbonate 1%. The conventional post tanning recipe used includes total retanning 21% and total fat liquoring 12% with acrylic 5%, melamine 5%, phenolic 6%, mimosa 5%, dye 4%, synthetic fatliquore 4%, semi synthetic fatliquore 4%, lectin 2%, Neatsfoot 2%, rechroming is done for both the conventional chrome tanned and waterless chrome tanned.

Conventional post tanning (no rechroming) (Sample code IZi and IXZi)

In this experiment every process is the same as the above conventional post tanning except here there is no rechroming for both the conventional chrome tanned and waterless chrome tanned

Trial 1 sample code (IY AND IXY)

In experiment 1 sodium bicarbonate is increased by 0.5% to a total of 1.5%, the acrylic is reduced by 1% to have a total of 4% acrylic and to compensate for the reduction of acrylic, melamine is increased by 1% to a total of 6%, while all the other retanning and fat liquoring chemicals remain constant. The conventional chrome tanned sample is re chromed while waterless chrome tanned sample is not re chromed.

Trial 2 sample code (IIY AND IIXY)

Acrylic is reduced by 1% to a total of 3% and to compensate for the reduced acrylic, phenolic is increased by 1% to a total of 7% while making all the retanning and fat liquoring chemicals remain constant. The conventional chrome tanned sample is rechromed while waterless chrome tanned sample is not rechromed.

Trial 3 sample code IIIX1

acrylic melamine and phenolic are made constant but mimosa is reduced by 1.5% percent to total of 3.5% and the dye is given in two batches (first 1% dye together with retanning chemicals) and (2% finally after fatliquoring)

Trial 4 sample code IIIX2

Everything is similar to experiment 3 except Acrylic is increased by 0.5%

Trial 5 sample code III X3

This experiment is similar to experiment 4 the only difference is in experiment 4 the neutralization chemicals are sodium formate 0.5% and neutralization syntan 2%.

3.2.3 Dyeing trials

Here to determine the relationship between dye % and organoleptic properties (color uniformity) 5 samples are processed with different dye % using trial 4 recipe, here also all the other process are made to be constant except for the dye%, the dye used is from the manufacturing company BASF that is called luganil black anionic dye. At the end after fixing the dye with formic acid, the final liquor color is assed for each samples so that we know whether the dye% is enough or in excess, the final color is assessed by first taking the liquor with hand and seeing its color. If the liquor color is too dark there could be different reasons such as the dye % is too much, the leather might have some problem due to previous processing error and can't react with dye, there could be a problem with the dye etc…

3.2.4 Neutralization trials

Neutralization is one of the important stages in post tanning, so it is important to have the correct alkaline percentage, using low alkaline % will cause the leather to have lower pH and this will affect the properties of the final leather for example for upper leather the pH must be 5 so that the re tanning, dyeing and fatliquore chemicals will properly and evenly react with the leather and produce a final leather with the properties of the upper leather. So in these trial different percentages of an alkali sodium bicarbonate are used while making the sodium formate constant. Then the pH of the leather is measured at the belly, butt, neck and surface sections. In these trials

the time is also important, the longer the time the higher the pH but this applies only if the alkali percentage is higher than needed. The first pH is tested at 60 min then at 65,70,75, etc until the pH 5 is determined, if the pH is lower than 5 at all those times or the solution is in equilibrium then another trial is started with higher alkali percentage.

Trial to see the relation between time and Neutralization pH for WCTT

During neutralization there are two factors that affect the pH these are the amount of the alkali used and the time taken; in the previous trials the best percentage of the alkali is determined and the time is also determined, but in this trial the pH is tested at different interval of time so that the relation between the time and pH is determined and also the speed the pH is rising can be determined. The equilibrium point or how high the pH can rise also can be found.

3.2.5 Physical testing methods

3.2.5.1 Tensile Strength

Tensile strength is the ultimate strength of the leather that includes grain, corium and flesh layers. In this test elongation property of the leather can also be measured. Permanent elongation that is responsible for permanent set (pas-tic character) of the leather also can be tested. Tensile strength is defined as strength of material in terms of force per unit area of cross section while applying force in linear direction. Tensile strength = Force (N) Area (Width in mm x Thickness in mm) Tensile strength testing Machine (Dynamometer):

Tensile testing machine used for physical testing of leather is generally working in tension method. It consists of a rigid main frame with two vertical columns. It is provided with a fixed horizontal cross head between these two columns. A movable cross head is also provided with a mechanism that smoothly moves up and down in between these two columns with the help of a driving system. A load cell capable of measuring up to 1000N force is mounted below the moving cross head with a swing assembly with sample holding rubber faced grip to accommodate the test specimen. A similar fixed sample holding grip assembly is provided in the bottom fixed cross head. The speed of the Movement and force applied on the test specimen is controlled with an external software controlled operating system. Clamping of test specimen is

made with either mechanical screwing method or applying pneumatic pressure. The test results are documented with a PC system. (34)

3.2.5.2 Water Vapour Permeability

Water vapour permeability (WVP) – ISO 14268/IUP15/EN 20344 is the unique property of leather. Under normal conditions about 5 grams/ hour sweat is produced by a human when the atmospheric condition is between 30–35oC. Under Industrial working condition, the sweat produced by a human foot is around 10 gram/hour. This sweat has to be sent out from the shoe to ensure comfort. This process of transmission of sweat from inside the shoe to the atmosphere is known as water vapour permeability. In shoes, leather upper has the ability to absorb the sweat produced and transmit to the upper part of the leather through wicking process. Once it reaches the upper surface, the sweat evaporates into atmosphere. This process is known as water vapour permeability or water vapour transmission. This is possible by the porosity characteristic of leather. Filling, finishing and lubrication processes in leather making reduces this water vapour transmission property to a greater extent. The extent of available water vapour permeability rate is determined using a specific test method called Nice-Mitton test method. The leather sample under test is sealed on the mouth of a desiccant filled jar that provides a humid gradient across the test sample and, again, the test is carried out in a conditioned atmosphere. The sealed jars are held in a vertical wheel or disc, which rotates during the test. A large fan is also incorporated within the equipment, and this rotates in the opposite direction to the sample wheel. This creates air turbulence over the samples sealed in the mouth of the jar, thus removing the layer of still air. The sealed jars are weighed before and after test, and the increase in weight of desiccant is used to calculate the WVP of the sample, usually expressed as ‘milligrams of water vapor per square centimeter per hour.(34)

3.2.5.3 Tear Strength

Tear strength is also an important bulk property test. This test is the most preferable test for leather than tensile strength by many of the customers. There are two types of tear strength tests are followed for leather material. Double edge tear strength – Baumann Tear strength (DE) and Single edge tear strength - Tomgue/trouser tear strength (SE).

DE tear strength is carried out in such a way first Cut six test specimen (three test specimen from along direction and three test specimen from across directions) using a cutting knife 50 mm x 25 mm size having a central slot, Condition the test specimen for 48 hours and measure the thickness. Insert one of the test specimens through the slit into the sample holding "L" clamps that are fixed to the tensile tester. Conduct the test by operating the tensile tester at the rate of 100 ± 10 mm/ minute speed until the test piece is torn apart. Record the maximum force. Continue the test for remaining test specimen. Tear strength = Maximum tear force (N) / Thickness (mm) (34)

3.2.5.4 Grey Scales

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". This procedure of assessing is adopted for both textile and colored leather materials. Grey scale used to assess the color change in leather surface is called – Color change scale – ISO 105-A03 and Grey scale used to assess the color transfer to the rubbing felt or contact fabric material is called – Color transfer scale – ISO 105-A03 These scales consists of nine pairs of gray color chips each representing a visual difference and contrast. Grade 5 indicates no visual change (best rating) and grade 1 indicates a large visual change (worst rating). The grades are given as follows (1), (1/2), (2), (2/3), (3), (3/4), (4), (4/5), (5) (34)

3.2.6 Chemical Testing Method

3.2.6.1 Chrome oxide content

Chromium content was determined using the idiometric titration method, in which the wet blue leather is first digested using acid in digestion method by measuring 0.5g of wet blue, 0.5ml of nitric acid and 0.75ml of acid mix and adding all in a flask, then the flask is heated until color changes to yellow gold. After cooling the flask 50ml of water is added and heat for 10min. next titrate the liquid in the flask with sodium thiosulfate and KI. By measuring the amount of titrant the amount of chrome oxide can be calculated. (34)

4. Results and Discussion

4.1 Organoleptic properties

The organoleptic results for conventional and waterless chrome tanned leather are indicated in the table below, the conventional chrome tanned are IZ, IZi, IY, IIY and the waterless chrome tanned are IXZ, IXZi,IXY,IIXY,IIIX1,IIIX2,IIIX3. The organoleptic values are tested by a professional staff, the values include fullness, roundness, grain smoothness, looseness, grain tightness, colour uniformity and the general appearance is the average of all the other values. In the next Page there is a detailed description about each result.

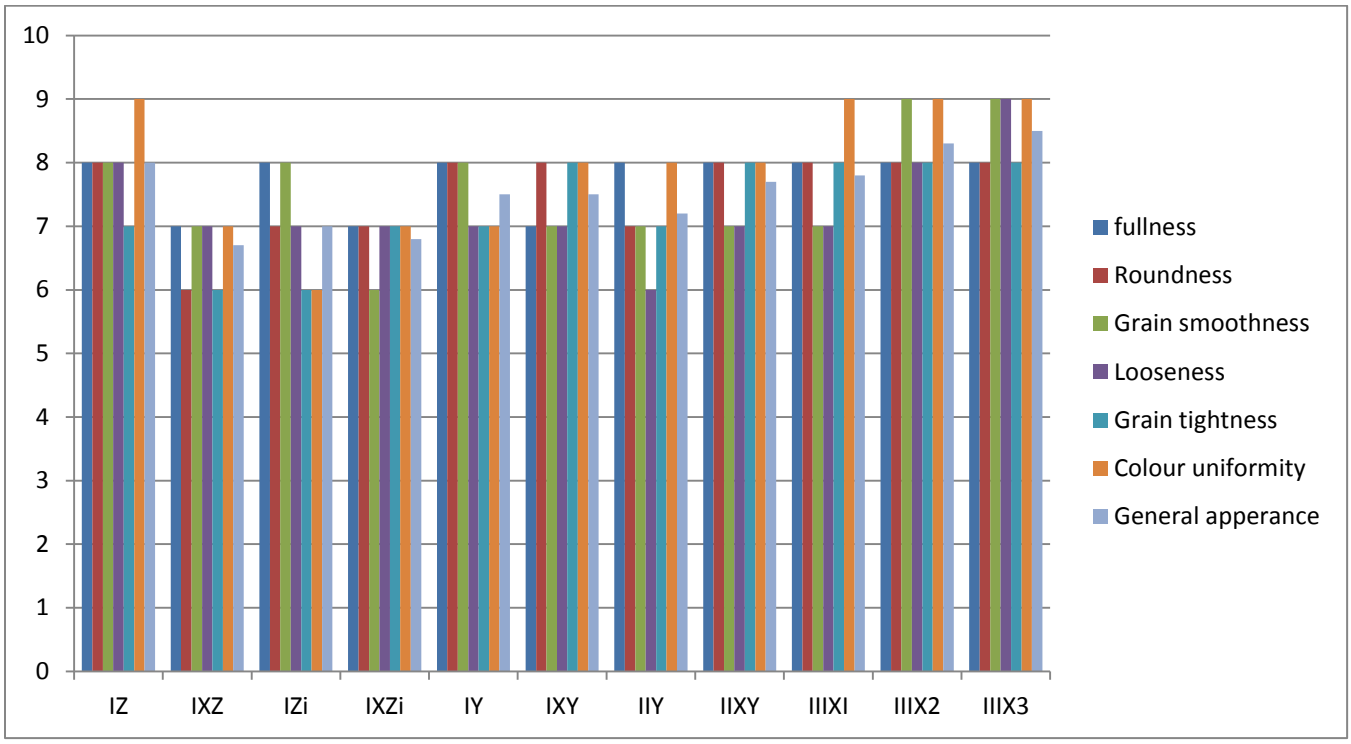

Fig 4.1 organoleptic properties

Conventional post tanning with re chroming (5% acrylic) (IZ and IXZ)

This is the first process done, its main goal is to determine what kind of differences are seen between the WCTT and conventional chrome tanned by processing them with the same conventional post tanning process, and as we can see from the organoleptic result the WCTT (IXZ) shows lower properties compared to the conventional (IZ). The general appearance for the WCTT is lower when compared with the conventional chrome tanned, the WCTT have lower organoleptic values. The conventional chrome tanned (IZ) with re chroming have good organoleptic properties; it is taken as a control. For the next results the conventional control will be taken as a standard.

Conventional post tanning without re chroming (IZi & IXZi)

When comparing this trial with the previous trial, for the conventional chrome tanned control without re chroming (IZi), there is a reduction in the roundness, looseness, grain tightness, colour uniformity. The general appearance is reduced. For the WCTT there is no significant difference.

Trial 1 acrylic -1%, melamin+1% (IY & IXY)

Comparing (IY) with standard (IZ) there is a reduction in looseness, colour uniformity for IY while the other properties remain same, as we can see from fig 4.1 the general appearance is reduced. It shows that for the conventional chrome tanned reducing the acrylic% negatively affects the organoleptic properties. For the WCTT comparing (IXY) with the previous trial (IXZi) there is improvement in roundness, grain tightness and colour uniformity.These improvements is due to the increase in melamin which predominantly Improves grain tightness and the reduction of acrylic. Here reducing the acrylic% didn't negatively affect the organoleptic values as it did for the conventional chrome tanned.

Trial 2 acrylic -1%, phenolic+1% (IIY & IIXY)

Comparing the conventional chrome tanned (IIY) with (IY) there is a reduction in roundness, grain smoothness and looseness but there is improvement in colour uniformity the continuous reduction of looseness could be due to reduced acrylic. For the WCTT comparing (IIXY) with (IXY) there is slight improvement in fullness while the other values look similar. There is slight improvement in general appearance for WCTT (IIXY) compared to the previous (IXY).

Trial 3 Memosa -1.5%, dye in 2 batch (IIIX1)

Comparing (IIIX1) with (IIXY) there is better colour uniformity this is due to adding the dye in two batches in IIIX1, the first chemical added in post tanning gets all the chemical reaction sites that's why adding the 2 % out of the 3.5% dye together with the re tanning chemical improved the color uniformity and adding the rest 1.5% dye next. At this trial all the organoleptic values are good except for grain smoothness and looseness.

Trial 4 acrylic +0.5% (IIIX2)

Comparing (IIIX2) with (IIIX1) there is improvement in the grain smoothness and looseness, this trial have best general appearance which is slightly better than trial 3. Comparing the general appearance of (IIIX2) with the first (IXZi) it can be seen that there is a significant improvement; all the organoleptic values have increased.

Comparing WCTT (IIIX2) to the conventional chrome tanned or control IZ here also it can be seen WCTT (IIIX2) have slightly better general appearance than the conventional chrome tanned IZ. Especially the WCTT is better in grain smoothness, looseness and grain tightness.

Trial 5 sodium formate & neutralizing syntan (IIIX3)

Comparing (IIIX3) with (IIIX2); there is improvement for (IIIX3) in looseness this could be due to using neutralizing syntan agent which is known for neutralizing without negatively affecting the other properties of the leather. Comparing this IIIX3 with IIIX2 it can be seen that the general appearance have increased.

Fig 4.2 Trial 4 (IIIX2), (WCTT IXZi) & Conventional chrome (IZ) respectively (the two at right end are conventional post tanned)

4.2 Chrome Oxide content

Table 4.1 Chrome Oxide Content *(values in braces are repeated trials)

%Chrome oxide content (ASTM standard of Cr oxide 1-5%)		
	At wet blue stage (No re chroming)	Re chroming (Bcs 4%,Cr syntan 2%)
Conventional chrome tanned (7% BCS at chrome tanning)	3.3 (IZi) (3.5)	5.0 (IZ) (5.1) 4.8 (IY) 4.7 (IIY)
WCTT (with 6% BCS at chrome tanning)	5.0 (IXZi) (4.8) 5.0 IXY 4.8 IIXY 5.0 IIIX1 4.7 IIIX2 4.9 IIIX3	5.2 (IXZ) (5.4)

For conventional chrome tanned upper leather re chroming is recommend so that the leather will have higher amount of chrome content and from the table it can be seen that for the conventional chrome tanned the Cr oxide content increases from 3.3 to 5.3 with re chroming for samples IZi

and IZ respectively. The WCTT samples IXZi, IXY,IIXY, IIIX1, IIIX2, IIIX3 are not re chromed and have chrome oxide % with in ASTM standard range of 1-5% with (deviation from the standard is acceptable in the range +-0.5%), it can be concluded that there is no need of re chroming for WCTT since sufficient chrome content is already found in the wet blue stage and re chroming the WCTT gives it little change.

4.3 Physical properties of hide upper leather

Conventional post tanning with re chroming for both

Table 4.2 physical properties for (Conventional control) IZ and (WCTT) IXZ

Sample conditioning 23±2^{o}c, 50±5%			
	Min requirements	Control IZ	Experiment IXZ
Tensile strength (N/mm^2) or (MPa)	15 N/mm^2 (minimum)	19.2	18.8
Tear strength (N)	40 N (minimum)	97.5	98.11
Color fastness to rubbing DRY WET	5 good (no visual change) 1 worst (large visual change)	4/5 4/5	2/3 3
Elongation at break %	40-80	58.9	60.1
Water vapor permeability ($mg/cm^2/hr$)	0.8	9.5	10.6
Water penetration,(min) Water absorption, %	60 35% max	63.5 29.0	52.1 31.2

Here the physical properties of both conventional (IZ) and the WCTT (IXZ) are shown; tensile strength and tear strength are above minimum requirement, the colour fast ness to rubbing is good for conventional but for the WCTT it is lower especially for wet rubbing test. The water

penetration for conventional is better than WCTT meaning that the water takes more time to penetrate which is ideal for upper leather.

Conventional post tanning without re chroming for both

Table 4.3 physical properties for (Conventional control) IZi and WCTT (IXZi)

Sample conditioning 23±2^{o}c, 50±5%			
	Min requirements	Control IZi	Experiment IXZi
Tensile strength (N/mm^2) or (MPa)	15	18.8	19.1
Tear strength (N)	40	96.6	98.51
Colour fastness to rubbing DRY WET	5 good (no visual change) 1 worst (large visual change)	 4 3/4	 3 3
Elongation at break %	40-80	59.1	61.2
Water vapour permeability (mg/cm^2/hr)	0.8	8.8	9.8
Water penetration,(min) Water absorption, %(60min)	60 min 35% max	58.6 31.4	53.3 29.9

The physical properties for the conventional IZi (no rechroming) show the tensile and tear strength above minimum requirement. The Colour fastness is still good but when we compare it to the previous (IZ) there slight reduction in both wet and dry rubbing tests results. Comparing IZi with IZ the water vapour permeability is slightly better for non rechroming (IZi). The water penetration time is slightly lower for IZi comparing it with IZ. For the WCTT with no rechroming (IXZi) the tensile and tear strength are also above minimum requirement, the color

fastness is slightly better when comparing it with IXZ with rechroming WCTT. The water penetration time for IXZi is also better than IXZ.

Trial 1 (IY and IXY) acrylic -1, melamine +1,

(WCTT) NAcO3 +0.5

Table 4.4 physical properties for Conventional IY and WCTT (IXY)

Sample conditioning 23±2°c, 50±5%			
	Min requirements	Control IY	Experiment IXY
Tensile strength (N/mm^2) or (MPa)	15	18.4	18.8
Tear strength (N)	40	98.1	98.51
Color fastness to rubbing DRY WET	5 good (no visual change) 1 worst (large visual change)	 4 3/4	 3/4 3
Elongation at break %	40-80	58.6	62.3
Water vapor permeability (wvp) ($mg/cm^2/hr$)	0.8	8.9	9.3
Water penetration,(min) Water absorption, %(60min)	60 min 35% max	55.8 29.4	55.2 28.1

The tensile strength and the tear strength are above minimum requirement for both IY and IXY, the colour fastness is slightly lower for the IY when comparing to IZ, for the WCTT IXY the dry rubbing is better when comparing to IXZi. For the water penetration time IY is lower when compared with IZ and the water absorption % is slightly higher compared to IY. For WCTT (IXY) both the tensile and tear strength are above minimum requirements, the colour fastness dry

rubbing is better from the previous IXZi. The water penetration time of WCTT (IXY) is also slightly higher compared to the previous IXZi and the water absorption is reduced which is a good indication we are in the right track.

Trial 2 (IIY AND IIXY) acrylic -1, **phenolic +1**,

Table 4.5 physical properties for Conventional IIY and WCTT (IIXY)

Sample conditioning 23±2^{o}c, 50±5%			
	Min requirements	Control IIY	Experiment IIXY
Tensile strength (N/mm^2) or MPa)	15	18.2	18.9
Tear strength (N)	40	97.8	99.1
Colour fastness to rubbing DRY WET	5 good (no visual change) 1 worst (large visual change)	 4 4	 4 3
Elongation at break %	40-80	57.7	60.3
Water vapour permeability (wvp) (mg/cm^2/hr)	0.8	8.4	9.1
Water penetration,(min) Water absorption, %(60min)	60 minute 35% max	50.6 30.4	55.5 27.3

The tensile strength and the tear strength are above minimum requirement for both IIY and IIXY, For IIY the color fastness is good with a value of 4; when comparing with previous IY, the IIY shows slight improvement in the wet rubbing, the elongation at break for IIY is within the minimum requirement at 57.7%, the water vapour permeability for IIY is good at 8.4 mg/cm^2/hr, water penetration for IIY is slightly lower compared to IY and water absorption is within the min requirements. For IIXY the color fastness to rubbing is good for dry rubbing but slightly lower

for the wet rubbing with a value of 3, comparing with the previous IXY there is improvement in dry rubbing but no change in wet rubbing, elongation at break is within min requirement at 60.3%.Water vapor permeability is good at 9.1 mg/cm^2/hr. water penetration is almost similar to the previous trial with a value of 55.5min, water absorption is within minimum requirement of 27.3%

WCTT trial 4 and 5

Table 4.6 physical properties for Trial 4(IIIX2) and Trial 5(IIIX3)

Sample conditioning 23±2^{o}c, 50±5%			
	Min requirements	Trial 4 (IIIX2)	Trial 5 (IIIX3)
Tensile strength (N/mm^2) or MPa)	15.0	19.5	19.3
Tear strength (N)	40.0	98.6	97.5
Colour fastness to rubbing DRY WET	5 good (no visual change) 1 worst (large visual change)	4/5 4/5	4/5 4
Elongation at break %	40-80	60.0	61.2
Water vapour permeability (mg/cm^2/hr)	0.8	8.5	9.0
Water penetration,(min) Water absorption, %	60.0 35% max	60.4 28.4	62.0 29.1

Tensile and tear strength for both trial 4 & 5 is above min requirement, the colour fastness for dry rubbing is the same for both trials at 4/5 and the colour fastness for wet rubbing is slightly lower for trial 5 when compared with trial 4.water penetration for both is above 60 min above min requirement and also the water absorption is also below 35% which is preferable. Out of all the trials these two trials have the best physical property results.

If we compare IXZi (conventional post tanning) with trial 4 there are improvements in color fastness from a value of 3 to 4/5, the water penetration is improved from 53.3 min to 60.4 min meaning it takes little longer for water to penetrate, Tensile and tear strength have small change but both have above minimum requirement result.

4.4 Effect of dye percentage

Using trial 4 recipe for WCTT at 70 min

Table 4.7 Effect of dye percentage *(values in braces are repeated trials)

Dye %	2.0	2.5	3.0	3.5	4.0
Colour uniformity (organolptic) 1-10	7.0, (7.4)	8.0	9.0, (8.8)	9.0	9.0, (9.0)
Cross section	Thin line	No line	No line	No line	No line
Final Liquor colour	light	light	medium	Above medium	Heavy

Here as we can see from the table different trials are done on dyeing section for WCTT, using different dye percentages starting from minimum 2% to 4% the color uniformity, cross section and the color of the final liquor is checked. At 2% of dye it can be seen the color uniformity is the lowest and when checking the cross section it can be seen that there is a thin line where the dye didn't reach the cross section of the leather, the color of the final liquor is light this is good. Generally at 2% it shows the dye % is not enough and more is needed. As the dye % is increased the organoleptic property related with dyeing is increasing, at 3% the color uniformity is good and there is no line in the cross section meaning there is a through and through dyeing, the color of the final liquor is medium which is good, the ideal color of the final liquor is light but the color might be medium due to different factors such as the quality of the dye, processing error, etc. at 4% dye the color uniformity is excellent at value of 9 and there is no line in the cross section but the color of the final liquor is heavy this shows we are using too much dye% and the excess dye is making the color of the liquor heavy so at 4% dye too much it will cause unnecessary dye wastage and increase the pollution of the final waste water. So the best dye % is

at 3%. In trial 4 the dye used is 5% but here by using different dye % while making the other post tanning chemicals constant, it is able to find the best dye % which is 3%, when compared with conventionally used dye % (5%) the WCTT needs only 3% dye to have good color uniformity.

Using Conventional post tanning with re chroming at 60 min (conventional chrome tanned)

Table 4.8 Effect of dye percentage for conventional chrome tanned*(values in braces are repeated trials)

Dye %	2.0	2.5	3.0	3.5	4.0	5.0	6.0
Colour uniformity, depth (organoleptic) 1-10	6.0, (6.5)	7.2	8.0, (7.8)	8.2	8.5	9.0,(8.8)	9.0
Cross section	Thin line	Thin line	No line	No line	No line	No line	No line
Final Liquor colour	light	medium	medium	medium	medium	medium	heavy

For conventional the best dye percentage is around 5% and adding above that causes no change except an increase in waste in the final liquor and just like WCTT as we decrease the dye% the color uniformity; through and through dyeing will decrease, below 2.5% a thin line occurs.

4.5 Neutralization

Effect of sodium bicarbonate on the pH on WCTT

Table 4.9 Neutralization/ effect of Sodium bicarbonate for WCTT

Sodium formate Sodium bicarbonate	0.5 0.5	0.5 1	0.5 1.5	0.5 2
pH at Belly area	4.5	5.0	5.5	5.5
pH at Butt area	3.5	4.5	5.0	5.5
pH at Neck area	3.5	4.5	5.0	5.5
pH at Surface	4.5	5.0	5.5	6.0

Sodium bicarbonate is a basic chemical and as we can see from the above table as the amount of sodium bicarbonate is increased the pH also increase, for upper leather the required pH is around 5, so out of the above combinations the best is 0.5% sodium formate and 1.5% sodium bicarbonate, below this combination the pH at butt and neck will be lower than 5 and this will have a problem in the next post tanning operations such as problems associated with dye penetration, etc. and if the combination is above 0.5% and 1.5% , as we can see from the table the pH will be higher than 5, higher pH will give the final leather properties that are not suitable for uppers leather such as being too soft etc…

Neutralization pH vs Time for waterless chrome tanned

Table 4.10 Neutralization pH vs Time for WCTT

Neutralization pH vs time for **waterless** chrome tanned	
Sodium formate=0.5% **Sodium bicarbonate=1.5%**	
pH at butt area	time
3.2	0
3.8	30
4.0	60
4.5	70
5.0	**70**
5.5	87
>6	105

The above table shows the relation between the pH and time for WCTT, at the start of neutralization the pH is around 3.2 which is slightly lower when compared to conventional chrome tanned, at around 70 min the pH reaches 5 this is the pH that is required for upper leather, the equilibrium point or the point when the pH stabilizes is after 105 minutes and the pH is above 6.

Neutralization pH vs time for **conventional** chrome tanned

Table 4.11 Neutralization pH vs Time for conventional chrome tanned

Neutralization pH vs time for **conventional** chrome tanned	
Sodium formate=0.5% **Sodium bicarbonate=1%**	
pH at butt area	time
4.0	0
4.5	30
5.0	**63**
5.5	76
6.0	89
>6.0	95

The above tables shows the relationship between the pH and time for conventional chrome tanned leather, at the start of the neutralization the pH is around 4, at around 60 min the pH gets to 5, the pH stabilizes when the time reaches above 95 min with more than a pH of 6. Comparing the above two tables (table 4.12 and 4.13) it can be seen that at the start of neutralization WCTT have a pH of 3.2 while conventional chrome tanned have a pH of 4, due to this it will take little more time for WCTT to reach a pH of 5 when compared to the conventional chrome tanned.

5. Conclusion and Recommendations

5.1 Conclusion

Conventional post tanning recipe was first used for both WCTT and conventional chrome tanned and when comparing the organoleptic and physical properties of the two, the WCTT shows lower organoleptic and some of the physical properties such as the color fastness, this is due to the re tanning chemicals not able to fully penetrate and this can be corrected by adjusting the amount and time of the post tanning chemicals.

At first to check if re chroming is required for WCTT, a trial was done such that one with re chroming and other without re chroming the result from the organoleptic and chrome oxide content shows that there is no difference between the re chromed and no re chromed so if there is no difference it can be concluded that re chroming is not important for WCTT. But for the conventional chrome tanned the same test was done; one test with re chroming and another test without re chroming; a lower organoleptic and chrome oxide was observed for no re chromed leather and from this result the conventional chrome tanned have to be re chromed. Here since the WCTT at wet blue stage contains enough chrome content that's why re chroming is not important.

The next process that needs adjusting is neutralization and when both WCTT and conventional chrome tanned was both neutralized with the same conventional neutralization (0.5% Na formate & 1% Na bicarbonate) after neutralization the WCTT pH was not enough for upper leather especially the cross section pH was around 4.5 instead of a pH of 5 so using different percentage of sodium bicarbonate at 0.5%, 1%, 1.5%, 2%. A pH of 5 was observed for 1.5% sodium bicarbonate. The surface pH was around 5.5 but this is reduced washing after neutralization. The average time taken is around 78min.

For the re tanning section first both the WCTT and conventional chrome tanned were re tanned with the same conventional post tanning recipe and the result form organoleptic and physical properties show a lower result for the WCTT so to adjust this different trials were done. From trail 1 & 2 by decreasing the acrylic and increasing melamin and phenlolic there is a slight

improvement in organoleptic values. So finally trial 4 shows best organoleptic and physical property result.

For the dyeing section when conventional chrome tanned & WCTT were both processed with the same conventional post tanning recipe, the WCTT showed insufficient cross section dyeing lower colour uniformity and a heavy final liquor color but this was fixed by adjusting neutralization pH, adjusting re tanning chemicals and reducing the amount of dye%. From the table showing the effect of dye percentage for WCTT it can be seen that at 3% colour uniformity shows best value of 9 with medium final liquor colour and no line in the cross section. The conventional chrome tanned needs around 5% dye, comparing the WCTT with conventional chrome tanned it can be seen that the WCTT requires lower dye%

To sum up the WCTT is a new technology with multiple benefits including environmental safe, reduced BCS cost etc… with simple adjusting of the post tanning such as lowering the acrylic%, adjusting the neutralization and dyeing amounts we can have a quality final product.

5.2 Recommendation

This research is focused on standardizing the post tanning of water less chrome tanning upper leather using conventional post tanning chemicals that are used in tanneries so that it can be shown this new technology (WCTT) works fine using conventional post tanning chemicals with some adjustment, but for next research there needs to be more focus given to see what the effects are when using different types of newly discovered post tanning chemicals on the WCTT And also there needs to be more study on the final crust leather after ageing to know its durability.

WCTT is a new technology with a lot of advantages and all this advantages related with the cost saving such as reduction in water usage, reduction in BCS usage, etc… should be quantifiable and presented so tanneries will be more accepting to the WCTT.

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7. Annexures

Annex 1 RECEPE conventional chrome tanning

Process name	Name of chemical	%	Time in min	remarks	
soaking	water	Hide under water	1-2day	Check for complete soaking or wetting with hand	
	Wetting agent	0.5			
	preservaive	0.5			
Drain/wash/drain					
liming	water	200	1day		
	lime	10			
	Sodium sulphide	4			
unhairing					
Relime	lime	1.5	1day	Check the plumb using hand	
Drain/wash					
Fleshing and scudding					
De liming	water	40	60min		
	Ammonium chloride	1.5			
	Sodium bisulphide	0.2		Colourless using phenophtaline indicator	

				(check cross section)	
Drain/wash 2x					
bating	water	50			
	Alkali bating enzyme	0.5	60min		
Wash/drain 2x					
Degreasing	water	40	60min		
	Degreasing agent	1			
Drain/wash 2x					
pickling	water	50			
	salt	5	10min		
	Formic acid	0.8			
	Sulphuric acid	0.7	180min	pH=2.8-3	
L/O/N					
Tanning	Water	50			
	BCS	4	30min		
	BCS	3	90min	Check chrome penetration through the cross section	
	Sodium formate	0.5	30min		
	Sodium bicarbonate	1.2	3hr	pH=3.8-4	
	Fungi cide	0.3	10min		
Pile—24hr age---samming---shaving---posttanning					

Annex 2 Waterless chrome tanning Same process with the conventional from soaking to degreasing

Process name	Chemical name	%	time	remarks
Soaking to degreasing recipe same with conventional				
Pretreatment	water	40		
	Pretreatment chemical	1	2hr	l/o/n pH=
L/O/N AND DRAIN				
Tanning	BCS	6		
	Sodium formate	0.5	6 hr	
	Fungi cide	0.3	10min	pH=3.2
Drain and pile wet blue				

Annex 3 RECEPE for conventional post tanning

Process name	Name of chemical	%	Time in min	remarks	
Wet back	water	200	30		
	Wetting agent	1			
Drain/wash/drain					
Rechroming	water	100			
	Formic acid	0.3	10		
	Chrome syntan	2			
	BCS	4	30		
Basification	Sodium formate	0.5	20		
	Sodium bicarbonate	1	60		
Neutralization	water	100			

	Sodium formate	0.5	20		
	Sodium bicarbonate	1	60	pH= 5	
Drain/wash 2x					
Retanning	water	100			
	acrylic	5	20		
	phenolic	6			
	melamine	5			
	mimosa	5			
	dye	5			
	Dye leveling	1	60		
Fatliquoring	water	100		50^{o}c	
	Synthetic	4		emulsify	
	Semi synthtic	4			
	Neats foot	2			
	lectin	2	60		
Fixing	formic	3	3x15+30		
Pile for 24 hr----samset----over head dry----conditioned----staked----buffed----trimmed---					

Annex 4 Recipe for WCTT trial 4

Process name	Name of chemical	%	Time in min	remarks	
Wet back	water	200	30		
	Wetting agent	1			
Drain/wash/drain					
Basification	Sodium	0.5	20		

	formate				
	Sodium bicarbonate	1	60		
Neutralization	water	100			
	Sodium formate	0.5	20		
	Sodium bicarbonate	1.5	*	pH= 5	
Drain/wash 2x					
Retanning	water	100			
	acrylic	3.5	20		
	phenolic	7			
	melamine	6			
	mimosa	3.5	60		
	dye	3			
	Dye leveling	1	75		
Fatliquoring	water	100		50^{o}c	
	Synthetic	4		emulsify	
	Semi synthtic	4			
	Neats foot	2			
	lectin	2	60		
Fixing	formic	3	3x15+30		
Pile for 24 hr----samset----over head dry----conditioned----staked----buffed----trimmed---					

Post tanning chemicals

Acrylic syntan : Relugan RE acrylic co polymer based syntan from BASF

Phenolic syntan: phenol condensate based syntan from BASF

Melamin syntan: melamine formaldehyde based syntan from BASF

Momosa: vegitable tanning

Synthetic fatliquore: lipoderm from BASF

Semi synthetic: from BASF

Lectin: from BASF

Neasfoot: from BASF

Dye: luganil black anionic dye from BASF

Dye levelling:

Annex 5 Time and pH for neutralization

Sodium formate=0.5% Sodium bicarbonate=1%	Sodium formate=0.5% Sodium bicarbonate=1%
Iz	IXz
Belly 5.5	Belly 5
Butt 5	Butt 4.5 after 5
Neck 5	Neck 4.5 after 5
Outside surface 5.5	Outside surface 5 adjusted with adding 0.5% sodium bicarbonate and additional 20 min
Total time = 65min	Total time = 70+20= 90min

Sodium formate=0.5% Sodium bicarbonate=1%	Sodium formate=0.5% Sodium bicarbonate=1.5%
Izi No rechroming	IXZi No rechroming
Belly 5	Belly 5
Butt 5	Butt 5
Neck 5	Neck 5
Outside 5.5	Outside 5.5
Total time=60min	Total time= 70min
Sodium formate=0.5% Sodium bicarbonate=1%	Sodium formate=0.5% Sodium bicarbonate=1.5%
IY	IXY
Belly 5.5	Belly 5
Butt 5	Butt 5
Neck 5	Neck 5
Outside 5.5	Outside 5.5
Total time 63min	Total time 72min

Sodium formate=0.5% Sodium bicarbonate=1%	Sodium formate=0.5% Sodium bicarbonate=1.5%
IIY	IIXY
Belly 5.5	Belly 5
Butt 5	Butt 5
Neck 5	Neck 5
Outside 5.5	Outside 5.5
Total time 60min	Total time 68min
Sodium formate=0.5% Sodium bicarbonate=1.5%	Sodium formate=0.5% Sodium bicarbonate =1.5%
IIIX1	IIIX2
Belly 5.5	Belly 5
Butt 5	Butt 5
Neck 5	Neck 5
Outside 5.5	Outside 5.5
Total time 71min	Total time 72min
Sodium formate=0.5% Neutralizing syntan=2%	

IIIX3
Belly 5
Butt 5
Neck 5
Outside 5.5
Total time 68min

Annex 6 Time taken for Re tanning, Dyeing and Fat liquoring

Post tanning operation	Time IZ (min)	Time IXZ (min)
Re tanning	60 min	60 min
Dyeing	64 min	90 min
Fat liquoring	60 min	60 min

Post tanning operation	Time IZi (min)	Time IXZi (min)
Re tanning	60	60
Dyeing	72	88
Fat liquoring	60	60

Post tanning operation	Time IY (min)	Time IXY (min)
Re tanning	64	60
Dyeing	65	85
Fat liquoring	60	55

Post tanning operation	Time IIY (min)	Time IIXY (min)
Re tanning	60	60
Dyeing	66	80
Fat liquoring	58	60

Post tanning operation	Time IIIX1 (min)	Time IIIX2 (min)
Re tanning	60	60
Dyeing	74	72
Fat liquoring	60	60

Post tanning operation	Time IIIX3 (min)
Re tanning	60
Dyeing	69
Fat liquoring	60

Annex 7 semi processed leather


WCTT chemical pre treatment

WCTT wet blue (Left) and Conventional chrome tanned wet blue (right)

Wet blue Cross section WCTT (left) and conventional chrome tanned (right)