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"Study on Effect of Drying Techniques on Area Yield and Quality of Leather"

By

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This is to certify that the thesis prepared by Endale Dabeta, entitled: "Study on effect of Drying techniques on Area yield and Quality of Leather" and submitted in partial fulfilment of the requirements for the Degree of Masters of Science in Chemical Engineering (Leather Technology) complies with the regulation of University and meets the accepted standards with respect to originality and quality.

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Abstract

Drying is an important process in leather making in which tanning agents, dyestuffs and fat-liquoring agents combine with collagen further and water is evaporated to fulfill the demands of final leather product, therefore drying is one of mechanical operation which has significant effect on leather chemical and physical properties. Using different techniques of drying in the processing of Garment leather affect the change in the area yield of the leathers as distinct from each other's. The area yield has great significance for the commerce since the price of piece of finished garment leather is sold based on its area yield. In this research, the effects of normal, toggle and vacuum drying techniques on the area yield of garment leather and the quality of the garment leather dried under each techniques of drying characterized based on moisture content, softness, tensile strength and elongation at break, subjective property and Scanning Electron Microscope (SEM) analysis was studied. Moisture content, softness and tensile and elongation at break of leather steadily decrease with increase in drying period and area yield. More porous and less adhesion of fibre is obtained by toggle drying techniques and some grain surface damages observed in vacuum drying techniques from microscopic images. Toggle drying techniques for drying of garment leather is preferable drying techniques because of the better area yield of 14.5% with good tensile strength and more porous leather.

Key words: Drying techniques, Area yield, Garment leather, Softness

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Acronyms and Abbreviations

SEM	Scanning electron microscope
CLRI	Central leather research institute
LIDI	Leather industry development institute
EHSG	Environmental, health and safety guidelines
C.R.C	Cell rotary conditioning system
IULTCS	International union of leather technologist and chemist society
JALCA	Journal of American leather chemists association
LIM	Leather international magazine
IUP	International Union for physical testing
S.C.	Share Company
ELICO	Ethiopian Leather Industry Private Limited Company
ISO	International Standards Organization
MPa	Mega Pascal
CSA	Central Statistical Authority
Min.	Minimum
Max.	Maximum
µ	Mean
S.D	Standard Deviation
TD	Toggle Drying
VD	Vacuum Drying

1. Introduction

1.1. Background

Production of leather from raw hides and skins, by-products of meat industry, has been one of the most important industrial processes since ancient times [1]. The Ethiopian leather industry is a relatively older industry with more than 80 years of involvement in processing leather and leather products [2]. Ethiopia is one of the leading countries that have the largest livestock populations in the world providing a strong raw material base for the leather industry. The livestock population of Ethiopia estimated to be 57 million cattle, 28 million sheep and 29 million goats [3]. About 80% of all hides and skins entering the formal market come from rural areas where they are collected by private traders. The remaining 20% are derived from slaughtering facilities found in major town and cities. About 18.9 million pieces of sheep and goat skins and 1.4 million pieces of cattle hides are supplied to the tanneries per annum [4].

There are presently 27 tanneries operating in the country, employing over 7,000 people and having soaking capacity of 1.3 million pieces of hide and 32 million pieces of skins annually. The existing daily soaking capacity of tanning industries is 172, 080 pieces of skins and 11,110 pieces of hides (see Annex 1). About one-third of these tanneries are found in Addis Ababa and its surrounding [5].

Leather making involves a series of unit processes and operations. Leather making process is broadly classified as pre-tanning, tanning, post-tanning and finishing [6]. Skins / hides are dried out following their post tanning processes to form crust leather, as this is a convenient point at which to grade the skins. In a hydrated state, leather is fully lubricated with water that is held between the elements of the fibre.

In this state it can be molded or deformed, stretched and flexed into any shape. However, as the leather is dried, the fibres approach each other and have a tendency to stick together to an extent that depends on how the water is removed [7]. One of the important mechanical operations in the leather making process is the removal of excess water from leather-drying [8].

Drying is one of the most important leather production processes which is necessary to obtain usable leather form from skin and determines the basic structural, chemical and physical properties of the leather [9]. Leather softness, tensile strength, tightness of the grain, and many other properties are a consequence of the drying conditions employed, especially, temperature, moisture content or humidity and time. Therefore, drying process in which the leathers are dried to the desired extent without affecting the feel of the leather is one aspects of quality control. In addition to achieving desired quality, one of the most important aspects of drying operation is area yield for the leather producer. Since the price of piece of finished leather products is determined by its area yield. Leather production is a subject of commerce, so that gaining or retaining of the leather area yield is had to handle as a very important concept [10].

Therefore, investigation of the effects of different drying techniques and conditions on area yield of leather without affecting the quality and characterization of quality of crust leather dried under different techniques of drying is one of the very important aspects research topics.

1.2. Problem of statement

In the manufacturing of the leather, the raw hides and skins are purchased by weight, whereas the price of piece of the finished leather product is determined by its area yield. Since leather production is a subject of commerce, any permanent improvement in the area yield of leather must be of considerable commercial importance. Therefore, most tanneries strive to improve area yield of leather as it has a direct impact on profitability. This normally achieved by some degree of in process stretching. Such stretching can be imparted by a setting or sammying machine and drying process under tension. But area obtained by sammying or setting machine may be lost due to subsequent relaxation of leather. A durable increase in area yield is achieved by drying leather under tension.

However, whilst in-process stretching may improve area yield of leather there is concern that it may also degrade the quality of the finished leather product. Therefore, uncontrolled drying process is not advisable in the manufacture of leather and drying process needs a watchful eye because the tanner may gain or lose money depending on the drying techniques and conditions.

This research work was designed to develop appropriate techniques of drying process which yields the required leather with the optimum area yield without affecting the quality required for its end use.

1.3. Objectives

1.3.1. General objectives

The general objective of this study was to establish the drying techniques required to give optimum area yield without compromising on leather quality.

1.3.2. Specific objectives

The specific objectives of this study includes:-

1. To investigate the effects of different drying techniques and conditions on area yield of leather

2. To characterize the crust leather dried under different drying techniques and conditions depending on desired end use

3. To select preferable drying techniques for garment leather

1.4. Framework of the study

The framework of this study categorized into two main groups: - the first one is investigation of the effects of different drying techniques and conditions on area yield of leather and secondly, characterization of crust leather dried under different techniques of drying process for developing qualitative measurements. The general conceptual framework of this study is shown in Figure 1.1 as below

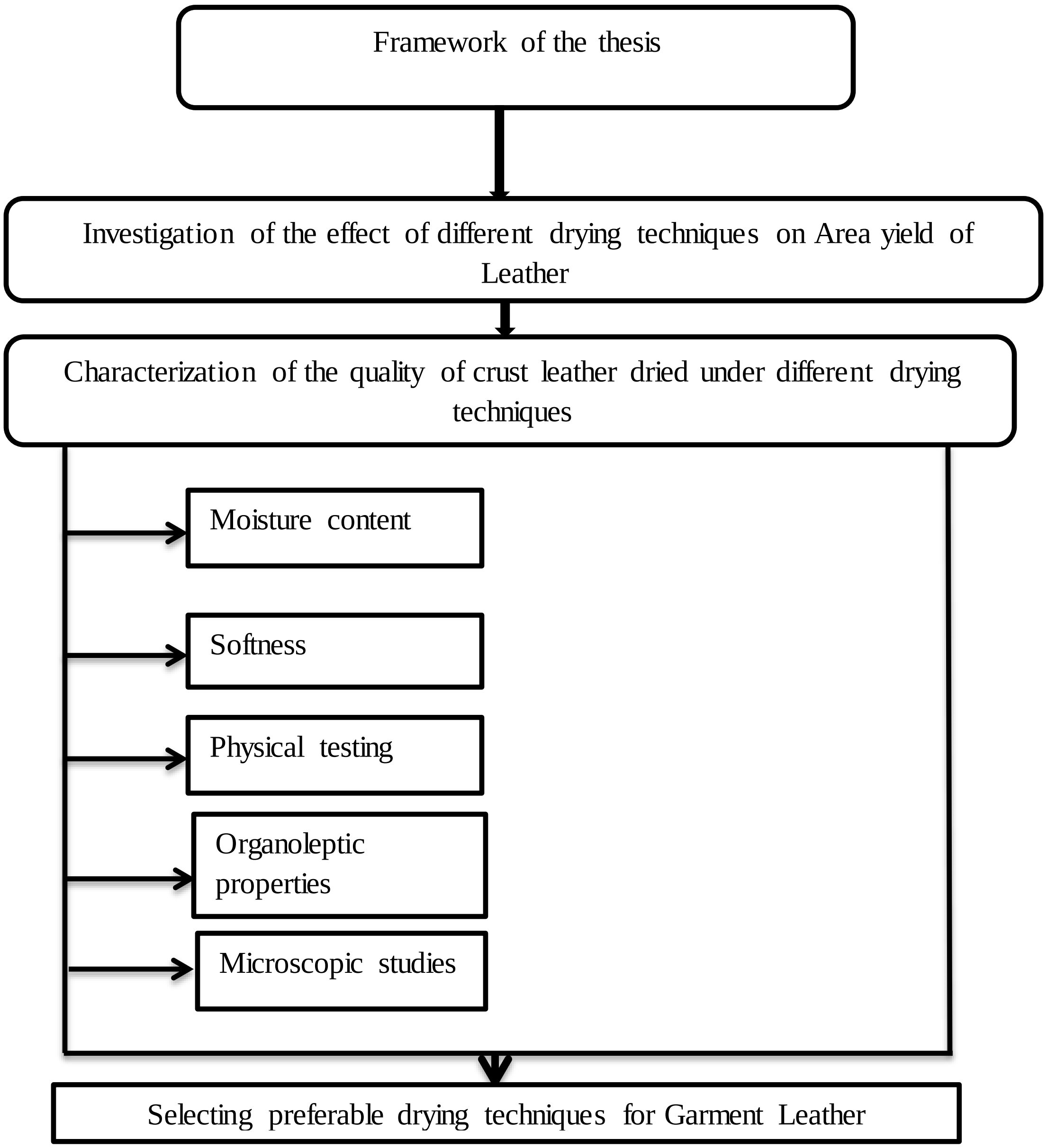


Figure 1.1:- Overall Framework of the Thesis

1.5. Scope of study

This study includes conventional wet finishing processes (retanning, dyeing and fat-liquoring) with a recipe suitable for the production of garment leather, investigation of different types of drying techniques on area yield of crust leather by controlling drying conditions, determination and characterization of crust leather by quality measurements (physical testing, softness, moisture content and organoleptic properties) and microscopic studies (SEM analysis) to examine the morphology of crust leather with different types of drying techniques. The schematic representation of the thesis to show the scope of study in simple way is shown in Figure 1.2 as below

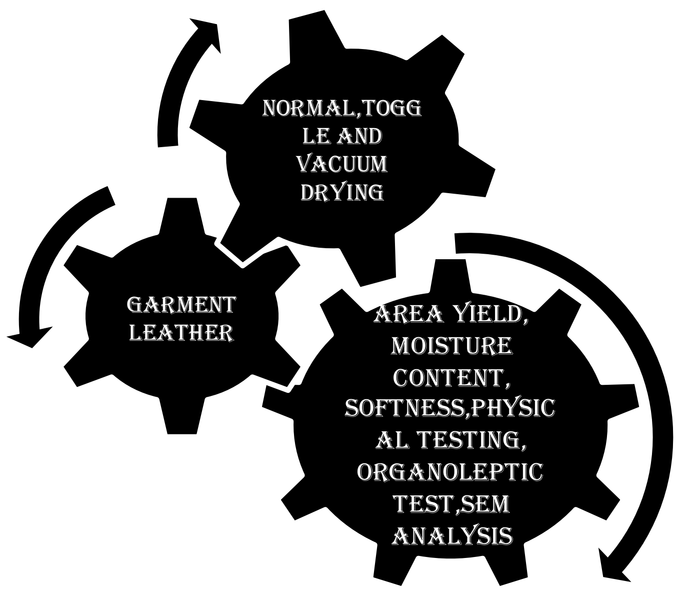


Figure 1.2:- Schematic Representation of the Thesis

1.6. Significance of study

The significance of the study was developing proper drying techniques which gives optimum area yield with achieving desired quality to the leather manufacturing process and knowing the effect of leather making conditions on the resultant area yield because the price of a piece of finished leather product is determined by its area. Also, to consult and sharing experience to Ethiopian leather industries in corporation with LIDI technician on techniques of drying process and conditions how to optimize area yield of leather without affecting quality.

2. Literature Review

2.1. Introduction

The principal aim of the leather industry, which plays a significant role in today's global economy, is to transform animal hides/skins into physically and chemically stable material by subjecting them to chemical and mechanical sequential processes, and therefore to obtain products for meeting various needs of people [11]. The processing of hides and skins into leather is a complex procedure that requires a precise combination of many chemical and mechanical operations. Drying is one of the key mechanical operations in tannery process and is one of the key steps governing leather quality. Leather physical properties, such as area retention and softness, were affected by the drying techniques and dry condition. There are many predictive drying models and mathematical relation for toggling, vacuum and environmental leather drying [12].

The objective of drying is to dry the leather while optimizing leather quality. Drying techniques include sammying, setting, hang drying, vacuum drying, toggle drying (leather dried while held under tension on frame using toggles), and over drying. Sammying and setting are used to reduce moisture content mechanically before implementing another drying technique [13]. An effect of drying regime is important implications of the water-leather relationship for leather properties particularly the effects of drying process on leather softness [14].

Because raw materials are purchased by weight but leather is sold by its area, it is common practice to stretch leather during manufacture. Some area increase may be achieved in mechanical operations such as sammying or setting but may be lost due to subsequent recovery. It has been shown that more permanent increases in area can be achieved by drying leather whilst it is maintained in a stretched condition such as when using a split toggle frame. However, there is concern that in-process stretching of leather may affect important aspects of quality such as stiffness and strength [15].

The importance of knowing the effect of leather making conditions on the resultant area yield cannot be over-emphasized because the price of a piece of chrome-tanned leather is determined by its area yield [16].

In the process of leather manufacturing, apart from various chemical operations, there are a number of mechanical operations, which also affect the quality of the leather product. Some of the mechanical operations involved are: (a) splitting and shaving by which an uniform substance is obtained (b) drying process in which the leathers are dried to the desired extent without affecting the feel of the leather (c) staking by which leathers are conditioned and made soft by staking the fat-liquored leathers and (d) buffing in which the clean flesh side is produced and improvement is effected on the flesh side. Among this mechanical operation drying is a critical leather-making process to attain the required physical properties for leather products.

Thus, one can appreciate that in the process of leather manufacture, there are so many controlling factors and it is necessary that standardization and quality control be maintained in each stage of leather processing so that the quality of the leather produced will be of a consistent quality from which various consumer products can be produced and drying operation plays a great role in the process of leather manufacture by controlling the quality of leather product for its end use. Therefore, optimization of the area yield of the leather without affecting the quality of leather is very important concept of this research topic.

2.2. Processes of Leather Manufacturing

Hide or skin is the natural covering material for an animal and forms the physiological functions during the life time and acts as a thermoregulatory. Leather making involves a series of unit processes and operations. Leather making process is broadly classified as pre-tanning, tanning, post-tanning and finishing. Leather is produced from them through a series of processes detailed below [17].

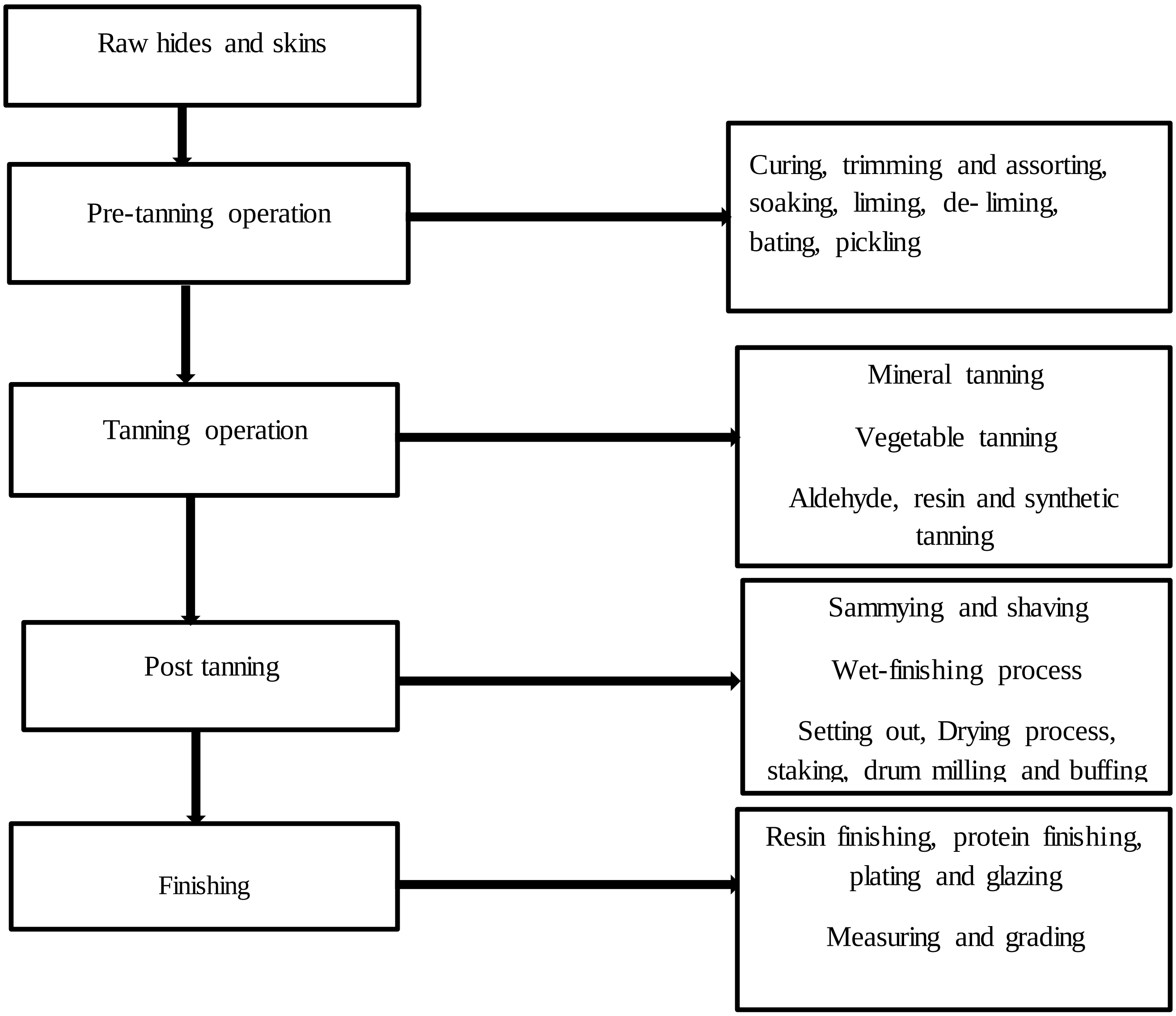


Figure 2.1:- Leather processing - Sequence of operations

a) Pre- tanning operations or Beam house operations

Curing, wet salting and dry salting: - Once the animal is dead, bacteria begin to be active and putrefaction sets in. The process known as curing, in which the bacterial action is getting inhibited temporarily, preserves the hides and skins, which are removed from the carcass. During the process of curing, the skins are dehydrated and unfavorable conditions are created for the bacteria to grow. This is done primarily by the application of common salt on the flesh side of the skin using about 30 – 40% on the weight of the skin. Sometimes, the skins are dipped in a saturated brine solution and piled. In countries like India, drying in sunlight known as flint drying is done to remove the moisture.

Trimming and assorting: - The cured skins, which arrive in the tannery, are first sorted out and trimmed. In the case of skins, they are ripped open and in the case of hides, they are cut into sides or processed as full hides as per the requirements.

Soaking: - Soaking of the raw hides and skins is the first and a very important operation, as succeeding operations and the final quality of leathers depend on proper soaking of the raw stock. Preservatives and wetting agents are added in order to accelerate the processes of soaking and to prevent the bacterial action in the presence of water. During the process, the dehydrated skin is hydrated back and brought to the original condition, which existed when the animal was flayed.

Liming: - During this process, chemical agents like lime and sodium sulphide are used to help in loosening the hair, open up the fibre structure and help in removal of the flesh layer and the other unwanted materials not required for leather processing. This is also done in pits or paddle or drums. After this operation, the hair and the adhering flesh are removed and the raw material at this stage is known as pelt. After liming, the pelt is pressed through a machine to remove fleshly tissue from the flesh side.

Deliming: - The lime that is present in the skin should be removed by the process known as deliming in which mild organic acid salts of weak bases like ammonium chloride, ammonium sulphate, etc., are used. The lime is removed from the skin and the skin is ready for subsequent operations of bating, pickling, etc.

Bating: - This is carried out by enzymatic process in which some of the unwanted materials get removed and the pelt presents a cleaner appearance. This is mainly done for the skins.

Pickling: - The process of pickling is mainly done to condition the pelt to a stage at which they can be preserved for a long time and also can be assorted for different types of tannages. This is achieved by treating the pelt with common salt and sulphuric acid and pH of the pelt is brought to about 2.5 to 2.8 and sometimes preservatives are also added to keep the skins without any further damage for quite a length of time.

b) Tanning operations

Tanning can be defined as the process of converting the putrescence protein material into non-putrescence form and making the leather resistant to moisture and micro-organism. Different agents bring this about and these chemicals are known as tanning agents. Several tanning processes viz. vegetable tanning, mineral tanning, aldehyde tanning, resin tanning, synthetic tanning, etc. are used for tanning leathers.

Mineral tanning: - In this method, the most commonly used material is basic chromium sulphate and to some extent salts of aluminium and zirconium. Apart from it, other tanning agents like formaldehyde, fish oil, resin tannages, etc. are used. There are characteristic differences between mineral tannages and vegetable tannages. The chrome-tanned leathers are soft, supple and stretch more than the vegetable tanned leathers. These tanned leathers are called wet-blue, which is the intermediate stage of leather processing.

Vegetable tanning: - This is a method in which the pelt is treated in an infusion of leaves/barks/nuts/roots.

Aldehyde tanning: -Aldehyde tanning is used to produce very soft white washable leathers usually from sheep or lamb skin with the grain split or shaved off. The leathers so produced are used for water washable gloves and clothing.

Resin tanning: - Resin tanning gives filler effect and grain tightening effect and reduces stretch. It provides good light fastness suitable for white leathers.

Synthetic tanning: -Synthetic tanning gives silky touch, tight and fine grain, surface feel, high degree of softness, light fastness, etc. to the leather. It is used to produce high fashion leathers.

The leathers, so produced depending upon the specific characteristics and nature, are used for different purposes. As a result of this variation in properties, in commercial practice, more than one tanning agent is applied, so that advantageous properties of different tannages could be imparted to the leather.

c) Post-Tanning operations

Sammying: - Sammying is the process in which excess moisture is squeezed out by pressing through large rollers under pressure.

Splitting and shaving: -The wet blue leather is split through the middle to the required thickness for end use, especially for thicker hides. Any further reduction of thickness can be done by shaving off the unwanted fleshy material of the leather.

Neutralization:-In the process of neutralization, the acidity of leather is removed and the leather is made to combine with subsequent chemicals that are used in latter stages in a more effective and uniform way.

Re-tanning:- In the process of retanning, synthetic tanning agents, resin tanning agents and vegetable tannins are employed and the various proportions are used depending upon the type of leathers to be produced.

Dyeing: - In the process of dyeing, the leather is made to combine with different types of dyestuffs and the colouring is imparted to the leather. The most important class of dyes that are used in the leather industry are anionic dyes, basic dyes and pre-metallized dye stuffs, each having its own property with respect to fastness to light, fastness to washing and penetrating capacity inside the leather. The tanner chooses his dyestuff depending upon the type of leather he is going to process.

Fat-liquoring: - In this operation, oil is introduced into leather in the form of emulsion, which breaks inside the fibre structure depositing a layer of oil or fat over the fibre structure. This helps in the fibres to move easily over the other giving sufficient softness and pliability to the leather. In this process, which is technically known as fat liquoring, emulsions based on vegetable oils, marine oils, animal fats and synthetic fats are used to get the desired property.

Setting out: - The process of setting is done for smoothing the grain of the side and removing excess moisture so that the leathers are put in proper condition for drying.

Drying: - Drying is an operation, which removes water from the leather. Before leather is subjected to the drying process, the superfluous water, which is adhering to leathers, is removed for making the surface of the leather smooth. Then, the leathers are conditioned and set on the grain side. Setting is essential for removal of wrinkles and folds as well as for smoothening out coarse and drawn grain. Drying is an important function and needs a watchful eye. Drying is carried out by toggle drying or vacuum drying. The leathers are stretched and kept over a metal frame by means of toggles. These are kept inside driers having controlled temperature and humidity. Vacuum drying imparts smoothness to grain and also increases yield. This method has the advantage of controlling the time cycle. After drying, the leathers are conditioned, staked and toggle dried for the process of finishing.

Staking: - After the hides are dried, they become stiff and less flexible. The leathers are therefore staked by mechanical process to make the leather soft and supple.

Milling:- is a mechanical process to improve the softness of the leather and gives the grain a more precise design. A drum similar to the one used in the wet phases is used.

d) Finishing Operations

In this operation, the leathers are subjected to the application of suitable finishing formulations based on binders, pigments, dyes, wax emulsion, etc. This surface coating not only helps to upgrade the leather by covering minor defects but also improves surface properties of the leather such as scuff resistance, water resistance that are necessary when they are converted into consumer oriented products. There are quite a number of finishes viz. resin finish, protein finish, etc. available in the market as well as topcoat formulations, which impart these characteristics.

Coated finish:-The leathers are finished by application of finish mixes to varying degrees. Depending upon the nature and coating applied, the leather surface and the defects can be covered.

Natural grain finish:-The leathers are finished with grain intact. The leathers should have good grain quality without deep scars or looseness.

Full aniline finish: - The leathers are dyed into a colour close to the required colour. Two or three coats of transparent finish with or without dye is applied which serves as a protection to the surface. Binders can be subjected to high temperature by friction to give a brilliant glossy look to the leather surface. These types of finishes enhance the natural appearance of the surface.

Semi-aniline finish: - Semi-aniline leathers contain small amount of pigments along with the dye to give coloured finish. The pigments used in the finish can cover minor scratches and superficial scars. They present a natural grain surface without too much of loading of the grain.

Pigment finish: - Pigment finished leathers are those types of finished leathers with relatively high amount of covering material. The covering of defects is very good in this finish.

Imitation grain finish:-These types of leathers are made from relatively poor quality hides. The hide surface has a number of deep scars and cannot be finished to a uniform look without modifications. So, the grain is removed by snuffing. Special resin binders are used to reduce the looseness of the grain layer and heavy finish coat is applied to get a uniform finished surface, which is embossed.

Corrected grain finish: - The crust is buffed to remove the top grain pattern and treated with a filling type of resin, which makes the grain layer tight. It is then embossed to stimulate an attractive grain surface. Special effects such as brush off effect can be obtained by using suitable binders and colouring mixes.

Printed finish: - These leathers are finished similar to corrected grain leathers, but with deeper print on the surface by embossing with suitable heat and pressure. A variety of print patterns such as crocodile print, lizard print, etc. can be effected.

Split surface finish: - Split leathers cannot hold the finish coating well due to its coarse and fibre network Special techniques can be used to apply finish coatings on the split surface to upgrade the performance similar to finished leathers.

Nubuck finish: - The leathers are finished with velvet like surface on the grain layer. Since the fibres in the grain layer are compact and short, the nap is fine and smooth and the textured surface will show a difference in shading when run by the hand over it.

Oil pull-up finish: - Special oils are applied on the surface of the leather with or without transparent finish coatings. The oils provide protection as well as a unique look to the surface. Oil pull-ups are made from full grain leathers with application of oil. The oil can migrate when pressure is applied on the surface and come back when the pressure is released. Thus, the surface will show two-tone effect when pressed or pulled.

Antique finish: - The leathers are applied with special wax to the buffed grain surface. The wax can melt and migrate under frictional heat. Because of this, when the surface is rubbed, the colour of the rubbed portion changes which does not reverse immediately.

Plating: - Plating is a mechanical smoothening of the finished leathers. It is the process in which a texture can be created on leather by impressing it with a pattern. Some of the leathers are given plating, which may be smooth plating in hydraulic press or continuous plating in a feed through machine. It is also possible by means of hydraulic press to impart the various types of designs on to the surface of the leather, which is known as embossing. In recent years, there has been a lot of development on newer embossing machines, which produce various types of effects on the surface of the leather so that they can be used for a variety of purposes.

Glazing: - Glazing is known as top coating. In this process, a clear aqueous finish is commonly applied to protect the grain surface of the leather. The leather surface is then polished to a high lustre by the action of a glass roller under pressure, which operates like a giant arm.

Measuring: - Almost all the leathers are measured by area, which is done either by a mechanically operated machine or electronically operated machine and the area is indicated in leather as square feet or square decimeter.

Grading: - All the leathers are finally graded mainly by visual examination and a lot of expertise is needed. Depending upon the grain characteristics, feel, substance, etc., every batch of leathers is normally given number of grades with each one fetching different prices.

2.3. Drying Operation of Leather

After dyeing and fat-liquoring the leather is ready for drying operation. The wet blue has been retanned; the colouring matter (dye) and the lubricant (fat-liquor) are in intimate contact with the fibres. Dyeing and fat-liquoring operations are the last wet processing in the tannery. Drying operation (i) facilitates the further processing like buffing and finishing, (ii) permits satisfactory utilization of the final product in making leather goods and footwear; (iii) prevents damage by micro-organisms; (iv) prevents migration of chemicals in the leather i.e. more fixations is there during drying; (v) it is possible to store the dried leather for a very long time without appreciable damage[18].

Proper drying and mechanical handling are amongst the vital operations in leather manufacturing. Drying was previously considered to be an operation to be done quickly and cheaply without considering the atmospheric conditions and changing the rates of drying. Most often the tanners dried the leathers in drying tunnels equipped with fans to circulate the air and heating coils to raise the temperature whenever the leather refused to dry at a reasonable rate. It is of late that the importance of drying operation has been realized. Drying needs a watchful eye. If the leather dried too quickly they shrank to smaller areas, became rough and horny due to case hardening and badly distorted in shape. These effects partly overcome by dampening the leathers after drying, flexing it by staking and then tacking it on boards to dry again in a flat extended conditions.

On the other hand, slow dried leather generally shows fungus growth and mould growth on the surface of leather and due to oxidation of the tannins, the vegetable tanned leathers generally get darkened in colour. These difficulties are not so pronounced in the case of skins, one must be very careful during drying of heavy leathers especially when they are vegetable tanned [19].

To understand the drying it is necessary to know the fibre structure of the leather and the interactions of collagen with water. Wet leather contains different kind of water usually divided up in three main groups:

- Bulk water: liquid-like, can form ice at 0°C
- Bound water: structure between solid and liquid
- Structural water: part of the fibre structure

Each portion of the three kind of water may be different and depends upon the process and the chemical products that have been used. The relation between the water molecules and collagen fibres is paramount to the leather properties. The drying rate through evaporation of wet leather was discussed by Friedrich. He defines three main stages: (α) Constant rate period: water between fibres removal, the surface completely wet so that the water can migrate to the surface from the Centre of the hide at the same speed that it evaporates. This is unbound water and the heat of the drying does not affect the leather temperature because of the evaporation effect. (β) First falling rate period: water between fibrils removal when the surface is only partially wet and the temperature of the leather itself will start to rise. This is a critical stage and can damage the leather if moisture is trapped in the Centre. During this stage both bound and unbound water removed and (γ) Second falling rate period: water within the fibrils removal.

The second falling rate period begin when the surface is completely dry. During this stage the drying rate depends upon the diffusion or on the rate of moisture flow from the inside of material to its surface.

Undue rapid drying exposed surfaces frequently produce the phenomena of case hardening wherein the drying surface becomes covered with dry layers which surrounds or covers the solid like a dry case or shell such an effect is generally undesirable and usually results in a defective and inferior dry product. Usually the constant rate period ends at 50% and the first falling rate at 30% moisture (expressed on dry leather basis) [20].

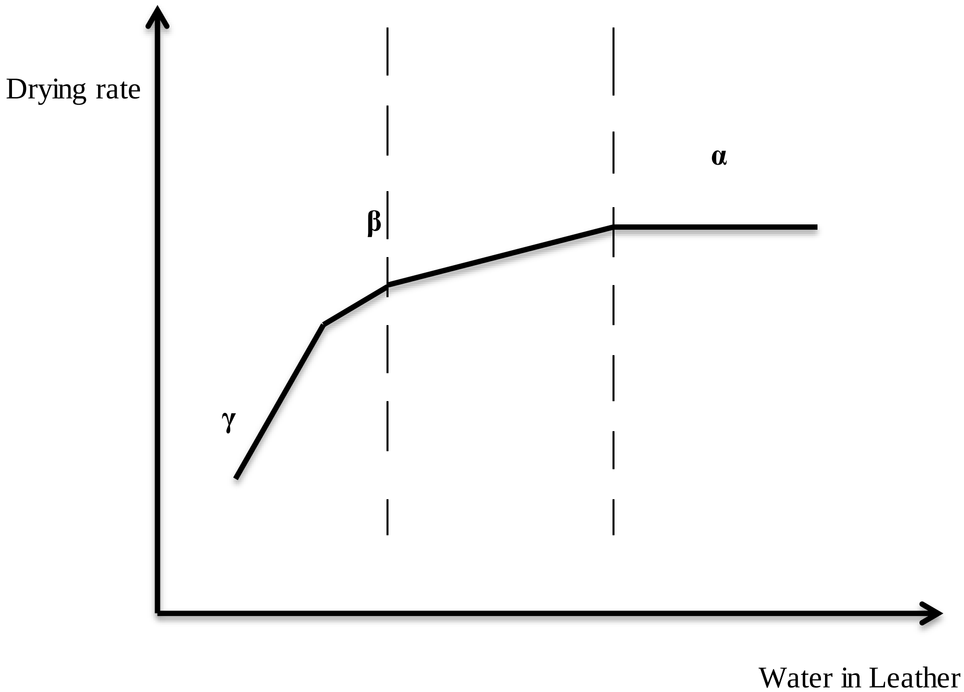


Figure 2.2:- Rate of drying vs. water in leather

Leather is a viscoelastic material and the water content changes its properties like a plasticizer. It is also a micro porous material where water is evaporated from its surface and is constantly replaced by other water from inside. The water diffusion is regulated by the capillary force and the evaporation occurs at constant rate. The mathematical model of the leather drying examined [21] shows that the drying rate is a function of four main parameters: water content, leather thickness (with exponent -2), drying time (with exponent -2), and air velocity (with exponent -0.6).

Starting with wet leather, experimental data were obtained measuring the elastic bending modulus (E) during the time at different air temperature. The elastic bending modulus indicating the stiffness of the leather increases from wet to dry leather but the curve obtained shows two inflection points. Different tanned leather shows the same curve's shape in a diagram E vs. time (fig.2.3) with two characteristic inflections. The critical points are around 60 and 30% moisture (water weight / dry weight) for chrome tanned leather and around 10% less for organic tanned leather. This value may be influenced by the chemical used and is very similar, for chrome and chrome-free tanning, if the water content is calculated on the dry collagen basis.

Increasing the temperature the drying rate is higher and curve shifts to the left, the inflection point compress to the ordinate axis (T2)

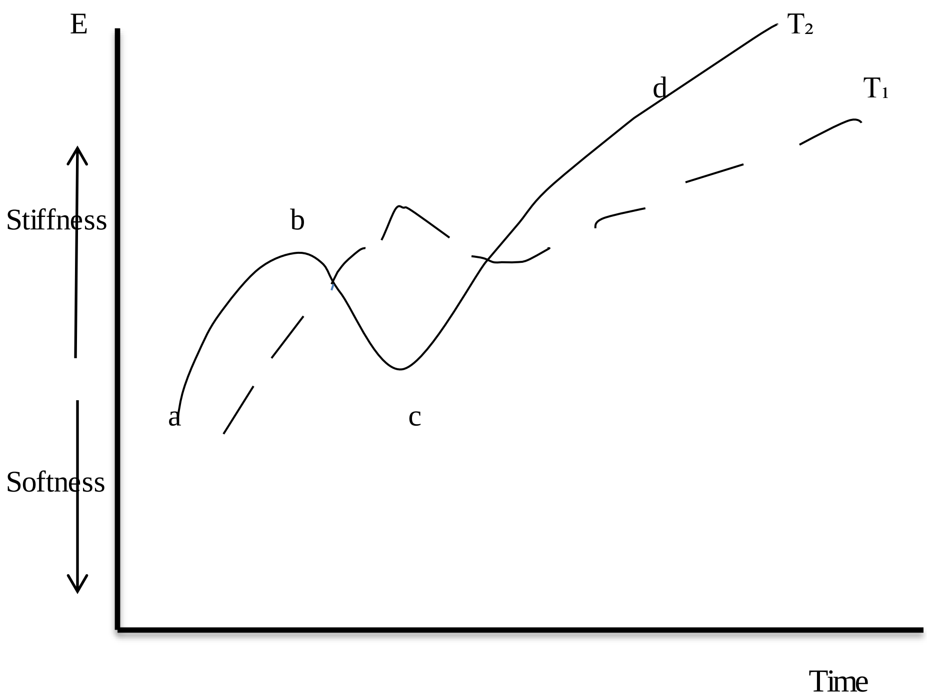


Figure 2.3:- Bending modulus vs. time for same leather at different temperature (T1<T2)

For the three stages of the curves:

a ⟶ b:- removal of the freezable water. The molecular packing increases and so the bending modulus,

b⟶ c: - the fibrils dimension changes and allows more freedom of movement

c ⟶ d :- the water lose in this stage is bound to the side chains, the fibrils dimension decreases and reduces the volume

Many experimental data obtained on chrome and organic tanned leather prove that the softness is independent of the drying condition (temperature and humidity) reached in the first step of the process (point "c" in Fig.2.3). Only the loose of the structural water may change the leather softness so in the past ten years authoritative research suggests a two steps drying like the best way [22]: a first step to remove moisture until approximately 30% and a second step to give the final moisture.

Also the toggling tension was experimentally investigated [23]. There are evidences that during drying, collagen fibres become adhered to each other and this explains why the stress-strain curves for the dried leather are different in shape from wet leather.

2.3.1. Drying of Vegetable Tanned Leather

After the vegetable tanned leather has been dyed and fat-liquored and slicked, each skin is laid flat on a smooth table, grain side up and the grain surface is coated with oil. The nature and composition of oil varies from tannery to tannery. According to Wilson three parts of denatured olive oil and one part of light paraffin wax can be used. This oil retards the evaporation of water from the surface of the leather, preventing the rapid drying of the leather and also protects the tannins on the grain surface from getting oxidized and hence the leather from discolourations. The oiled skin are tacked all round edges and on drying the leathers tend to shrink but its area is maintained by the tacks and the leather after drying is smooth.

After the skins have been tacked onto the frame, the frame is stacked vertically with many other frames. There is enough space between the skins of one frame and that of the next. This is done to prevent the skins from touching during drying and to allow sufficient space for ventilation. A fan is placed above the frames which forces a circulation of air between the frames. Where there is no temperature and humidity control of the air, the skilled worker regulates (i) the operation of the fan, (ii) the temperature of the air, and (iii) the position of the frames with respect to the fan, so that the drying proceeds uniformly. If by chance the speed of drying increases and causes discolouration by oxidation, the worker shuts off the fan.

When the leather is taken out from the tacking frame it usually contains 10 to 12 % by weight of water. At this stage the leather may feel a little firm, but it is easily made soft and flexible by slight staking.

The proper drying of vegetable tanned leather is of importance because of the unfixed tannins and non-tans present in the leather. If the drying rate is very fast these unfixed tans and non-tans tend to be carried over the surface along with the water.

2.3.2. Drying of Chrome Tanned Leather

Chrome tanned leather after drying was so hard and tinny, that it could not be stacked without damage to the leather. It was found necessary to dampen the leather with water and allow it to condition for a day or more before it could be staked and made flexible enough. Chrome tanned leather shrank to a larger extent on drying. Tacking the leather on frames and then drying prevent the shrinkage, but only by rupturing the fibres to such an extent so as to make the finished leather loose and pipey. It was found best to hang the leathers to dry without tension and then dampen it by piling it in damp saw dust for a day or more, then stake it to make it flexible and then tack it for final drying.

When the leather has dried completely the fibres cohere so strongly that any attempt to separate them by flexing will result in actual rupture of the fibres. During the drying of chrome tanned leather it undergoes considerable shrinkage in volume and this drying is greatly increased by the cohesion of the fibres. The leather finally becomes dense, hard and tinny [24].

2.4. Types of Dryers in Leather Manufacturing

The nature and species of skin or hide, its treatment in the beam-house, the type and extent of tannage, as well as the grease content and its distribution, are influencing factor in obtaining successful drying results. The dryers used may be provided with wet and dry bulb temperature control so that any temperature and humidity within a required range may be maintained depending upon the individual schedule. Chrome tanned leather may be safely subjected to higher temperatures during drying than vegetable tanned leathers due to the higher shrinkage temperature in chrome tanning. Thus chrome tanned leathers can be dried rapidly and successfully under conditions which would ruin vegetable tanned leather.

Drying is one of the operations during leather making that has a great effect on leather quality. Leather softness, tightness of the grain, area yield and many other properties are a consequence of the drying conditions employed, especially, temperature, humidity and time. In a hydrated state, leather is fully lubricated with water that is held between the elements of the fibre. In this state it can be moulded, stretched and flexed into any shape. However, as the leather is dried, the fibres approach each other and have a tendency to stick together to an extent that depends on how the water is removed. The technique of drying is therefore adapted to the characteristics of the required leather. An ideal technique of drying is one that gives maximum area yield without compromising quality. There are different techniques of drying used in the manufacturing of leather.

2.4.1. Hook (Normal) Drying

The leather is dried as smoothly as possible by hanging on hooks or over bars at normal room temperature and increased air movement, if possible. Depending on the type of leather, this can take up to several weeks. It is a suitable method for thin and soft leathers. The deformation of the leather is higher, because it is not hindered.

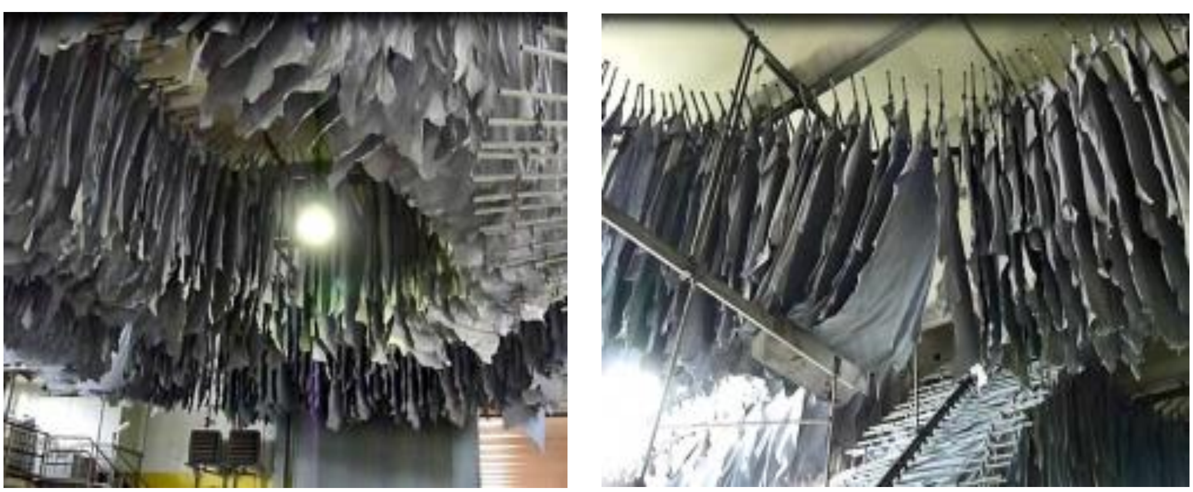


Figure 2.4:- hook (tension free) drying

2.4.2. Toggle Drying

To dry hide or skin, they are placed on a bed of perforated metal plates and stretched using toggle clips. These plates move through drying tunnels with hot-air circulating. A modern machine dries a hide or skin in a couple of hours. The tension applied during the toggling operation can retain much of the yield gained and preserve a better shape. This tension also increases the firmness, coarseness of the grain and the break characteristics. A new development in the drying of furniture leather increases the smoothness and the surface yield of the leather by hydraulically re-tensioning the perforated frames.

Figure 2.5:- Toggle drying

2.4.3. Vacuum Drying

Vacuum drying is based on the physical principle that water evaporates at low pressure and low temperature. In the vacuum dryers, leather is placed with the grain side on heated polished metal surfaces and then the water vapour is sucked out of the vacuum chamber. This process has the advantage that the liquid flow goes through the flesh side and draws possible greases from the grain side into the inner zone. The manual work involved is not excessive, as the hides or skins are placed onto the metal plate without clamps or adhesives and the drying time is very short.

Figure 2.6:- Vacuum drying

2.4.4. Drying with air using a drier or a drying chamber

This is accomplished by passing both air (at appropriate temperature and humidity) and leather in opposite directions in a drier. In this operation the incoming air at first comes in contact with nearly dry leather leaving the drier. At this stage, the drying potential of air is the highest. As it becomes increasingly more saturated, the same air comes stepwise in contact with increasingly wetter leather. To increase its water uptake capacity in several of its final stages, the air has sometimes to be reheated.

2.4.5. High frequency drying

One method of reducing the water content of the leather to a desired level is provided by high-frequency drying. After dewatering by pressing, humid leather is brought into an electric field of high frequencies by a belt conveyor system. The energy density in the humid, conductive areas ensures internal heating and evaporation of the water. This type of drying is only used to a limited extent in the leather industry [25].

2.4.6. Paste drying

In these techniques of drying the leathers are pasted on to large glass or metal plates (using starches, casein, carboxyl methyl cellulose, plasticizers, preservatives etc.) with the grain surface to the sheet. This gives maximum smoothness of grain and area yield (5-8% extra yield compared to naturally dried leather). A glass plate is coated with a thin starch paste and the wet skins are slicked on this, grain side to the glass, thereby preventing shrinkage on drying. The type of paste used varies, to suit the thickness of the skin, its wetness, its tannage and particularly its grease content and the temperature and speed of drying.

Paste drying is widely used for corrected grain sides for shoe uppers, giving a suitable, flat and smooth grain surface.

Paste leather dryers are built in various sizes according to the individual production. These dryers are divided into distinct drying zones throughout their lengths, the temperature and humidity being automatically in each zone. Each individual is provided with its individual air supply, heating and exhaust air system. The leather should have an initial moisture content of 55% to 65% from the putting out machine and on leaving the dryer 10% to 12% moisture. With full grain leather it is necessary to wash thoroughly the paste from the grain side so that the paste particles will not afterwards prevent the adhesion of the finish, but for corrected grain the paste is buffed or snuffed off with the grain.

The pastes for pasting are mounted in a steel frame work and carried through the drying zones on an overhead mono rail system. Many type of leathers, both chrome and vegetable tanned leathers are presently being dried by the pasting process. The pasting process will not entirely replace tacking or toggling for certain leathers.

Stainless steel, Aluminium, plastic and glass has all been used in paste dryers. The type of plate depends upon the type of leather to be processed and the design of the drying equipment. The various plate materials have different specific heats and thermal conductivities affecting the drying rate and in addition showed the defects on the grain of leather.

Table 1:- Specific heats and thermal conductivities of various materials

Materials	Specific heat (Cal/gm./ °C)	Thermal conductivity (BTU/lb./hr./°F/ Ft²)
Aluminium	0.23	305
Glass	0.19	6.6
Stainless steel	0.15	184
Air	0.24	-
Leather	0.33	-

Average specific heats of different leather products are shown below.

Table 2:- Average specific heats of leather at raw (collagen) and tanned stage

Materials	Specific heat (Cal/gm./°C)
Collagen	0.37
Chrome- retanned leather	0.34
Vegetable tanned leather	0.33
Chrome tanned leather	0.30

Thermal conductivity of different leather products shown below.

Table 3:- The thermal conductivity of different types leather

Materials	Conductivity , K × 10^ ⁻4 (Cal/ cm²/° c/ sec)
Vegetable tanned sole	1.18 – 1.58
Chrome sole fat- impregnated	1.25 – 1.68
Chrome upper- low fat content	0.44 – 0.77
Chrome upper- high fat content	0.98 – 1.34

The thermal conductivity values obtained for leather when compared to those values of the various plates, it is clearly seen that only glass is near the leather in conductivity. The other material conduct the heat at a much greater rate could damage the grain of the leather unless proper precaution as to drying temperature is taken.

Advantages of paste drying as compared naturally dried leather

(a) Smooth grain
(b) Increased surface area

Disadvantages

(a) Increase in area is obtained at the expense of fullness and handle. The leather become flatter and harder (these can overcome by suitable retannage and fat liquoring)

(b) Moisture content should be about 60 – 65 % before pasting. Too much or too less moisture content causes the leather Pell off while pasting.

2.5. Chemical changes during drying process

During drying process certain changes takes place in chrome tanned leathers as it's evident from the following facts:-

1. After drying process chrome tanned leathers cannot be wetted back readily with water.
2. After drying process the chrome tanned leathers which stood boil test earlier will no longer to do so.
3. In fresh chrome tanned leathers the acid bound to chrome is practically in ionic form and can readily remove by washing. No such ionic bound acid is present in dried chrome leathers.

The causes for all these changes lie in changes of chrome complex occurring in drying process. Ionic bound acid gets into the chrome complex in drying with the formation of acid complexes. When chrome leather is dried, it partly loses its strong affinity to combine with ionic dyes. Similar effects are also obtained in, if freshly chrome tanned leather is neutralized with salts containing complex active acid, radicals such as sulphates, phthalates, adiphates etc.

Also freshly tanned chrome leather which does not have affinity for basic dyes shows the capacity for binding basic dyes after drying process. Therefore, it may be concluded that at least part of chrome present in leather are converted into anionic complexes in the course of drying process. It is also noticed that the iso electric point of leathers tanned with cationic $Cr\ (SO_4)_3$ is reduced from pH (7 – 7.5) to pH 4 by drying process. In view of the above it is concluded that when chrome leather is dried, the basic groups of hide collagen come into close proximity with the chromium atom and then incorporated into the complex thus weakening the cationic and promoting the anionic properties of leathers [26].

2.6. Area yield and Leather Quality

Leather is made to meet various end use purposes that need varying qualities that must not be sacrificed at the expense of area yield. Apart from the raw hide from which leather is made, the major components determining leather quality [27] are:-

- The chemical processing from the raw hide to the tanned condition
- The modification of the basic tanning method by a variety of retanning and fat liquoring materials.
- Mechanics associated with the process vessels and leather making machinery
- The drying techniques employed.

Each of these components needs to balance with the others. If one or more of these components does not harmonize with the required characteristics, then it is necessary to attempt to build these properties into the leather using the remaining options. With chrome leathers it is general practice to manufacture or purchase a versatile wet-blue which can be adapted to a reasonably wide range of leathers as opposed to a specialized tanning procedure. Thus enhancement of wet-blue towards a set of target properties is normally achieved by using the correct mechanical and drying techniques.

3. Materials and methods

3.1. Materials

Twenty one wet blue sheep leathers for production of garment leather were used as material for this study.

Chemicals and Equipment's

- **Chemicals: -** Commercial wet finishing chemicals were used (see the recipe on annex 2 and 3).
- **Equipment's used were: -** Digital balance, Testing drum, Post tanning mechanical operation machine (shaving, setting out, hang dryer, toggle dryer, vacuum dryer, staking and drum milling machine), Area measuring machine, Precisa gravimetric AG moisture analyzer, St-300 digital softness tester, Instron 1122 physical tester, JSM-IT300LV scanning electron microscope (Japan Electronic Co. Ltd., Japan) and Edwards E306.

3.2. Methods

The sheep wet blue with thickness of 0.9 mm was prepared and subjected to wet finishing process (retanning, neutralizing, dyeing and fat liquoring) with a conventional process recipe for making garment leather to get wet crust. The chemicals used for wet finishing chemicals were commercial grade and the design of process recipe according to annex 2 and 3. (See on annex 2 and 3). After wet finish process they were setting out after being horsed-up for one night before drying process.

3.2.1. Drying Techniques

After setting-out process, they were divided into three groups for applying different drying techniques. Drying techniques and conditions applied to the leathers are given below.

Hang drying:-The drying hanger unit with 1.5 m/min speed was used. The temperature of closed drying cabin unit placed at the end of hanger unit was adjusted at 65˚c and duration of time for 18 hrs.

Toggle drying:-The temperature of toggle drying cabin was adjusted at 55˚C and the drying was applied for two different duration of timeline 3 hrs. and 3.5 hrs.

Vacuum drying: - The temperature of the vacuum drying unit was adjusted to 60˚c. The vacuum gauge pressure was maintained at 0.8 bar (absolute pressure of 21.3 KPa). It is a typical pressure used in a Vacuum drying operation. Four different drying times i.e. 60, 90, 120 and 150 seconds were applied. Before vacuum drying operation was done, Sam-setting operation was applied in order to reduce the moisture content.

After each techniques of drying the crust leather undergo staking operation to increase pliability and softness of leather and drum milling operation to further increase the softness of leather for 3 hrs.

3.2.2. Area Measurement

The Areas of prepared sheep wet blue leathers, crust leathers that were staked after the drying techniques and drum milled after the staking process were measured by using area measuring machine in order to determine the changes in the areas at wet blue stage (before wet finishing process) and at crust stage (after wet crust process) by drying techniques and mechanical processes after drying. The measurement of area was done following IUP 32 test method. The area is indicated in leather as square feet or square decimeter.

The percentage increase (% area change) was determined by:-

D_a or D_b = (A_2or B – A_1)/ A_2 or B× 100; where A_1:- Area of leather before drying process

A_2:- Area of leather after (drying process + staking operation) and B: - Area of leather after Drum mill operation.

D_a or D_b: - percentage increase or decrease (% area change) of leather

3.2.3. Characterization crust leather

The following methods were used to determine the moisture content, softness, tensile strength and elongation at break, organoleptic properties and microscopic studies of crust leather.

3.2.3.1. Determination of moisture content of leather

Moisture content of crust leather after each drying techniques measured by precisa gravimetric AG moisture analyzer which is used as a quick and reliable means of determining the moisture content of leather by thermo gravimetric process. After immediate drying process of leather, the sample should be packed in air tight containers so as to ensure that the sample do not change while they are in storage. For each measurement 5 g of leather sample is taken and the sample distributed evenly and thinly on the weighing pan in order to achieve reproducible results. Then, the temperature of heating and drying time adjusted at 105^{o} c and 15min. – 25min. respectively. All the experiments were performed in triplicates.

3.2.3.2. Determination of softness leather

Softness was measured following IUP 36 test method (which is equivalent to ISO: 17235:2002) using ST 300 digital softness tester [28]. The ST 300 D is a means of determining the softness of leather without defacing the hide or skin, as it does not require samples to be cut from the leather prior to testing. This enables a quality system to be set up between supplier and customer whenever leather softness is an important factor.

The size of the reducing ring (aperture) used in the softness tester was 20 mm (the aperture size used for measurement of garment leather). The leather samples conditioned at 20 ± 2 ˚C and 65 ± 5 % RH for 48 hrs. before testing. The softness of leather expressed in terms of distention value (mm). All the experiments were performed in triplicates.

3.2.3.3. Tensile strength and Elongation at break of leather

The sampling protocols for physical testing were carried out as specified in the official sampling method (International Union for Physical Testing (IUP2), 2000) [29]. After cutting three samples from parallel to back bone direction of leather (along direction) and three samples right angle to back bone direction (across direction) and samples were conditioned at 20±2 ˚C and 65±2 % RH for 48 hr. prior to testing (International Union for Physical Testing (IUP3), 2002) [30]. The physical properties such as tensile strength and percentage elongation at break were measured according to IUP6: ISO 3376 (International Union for Physical Testing (IUP6), 2000) [31]. Tensile strength is the ultimate strength of the leather that includes grain, corium and fresh layers. In this test elongation property of the leather can also be measured. All the experiments were performed in triplicates. The tensile strength expressed in terms of N/mm^2 (Mpa) and elongation at break of leather expressed in %.

3.2.3.4. Organoleptic properties

The Organoleptic properties of garment leathers dried under each techniques of drying process were accessed for the functional properties such as smoothness of grain, grain tightness, and grain break, uniformity of Shade and overall appearance rated as on a scale of 0-10 points, higher values indicate better property.

This visual and hand evaluation were carried out by experienced researchers and tanners from leather processing division of Central Leather Research Institute, Chennai, India.

3.2.3.5. Microscopic studies (SEM analysis)

Samples from crust leathers dried under each techniques drying process and conditions were cut from official sampling position. Samples were directly cut into specimens with uniform thickness without any pretreatment. All specimens have been then coated with gold using Edwards E306 sputter coater. The micrographs for the grain surface and cross section were obtained by operating the SEM at an accelerating voltage of 15 KV with different lower and higher magnification levels.

4. Results and Discussion

4.1. Effects of Drying techniques and Conditions on Area Yield of Leather

A significant area increase of 16% can be achieved by using a combined drying process of vacuum plus stretching (toggling), compared to the regular vacuum dried leather without stretching [32]. Thus, toggle drying produces high area yield, but may result in stiffer leather [33]. Surface area measurement values of leathers after staking process are higher than the surface area measurement values of wet-blue leathers in all drying techniques and conditions as shown in annex 4.

Generally, the area yield of leather increases steadily with the increase of drying period. Because, the longer drying period causes to remain less moisture in the leather and the lower residual moisture content enables higher area yield. Decreasing the initial moisture content to a certain level, this tendency steadily becomes reverse. With the increase of the drying period, this behavior much more revealed. Probably, the leather is too dry and loses the elongation ability during toggled drying lead to lower area yield [34]. After the leather has been dried following the re- tanning process, and even though the leather fibers had been lubricated with fat liquors, without additional mechanical force, the fibers of the leather can still stick together, leaving the leather rigid and hard. Therefore the leather must be physically conditioned by staking and/or milling. Staking is a mechanical method that increases the pliability and softness of the leather. The hide travels through the machine on a conveyor belt and is pounded by several thumb-sized rounded pins that stretch the fibers in every direction, thus separating the fibers and softening the leather. It can be showed that, the area yield of the leathers dried by using different drying techniques and conditions were increased according to their area in wet-blue stage, but there is little decrease in area yield of leather during drum milling operation as shown on Figure 4.1.

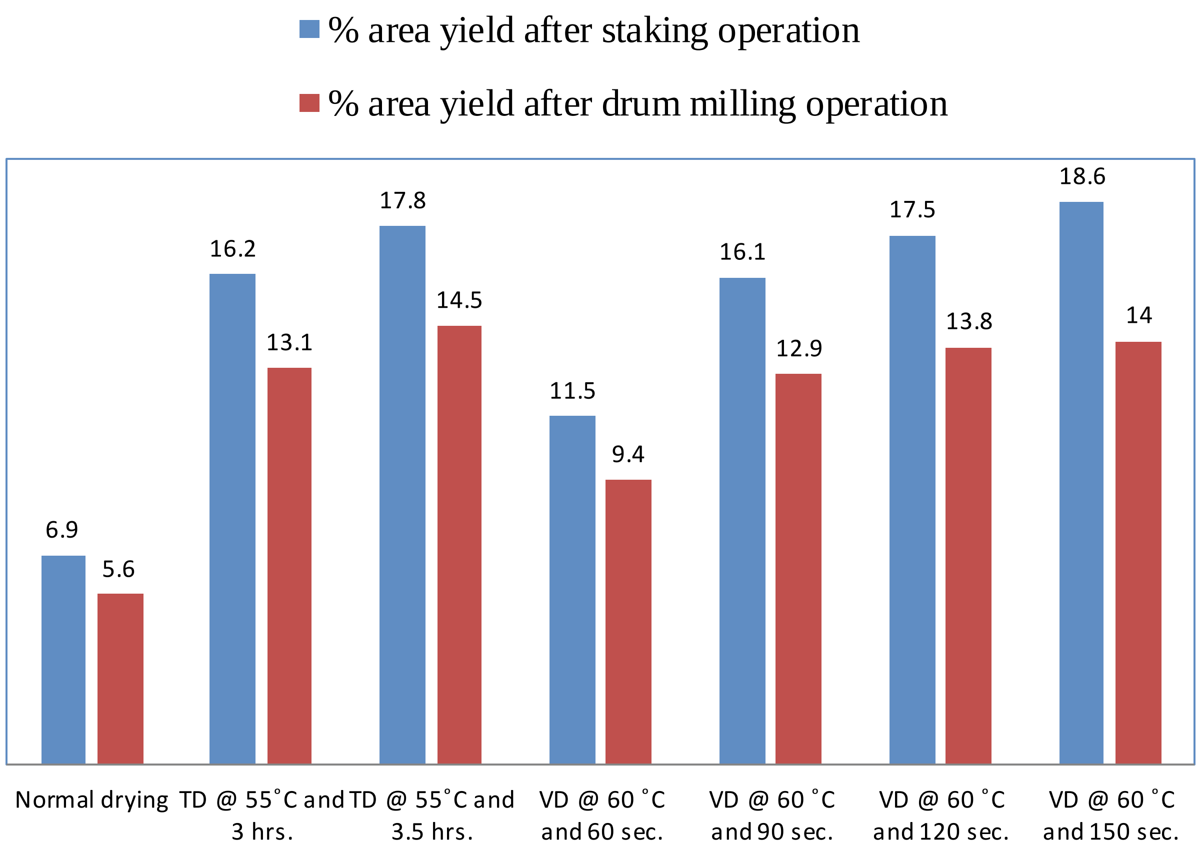


Figure 4.1:- Percentage increase of area yield after staking and drum milling operation

After staking process, the leather usually goes to the drum milling process for increasing the softness of the leather. Desired softness can be generally obtained by carefully control of the drum speed, period and humidity inside the drum [35].

The cost of labour is low in the drum milling process and a more effective softness can be achieved than the other staking methods. There is no negative effect of drum milling on the strength of the leather, but the area loss is between 3-6%. Decrease of the area of leather in the first four hours is highest [36].

Liu et al. (2011) investigated that the effects of conditioning, staking and drum milling processes on the retention of surface area gained by toggling process. The results indicated that toggling has markedly effect on surface area yield, conditioning and staking have a little effect on area yield, whereas the drum milling significantly decreased the surface area yield. It is seen that drum milling process applied after staking process is shown to reduce the area yield of leathers in all drying techniques as shown on figure 4.2

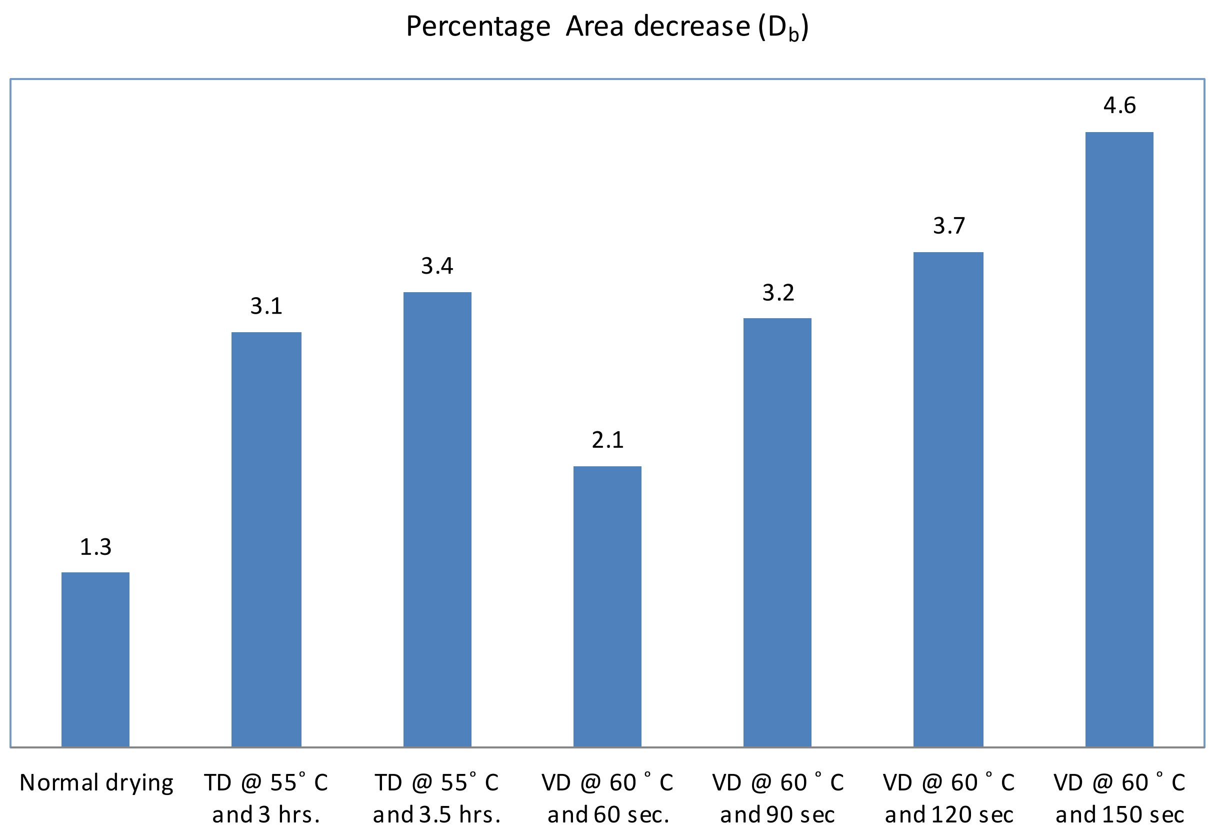


Figure 4.2:-Percentage decrease of area yield under each drying techniques after drum milling operation

It is observed that the tendency of decreasing on area of leather after drum milling is also higher in the drying techniques which provide higher area gain after staking process. Despite this decrease, it is also seen that the area yields after drum milling in all the drying techniques are higher than the areas of wet-blue leathers.

4.2. Characterization of Crust Leather

Although the properties of leather depend on the structure of the skin/hide from which it was made, its quality is influenced by the post-tanning mechanical operations that are carried out for various reasons. Drying is one of the most important processing steps affecting leather quality. Quality measurement and leather properties such as moisture content, softness, strength properties and tightness of the grain are affected by drying process. The techniques of drying have to be adapted to the characteristics required of the leather.

a) Moisture content of leather

The moisture content difference can happen due to the difference in the original moisture content in the wet blue (over aging in a pile will have reduced the moisture level), difference in the efficiency of sammying before shaving, seasonal variation (in summer/dry season the shaved leathers may loose water more rapidly than in winter/wet season and also will depend on how long the shaved leathers are left in the shaving yard prior to weighing. So a suitable strategy may be evolved to measure the shaved weight to minimize the batch-to-batch variation. Some of the options available are (i) to document regularly the ratio of shaved weight to area for a particular thickness over a period of time and from this data, calculate the area to shaved weight ratio and use this as a parameter to correct for the inconsistency and (ii) Determine the hide substance and base the % of chemicals on this rather than on the shaved weight (this procedure is time consuming and the sampling for analysis should carefully be done to avoid variations. Probably, drawing samples from different positions in the pile and mixing the samples prior to analysis may help). After each techniques of drying process the leathers are intermediately stored in order to compensate for over dried or over wet sections in the leathers. The mechanical operations after drying process serve to further treat the leathers to achieve desired softness or firmness (staking) to further increase softness of leather (drum-milling), to process the fibers on the grain or flesh side (buffing/snuffing). In order to facilitate these mechanical operations, the moisture content of the dried leather should be around 12-18%. If the moisture content is above the standard values the resultant leather becomes looser and below the standard values will result in hardened leathers with grain crack.

The mean moisture content of the garment leather produced by different techniques of drying process and conditions are shown in Table 4 along with standard deviation.

From the result, as drying period increases, the water is evaporated from the surface of the leather and is constantly replaced by other water from the inside and continuous through the three stages of drying rates; in turn decrease in moisture content of leather. The mean moisture content of leather has been plotted against the drying time in case of vacuum drying process as shown on Figure 4.3. It indicates that as drying time increases, the moisture content of the leather decreases which correlates inversely when fitted linearly using Minitab software. The value of correlation coefficient (R^2= -0.9) indicates excellent correlation between mean moisture content of leather and drying time of leather.

Table 4:-moisture content of leather dried under each drying techniques and variables before staking operation.

Drying techniques	Moisture content (%)
Normal drying	16.8 ± 1.7
Toggle drying 55˚C and 3 hrs.	15.9 ± 2.5
Toggle drying 55˚C and 3.5 hrs.	13.1 ± 1.3
Vacuum drying 60˚C and 60 sec.	16.9 ± 2.2
Vacuum drying 60˚C and 90 sec.	16.1 ± 1.1
Vacuum drying 60˚C and 120 sec.	14.9 ± 0.8
Vacuum drying 60 ˚C and 150 sec.	11.6 ± 1.0

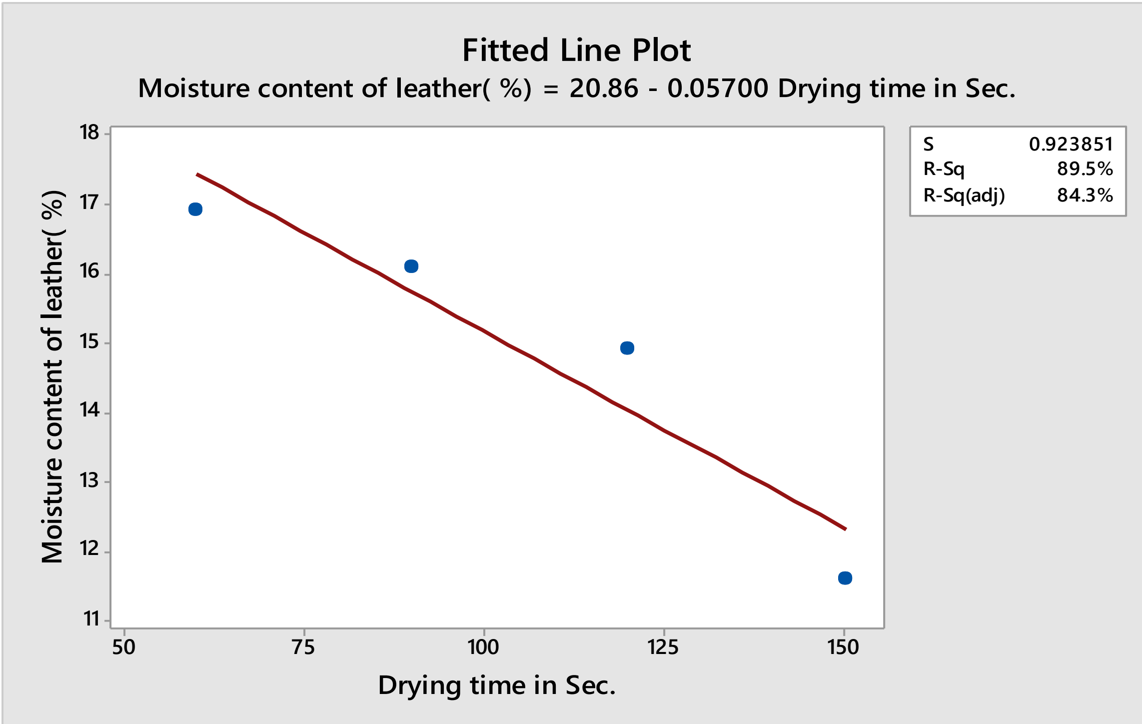


Figure 4.3:- mean moisture content of leather vs. drying time in case of vacuum drying.

b) Softness of Leather

The development of leather softness first originates in the beam house with the chemical opening up of the collagen fibres. To retain the open fibre structure and tendency towards softness originally imparted by chemical processing, it is important to ensure adequate lubrication of the fine fibrils as well as of the coarser fibril bundles/fibres. This is achieved by the use of fat liquor emulsions of small particle size capable of penetrating down the hierarchy of the leather structure. This, in conjunction with the use of relatively mild drying conditions minimizes the extent of fibril, as well as fibre, re-adhesion during drying process. This promotes leather softness and reduces the need for subsequent stress softening. The current view of the changes in ultra-structure that occur during drying process is that the diameter of collagen fibrils shrink during drying and the cracking of the fat liquor emulsion allows the neutral fraction to lubricate the fibril and prevent sticking during drying process [37]. Without fat-liquors, the leather would dry hard and any mechanical action would damage the fibre and limit the quality potential. It controls the feel of the dry leather. The softening action of staking only becomes effective after the fat liquor concentration reaches a certain level.

After being staked, the leather will usually go through the milling process to further soften the leather. Dry-milling is a fast revolving dry drum and is applied when very soft leather must be produced. It could be for upholstery, garments or very soft nappa for shoes. Milling is a physical softening process in which leather is tumbled in a dry drum fitted with wood dowels with atomized moisture injected into the tumbler. An acceptable softness can generally be obtained by careful control of the drum speed, time and humidity inside the drum.

Mean softness values of the Garment Napa leathers procured from different drying techniques and conditions are given in Table 5 along with standard deviation. Softness was expressed in mm of leather deflection. The mean softness values in case of vacuum drying ranges from 4.0 to 4.8 mm. From observation of the result, generally as drying time increases, there is small variation in softness of leather and softness of leather steadily decreases. The standard values softness of leather for more softy leather is above 5 mm and for more firm leather is below 3 mm.

Table 5: - Softness of crust leather after drum milling process

Drying techniques	Softness in terms of distention value (mm)
Normal drying	4.7 ± 0.3
Toggle drying 55˚c and 3 hrs.	4.4 ± 0.5
Toggle drying 55˚c and 3.5 hrs.	3.9 ± 0.3
Vacuum drying 60˚c and 60 sec.	4.8 ± 0.4
Vacuum drying 60˚c and 90 sec.	4.5 ± 0.4
Vacuum drying 60˚c and 120 sec.	4.2 ± 0.2
Vacuum drying 60 ˚c and 150 sec.	4.0 ± 0.6

The softness values of sheep nappa are higher than the values reported in the literature for cow nappa leathers [38].

The mean softness values of sheep nappa Garment leathers have been plotted against the mean percentage area yield of leather as shown on Figure 4.3. From the observation, the mean softness of leather steadily decreases with the increase in percentage area yield of leather as demonstrated by the inverse correlation when fitted linearly using Minitab software. The value of correlation coefficient (R^2 = - 0.64) indicates fairly good correlation between the mean softness values of the leather and mean percentage area yield of the leather.

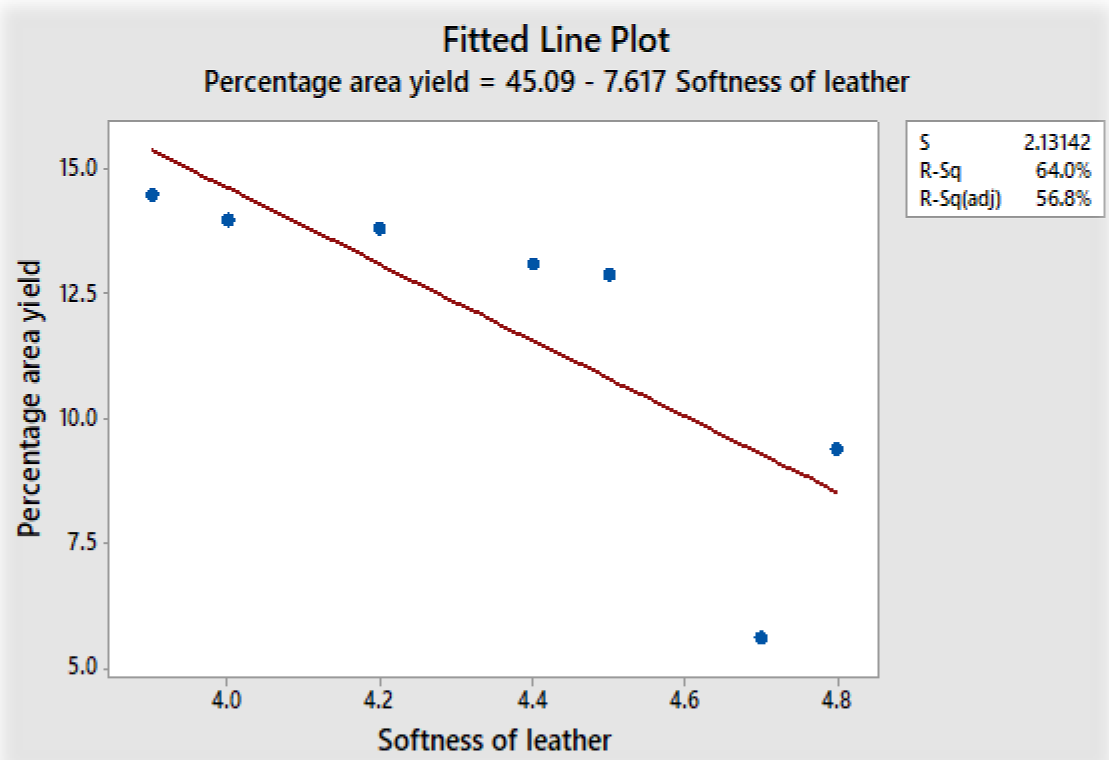


Figure 4.4:- Percentage area yield vs. softness of leather

Residual moisture content of leather plays an important role in controlling the softness of leather. Also, the mean softness values of leather have been plotted against the mean moisture content of leather as shown on Figure 4.4. From the figure, the mean softness of the leather increase with increase in moisture content of leather which is directly correlated when fitted linearly using Minitab software. The value of correlation coefficient (R^2 = 0.84) which indicates a very good correlation between mean the softness of the leather and moisture content of the leather.

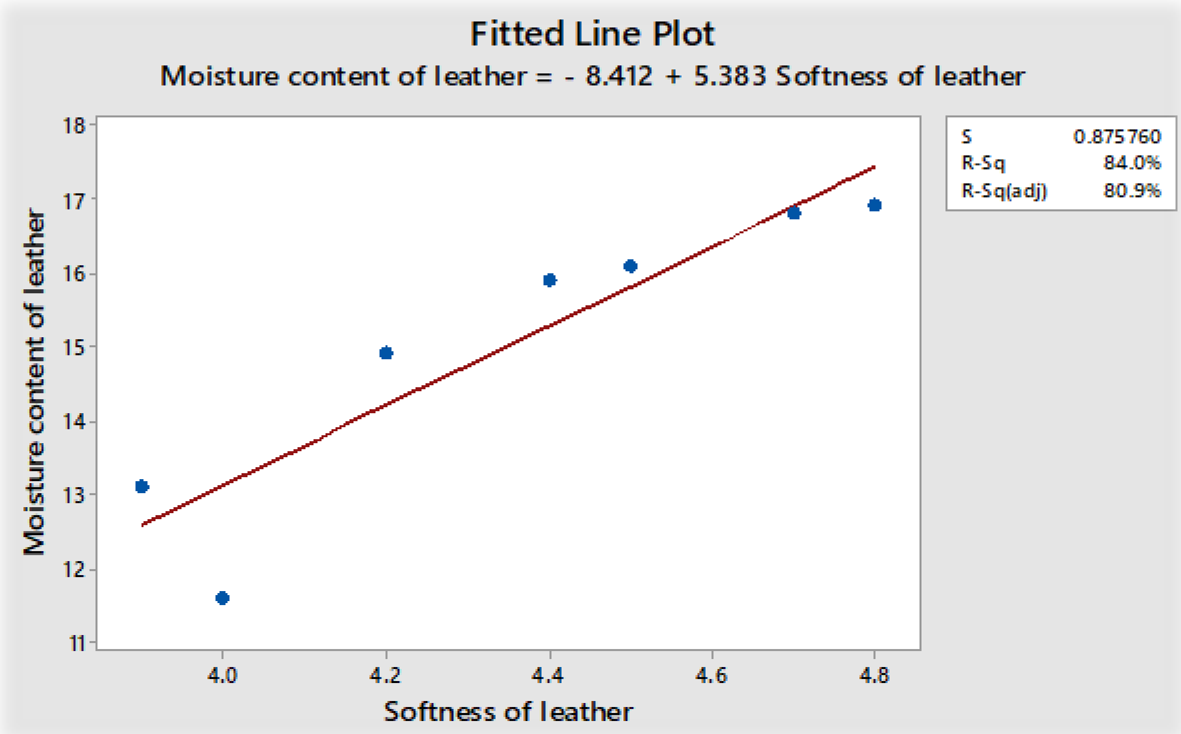
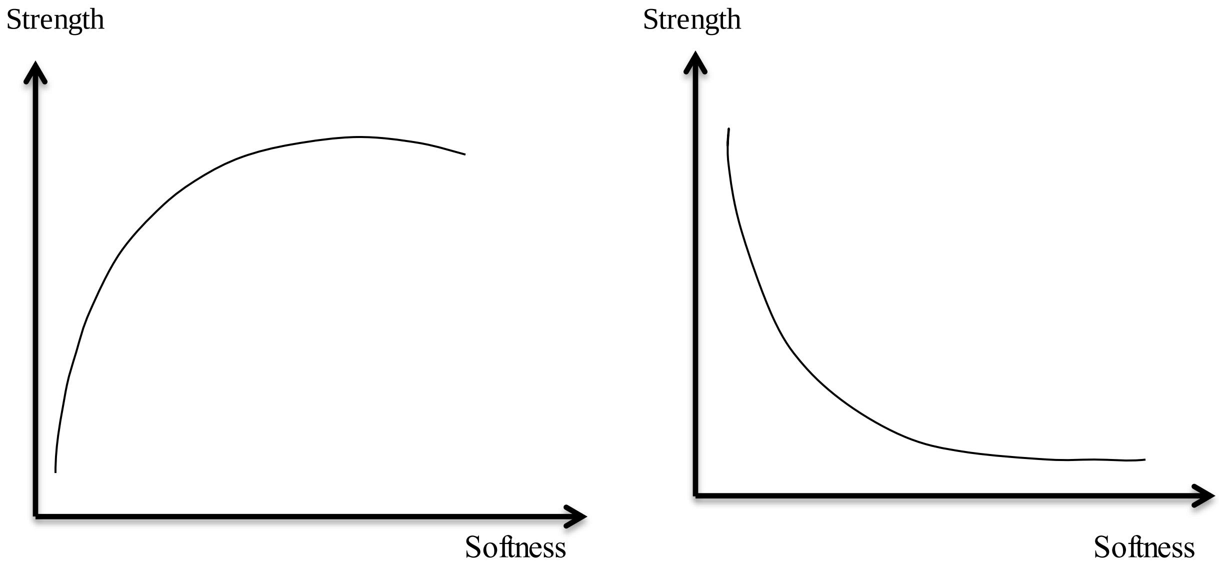


Figure 4.5:- Moisture content of leather vs. softness of leather

The development of softness in leather is intimately associated with mechanical action, because the process of drying causes adhesions to occur, weak adhesion in the case of well fat liquored leather, which must be broken to soften the leather. This is achieved by the process of staking, in which the leather is mechanically stressed: in industry the process used to involve bending the leather by hand through an acute angle over a blunt blade, but now machines pummel the leather automatically and with precisely controlled force. A crucial feature of the staking process is the water content of the leather: more than equilibrium moisture content is required, 15–20%, to provide additional lubrication of the fibre structure [39].



Developing chemical softness = stress softening Over staking fibre structure = stress Weakening

Figure 4.6 a) chemical softness; b) stress softness

c) Tensile strength and elongation at break of leather

Tensile strength is one of the most important properties to evaluate the qualities of leather and governs its end use. Leather quality depends on the arrangement and strength of its fibres. The tensile strength of leather depends on the number of fibres in the woven fibre network that are oriented in the direction of the applied load. The mean tensile strength and elongation at break values of the Garment Napa leathers procured from different drying techniques and conditions are given in Table 6 along with standard deviation. From the result, Collagen materials such as leather in general have very poor heat resistance. Thus prolonged drying not only shrinks the leather, but also makes the leather fibres brittle and stiff, thereby decreasing the tensile strength. When leather is stretched, the observed elongation is the sum of the elongation of the constituent fibres and the distortion of the collagen fibre network.

Elongation at break is an important leather quality and it demonstrates that elongation at break of leather steadily decreases as drying time increases. The standard tensile strength for garment leather according to IUP 6 (international union for leather physical testing) is 12 Mpa and the standard values of elongation at break of sheep garment nappa leather minimum 40% and maximum 80%.

Table 6:- Tensile strength and elongation at break of leather

Drying techniques	Tensile strength (MPa)	Elongation @ break (%)
Normal drying	16.3 ± 1.7	67.8 ± 4
Toggle drying 55˚C and 3 hrs.	13.7 ± 2.1	60.7 ± 3.5
Toggle drying 55˚C and 3.5 hrs.	12.6 ± 3	58 ± 5
Vacuum drying 60˚C and 60 sec.	17.4 ± 1.3	74.8 ± 6
Vacuum drying 60˚C and 90 sec.	14.7 ± 3.1	70 ± 2.5
Vacuum drying 60˚C and 120 sec.	13.3 ± 0.9	65.6 ± 8
Vacuum drying 60 ˚C and 150 sec.	11.8 ± 1	61.5 ± 2

These physical properties are likely to depend on the fundamental properties of the individual components of leather and the arrangement of these components in leather. However tensile strength of leather is usually considered as an indicator of leather quality. The prediction of leather strength is not only important to the tanner but also in the design of any component that uses leather. There is need therefore to develop methods of predicting leather strength so as to effectively optimize the leather making processes.

The mean tensile strength values of sheep nappa Garment leathers have been plotted against the mean percentage area yield of leather as shown on Figure 4.7. From the observation, the mean tensile strength of leather steadily decreases with the increase in percentage area yield of leather as demonstrated by the inverse correlation when fitted linearly using Minitab software. The value of correlation coefficient (R^2 = - 0.68) indicates fairly good correlation between the mean tensile strength values of the leather and mean percentage area yield of the leather.

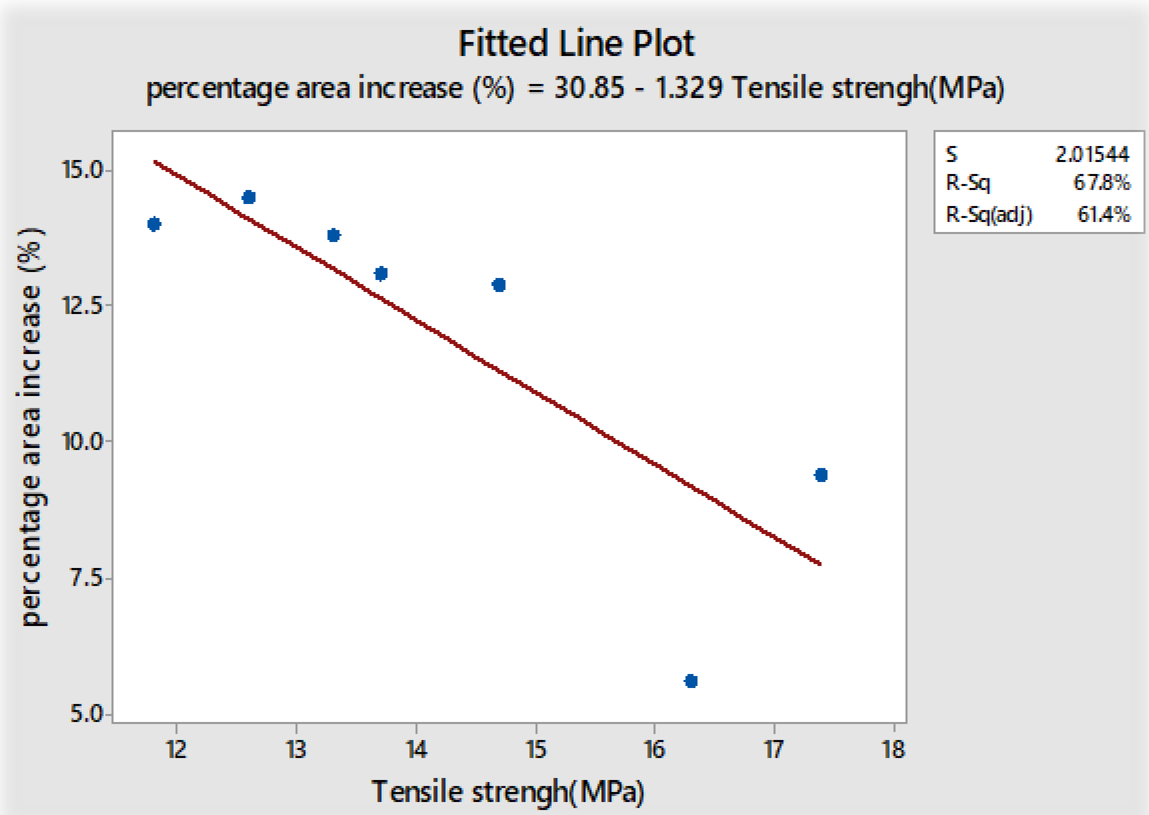


Figure 4.7:- Percentage area increase (yield) vs. tensile strength of leather

d) Organoleptic properties

The organoleptic properties were evaluated by experts from CLRI model tanneries. Three tanners have evaluated the crust leather dried under each techniques of drying process and conditions. The ratings have been provided in a scale of 1-10. The average of the rating for the leathers corresponding to experiment has been calculated for each functional property as shown on annex 5.

Generally, the overall appearance of crust leather in all drying techniques is almost similar, but as drying time increase, the functional properties decreases as compared to Normal (tension-free) drying techniques.

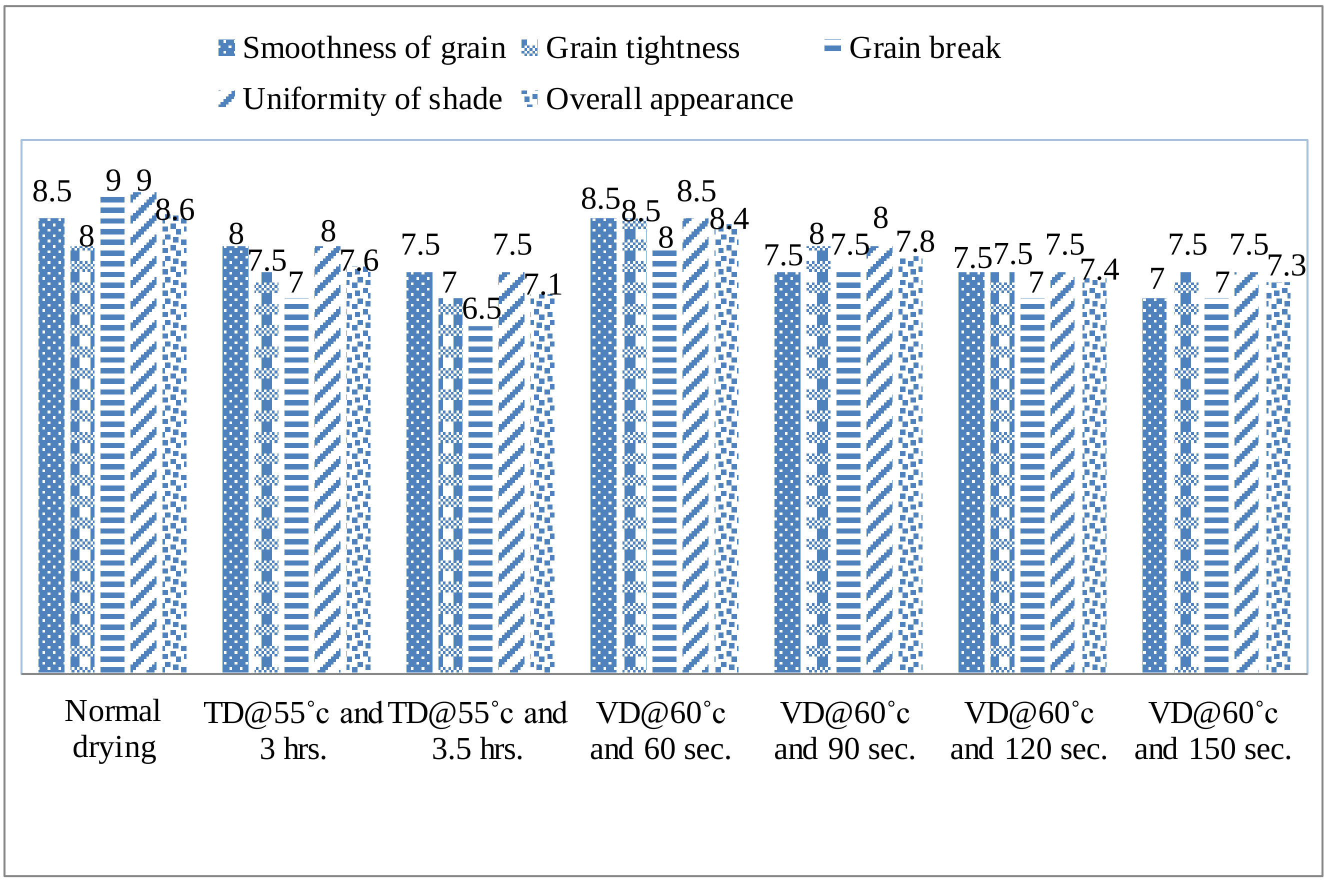
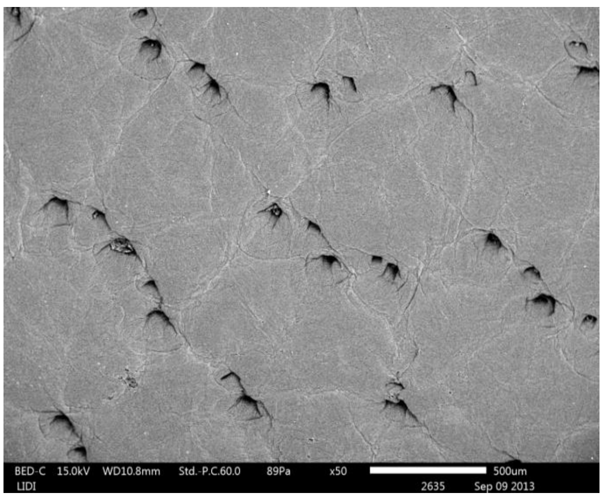


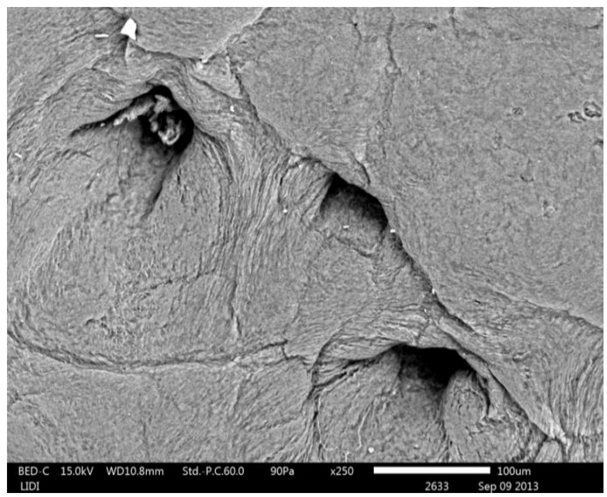
Figure 4.8:- Visual examination (subjective properties) under each dries techniques of crust leather.

e) Microscopic Studies (SEM analysis) of crust leather

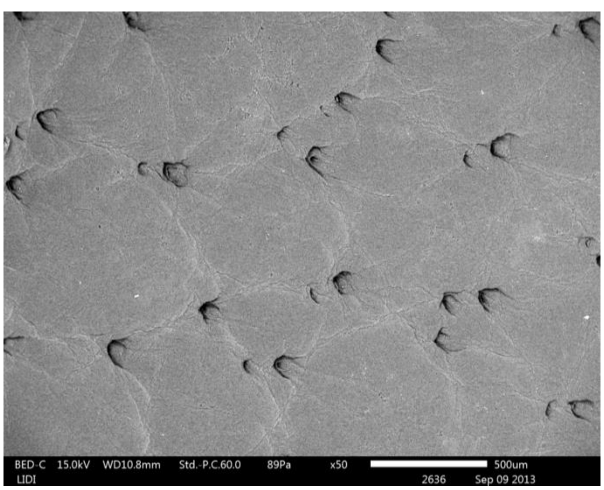
Scanning electron micrograph has been performed to investigate the grain characteristics and fibre structure of crust leather that has been dried by different techniques of drying process. SEM study showed that drying causes agglomeration the leather [40]. This agglomeration phenomenon is undesirable since it results in area loss; therefore, most tanneries rely on drying processes that are carried under natural slow conditions. However, forced drying conditions i.e. vacuum and toggle drying may be used to speed up the drying process while trying to maintain the leather area. The grain surface and cross section crust leather shown below.



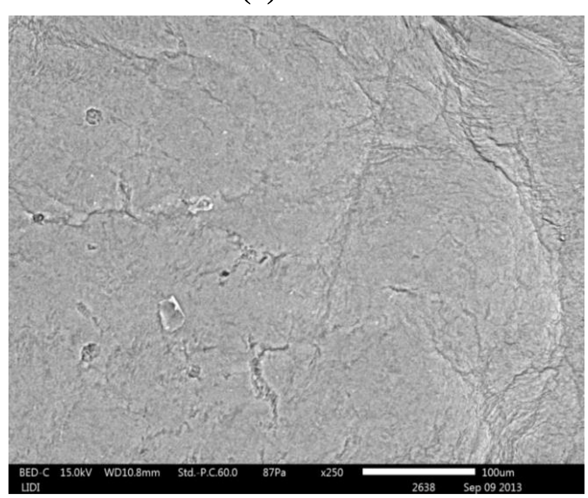
(a)



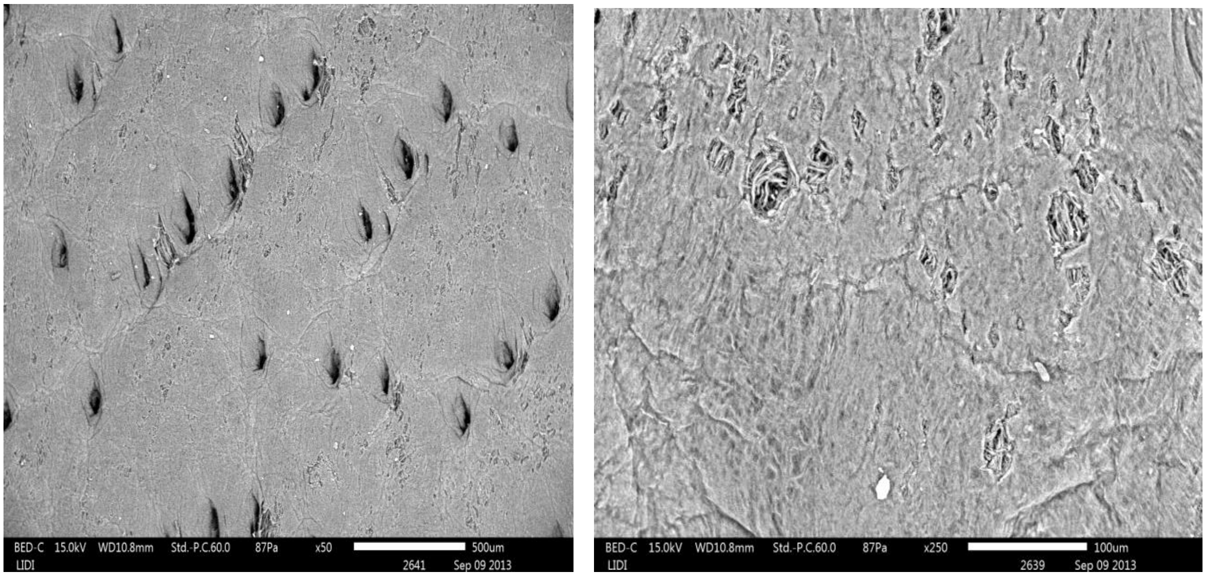
(b)



(c)

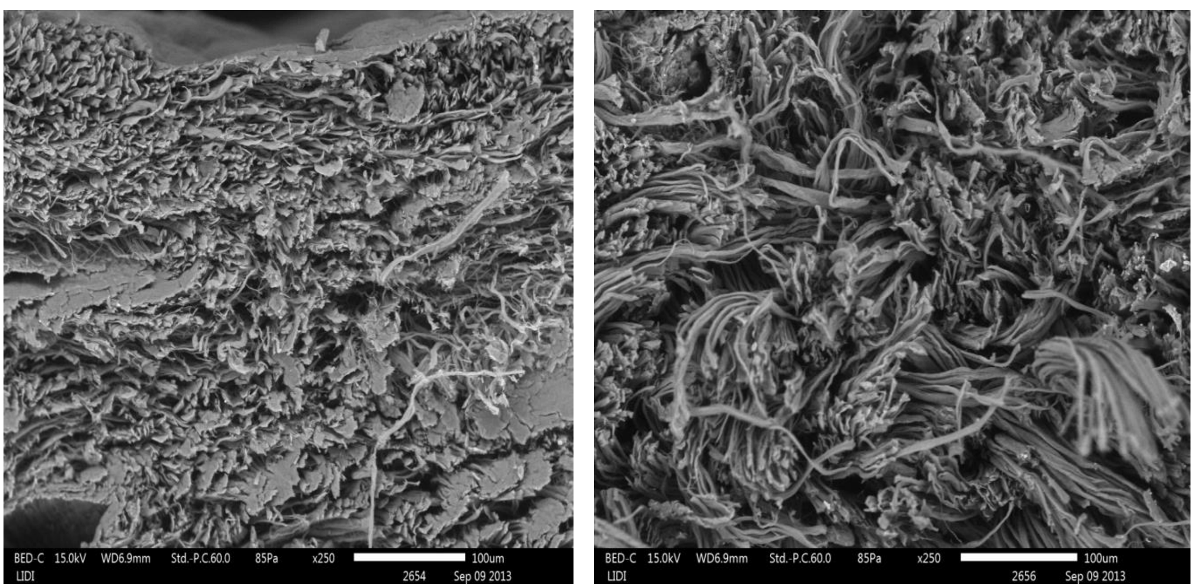


(d)

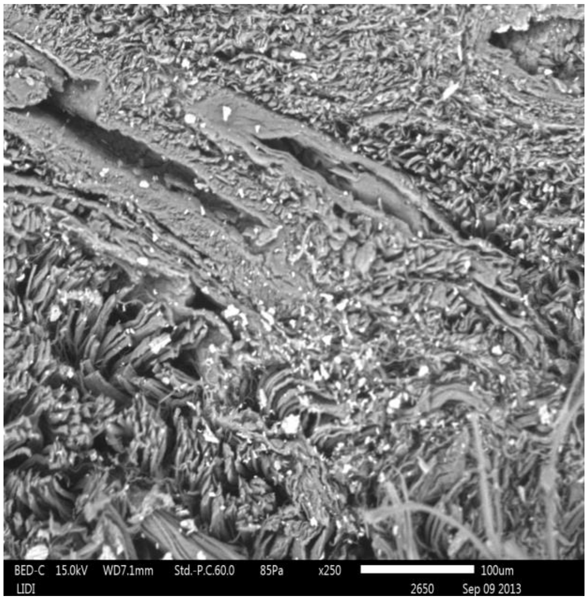


(e) (f)

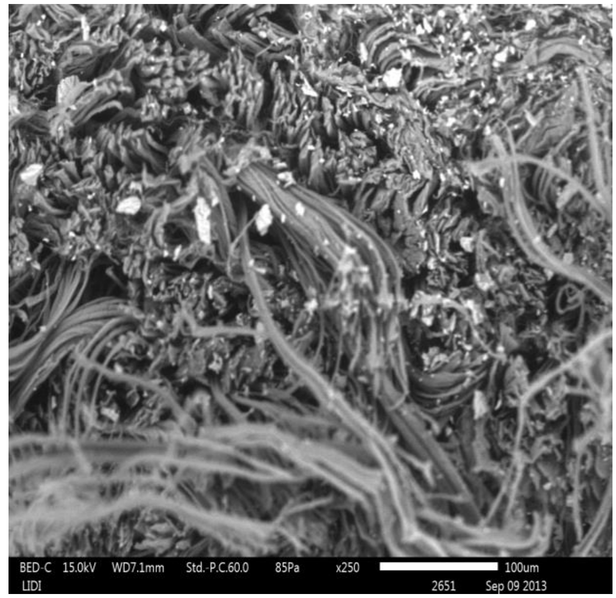
Figure 4.9:- Scanning electron micrographs (50× and 250×), (a) and (b) grain surface of Normal dried crust leather, (c) and (d) grain surface of Toggle dried crust leather and (e) and (f) grain surface of Vacuum dried leather respectively.



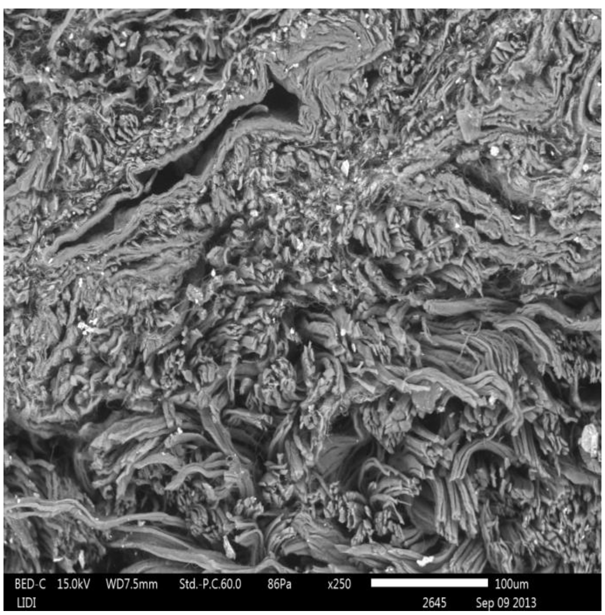
(a) (b)



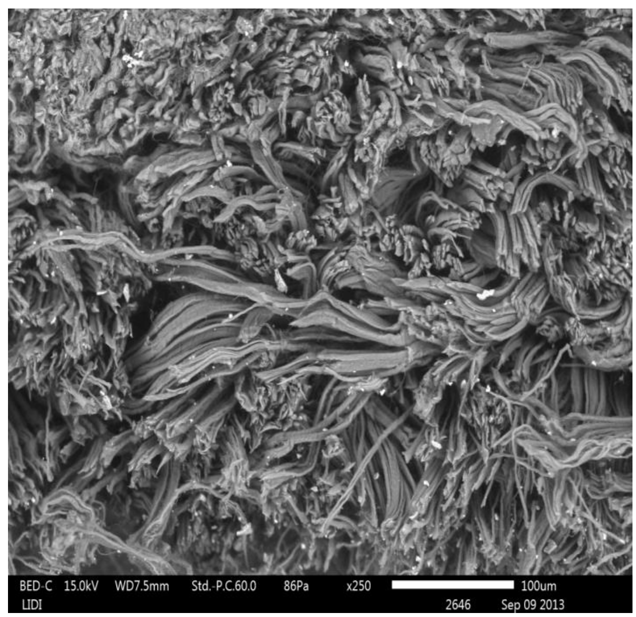
(c)



(d)



(e)



(f)

Figure 4.10:- Scanning electron micrographs (250×), Cross section of, (a) and (b) Normal dried, (c) and (d) Toggle dried, and (e) and (f) Vacuum dried crust leather respectively.

The grain surface and cross section (fibre structure) of normal dried leather shows smooth grain surface and very thick and compact fibre structure with more fibre adhesion respectively

The grain surface of crust leather dried by vacuum drying techniques shows some scratches and damages, this is due to contact between leather and plate which makes the resultant leather flat and thin taking the impress of the smooth plate. The fibre structure of collagen is more weaving and adhesion between fibres in case of normal and vacuum dried leather compared to toggle dried leather. The cross section of toggle dried leather shows less fibre adhesion and more porosity with thin and less compact fibre structure.

4.3. Selecting preferable Drying Techniques for Garment Leather

A significant area yield of 14.5% is achieved by toggle drying techniques at a condition of 55 ˚C and 3.5 hours. Thus, toggle drying techniques produces high area yield when compared to normal and vacuum drying techniques. Literature survey indicates that one of the preferable techniques and widely used for the final drying of garment leathers after staking or dry drumming is toggle drying techniques. The characterization of crust leather at these preferable drying techniques indicates that the moisture content, softness and tensile strength was found to be 13.1%, 3.9mm and 12.6 Mpa respectively which is higher than the standard values. The SEM images also shows that smooth grain surface and more porous with less fibre adhesion crust leather is obtained by toggle drying techniques. Therefore, toggle drying techniques is preferable and feasible drying techniques in obtaining better area yield with achieving desired quality of garment leather.

5. Conclusions and Recommendations

5.1. Conclusions

From the study made on effect of drying techniques on area yield and quality of leather in case of garment leather the following conclusions were drawn.

Area yield of the leathers has been increased in all techniques of drying process and conditions compared to the wet-blue status. The maximum area yield was observed in the leathers that are subjected to toggle drying techniques. This was followed by vacuum drying techniques. The leathers that were subjected to the normal (tension free) drying have been minimum area yield when compared to leather dried under tension. As the period of drying time increase in vacuum drying techniques maximum area yield is obtained. The drum milling process that applied after staking process reduces the area yield of leather in all drying techniques and conditions. It is observed that the area reduction after drum milling is also higher in the drying techniques which provide high area yield. Despite this decrease, it is also seen that the area yields after drum milling process in all the drying techniques are higher than the areas of wet-blue leathers.

The moisture content of leather decreases steadily with increase of drying period, which in turn increases steadily the area yield of leather. It indicates that, the longer drying period causes to remain less moisture in the leather and the lower residual moisture content enables higher area yield. It is found that, the correlation of mean softness of leather and mean tensile strength of leather steadily decreases with the increase in percentage area yield of leather. There is also direct correlation between mean softness and mean moisture content of leather. The overall appearance and properties of crust leather dried by toggle and vacuum drying techniques decreases compared to normal (tension free) drying techniques as drying period increases. The microscopic image shows that some grain surface damages observed in case vacuum dried leather and less fibre adhesion and more porous leather is observed in toggle drying techniques. In general, the result of this study revealed that area yield of leather increases compared to wet blue status in all drying techniques and conditions.

5.2. Recommendations

The following recommendations were made on the subject area of drying techniques on area yield and quality of leather

- The study was conducted for garment leather, further study has to be conducted for other types of leather products i.e. upper and glove leather
- Energy versus cost estimates have to be studied
- Drying process needs a watchful eye; therefore uncontrolled drying process is not advisable
- Optimizing the area without affecting the quality of leather

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Annexes

Annex 1. Daily soaking capacity of Tanning Industries

S.No	Name of Tannery	Soaking Capacity (Pieces / day)		Soaking Capacity (tons / day)	
		Skin	Hide	Skin	Hide
1	China Africa overseas	12000	400	18	10.2
2	Dire Tannery	6,000	600	9	15.4
3	Wallia Tannery Plc.	5,000	1000	7.5	25.6
4	Hafde Tannery Plc.	6000	250	9	6.4
5	Batu Tannery Plc.	2500	1000	3.75	25.6
6	Modjo Tannery S.C	8,000	500	12	12.8
7	ELICO	13,000	1050	19.5	26.9
8	Bahir Dar Tannery Plc.	2000	300	3	11.5
9	Debrebrehan Tannery	6000	0	9	0
10	Addis Ababa Tannery	3,200	900	4.8	23
11	Sheba Tannery	6,000	600	9	15.4
12	Gellan Tannery Plc.	3000	0	4.5	0
13	Friendship tannery	10,000	1000	15	25.6
14	Habesha tannery	4000	0	6	0
15	Ethiopian share tannery	12000	1200	18	30.7
16	Farida tannery	7000	0	10.5	0
17	Hoandachen tannery	10000	0	15	0
18	Dx industrious	8000	0	12	0
19	Kombolcha Tannery	6000	0	9	0
20	New wing tannery	180	10	0.27	0.25
21	Ethiopian share tannery	12,000	1,200	18	30.7
22	Xiang xin xhange	5000	500	7.5	12.8
23	Sun industrial	3000	0	4.5	0
24	United Vasn tannery	5000	0	7.5	0
25	Kolba tannery	6000	600	9	15.4
26	Hora tannery	3,200	0	4.8	0
27	East Africa tannery	8000	0	12	0
	Total	172,080	11,110	258.12	288.3

Annex 2. Trial 1:- Process design for garment nappa processing (weight=3.7 kg)

s.no.	Process	Chemical	Percentage (%)	Weight	Time(min)	Remarks
1	*rechroming*	Water	100			
		Acetic acid	0.5		30	
		Bcs	2		40	
		Chrome syntan	2		30	
		Sodium formate	0.5		30	
		Sod.bicarbonate	0.5		2×10+30	Check PH=4.0 D/W/ pile
2	*neutralization*	Water	150		3×10+30	Check PH=5.6-5.8
		Sodium formate	2			
		Sod.bicarbonate	1-1.5			
		Proval BA	2		30	D/W
3	*Retanning*	Water	100			
		Novaltan MAP	3		30	
		Proval BA	3		20	
		Tanigan BN	4		40	
		Melamine	4			
		Dye leveling	0.25		30	
		Dye	2.5			
		Water	100		15	Check cross section
		Filler	2			
		94S	4		15+60	
		Proval BA	4			
		Ombuslon PM	4			
		Syncurol MAX	4			
		Novaltan MAP	1.5-2.5		30	
4	*Fixing*	Formic acid	3		3×10+30	Check :D/W/pile

Annex 3. Trial 2:-Process design for garment nappa processing (weight=4.78 kg)

s.no.	Process	Chemical	Percentage (%)	Weight	Time(min)	Remarks
1	*Rechroming*	Water	100	4.78		
		Acetic acid	0.5	23.9	30	
		Bcs	2	95.6	40	
		Chrome syntan	2	95.6	30	
		Sodium formate	0.5	23.9	30	
		Sod. Bicarbonate	0.5	23.9	2×10+30	Check PH=4.0 D/W/ pile
2	*neutralization*	Water	150	7.17	3×10+30	Check PH=5.6-5.8
		Sodium formate	2	95.6		
		Sod. Bicarbonate	1-1.5	71.7		
		Proval BA	2	95.7	30	D/W
3	*Retanning*	Water	100	4.78		
		Novaltan MAP	3	143.4	30	
		Proval BA	3	143.4	20	
		Tanigan BN	4	191.2	40	
		Melamine	4	191.2		
		Dye leveling	0.25	11.75	30	
		Dye	2.5	119.5		
		Water	100	4.78	15	Check cross section
		Filler	2	95.6		
		94S	4	191.2	15+60	
		Proval BA	4	191.2		
		Ombuslon PM	4	191.2		
		Syncurol MAX	4	191.2		
		Novaltan MAP	1.5-2.5	110	30	
4	*Fixing*	Formic acid	3	143.4	3×10+3	Check, D/W/pile

Annex 4:- Area measurement of Garment Leather under each dries techniques and conditions in ft^2

Drying techniques	N		Wet blue stage(A_1)	Vibratory staking (A_2)	Percentage increase (D_a)	Drum milling (B)	Percentage decrease (D_b)
Normal drying	3	Min.	3.12	3.23	3.4	2.5	0.9
		Max.	3.66	4.09	10.5	8.5	2.0
		μ ± S.D	3.3 ± 0.3	3.5 ± 0.5	6.9 ± 4.3	5.6 ± 4.2	1.3 ± 0.9
Toggle drying 55˚c and 3 hrs.	3	Min.	2.58	3.12	14.7	11.4	3.3
		Max.	3.23	3.87	17.3	14	3.3
		μ ± S.D	3.0 ± 0.3	3.6 ± 0.4	16.2 ± 1.3	13.1 ± 1.4	3.1 ± 0.3
Toggle drying 55˚c and 3.5 hrs.	3	Min.	3.3	4.0	14.6	12.7	1.9
		Max.	4.1	4.8	21.4	17.5	4.3
		μ ± S.D	3.5 ± 0.5	4.3 ± 0.1	17.8 ± 3.4	14.5 ± 2.6	3.4 ± 1.3
Vacuum drying 60˚c and 60 sec.	3	Min.	3.12	3.44	9.3	7.87	1.34
		Max.	4.1	4.84	15.5	12.4	3.1
		μ ± S.D	3.7 ± 0.5	4.2 ± 0.7	11.5 ± 3.4	9.4 ± 2.6	2.1 ± 0.9
Vacuum drying 60˚c and 90 sec.	3	Min.	3.2	3.9	14.6	11.34	2.1
		Max.	4.3	5.0	17.9	15.8	4.36
		μ ± S.D	3.9 ± 0.6	4.6 ± 0.6	16.1 ± 1.7	12.9 ± 2.5	3.2 ± 1.1
Vacuum drying 60˚c and 120 sec.	3	Min.	3.0	3.6	16.6	12.8	3.3
		Max.	4.2	5.1	18.4	14.4	4.0
		μ ± S.D	3.4 ± 0.6	4.1 ± 0.8	17.5 ± 0.9	13.8 ± 0.9	3.7 ± 0.4
Vacuum drying 60˚c and 150 sec.	3	Min.	2.8	3.2	12.5	9.7	2.8
		Max.	4	4.9	25	17.5	7.5
		μ ± S.D	3.4 ± 0.6	4.2 ± 0.9	18.6 ± 6.2	14 ± 4	4.6 ± 2

Annex 5:- Organoleptic properties under each drying techniques of crust leather

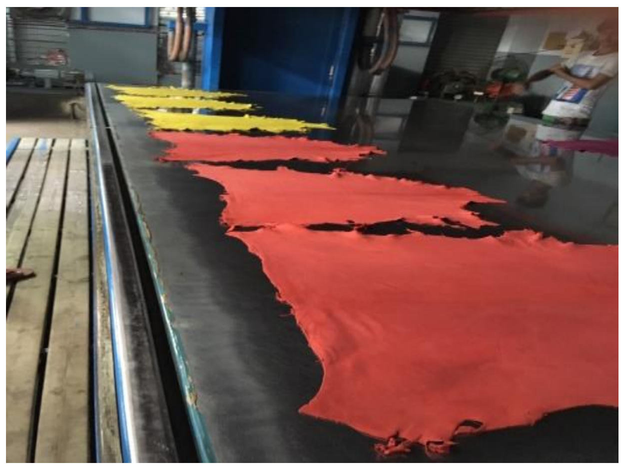
Drying techniques	Smoothness of grain	Grain tightness	Grain break	Uniformity of shade	Overall appearance
Normal drying	8.5	8	9	9	8.6
Toggle drying 55˚c and 3 hrs.	8	7.5	7	8	7.6
Toggle drying 55˚c and 3 .5hrs.	7.5	7	6.5	7.5	7.1
Vacuum drying 60˚c and 60 sec.	8.5	8.5	8	8.5	8.4
Vacuum drying 60˚c and 90 sec.	7.5	8	7.5	8	7.8
Vacuum drying 60˚c and 120 sec.	7.5	7.5	7	7.5	7.4
Vacuum drying 60˚c and 150 sec.	7	7.5	7	7.5	7.3

Appendices

Wet finishing process

Toggle drying

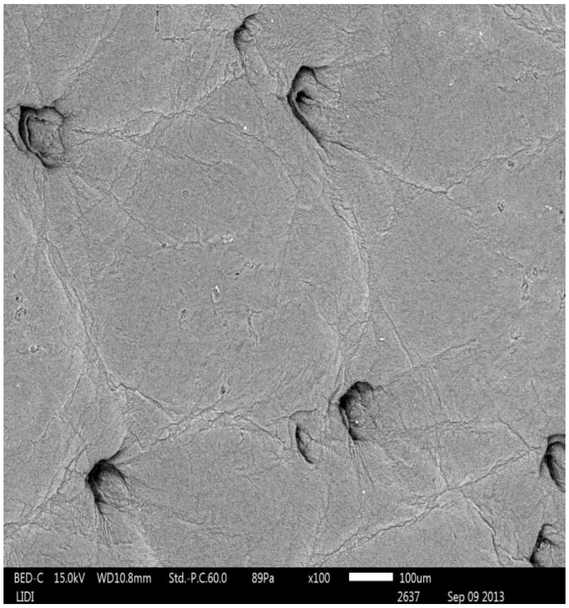
After setting out operation

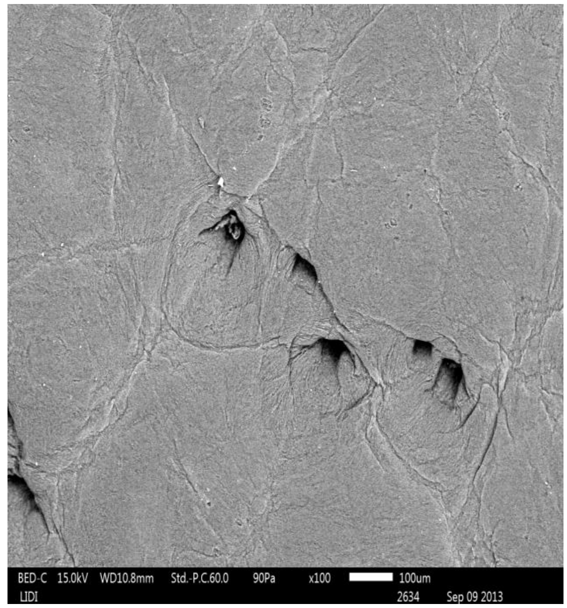


Vacuum drying

Area measuring machine

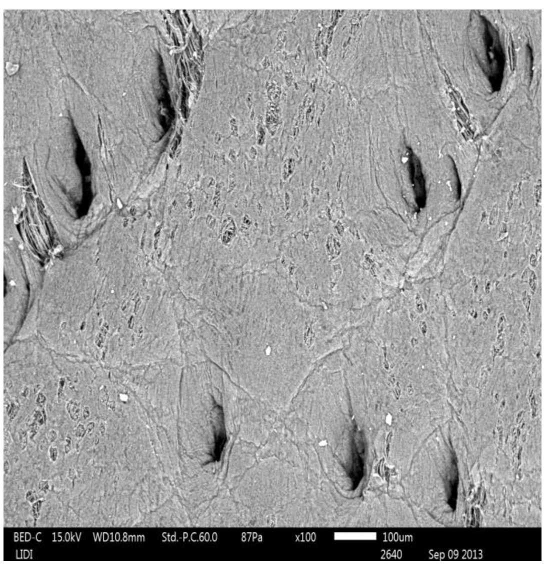
Scanning electron microscope (SEM)

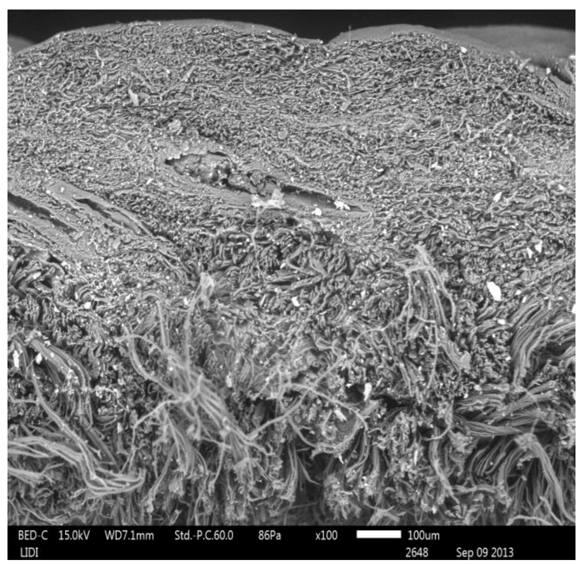




Surface of Normal dried leather

Surface of Toggle dried leather





Grain surface of vacuum dried leather

Fibre structure of Toggle dried leather

Glossary

Crust Leather: - Leather processed to a point when it can be dried: this is usually after post tanning, but may apply to leather given a primary tanning, possible including some lubricant to prevent fibre sticking during drying.

Fat liquoring: - Lubrication of the leather often uses partially sulfated or sulfonated oils, which may be animal, vegetable or mineral in origin. The partially sulf (on) ated sulfo fraction is the emulsifying agent used to carry the unreacted, neutral oil into the leather: it is the neutral oil that performs the lubricating action.

Fixation: - A general term refers to the chemical binding of a tanning agent to collagen.

Leather:- 'Hide or skin with its original fibrous structure more or less intact, tanned to be imputrescible' (British Standard Glossary of Leather Terms, British Standards Institution, BS 2780:1983).

Napa: - General name for soft smooth leather. The term "Napa" particularly is good quality or a special softness.

Neutralization: - Process of raising the pH after main tanning, prior to initiating post tanning reactions, to adjust the charge on the leather. Despite the term, the final pH may be significantly below conventional neutrality (pH=7).

Shaving: - Mechanically cutting through the surface to produce accurate and consistent thickness.

Setting:-Squeezing (sammying) the pelt, but with a spreading action over the grain of surface from the rollers – to flatten the leather and remove creases.

Retanning: - Following the first and main tanning process, usually chrome tanning, the leather is tanned again, typically to modify the handle properties. Any tanning agent may be used for this purpose, depending on the desired leather properties.

Wet-blue: - Chrome tanned pelt: it is wet because it not usually dried before progressing to post tanning and it is blue because of the nature of the chrome complexes bound to the collagen.

Declaration

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

Declared by:

Name: __Endale Dabeta___

Signature: ____________________

Date: ____________________

This is to certify that the above declaration made by the candidate is correct to the best of my knowledge.

Advisor

Name: Prof. Dr. Eng. Belay Woldeyes

Signature: __________________________

Date: __________________________