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Sudan University of Science and Technology
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**Development and Application of Cleaner
Production in Rural Tanneries**

تطوير وتطبيق الانتاج الانظف في المدابغ الريفية

A thesis

Submitted in fulfillment for the requirements of PhD degree in leather
engineering

By

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Dedication

I dedicate my thesis work to my loving parents whose words of encouragement have pushed me to success.

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Abstract

Sudanese rural tanning is an inherited craft. The methods and the indigenous materials employed by the rural tanners have remained unchanged for a long time. This is due to poverty, illiteracy, poor communications and lack of access to modern scientific technologies of leather production. As a result, the leathers produced by rural tanners are hard, crusty, liable to crack, tear. Moreover, the process period is long. The objective of the study is to investigate the possibilities of adoption of modern tanning methods to rural tanning with appropriate modifications (1) to speed up the process, (2) take out some of the hard manual work, (3) improve the quality of the produced leathers, (4) increase the production of the rural tanneries and (5) direct rural tanners toward cleaner production. For this purpose, a hand-operated drum was designed to carry out all wet processes through soaking to retanning. Modern tanning materials were introduced in all processes. Little amounts of chromium were used as a pre-tanning agent. The optimum amount of chromium was found to be 3% (based on the fleshed weight) which gave acceptable shrinkage temperature and good physical properties. After developing the tanning recipe and selecting the optimum chrome powder to be applied by rural tanneries, recycling of spent liquors was carried out to (1) minimize the environmental impact and to (2) reduce the production cost. Considerable savings on chemicals and water were obtained. Rural tanneries play a vital role in national economy and they have to be improved. Rural tanneries can create employment opportunities for a large number of people if attention has been paid for revamp and modification.

المستخلص

الدباغة البلدية مهنة متوارثة في السودان. الطرق والمواد المحلية المستخدمة بواسطة الدباغين البلديين لم تتغير منذ زمن طويل. ويعزى هذا الي الفقر والامية و ضعف وسائل الاتصال وعدم مواكبة التكنولوجيا الحديثة في صناعة الجلود. و نتيجة لذلك فان الجلود المنتجة بواسطة الباغين البلديين صلبة وقشرية وقابلة للكسر والقطع. بالاضافة الي طول فترة العملية. لذلك تهدف هذه الدراسة الي بحث امكانية تطبيق اساليب الدباغة الحديثة علي الدباغة البلدية مع بعض التعديلات وذلك (1) لتسريع العملية (2) والتقليل من بعض العمل اليدوي الشاق (3) وتحسين من جودة الجلود المنتجة (4) وزيادة انتاج المدابغ البلدية (5) وتوجيه هذه المدابغ نحو الانتاج الانظف. لهذا الغرض تم تصميم برميل يعمل يدويا لاجراء جميع العمليات الرطبة من مرحلة البلل وحتى مرحلة اعادة الدباغة. كما تم ادخال مواد الدباغة الحديثة في كل هذه المراحل. وكذلك استعمال كميات قليلة من الكروم كمادة دابغة اولية ووجد ان نسبة 3% (علي اساس وزن الجلد بعد ازالة اللحمية) من بكرة الكروم هي النسبة المثلي للدباغة البلدية لانها اعطت درجة انكماش وخصائص فيزيائية مقبولة للجلد. بعد وضع وصفة الدباغة المناسبة واختيار نسبة الكروم المثلي للدباغة البلدية ، تم تدوير واعادة استخدام المخلفات السائلة الناتجة من كل المراحل من مرحلة البلل وحتى مرحلة اعادة الدباغة . وقد تم توفير قدر كبير من الماء والمواد المستخدمة. تلعب المدابغ البلدية دورا حيويا في تنمية الاقتصاد الوطني لاتها تقوم بدباغة عدد كبير من الجلود الخام. لذلك لابد من تحسينها. بالاضافة الي ذلك فان المدابغ البلدية يمكن ان تخلق فرص عمل لعدد كبير من الناس اذا ما وجدت الاهتمام بالتحديث والتعديل.

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Introduction

1.1 Leather

Leather which has been used by man for many purposes for thousands years, is remarkable for possessing a combination of properties to be found in no other natural or man-made materials. It can be so hard and tough that it requires working with a saw or lath; yet it can also be as a fine textile, a fit material for needlewomen. Leather is not only strong, durable (when properly prepared, it will resist decay for centuries) and flexible; it has a unique porous structure which enables it to “breathe” that is to permit the passage of air and water vapour through it. It can be easily worked, cut, joined, stitched, embossed, dyed and gilded. When it is cut, the edge does not fray a characteristic which for some purposes make it superior to woven materials. In the hand of a craftsman, leather will yield articles of use and arrangement which cannot be produced in any other way. [1]

During the present century many attempts have been made to produce substitutes for leather such as impregnated textiles, rubber and plastic materials. Although these products have found wide use in the manufacture of footwear and other articles of everyday use, they have not been able to reproduce the particular properties of leather.[1]

Visco-elasticity and pore size distributions are two important properties of leather that have rendered it a unique material. The ability to breathe and readjust to volume fluctuations of the foot has made leather a unique material of choice in footwear industry.[2] Moreover, aesthetic appeal, feel, texture, toughness, non-flammability, resistance to heat, impermeability to water, and permeability to air and water vapour are other distinctive

properties [3]. Major product applications for leather are leather goods, garments, and footwear. More than 60% of the leathers produced are being converted to footwear [4].

1.2 Tanning

This versatile material is obtained by the conversion of hides and skins through a treatment process known as tanning. The tanning process involves specific reactions among carboxylic groups of the protein fiber network of animal skin (collagen) and tanning agents.[5] Due to these reactions the putrescible hides and skins of animals are converted into non- putrescible leathers with definite physical and chemical and biological properties so that they can be used to produce various leather products [6]

There are two ways of tanning one is old method, in which plant is used as tanning materials which we call “rural tanning” and the other is the one in which chemicals and machines are used instead of manual working and this is normally done in the modern factories [7]

Various techniques were employed over time to preserve and condition hides and skins. These included the use of animal fat, brain and other substances which were used purposely for softening and arresting putrefaction. The different techniques and methods continued until “vegetable tanning” using plant parts such as leaves, barks and fruits containing tannins was discovered [8]. With increasing demand for aesthetic appeal and softer types of leathers as well as the need for reduction in process time and to increase the production, modern tanning techniques employing the use of chemicals had to be developed.[2]

The discovery of chromium as a tanning material is a landmark in leather processing. Although many alternative mineral tanning materials have been

known, chromium was used in the manufacture of light and softer types of leathers giving leather with good physical properties [2].

Leather processing has undergone significant changes since 1980s when the availability of inexpensive automatic and manual machines began a radical changes in the touch, appearance and finishing of leather. Pressure associated with increase competition, rapidly changing economic conditions, more stringent environmental regulations and the need for more flexible, yet simpler processes have given leather processing technologist an expanded role in design and operation of processing tanneries.[7]

Clean production, high performance, high quality and safe protected environment play a critical role in making tanneries economically competent. Now and in the future there will be an expanded use of recycling systems of all wet processes from soaking through retannage without loss of quality. The rationalization of recipes should go parallel to recycling with no waste of chemicals and water[7]

1.3 Modern tanning method

The production processes in a modern tannery can be split into four main categories: hide and skin storage and beamhouse operations, tan-yard operations, post-tanning operations and finishing operations. After the hides and skins are flayed from the animal at the abattoirs, they are delivered to the hide and skin market, directly to the tannery. Where necessary, hides and skins are cured before transport to the tannery in order to prevent putrefaction. In the tannery, hides and skins can be sorted, trimmed, cured and stored. In the beamhouse of a tannery, the following processes are typically carried out: soaking, unhairing, liming, fleshing and splitting. The main processes, carried out in the tan-yard are: delimiting, bating, pickling, and tanning. Sheepskin tanneries may degrease the skins prior to, or after,

pickling or after tanning. The tanned hides and skins are tradable intermediate products (wet-blue) as they have been converted to a non-putrescible material called leather. Processes typically carried out in post-tanning operations are: samming, setting, splitting, shaving, retanning, dyeing, fatliquoring and drying. At this stage the leather is called 'crust'. Crust is also a tradable intermediate product. Finishing operations include several mechanical treatments as well as the application of a surface coat. The selection of finishing processes depends on the specifications of the final product. Tanneries generally use a combination of the following processes: conditioning, staking, buffing, applying a finish, milling, plating and embossing [9].

1.4 Sudan leather industry

Modern mechanized tanning started in 1945 by establishment of the Omdurman military factory, followed by the Khartoum tannery in 1962, the White Nile tannery in 1975 and continued. Now there are about 12 modern mechanized tanneries, and 290 traditional tanneries. The former are large capacity tanneries, which use mechanical methods, imported chemicals and new technologies, while the latter are tanneries of low capacities use local materials, manual production and produce less quality leathers mainly for the local market[10].

Sudan is one of the Largest Countries in Africa and rich in live stock population. It is estimated to be 104 million heads of Cattle, Sheep, Goats and Camels. Statistics of annual availability and animal population estimated from 1990 to 2010 as total of 140,000000 heads of sheep, goats, cattle and camels. The estimated annual production of hides and skins are 20 millions. There are about 20 working tanneries most of them are small tanneries. Most of the tanneries are facing problems such

as low capacity utilization, high cost of production, non-availability of liquid money-and low quality of produced leather; they are processing a large number of raw hides and skins. The rural tanneries are tanning low quality raw materials. The leathers produced in the modern and rural tanneries satisfy the local market and they export part of their production as semi processed leather[11].

1.5 The study problem

The craft of tanning has been inherited from father to son. The methods and the indigenous materials employed by the rural tanners are the same and have remained unchanged for a long time. This is due to poverty, illiteracy, poor communications and lack of access to modern scientific technologies of leather manufacture. As a result, the leathers produced by rural tanners are hard, crusty and liable to crack and tear and the production cycle is long.

1.6 The importance of the study

The importance of the study came from the little information available about this craft. Moreover, rural tanneries play a vital role in national economy; they process a large number of low quality raw materials besides good ones and reptiles. This low quality hides and skins are not processed by modern tanneries because they probably be damaged during processing especially in fleshing machine and if not be processed cause environmental problems and it is also a great loss of valuable materials. Furthermore, rural tanneries can create employment opportunities for a large number of people if attention has been paid to them.

1.7 General objectives

- a. Improvement and upgrade of rural tanneries
- b. Adoption of cleaner production in rural tanneries

1.8 Specific objectives

- a. To improve leather quality
- b. To ease the process
- c. To shorten process time
- d. To protect the environment
- e. To create employment opportunities
- f. To improve rural tanner's working condition

1.9 About the study

The study was divided into three parts; the first part was to collect and document information about rural tanning in Sudan. The information was collected by interviewing 10 tanners in Khartoum state using a structured questionnaire from 5th to 11th of June 2013. Data was also collected by direct observation, Photographs and films captured from the site. These information were in chapter two under the title "rural tanning in Sudan". The second part is to investigate the possibilities of mechanization rural tanneries to ease the process, shorten the process time and to enhance the quality of leathers. For this purpose a hand- operated drum was designed to carry out all the wet processes from soaking through to re-tanning. The third part dealt with the possibilities of improving the quality of leathers by using of the modern materials and methods to replace the indigenous materials and methods those were used. The fourth part was to investigate the possibilities of adoption the recycling of the spent liquors in rural tanneries in order to direct them towards cleaner production.

Literature review

2.1 Raw materials

Hides and skins are the raw material of leather manufacture. In the tanning trade the outer coverings of large domestic animals are called “hides”. Hides are larger in size, thicker in substance and heavier in weight than skins such as cowhide, buffalo hide, horsehide etc.

The outer coverings of small domestic animals and wild animals are called “skins”. Skins are smaller in size, thinner in substance and lighter in weight than hides such as goatskin, sheepskin, tiger skin, crocodile skin etc[6].

The surface of hides and skins contains the hair and oil glands and is known as the grain side. The flesh side of the hide or skin is much thicker and softer. The three types of hides and skins most often used in leather manufacture are from cattle, sheep, and pigs[12].

Hides and skins have the ability to absorb tannic acid and other chemical substances that prevent them from decaying, make them resistant to wetting, and keep them supple and durable[13].

2.1.1 Structure of hides and skins

All mammalian hides and skins are more or less similar in their structure. They have a very complex and intricate structure. They consist of three layers namely; the epidermis, the corium or dermis and the hypodermis which are distinct both in structure and origin[1].

The epidermis is the outer layer of the skin. It is composed of the protein keratin which belongs to the same group of keratinous substances as nails, claws, hooves, scales and feathers. The cells of the innermost layer of the epidermis contain pigment granules which give color to the hairs and the skin[1].

The corium or dermis is the true skin and is the main portion of the integument, the natural covering which is subsequently converted into leather. The dermis is composed mainly of connective tissues fibers. Three different types of connective tissues, collagen, elastin and reticulin are found in the dermis. Collagen is largest portion and the chief leather forming constituent [1].

The hypodermis or subcutaneous tissue is the loose connective tissue which joins the corium to the underling part of the body it consist mainly of collagen and elastin fibers. These are loosely arranged and they contain the adipose tissue which is the seat of the fat deposits. Together these tissues are what the tanner calls the flesh. It is removed mechanically in the fleshing operation before tanning[1].

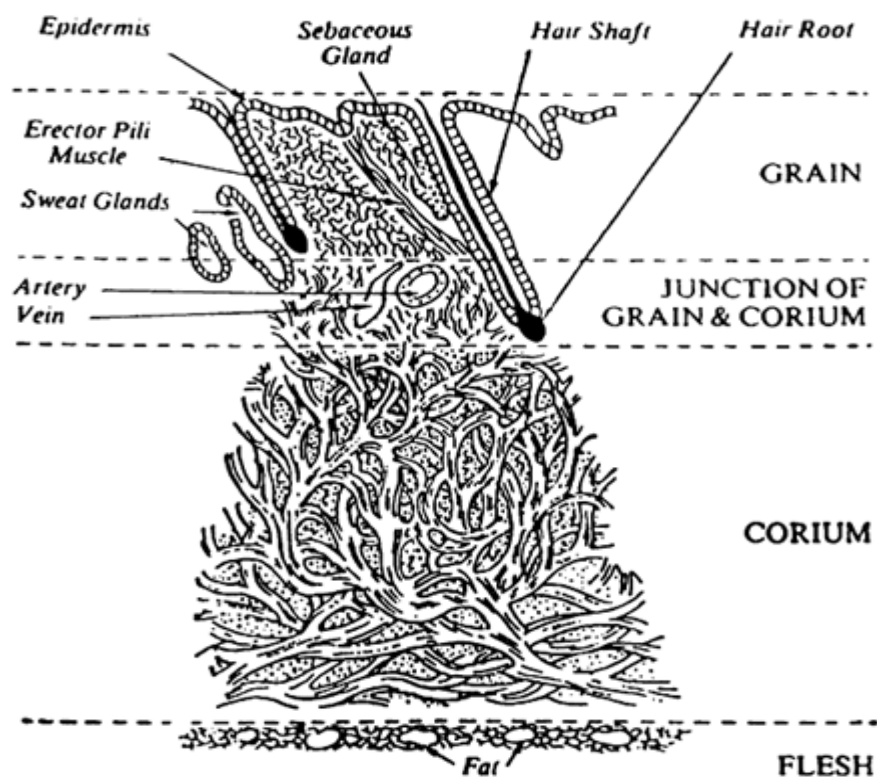


Figure 2.1: Structure of an animal skin[14]

2.1.2 Chemical constituents of hides/skins

The chemical constituents of hides and skins can be divided into four main groups such as:

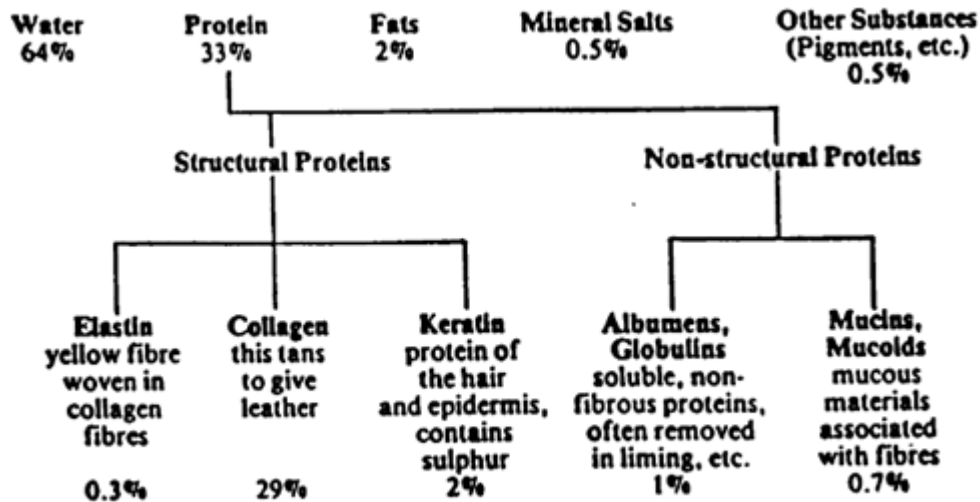


Figure 2.2: Approximate composition of a hide [14]

The relative proportions of these materials vary from skin to skin depending on the species, age, breed, feeding and other habits of the animals. For example, fatty matters vary according to species such as: cattle, calf 2.0 %, goat 2.0-10 % and sheep 5.0-30 %.[14]

2.1.3 Types of raw materials

Hides and skins are divided into four types of raw materials. And this is the first process in whole tanning operations which is called “sorting or selection”

Hides and skins from freshly slaughtered animals are termed “green” they must reach the tannery within the shortest possible period and certainly within few hours.

Dry salted hides are preserved by a combination of two processes, first by salting and then by drying. They are easier to soak.

Air dried goods are hanged on the wall or on the wood or glass board until they are dried, they are called air dried goods.[14]

Ground dried goods in drying they have been invariably dried on the outside, while the inside is still wet and liable to putrefaction, they will hardly absorb water and they are difficult to be soaked. This method of drying is not recommended and it may lead to “case-hardening or sun blister”, horny and pipey leather. [14]

2.1.4 Quality of hides and skins

Many factors influence the growth and quality of the skin and hide of any animal, whether wild or domestic. The breed and origin of the animal, its mode of life and its food, its general condition, its age and sex and the purpose for which it is bred affect the growth and properties of the skin during the animal’s lifetime. So every care must always be taken to produce and to select for tanning a raw material which is as free from defects as possible. Defects which influence the quality of raw hides and skins are classified in two groups: “anti – mortem defects” and “post- mortem defects”. Anti- mortem defects are damages caused on the living animal and may be caused by parasites, diseases, old age, and mechanical means [1].

2.1.5 Curing of hides and skins

Curing means temporary preservation of hides and skins. It is not always possible to send the hides and skins to tannery immediately after flaying because the source of collection and the tannery are not generally located in the same area. The time gap between the flaying operation and the start of tannery operations vary and may be longer. Failure to flay immediately after slaughter and any delay in the start of the curing, allows post- mortem

changes to diminish the value of the hide or skin. This is initially seen as “hair slip” leading subsequently to putrefaction within hours depending on the climate.[6]

The majority of hides and skins of the world are cured by the application of common salt and the final cured materials are known as “wet- salted” hides and skins. Such hides and skins produce very high quality leather, if curing is carried out properly. Wet-salted hides and skins are produced by either simple salting or simple brining.[6]

2.2 Pre- tanning operations

In this stage hides and skins are firstly sorted and weighed to pass through these processes: soaking, unhairing, liming, fleshing, splitting, deliming, bating and pickling.

2.2.1 Soaking

Soaking is the first process of leather manufacture. It is essential to soak the skins well, if one is to obtain uniformly tanned and dressed leather of good strength and flexibility. It is simply done by immersing the hides and skins in a pit full of water. The aim of soaking is to allow the skin to re- absorb any water which may have been lost after flaying in the curing process or during transport. This absorbed water re-hydrates any dried inter-fibrillary proteins, loosening its cementing action on the fibers. The collagen fibers and keratin cells of the hair and epidermis also take up water and become more flaccid and flexible. The length of time and the conditions required depend on the size and thickness of the skin, the curing method used and often greasiness of the skin[14].

To prevent bacteria from attacking the soaked hides and skins, disinfectants (bactericides), should be added to the soak liquor. The most common bactericides used are sodium hypochlorite and sodium trichlorophenolate. Other

materials which may be used under some circumstances are sodium pentachlorophenate, formic acid, and many proprietary products. [14].

Speeding up the water uptake of the skin reduces the chance of putrefaction. Also very hard hide need mechanical assistance to help the softening. Mechanical assistance can be done either by hand such as trampling, working over a beam, kneading or flexing the skin in the water, or vigorously circulates the water round the skin. For this purpose paddles and drums are commonly used. [14]

2.2.2 Unhairing and liming

The aim of unhairing and liming is to destroy or soften the epidermis whereby the hair or wool is loosened, to destroy sweat glands, nerves, veins and blood vessels in the hide substance and to some degree the inter-fibrillary tissues which keep the fibrils together, to open and plump the fibers and fibrils to facilitate the penetration of the tanning materials, to cause swelling and plumping of loose meat and connective tissues on the flesh side and to facilitate its subsequent removal by fleshing process. Unhairing can be done by sweating, enzyme, painting and liming [14]

2.2.3 Mechanical operations after liming

After liming, if the hair has not been removed by the liming process, it must now be removed either by unhairing machine or by a hand knife. Hand unhairing is laborious and only used for hides and skins which for some reasons cannot be machined. Then the skins must be trimmed, and fleshed.

Trimming is the removal of uneconomic edges, pieces of flesh, and so on by using a hand knife. Fleshing is the removal of the hypodermis either by hand or by fleshing machine or by hand.[14]

2.2.4 Deliming

After liming the unhaired and fleshed hides and skins, known as pelts, are taken for the next operation called deliming. The object of this deliming operation is to remove the lime and other alkalies from the limed pelt used in liming, either by repeated washing in water to remove free alkali or by chemical treatment to remove combined alkali or by both. The removal of alkali from pelt before tanning is important and essential for the production of good quality leather [6].

The degree of deliming; partial or complete depends on the type of leather to be produced. Unless the lime is removed, the finished leather will be hard and the grain will be brittle and discolored. The aim of deliming is to obtain a flaccid pelt soft and fallen by complete removal of lime. Also to produce firmer leather such as sole leather by partial removal of lime [1].

2.2.5 Bating

Bating is the treatment of pelts with a warm infusion of dog, hen or pigeon dung. The objects of this process are to produce soft, smooth and pliable leather. And to obtain a certain degree of stretch, suppleness and smoothness for shoe upper, gloving, clothing and other light leathers. Moreover, to remove the plumpness caused by the lime process to ensure production of a soft pliable leather.[6]

Dog or pigeon dung is unpleasant to use and difficult to control thus, in recent time, it has been replaced by synthetically produced material, such as the patented pancreol, peroly, cutrilin, orpon and similar products. These materials are commercially prepared bate made of animal juice or minced pancreas. In rural tanneries, hen or pigeon dung is still used for bating process.[6]

The amount of bate which should be used depends on the type of skin, but as a rule it does not exceed 0.5% of the weight of the pelt. It is always used in water at a temperature of 32 to 35°C. [6]

Degraded protein is normally solubilised by pancreatic enzyme action at pH 8.2 -8.4. The process can be assisted by stirring, paddling or drumming. The completion of the process is checked by gathering the skin into the form of a bag which contains some of the bating liquor and air the bag is then squeezed. If the air passes through the pores of the skin, bating is complete, if not bating should continue. Another test is to press the sump firmly against the grain side of the skin if the sump impression remains, bating is complete. The skins are then washed in water before they are tanned and a small amount of boric acid may be added to the water to ensure neutrality. Prolongation of enzyme action further loosens the fiber structure.

These pre-tanning processes influence greatly the character of the resultant leather. Throughout this period the stock is still a heat sensitive biological tissue and temperatures should not exceed 37°C [6].

2.2.6 Pickling

Pickling is the treatment of delimed, bated and scudded pelts with a solution of salt and acid which must be carefully carried out to suit a particular tannage. The main function of salt in the pickle is to avoid the pelts from swelling in the acid condition. The pickle acid shifts the equilibrium in favour of the positive charges in the amino sites. If there would be no salt in the pickle, this would generate repulsive forces within the structure, forcing the polypeptide chains away from each other. This would then create empty spaces in which water would penetrate rapidly. The very strong osmotic pressure would then destroy the pelt from within. Salt avoids this swelling process in the pickle by reversing the osmotic pressure. In a good pickle,

these two forces are balanced out. Pickle salt has a hydrotropic effect on the pelt that is increased substantially at a pH under the iso-electric point of 5.5. This effect is very important to give the leather inner softness, but in excess can lead to loose structured leather. Sulfates in pickling and tanning can have a positive effect on the tightness of the final leather since it stabilizes collagen[15].

The carboxyl groups are the important binding sites for the mineral tanning agents (like chrome). These binding sites have to be prepared for the tanning step and the collagen has to be activated. This is achieved by pickling process right before the tanning take place. The delimed or bated skin at pH 8.2 -8.3, must be adjusted to a suitable acidity for tannage by reduction of the pH at least to the iso-electric point (according to the type of tannage) and there are various processes for achieving this end.[16]

For chrome tannage the pH is lowered to a pH value of 2.5 and due to the low pH-value the collagen starts to swell. It is necessary to prevent this swelling and this is done by the addition of common salt to the acid liquors. If salt is not added, hides or skins will swell up giving hard, firm or even brittle leather after tannage. Also, for chrome tannage, if the skins are pickled to a low pH of 2, one gets a mellow light chrome tannage and if to a pH of 5, one may get rapid surface fixation (astringency) with little penetration and almost raw skin inside. The suitable PH for chrome tannage is between 2.8 to 3. Pickling is also used to facilitate the penetration of the tanning agents, for chrome tanning, it prevents too rapid fixation of chromium and ensures an even penetration of the chromium salts. [16]

Vegetable tannage may be done on pickled skins. Where pickling is undesirable, the bated or delimed hides or skins may be further acidified down to pH 4-4.5 either by naturally occurring weak acids in old tan liquors,

the addition of weak acids or by the use of slightly acid syntans in the absence of salt, because such acid syntans may be classed as none swelling acids, although they also have a slight tanning action. [14].

2.2.7 Degreasing

Degreasing is the removal of grease from the skin. Some sheep and other skins which are particularly greasy, and which have been given a good pickle, may be degreased at this stage before tannage. Extensive amount of grease in the skin may interfere with uniform penetration of tan or dye, cause difficulties in finishing processes and show as dark, greasy patches in the finished leather. Degreasing greasy skins before tannage is particularly important before chrome tannage, where chrome salt can react with some grease to produce chrome soaps, which are difficult to be removed [14].

The drained, damp pickled skins are drummed with half their weight of paraffin for two hours. A small amount of wetting agent may be added to the paraffin (e.g. 5% of non ionic wetting agent). At the end of the paraffin degreasing, the surplus greasy paraffin is drained off, then the skins are rinsed in a 5 percent salt solution at 27°C for 30 minutes. Afterwards they are well drained and drummed in 200 percent water and 8 percent salt and the tan is added directly to the liquor. Salt solution must be used, as water alone would result in acid swelling. The wash liquor is drained of, the emulsified greasy paraffin giving it a white milky appearance. This washing with salt water may be repeated until the wash liquor remains clear. [14]

Degreasing process can be aided by increasing temperatures which are usually attained merely by the mechanical action of running the load in the drum or by worming up the paraffin by steam, but the skin temperature must not exceed 32°C or the skin will shrink and suffer serious fiber damage.

Also, mechanical action is needed to break up the patches of grease into drops, etc to form an emulsion [14].

2.3 Tanning operations

Tanning is the fundamental stage, which gives leather its stability and essential character[17].

Tanning is defined as the conversion of the protein of the raw hide or skin, a highly putrescible material into leather a stable material which will not putrefy, resistant to heat, sweat, moisture, etc. and can be used in the manufacture of a wide range of products.[18]

There are many tanning materials produces leather with different characteristics, the method of using these materials, influencing the resultant leather. The most common tanning agents used is trivalent chromium and vegetable tannins extracted from specific tree barks. Alum, syntans (manmade tanning agents), formaldehyde, glutaraldehyde and heavy oils are other tanning agents.[19]

The tanning agent blocks carboxylic groups, in the case of mineral tanning agents, or the amine groups, in the case of vegetable tanning agents, and joins the proteinic colloid thus increasing the cross-linking of collagen fibres[20].

Most tannages consist of the following steps:

- a. A suitably prepared stock at a pre-determined pH.
- b. Addition of the tanning materials, preferably in one feed, to a measured float. For pickled stock the float contains sufficient salt to prevent swelling.
- c. Complete diffusion of the tanning agent, followed by alteration of pH and/or temperature to ensure combination.

- d. At the end of the process simple check are available, such as shrinkage temperature determination, visual examination of penetration in the thickest areas of the stock, and the PH of the exhaust tanning liquor.

Rapid fixation of vegetable tan is favoured by acid conditions, e.g. (low pH) low non – tan content, etc, whilst in the mineral tannages rapid fixation is caused by higher pHs (5-7) and low pHs will give penetration [14]

2.3.1 **Chrome tanning**

The salts of many metals have the capacity to combine with skin protein but, only a few makes satisfactory leather. The most commonly used is chromium sulphate in chrome tanning process because of the excellent properties of the chromium compounds that it renders to the leather along with simplicity of operation. It is very difficult for a single tanning agent to match chromium tanning salt with respect to its hydrothermal stability[21]. Chrome tanned leathers are characterized by their light weight, high tensile strength[19], top handling quality, high hydrothermal stability, excellent user properties versatile applicability[22, 23], a good mechanical resistance, and an extraordinary dyeing suitability[24]. Low cost of applications, colour of the leather and resulting stability are added advantages of using chrome tanning[25].

Although there are some disadvantages of chrome tanned leather, such as lack of fullness and coarse nap especially in suede leather, chrome tannage is still the most widely used method in the tanning industry[19].

Chromium ores occur naturally in many parts of the world. After heating with alkali and purifying, they are marketed in crystalline forms as sodium or potassium chromate K_2CrO_4 (yellow) or dichromate $K_2Cr_2O_7$ (orange).

Most commercial chrome tanning products are used in powder form; they contain about 25% Cr_2O_3 of 33% basicity. Basic chrome sulphate liquors are also used. These liquors are prepared by reducing the sodium or potassium dichromates to sulphate $Cr_2(SO_4)_3$ in the presence of sulphuric acid. As a rule reduction is carried out using sulphur dioxide (“sulphur dioxide reduced”) or technical sugars or glucose (“glucose reduced”).[14]

Increasingly today the preparation of chrome tanning liquor and powder is carried out by specialist firms and they are available as closely controlled standard products. They consist essentially of a solution of basic chromium sulphate in water. The exact nature of the chromium compounds formed depends on the method of preparation, so the “strength” of chrome liquor is defined as the percentage of weight of chromium or expressed as chromic oxide Cr_2O_3 ; traditionally the most usual strength was 11% chromic oxide, but stronger liquors containing 15% are now becoming more common. Most commercial liquors are prepared at either 33% or 50% “basicity”. [14]

Chrome liquor can be converted to a solid form by spray-drying. The water is evaporated and leaves a “chrome powder” of fine green crystals, containing about “26% chromic oxide”. This powder is cheaper to transport and it is easily dissolved, the tanner can make up his own chrome liquors as required. As with liquor, the powder may be glucose or sulphur dioxide reduced and is available in various basicities. The corresponding chrome offer in tanning is usually 1.5 -2.5% Cr_2O_3 on pelt weight. Under standard condition 60-80% float on pelt weight is used. [14].

Chrome salts are less astringent under very acid conditions and as the acidity is neutralized (i.e. the pH rises), they combine or fix more rapidly and readily. Chromium sulphate hydrolyses in water to produce sulphuric acid and a basic chromium sulphate. Such solutions may have low pH (2-3) and slight tanning power. By adding an alkali (soda ash, sodium bicarbonate, etc.) this acid is neutralized. However, the chromium sulphate will tend to hydrolyze further and produce more acid and more basic chromium sulphate to counterbalance this disturbance. Therefore, increasing amount of alkali, increase the amount of basic chromium sulphate, and consequently increase the liquor's astringency or tanning power. Further, chromium sulphate may have different degrees of basicity depending on the amount of alkali added. With the further addition of alkali, a stage is reached when the chromium sulphate can become no more basic, and indeed become chromium hydroxide, a pale-green insoluble precipitate with no tanning power. This is said to be 100% basic and the intermediate basicities up to this stage are expressed as a percentage of this (schloremmer scale). Schloremmer basicity is defined as the number of hydroxyl groups combined with the one unit of chromium, expressed as a percentage of the total number that could combine to form chromium hydroxide.[14]

From the above it is noted that, as the basicity increases, so does the astringency. This occurs up to about 66% basicity, when the basic salt becomes insoluble in water and hence useless for practical tanning. The addition of too much alkali relative to the amount of chromium sulphate causes complete loss of tanning power, as the chromium is precipitated as 66% up to 100% basic salts, causing stains on the leather and uneven dyeing. For mellow or gentle chrome fixation with good penetration, basicities of about 33% are chosen. For rapid fixation, i.e. high astringency basicities of

40 – 50 % are used. So that it is important in chrome tannage to do the following:

- a. The alkali (soda ash, caustic soda, borax, etc) should be dissolved in water and added slowly to the chrome liquor with very thorough mixing. Because if a high local concentration of the alkali occurs it will cause local precipitation of the chromium salt which is very difficult to re dissolve.
- b. The acidity of the stock must be correctly adjusted before the tanning process starts, because the acidity or alkalinity of the hides or skins as they go into the chrome liquor will affect its basicity and hence it's tanning power, as demonstrated by the following example using 33% basic liquor.[14]

Limed skins (pH12) into chrome liquor will precipitate the chrome as chromium hydroxide, reduce tannage and give hard leather. Delimed or bated skins (pH 8) into chrome liquor will increase basicity of chrome salts and may precipitate them as a sludge or give a very a stringent surface tannage only with a case hardened, drawn or linked wrinkled grain effect. Drenched skins (pH 4.5) may cause only a slight increase in the basicity of the skins and give quite a good, full tannage; there may be slight drawing or wrinkling of the grain. Pickled skins (pH 2-3) cause no increase in basicity of the chrome liquor and favour good penetration and a smooth, level flexible grain. The more acid pickled skins (low pH) will reduce the basicity of the chrome liquor to less than 33% and thus reduce its tanning power. It is obvious from the above that the pickling process is a necessary preliminary to chrome tanning, which is normally commenced with the hide and skin surface at pH's between 2-3 and basicities between 30-40%.[14]

The process is normally carried out in paddles or drums. After the chrome has penetrated thoroughly and uniformly, the basicity of the liquor is increased by the controlled addition of alkali in order to fix the chrome. This is known as basification and must be carried out very carefully to avoid the danger of precipitation of the unfixed chrome still in solution. So, it is a good practice to carry out “a precipitation figure test” on the used chrome liquor. An alkali solution is added to a known quantity of the chrome liquor until precipitation occurs. This indicates the amount of alkali which if added to the liquor, would just cause precipitation. It is then usual to add only half this amount to be of the safe side. The feel and handle of the leather may be varied by the basicity and condition of the chrome tannage. The degree of tannage varies accordingly to requirements, but modern practice calls for the tanned leather to withstand a shrinkage temperature of 97-100°C in the boiling test.[14]

Note that the more acid pickled surface layers, give less chrome fixation and allow the chrome to penetrate rapidly to the corium, which is more alkaline and therefore fixes more chromium this tend to give a flat, flexible grain and a firmer centre. The chrome is added in two portions, the first one to get a mild tannage and fix the grain and fiber structure, whilst the second portion is of high basicity to complete the tannage and give full resilient leather.

It is usual to check the degree of tannage by measuring the resistance of the leather to hot water commonly referred to as shrinkage or boiling test (Ts). A small piece of the wet leather is cut off and its shape outlined with a pencil on a paper. It is then immersed in water, which is slowly heated with constant stirring. When the predetermined temperature has been reached and the necessary time has elapsed. The sample is removed and compared with previously – marked paper outline. Raw or untanned skins shrink in area at

about 60°C in a very distinctive and definite way. Vegetable – tanned leather shrinks at about 65°C whereas a normally well tanned chrome leather withstand immersion in boiling water (100°C) for two minutes without shrinking. [14]

Freshly- tanned chrome leather which has not been dried out, is referred to as being “in the blue” (from the color which goes much paler on drying). It is very important to remember that all blue leather develop acidity on standing or aging. Subsequent processes are very sensible to variation in acidity, and consequently this must be carefully controlled (neutralizing). Blue chrome leather has a very strong affinity for many dyes, fat liquors and vegetable tans but this becomes much less after drying, owing to changes in the chrome sulphate complex during drying or ageing [14].

2.3.2 Basification

Basification follows tanning operation in order to neutralize pickling acids and any acids produced in reaction with the collagen. For good tanning the pH value has to be raised to 4. At the same time, the reactivity of chrome complexes is enhanced on account of their basicity; it increases from 33% up to 66% at the end of tanning process.[23]

Sodium carbonate is often used as a basification agent. Usually the dosage is given towards the end of the tanning process in several portions in a total amount of 0.8-1.2% on pelt weight in order to achieve a final pH 3.8-4.2 in the float.[23]

In a conventional procedure, the tanning and basification operation should be finished at a float temperature of 35-40°C. The drumming time should be at least 6-8 hours. [23]

The stability of leathers is checked through the determination of the shrinkage temperature (T_s). The shrinkage temperature is an accurate method

to determine the stability of the leather to heat. Another procedure used in industry is the boil test where leather is dropped into boiling water and the time recorded before it undergoes irreversible damage. A time of 2-3 min minutes before any signs of change would be considered acceptable in this type of test. A shrinkage temperature of 99°C would be high enough to pass the test[26].

2.3.3 **Vegetable tanning**

Vegetable tanning could play a dominant role in the future of leather industry. The leathers processed through vegetable tanning have distinct advantages such as comfort, compatibility with human skin and high dimensional stability. Moreover, the tanning methodology adopted affords easy disposal of spent liquors. However the problem with the vegetable tanning is its poor thermal stability. Vegetable tanning are not able to establish sufficient cross links with the fibers and fibrils of collagen which renders them a relatively weaker tanning system[21].

The vegetable tanning method does not need the prior preparation stage of pickling and therefore the contributions to pollution load from sulfate salts are lower. Vegetable tannins, however, are known to be hard to biodegrade, and hence wastes bearing vegetable tannins degrade slowly [4].

Vegetable tanned leather is used in making heavy leather such as furniture leather, garment leather and shoe upper leather [8].

Products from the leather tanned with tannins perfectly keep form. An extract of every plant dyes the leather by colour which is typical only for that extract. This is the reason why the tanned by tannins leather is used for the particular fashionable articles[27].

By the way, the tanning by vegetable tannins is one of the oldest tanning methods. Tanned with tannins leather is less thermo stable than chromed but it less swells in water and can be dyed using direct dyes [27].

Tannins are bitter substances present in barks, fruits, pods, leaves or seeds. They are used to convert hides and skins into leather. They come from plant sources and they are called vegetable tannins. They have different origins, however, and they differ in strength and in character, colour concentration and quality. Thus they produce leathers of different types, hard, soft, light colored, dark colored, heavy or light. These tannins can be used singly or in various combinations to produce different effects.

The most important tanning materials which are widely used in commercial tanneries and they are suitable for rural tanneries are: Black wattle or mimosa, Camachile, Chestnut, Catch, Divi-divi, Gambier, Hemlock, Nut-galls or Oak-galls, Mallet bark, Mangrove, Myrobalan, Oak bark, Quebracho, Sumac, Tara, Valonia etc. Concentrated and expensive tannins are available in two forms as a thick liquid which contains about 40% tannin or in a solid form which contains up to 60% tannin [1].

Sudan has various indigenous tanning materials. Some of these, such as Garad pods (*Acacia nilotica* sub. sp. *nilotica*) and Talh bark (*Acacia seyal*) are used extensively in the Sudan by rural tanners. The tannin content of garad pods is fairly high and amounts to approximately 30% of the total weight, soluble nontans are nearly 20%, while moisture and insolubles make up the remainder. The main constituent of the garad tannin is presumably leucocyanidin gallate i.e. gallic acid esterified with a flavanoid. Garad tannin is reported to contain chebulinic acid, gallic acid and to have a high sugar content, factors which are common in hydrolysable tanning materials. Garad

tannins are therefore mixed tannins i.e. containing condensed tannins as well as hydrolysable tannins containing gallic acid esterified with glucose[28].

When garad pods are crushed, they disintegrate into three parts, the husk with about 12% pure tannins, the seeds with no tannin content and the grain powder with approximately 55% tannins. The seeds and husk form about 63.6% of the weight of the pod, the remainder being the grain powder [28].

The Sudanese leather industry uses mainly imported vegetable (*A. mearnsii*) and mineral tanning materials (chrome). Local vegetable tannins such as garad (from the pods of *A. nilotica*) are abundant, but they do not produce the same quality of leather as wattle (*A. mearnsii* bark is used)[18].

For rural tanners of Sudan the acacia are one of the most important tanning bearing trees. Several species, such as *Acacia Arabia*, *Acacia nilotica*, and *Acacia adamsonia*, have supplied pods and bark since immemorial times. The leather produced by acacia pods is soft, plump, light colored and durable and it can be readily dyed. Their solutions are mellow. The acacia pods and bark are known variously in the countries where they grow as garad or sunt (Sudan) babul (Hindustan) babar (Sind), babla (Arabia), ne-neb (west Africa) and gabarua (Nigeria). According to the condition of the soil and the climate, their tannin content varies from 20 – 30%. The material contains an undue proportion of nontans and a high proportion of sugary matter in the seeds. This results in a rapid fermentation of the liquor. These seeds may be removed by ridding or by shaking the pods in a flat basket, thus separating them from the shattered pods. Good results are obtained by using a wooden pestle and mortar for pounding the leaves, pods or fruit. Small power driven mills, in particular for a group of cooperative organized tanneries can be also used for advantage. The bark of the *acacia Arabica* does not contain more than 14% tannin and is mostly used in northern India

under the name of babul bark. When babul bark is used for tanning, it gives a leather which has a darker colour and a tendency to crack and tear; but when it is suitably blended with myrobalan (3:1) or with avaram bark, it can be used with advantage, particularly in sole leather tannage [1].

The water extract of tannin bearing material consist of tans and non tans, tans being those parts which will combine with or fix on to hide or skin under usual conditions and the remainder being the non tans.

Chemically the tans belong to the polypolenols. There are two main classifications: (a) the catechol tans (or condensed tans) which are similar to catechol and (b) the pyrogallols (hydrolysable tans) which are esters of glucose and gallic acid and its derivatives, e.g. ellagic acid. The non tans have a somewhat similar chemical nature to the tans but they do not combine with the hide substance. Together with sugar like materials, flavones, acids, salts, starch, fermentations products and salts or acids, etc added by the tanner. Polyphenol non tans peptize the true tans, i.e. they disperse the large aggregated molecules of true tans to make it more water soluble, penetrate the hide more easily, and therefore produce less astringent liquor. Tan liquor is said to be astringent if the tan present combine very rapidly with the hide or skin substance. Stringent tan liquor can cause full or over tannage of the skin surface before the corium is fully tanned and so result in “case-hardened” and brittle grain.[14]

Vegetable tans, consist of large polyphenol molecules with some acidic groups and high secondary valency potentials (dipole H - Bonds). The acidic groups may combine with basic groups of the proteins displacing the hydrated water, and the numerous secondary valencies, dipole or hydrogen bonds to the peptide group, displacing their hydrated water. Consequently

vegetable tannage could be considered as dehydration of the wet protein, replacing the water molecules by a sheath of vegetable tans molecules.

On drying this will create some mechanical impedance to the fiber shrinking together and the presence of the vegetable tans will obstruct the formation of the cross links. The softness obtained will depend on the type and quality of vegetable tan given. With higher quantities of vegetable tans such as are given to sole leather, the leather become firmer again due to the filling action of the vegetable tans and the possibility of aggregate formation between those fixed on the fiber.[14]

Generally acid conditions and low non-tan content favour vegetable tan fixation in increasing the ionization of the protein basic groups and hence their ionic attraction for acid groups of the vegetable tan molecule; also acid conditions increase the secondary valency forces of the vegetable tan molecules (e.g. dipole moment and H – Bonds) increasing the fixation to peptide groups, etc, and also vegetable tan aggregate formation [14].

The penetration of the tan through the thickness of the skin substance is very important to get the required uniform distribution. It has been implied that most tannages cause some degree of fiber shrinkage and rapid tan fixation (astringency) may cause such shrinkage of the skin surface, as to cause wrinkling, pebbling and interfere with further tan penetration. Thus many tannages commence under conditions where tan fixations to the fiber is low until the tan is well penetrated, and then conditions are changed to favour more rapid tan fixation, thus avoiding the astringency effect.[14]

Vegetable tannins may have different chemical structures, but impart some common properties:

- a. They are miscible with water in any ratio;

- b. They are insoluble in organic liquids such as chloroform, ether, gasoline etc.;
- c. They are amorphous substances, very sensitive to oxidation and reduction in the presence of enzymes [29].

When tannins come into contact with hide proteins, they react together to form leather which is resistant to putrefaction.

Immersing hides directly into strong solutions of vegetable tannins cause the surface to tan so hard; draw together the grain of the pelt that the tannin cannot penetrate into the center and produce hard leather. Therefore, vegetable tanning has to be started with a weak liquor and gradually increasing the strength of the liquor. This may be achieved in two ways: (a) by passing the skins or hides through a series of vessels, each containing a stronger solution than the previous one or (b) by strengthening the liquor in the original container by adding more tannin to it. It is essential first to use mellow tan liquors to get a weak initial penetration of tan and to follow them by using astringent liquors. Very astringent tannins may produce a leather which is untanned inside, because the pores were contracted too rapidly or “case hardened”. This method gives slow and sometimes uneven tan penetration but tend to produce flat leather. Suspending the hides in pits or even better, rocking the suspending hides give a faster and more uniform tannage. It should be noted that some modern methods of tannage appear to contradict these postulates, in that good sole or light leather is made by adjustment of the pH of the hides before immersing them in strong liquors of 70° to 90°Bkr to obtain a rapid tannage but not case hardening of the surface, although such liquors would be ranked as very astringent [1, 14].

Rely on vigorous mechanical action, usually in a drum. The tan is added in concentrated form (even as a powdered solid) with little or no float of water

to the drum. Penetration due to mechanical action and diffusion from (high tan concentrations externally in to the wet skin) can be so fast that penetration is largely attained before any significant extent of tan fixation has occurred.

Exact conditions must be carefully maintained and it is important not to confuse the two methods i.e. the slow long float and the no float drum tannage. Conditions of PH, temperature, etc. which are suitable for one are not necessary suitable for the other [14].

Paddles give more thorough agitation, as the hides or skins will turn in the paddle and a large volume of liquor is permissible. Drums can give a very vigorous agitation which will speed tan penetration, especially if they are large and faster or if little liquor (“or short float”) is used.

Typical drum speeds are 8-12 rpm. This question of speed of tan penetration is important as, in some cases large amount of tan are necessary to produce firmness.

As the grain and flesh surfaces of the hide or skin are exposed to the tan first these may become “over- tanned” whilst the inside or corium of the hide or skin is under-tanned, not having sufficient process time or enough tan i.e. “case hardened”. Such conditions give hard, thin leather, often with cracky, distorted (drawn) grain so that great care must be taken to prevent it [14].

2.3.4 Alternatives to chromium

Many attempts have been taken to produce chrome free leather using iron complexes, synthetic resins with aluminium and titanium, tara-aluminium tanning, wet white pretannage and aldehydes/polymer combination etc. But these processes suffer from various disadvantages such as aluminium tannage gives inferior shrinkage, and light-fastness, titanium tannage gives full leathers with yellowish tinge, titanium tannins are also expensive. Using

vegetable tannins the leather cannot achieve the characteristics like chrome tanned leather. But the use of these minerals suffer from various disadvantages such as aluminium tannage gives inferior shrinkage, and light fastness, titanium tannage is expensive and gives full leathers with yellowish tinge. Using vegetable tannins the leather cannot achieve the characteristics like chrome tanned leather. [30]

The ideal tanning agent to rival chrome must be naturally abundant, easily obtainable, cheap, eco-friendly ease and safe to use and offer competitive tanned leather performances[12].

Total chrome replacement is possible if reduced hydrothermal stability and lower handling qualities are acceptable. However, most end uses of leather require high hydrothermal stability. For example shoe upper leather must withstand hot lasting and heat setting, while garment leather must withstand steam pressing [23].

2.3.5 Combination tannage

Different methods of tanning produce leathers with different properties, especially physical properties, and naturally their uses are limited in different fields of leather goods manufacture. Moreover, properties that a particular method of tanning renders to the leather are not always desirable to the user. So to eliminate those undesirable properties, combination tannages are carried out using more than one tanning agents. In combination method leather is first tanned by that method which can give the maximum number of desirable properties and followed by another suitable method of tanning to eliminate the undesirable properties and provide other desirable properties. [6]

Initially, no-chrome metal materials and other materials with tanning property are combined and applied to leather making, then the combination

tannage was developed step by step and the combining use of organic-organic tanning agents, organic –inorganic tanning agents and inorganic – inorganic tanning agents has been applied for many years

Among the mineral materials, aluminium, zirconium, copper, and iron are the potential metal substitutes for chrome. Their tanning effects enhance when they are used in combinations with vegetable tannins, aldehydes or other organic materials. Leathers tanned by these combinations have physical- mechanical properties adequate for a variety of applications and hydrothermal stability in the range of 85°C to 100°C. Nevertheless, these combination tannages have not been widely adopted [31].

In spite of the good properties of pure chrome tanned leathers, they have some undesirable properties such as emptiness, looseness, hardening due to rewetting and drying. These undesirable properties can be reduced to a great extent by retanning with vegetable tannins. [6]

Now- a- days most of the chrome upper leathers, as for example, must have mainly the properties of pure chrome tanned leathers and to a less extent of pure vegetable tanned leathers and therefore these leathers are produced by retanning chrome leathers with vegetable tannins. Also, chrome-retanning is preferred where the grain is buffed to produce corrected grain finishes, particularly where the leather is paste- dried. On chrome sheepskins, vegetable retannage reduces the looseness, grain pipeyness and run or stretchy of the leather, and is favoured for clothing leather and some lower grades of gloving leather. [6]

The reverse order of tanning has been followed also and is called semi-chroming; the hides or skins are first given a vegetable tannage (sometimes with some syntans) and then chrome tanned. To avoid hydrolysis of the chrome complexes in the wet semi-chrome leathers, some tanners suggest

pickling the leathers before chrome treatment with 0.3 to 0.5% formic acid and 3-4% salt. The supplementary chrome tannage gives more flexible and softer leather for gloving and clothing or more resilient leather for shoe uppers. It increases the resistance to damp heat or hot water and also the uptake of dye and with appropriate treatment the water proofness. Combination tannage of vegetable tan and chrome can give better resistance to rotting or ageing than vegetable tanning alone and better resistance to perspiration than purely chrome tannage [6,14].

Since the methods of chrome tanning and vegetable tanning are quite different, a lot of difficulties should be overcome to give vegetable treatment to chrome leathers. Vegetable tanning starts with a liquor of low specific gravity of high pH value (near about 5.5) and as tanning proceeds the specific gravity of the liquor is gradually increased with gradual decrease in pH value to a pH value (near about 3.0). But in chrome tanning on the other hand, specific gravity of the liquor is not so important even though the astringency of chrome liquor unlike vegetable liquor increases with dilution. Moreover, in chrome method the tanning is started at low pH values (near about 2.0) and with advancement of tanning the pH values are gradually raised to a pH value (near about 4.5). So to give vegetable treatment, therefore the pH of the chrome leather should be raised to a pH value of 5-5.5 which is far above the end pH of chrome tanning. So, if the chrome leather is brought to this pH by strong alkali treatment all the bound acids and free acids are removed and the leather becomes harsh, hard and gets ruined. But on the other hand, weak alkali treatment is not sufficient to solve the problem. The presence of acid, especially mineral acid, in vegetable tanned leathers deteriorates the leather very rapidly. Chrome leather neutralized with weak alkali like borax, bicarbonate etc., becomes acidic due to

hydrolysis of chrome complexes which causes acid rot to chrome- retan leather. Moreover, a portion of the vegetable tannin penetrates into the chrome complex in the leather by replacing the aqua radicals, so that additional binding sites arise. This causes rough and drawn grain to the leather. To eliminate this drawback, it is necessary to stabilize the chromium complexes in the leather. From the above discussion it is clear that for proper retanning of chrome leather with vegetable tannin the following requirements must be fulfilled:

- a. The chrome leather must be properly neutralized to a pH 5-5.5.
- b. The hydrolysis of the chrome complex in the neutralized leather should be stopped or reduced to a maximum possible extent.
- c. The affinity of the organic tannin for penetration into the chrome complexes must be reduced as far as possible.

The above three requirements can be satisfied if the neutralization of chrome leather is carried out with sodium or potassium salts of organic fatty acids. These salts can remove the free acids without affecting the bond or complexly held acids and the same time the acid portions of these salts have excellent power of penetrating into the chromium complexes by displacing the aqua radicals. The chrome complexes in the leather thus get masked. Under such conditions, the liberation of acid due to hydrolysis of the chrome complexes is reduced and the tannin cannot penetrate into the complexes by removing these masked radicals. Since the masking effects of different fatty acid radicals are different and the leathers produced show different characteristics, the selection of suitable salt for such neutralization is a difficult task. In some tanneries sodium lactate is used for this purpose. There are many neutralizing type of syntans in the market and many of them are suitable for neutralizing chrome leather before retanning with vegetable

tannins. Another important point to remember in chrome retannage is the fatliquoring of this type of leather with cationic fatliquor. The vegetable tannin in chrome retan leather remains in the outer layers whereas the central layer remains purely chrome tanned to impart chrome properties. Since vegetable tanned leathers require more fat than chrome leathers, the percentage of fat liquor for retan should be more than pure chrome tanned leather and this extra fat should remain in the outer layers where vegetable tannin are present. This is possible if the tanned leathers are fat liquored with cationic fat emulsions. But, on the other hand, cationic fat droplets penetrate up to the middle layer, if pure chrome tanned leathers are fatliquored with cationic fat and the droplets do not break so easily due to cationic nature of chrome collagen. Anionic fatliquor therefore, give better fatliquoring effect to pure chrome tanned leather. Chrome retanned leathers naturally require both cationic and anionic fatliquors. Since these two types of fatliquors cannot be mixed up, chrome leathers are fatliquored with anionic fatliquor before retannage and with cationic fatliquor after retannage [6].

2.4 Post- tanning Operations

After the hides or skins have been tanned, they require further treatment to improve their quality and appearance. These operations differ according to the type of leather and its further use [1].

Many chrome leathers for the shoe upper trade are neutralized, dyed and fatliquored before drying; whilst most vegetable – tanned leathers are dried out after tannage and are then wetted back for dyeing, because fresh vegetable tannage tends to wash out in the dye bath, giving a thinner, emptier leather. During drying the tan becomes more firmly fixed. Vegetable – tanned leathers usually wetted back fairly easily for dyeing, whilst chrome leather can be very difficult. Nevertheless, chrome tanned leather for suedes

and gloving is often dried out before dying in the former case to allow buffing of the dry leather to be carried out before dying, and in the later case to allow the skins to be staked and carefully sorted before dying [14].

After tannage it is common to allow excess tan liquor to drain off the hides or skins and to stand them in a damp condition for a day or more to obtain further fixation of tan and setting off the skin fiber. When a flat leather is required, the skins are drained flat to avoid any tendency for the fiber to set in a creased condition. This can be achieved by many methods such as horsing up, and piling [14].

To enable the leather to go through the splitting and shaving machines easily, its water content must be reduced to about 60% (of the wet weight) by squeezing out water through a sammying machine [14].

The thickness of the leather is usually termed its “substance”. If the hide or skin is thick enough, it may be split into two layers using the band - knife splitting machine. [14]

All types of animal skins are thicker in the butt and in the neck than in the other areas. If the uneven thickness of the skin is only in such small areas as to yield very small pieces on splitting, the hides or skins may be shaved so as to level off the thicker areas by using a shaving machine [14].

The splitting operation may be done on the limed and swollen goods, but accurate substance control of such leathers is achieved by splitting after tanning. With crusted stock, leveling of substance may take place after sorting and re-wetting. Occasionally, this operation is done on the finished stock, for example on clothing suede. [6].

In the case of light leather, e.g. fancy, gloving, lining, or shoe upper leathers, where firmness or solidity are not needed, it is common to wash the skins by running in a drum or paddle whilst a constant flow of water is fed in. The

water should be clean and free from ions salts harmful degree of hardness or alkalinity, all of which may cause stains. The aim is to remove loose, surplus tan from the surface only, as on drying it might give a patchy, dark-brown colour or a hard, brittle surface i.e. cracky grain or cracky edges. [14]

2.4.1 Neutralization

Chrome leather under acid condition is acid and develops acidity on standing. Under acid conditions the skin protein is cationic and that this is further accentuated by the mineral tannage. Consequently negatively charged colloids such as dyestuffs, vegetable tans, sulphated oils, etc, will readily precipitate on the skin surface. Neutralizing removes the acidity from the skin and hence reduces the cationic charge, so that there is less reaction with these anionic materials which then penetrate the skin more uniformly and thoroughly. The washed chrome leather is therefore neutralized by drumming in 200-300% water and 1-2% sodium bicarbonate or borax for about 30 minutes (percentage on drained shaved weight). A piece of leather is then rinsed with water, blotted and a pH or acidity of the cut cross- section measured with a pH indicator. Normally, it should be in the range of pH 5.4-6.5 i.e. blue-green to bromocresol green, but this standard may be varied for different leathers depending on dyeing and oiling requirements. If the leather is made too alkaline (above pH7.0) there is a danger of making the chrome tannage too astringent, so that flexibility of the grain is lost and the leather suffer from grain crack and is often stained or dyes patchily, caustic alkalis are avoided for this reason, and mild or weak alkalis, such as borax, sodium bicarbonate, sodium sulphite, or ammonium bicarbonate are used. The leather is then washed once again and the next process (dyeing or fatliquoring) should be carried out immediately. If this is delayed, even neutralized chrome leather will start to generate acid, so for some leathers

the neutralizing is deliberately left until thickness adjustment have been made.[14]

2.4.2 Leather Dyeing

Leather dyeing is difficult and tricky, it requires an intimate knowledge of the preparation of leather before dyeing, the application of suitable dyes, the use of mordants and various of after- treatment. Dye stuffs used for coloring are of two types: natural dyes and artificial dyes. Natural dyes are derived from plants or animals and cannot be used by themselves, for they will not stay on the leather. They must be fixed by means of certain chemicals which are called “mordants” or “strikers” the same will give different colour according to the mordant which is used. Although, natural dyes have been replaced by artificial dyes, rural tanner is well advised to start working with natural dyes before using the synthetic ones [1].

Artificial dyes are those prepared synthetically. The tanner divided artificial dyes into three main groups: acid dyes, basic dyes and direct dyes.

Acid dyes are readily soluble in water and they require no mordant for their vegetable or chrome tanned leather. Such dyes are: Orange G, Mtanil Yellow, Fast Red, Resorcine Brown, Acid Green, Nigrosine, Acid Black-Brown, Naphthol Blue-Black and Naphthalene Leather Yellow, Brown or Red and others. [1]

Basic dyes can be used on vegetable tanned leather. It is essential to give the leather a preliminary treatment because these basic dyes are readily precipitated by tannin. The leather therefore be washed, retanned slightly with sumac or any mild tanning material, washed again and then drummed in a solution of titanium potassium oxalate or other salts such as tartar emetic or lead acetate. This pretreatment not only precipitates the remaining tannin which might diffuse out of the leather and interfere with dyeing, it

also effects the final combination of leather and dyestuff and makes the color faster to washing and to light. [1]

If basic dyes are employed for chrome leather in the neutralized state, it is necessary to mordant with surface retannage and to use vegetable tanning materials, syntans or natural dyes which contain tannin. Afterwards the skins should be washed, drummed in a salt, such as titanium potassium oxalate, washed and then dyed. Examples of common basic dyes are Bismarck Brown, Magenta, Safranine, Methylene Blue, Basic Black, Indine Blue and Rhoduline yellow. Acid and basic dyes must never be mixed for they precipitate each other.[1]

Direct dyes can combined directly with chrome tanned leather without the aid of mordant. They can also deepen the colour of vegetable tanned leather, which has been previously died with a basic dye, but they have little affinity with vegetable tanned leather. They will only produce light shades on chrome leather mordanted with tannin. Dizole chrome brown, direct blue, direct fast, red and direct black are examples of direct dyes.[1]

The amount of dye used depends on many factors among them are, the type of dye, the kind of tanning, the quality of the leather, the strength of shade required and the degree of penetration the method of application and the nature of the water, but it falls between 0.5% and 5% of the weight of dry leather. 6% on the shaved weight is about the maximum of anionic dyestuff that can be fixed on vegetable - tanned leather (less if syntans is present), whilst paler shades may need only 0.5%. [1]

Dyestuff should never be dissolved in iron vessels; for iron may affect certain colors, instead wooden porcelain, aluminium, enameled or glass vessels can be used. The best way to dissolve dyes is first to make them into a paste with cold water and then to add more water and to heat to 70°C while

stirring vigorously. If only hard water is available, basic dyestuffs should first be made into a paste with an equal quantity of acetic acid (30% strength) before adding the hot water. Acid dyes are prepared by dissolving 5 to 20 parts of the dyestuff in 1000 parts of warm water (at 30-40°C). The amount of dye used depends on the depth of color desired. [1]

Acetic, formic or sulphuric acid is later added to this solution; that is, after the color has been absorbed by the leather. The amount of acid should be slightly less than the weight of dye used, i.e. for 2gms of dyestuff, 1.5gms of acid. Dyeing takes about 30 minutes. It is better to add the dye into two portions to obtain more even shades before the acid is added. [14]

Vegetable tanned leather are suitably damped by water dipping and piling to about 50-60% water content and their thickness adjusted by shaving or splitting; and the skins weighed. The skins are then given a light wash with water and “stripped”. stripping is usually carried out by drumming the skins in warm water (40°C) to which may be added a little mild alkali, e.g. 1% borax, or soda ash, or sodium carbonate (on the damp shaved weight) for one hour. This removes some of the surface tan and any superficial dirt or grease that might be with it. Anionic surfactants (0.5 -1%) are added, and cationic and non-ionic ones are avoided as they may precipitate with vegetable tans. [14]

It is often desirable to reduce the leather PH to a suitable level for the next process. Such simple acidification may be done with 0.5 – 1% formic acid.

If the leather suffers from blue black iron stains these will be accentuated by alkali and in this case the rinsed skins are drummed in cold weak oxalic acid (0.5% solution) for 20 to 30 minutes. This process clean or lighten the grain colour and remove the iron stains.[14]

If heavy stripping has been necessary, or if the original tannage was not satisfactory for the leather required, it is quite common to retan the leather at this stage. The skins may be retanned by drumming with 10 – 15% bleached mimosa extract or by using a mellow tannin such as acacia at strength 1-2% in warm water calculated on the dry weight of the leather and 300% water at 30°C for 1 -2 hours. After retanning the leather is washed thoroughly.[14]

Special syntans with good tan dispersing properties are favoured for obtaining pale level colours or pastel tints. The shaved skins are drummed in 200% water at 40°C and 5 -10% of such syntans added. Drumming is continued for half to one hour. Syntans is favoured for russet or pastel shoe linings. However, they tend to make the leather difficult to dye with acid dyestuffs to deep full shades.[14]

Discolored vegetable tanned goat or sheep skins should first be drummed in lukewarm water, horsed up for about one hour and drummed in a float of water at 30°C for 30 minutes and then drain. This is followed by “stripping” in the same drum or vat using about 1-2% borax or 0.25-0.5% soda ash based on the drained or “sammed” weight for about half an hour. The leather is washed again before it is retanned with a suitable light-colored tanning material. Basic or acid dyes can be used for delicate and pale shades; however, acid dyestuffs are preferred [14].

After the above process, the leather (at a pH about 5) is warmed up to 45°C and floated in 100 – 200% water at 45°C in the drum or 500 -600% water at 45°C in the paddle and the drum or paddle run. The dyestuff is weighed out, pasted and dissolved in sufficient hot water to dissolve it and slowly added to the agitated dye bath. Where very level dyeing is desirable the dye solution may be given in two or three portions at ten minutes intervals, although this

may give paler shades. Running time is usually 20 to 30 minutes, unless good penetration demands a longer period [14].

The dye bath may be exhausted in the case of small quantities of colour, otherwise it is acid exhausted by adding formic acid (diluted to 10 times with water) to bring the PH down to about 3.8 and running continued for a further 20 minutes. A common estimate of the amount of formic acid added is half the weight of the dyestuff, but more may be needed with pale shades and alkaline leather to get this PH, e.g. a minimum of 0.5 – 1% is often desirable to fix the dye [14].

The cationic blue chrome leather should firstly be neutralized before dyeing it with anionic and direct dyes to remove acidity and reduce the cationic charge; otherwise it will react very quickly with such dyes which will be rapidly fixed on the surface giving strong unlevel shades of poor penetration. The quantity of neutralizing agent used depends on the degree of the desired dye and fatliquor penetration. If a surface dyeing and fatliquor is needed, neutralizing with about 1% sodium carbonate is sufficient to give surface pH of 5 or over. If more thorough dye or fatliquor penetration is required, larger quantity of neutralizing agent such as borax and sodium bicarbonate is used to obtain a uniform neutralization throughout the cross section of the leather to a pH of 5-5.5. to avoid over neutralizing or basifying the grain tannage which may cause roughness or pebbling effect or a hard brittle crack grain, buffer salts are used e.g. ammonium bicarbonate, sodium or calcium formate or masking agents or syntans which reduces the cationic charge irrespective of pH e.g. sodium sulphthallate and neutral syntans.[14]

The methods used for retanning depends upon radical changes in the charge on the leather fiber primarily to control the deposition or distribution of the retanning agent or resin and the fatliquor. Such changes can affect the

penetration or fixation of the dye very considerably. Retannage with cationic metal salts (e.g. very basic chrome, zr or Al salts), cationic resins or fat liquors will give strong surface shades, whilst syntans and vegetable tans will give paler more penetrating shades. If the anionic dyestuff is given after a process giving a strong positive charge, a strong surface shades can be obtained, whilst with a lesser charge, some penetration will be obtained [14].

2.4.3 Fatliquoring and oiling

Oils and fats are often incorporated into the leather or its surface and can make some important changes in its properties; they play a fundamental role in governing the softness, pliability, and stretch, “run” or “handle”; the ability to take up or resist water and the smoothness or oiliness of the grain. They affect the resistance to abrasion, chemical attack and becoming dirty. The effect obtained will depend upon the type of leather, the type and quantity of oil, fat or wax, how it is applied and whether it is all on the surface or has penetrated into the internal structure. [14]

If the fiber structure is tightly woven, the leather will be firmer, and it will be more difficult for the oil to penetrate the fibers uniformly. In the absence of oil, chrome tanned leather dries out firm and rather hard. However, relatively small amount of oil, if uniformly spread over the fibers, readily reduces this hardness, and make the same leather remarkable for its softness and stretch. Vegetable tanned leather in the absence of oil, is less hard than chrome leather; on the other hand, much greater amount of oil must be added to vegetable tanned leather than to chrome leather to obtain the same softness or stretch. Normally the leather becomes softer and stretchier as more oil is used, but excessive amount of oil may give an undesirable, greasy feel, or may interfere with dyeing and finishing [14].

Oils and fats which are used for lubricating leather are of two types: mineral and natural oils and fats. Some mineral oils which are obtained from crude oil from oil wells or shale deposits may be used in leather manufacture. They are relatively cheap and chemically stable and they are not affected by moulds or bacteria. Mineral oils do not mix easily with water and therefore give good waterproof properties. They can be obtained at any viscosity. Despite these advantages, however, they have only a limited use in leather manufacture because they give a slightly oily or waterproof surface which is a disadvantage for many leathers which are to be dyed or finished. Also they have a poor feeling action and give thin or empty leathers but may be quite flexible. Moreover, these oils may migrate to the surface by heating giving an oily or discolored surface. As examples of these mineral oils and waxes are Paraffin wax, Montan wax and Ceresine wax [14].

Natural oils and fats are extracted from animals, fish and plants. They are compounds of fatty acids (glyceride) and glycerin or a waxy fatty alcohol. The fatty acids are insoluble in water. As lubricating oil, they are ranging from very fluid oily liquids to greasy pastes and hard waxy materials. The property of the natural oil is largely influenced by the type of fatty acid it combined off. Thus the oilier is the fatty acid present, the oilier will be the oil or fat, and the solid is the fatty acid, the solid will be the natural oil or fat. The fatty acids are also classified as saturated and unsaturated fatty acids. Unsaturated fatty acids are more chemically active than saturated ones. Thus highly unsaturated oils may cause trouble on ageing of the leather [14].

The various fatliquors are obtained by emulsifying the natural oils using surfactants; emulsifying, wetting, dispersing agents. Surfactants are materials which reduce the interfacial tension between the oil and water so that they can be mixed together and their emulsion is more stable.

Surfactants are classed as colloids and if the hydrophilic groups ionizes so that the large molecule has a negative charge they are termed anionic surfactants (soap and sulphated, sulphonated, sulphited alcohols and oils) or if the large molecule carries a positive charge as cationic surfactants (cetylpyridinium bromide).[14]

Anionic surfactants are more effective as wetting and emulsifying agents at high pH's and on anionic materials e.g. vegetable tanned leather. Their emulsions penetrate leather better under these conditions. They will lose efficiency or precipitate with heavy metal salts and cations. Cationic surfactants are more effective as wetting and emulsifying agents at lower pH's and on cationic materials (e.g. chrome leather). Their emulsions penetrate the leather better under these conditions. They are relatively stable to heavy metals (e.g. chrome, zirconium, etc.) but precipitate with anions, e.g. vegetable tans, acid dyes or anionic surfactants.[14]

In non ionic surfactants the hydrophilic group does not ionize and often consists of several hydroxyl groups. Consequently they retain their properties in the presence of anions, cations or with change in pH. Common types are made by condensing ethylene oxide on to a fatty molecule (e.g. the fatty cetyl alcohol or a fatty amin or amide). They are commonly used in the industry as auxiliaries in paraffin degreasing, as wetting agents and to stabilize fatliquors to obtain emulsion penetration into the leather. [14]

Fatliquors are therefore formulated as emulsions of oil in water which will have only sufficient emulsion stability to allow of suitable penetration into the fiber structure when in contact with increasing amount of reactive fibers neutralizes the agent present causing the emulsion to split depositing all the oil on the fiber.[14]

The art of fatliquoring consist of balancing this emulsion stability, with the reactivity of the particular tannage, the PH, the float the mechanical action and the particular leather to be treated.[14]

The fatliquors may be divided into non-ionic, cationic and anionic. Non-ionic fatliquors are made from raw oils and non-ionic emulsifying agent. The later is hardly affected by acids, alkalis or mineral tannages, and therefore gives fatliquors of good penetration under most conditions. Cationic fat liquors are made by mixing raw and a cationic emulsifying agent. In these emulsions the oil droplets have a positive electrical charge. Cationic fatliquors have excellent stability to acids and mineral salts and give good penetration on suede and chrome leathers. They tend to make the leather wet back easily. They do not readily mix with other fatliquors, vegetable tans and acid dyes, which then tend to precipitate. Anionic fatliquors such as soap, sulphated and sulphited oils, have a negative electrical charge.[14]

Multicharge fatliquors may be blends of two or more of these types, the emulsion being stable as long as one type predominates, if this becomes precipitated on the leather the another type present may come into play. Synthetic fatliquors are usually emulsifiable oils which have been synthesized from products of the chemical or oil industry. They should be of more uniform constitution than those derived from natural sources, have uniformity of colour, light fastness and free from spue or smell [14].

The application of oils and fats depends on the type of leather to be produced and the degree of softness, stretchiness, greasiness, smoothness and elasticity required. If softness and stretch are required without greasiness, each fiber should be coated with a microscopic film of oil without excess. If smoothness or elasticity of grain is important but the

centre of the leather is required to have some firmness, the oil is limited to the grain layers. These properties are achieved by the process known as the fatliquoring method. [14]

Almost all light leathers need a greater softness and flexibility than is imparted by tannage. The percentage of oil on the weight of the leather is quite small (from 3 – 10 %) and the precise manner in which this small quantity of oil is distributed throughout the leather materially affects the subsequent finishing operation and the character of the leather [14].

Despite the sophistication of oils available, the type of leather and its condition play an important part. Briefly anionic fat liquors will penetrate anionic leather well. The leather may be more anionic by raising the PH, tannage with aldehydes, tannage with anionic vegetable and syntan materials, or their use as retannage materials, and dyeing with anionic dyes, etc. Cationic fatliquors will penetrate cationic leather best, e.g. most mineral tannages, some resin tannages and cationic dyed leathers. [14]

After the completion of the drum process, leathers should be piled up to drain and to enable the fatliquor to stabilize within the stock. The fiber alignment disturbed by mechanical action in drumming, tends to return to its normal pattern. Omission of this rest period detracts from the “roughness” i.e. handle of the final product [6].

Excess water is removed by passing through rollers under high pressure (Sammying) and the leather is spread out (set) on a machine with bladed cylinders (setting machine) to gain maximum area and to minimize growth marks [6].

2.4.4 Drying

Many leathers are inconsistent from batch to batch if the drying conditions are not strictly controlled with respect to temperature, humidity, and air flow.[6]

Drying time and conditions depend on the weather and attention should be given to the effect of drying on the skin structure and how these changes may be modified by tannage, oils, etc. the actual drying technique also plays an important role in determining the feel, handle, softness, area, thickness and can also affect the colour. During drying the leather tend to shrink in area and these shrinkage forces can be quite strong. Vegetable – tanned leather usually shrink less than other types.[14]

Normally, higher drying temperatures produces greater shrinkage and “crustier” leather. In addition, the leather usually dries to a paler shade (a fact well known to dyers). Most tannages become more firmly fixed on drying and irreversible changes occur. Oils and fats spread more thoroughly on the fiber surfaces and dyes tend to penetrate more deeply and become more firmly fixed. However, any loose, unfixed tan, dye, oil or fat may migrate on drying, i.e. tend to creep to those parts of the skin which dry most quickly, such as the edges loose flanks, damaged grain, where they form darker coloured patches or stains. Such faults are accentuated by uneven drying conditions . Drying methods depend on the type of leather to be produced. It can be done by hanging, nailing, toggling and pasting. [14].

2.5 Finishing operations

The final processes, aimed at giving the leather its pleasing appearance and handle may be very simple involving only mechanical operations of softening, plating, rolling polishing, brushing, embossing, etc. as required. They can also be very complex, involving grain preparation and three or four

applications of different finish films, with intermediate and final mechanical operations [6].

2.5.1 **Mechanical Finishing operations**

There is a great variety of mechanical finishing processes, designed to enhance the appearance of the leather. Some grain leathers are sold with natural grain, while others have various colored finishes applied to the grain and may have artificial grain patterns embossed on them. Other skins are used for the production of suede leather. [14]

After dyeing and fatliquoring the leather is dried and, in order to make it suitable for the various purposes for which it is intended, some or all of the following operation must be carried out: trimming, conditioning, staking, buffing, brushing, glazing, ironing and pressing. [14]

2.5.2 **Finishing materials**

The wide variety of colored pigments, binders, waxes, etc. applied to the leather are known as finishes. Both the composition and application of these are varied to suit the requirements of the end product; not only in terms of colour, gloss, handle, resistance to water, solvents, heat, flexing, rubbing, etc, but also in terms of uniformity of surface appearance [14].

Finishing materials are divided into six main groups:

- a. Proteins
- b. Waxes
- c. Gums and mucilage
- d. Resins
- e. Pigments; and
- f. Miscellaneous; such as sulphonated oils soaps, metal salts, plasticizers and solvents.

The first four groups are the most important for the rural tanner.

The solutions of such finishes which give a transparent film or coating when applied to the surface of the leather but leave the natural appearance of the leather visible – the so called aniline look, are called seasons. These solutions modify the shine, handle or fastness properties. [1]

2.5.3 Pigment finishing

The bulk of the leather suffers some grain defects and the most effective and common method to hide these defects is by pigment finishing.

Pigments, unlike dyestuffs, are insoluble in water or solvents and are opaque. They have hiding or obliterating power, as is commonly seen in their use in paint. Pigments of smooth, fine texture are chosen from types which will not discolor or stain with chemicals in the leather or in the finish, and which are of good fastness to heat and light. They are prepared by grinding natural coloured rocks or ores to fine powders (e.g. some iron oxides) or by roasting these ores (e.g. titanium dioxide) or by chemical preparation, e.g. lead chromate [14].

As the pigment by itself, is not capable of adhering to the leather or forming a continuous film, other materials must be incorporated in the finish for this purpose, as in the case of ordinary paints. These agents are known as binders and are of two main classes – natural colloids and mucilages, e.g. casein, linseed, seaweeds, etc. or more recently, synthetic resins. [14]

2.6 Cleaner production in leather industry

The leather industry has high water consumption and, respectively, generates great amounts of wastewaters with a very complex composition, large quantities of solids and organic material, nitrogen, salts, in addition to some specific pollutants such as chromium and sulphide [32]. For 1 kg of processed hides, 3-5 l of tanning waste water is produced [33]. Therefore,

implementation of cleaner production technology is essential for the sustained growth and development of leather industry[34].

It is possible to minimize the pollution generated during leather processing by applying environment-friendly technologies and methods. In general, such technologies can be classified based on different approaches such as (a) higher exhaustion (b) recovery and recycle (c) alternatives to chromium and (d) safe utilization and disposal of chromium bearing wastes [2].

There are three main reasons for carrying out recycling operations in a tannery. These reasons are: (a) recycling in order to utilize excess of chemicals in a process which if not recycled would have been discharged, (b) recycling to reduce the pollution load in the effluent, and (c) recycling as a means of water saving. The last reason on its own is not so important, because of the cost and efforts involved in collecting, pumping and piping the liquor [35].

2.6.1 Cleaner technology in soaking

In conventional processing salt-preserved hides are commonly used. The most important pollutants in soaking effluents are: salt, hide surface impurities, dirt and globular protein substances dissolved in water and salt solution [36].

The primary aim here is to reduce the chloride load which can be reduced by several methods such as shaking the salt off by using special drums, decreasing the amount of salt used to preserve hides by adding some environmentally acceptable antiseptics (such as boric compounds, acetic acid and sodium sulphite) or commercial chemical bactericides based mainly on ethyldithiocarbamate and isothiazolin.[36]

Soaking water can be recycled in a countercurrent manner, dirt soak, main soak and rinse. The last two soak liquors, Main soak and rinse liquors could

be collected and re-used in the next soaking operation for the dirt soak and main soak respectively, the dirt soak liquor being discarded and fresh water being used for the rinsing operation. This type of operation gives only a saving on water.[35]

2.6.2 Clean technology in liming and unhairing

Although sulfide salts are very effective/efficient in breaking down hair, these reagents are potential environmental pollutants in that they contribute highly to the biological and chemical oxidation demand of the resultant waste stream. In addition, sulfide salts that are accidentally exposed to acid may be converted to toxic hydrogen sulphide gas, which poses a threat to tannery workers [37].

Satisfactory unhairing can be achieved when lime liquors are recycled without removal of either the soluble proteins or the solids; it is only necessary to replenish with lime, sodium sulphide and water. Fat builds up in lime liquors which are recycled without solids removal. In practice this fat may prove to be a problem as it may cause greasy leather or adhere to the drum and be difficult to remove. The use of green fleshed hides and/or surfactants may overcome the problem [38].

2.6.3 Clean technology in deliming and bating

Reducing the ammonium salt in deliming is more complicated than it may seem. Ammonium salts are economical and apart from having a low deliming value, they have a high buffering capacity and clean the pelt very well. They de-water and relax the pelt very well, allowing a good removal of lime. On the other hand, ammonium salts are toxic in surface waters and are an additional load for the biological waste water treatment. [15].

When considering the ammonium salts, we need to look more closely at the bating process as well. Most commercially available bating enzymes are

formulated with ammonium salts. In a normal process, this makes sense since the formulation salt is adding to the de-liming effect, whereas a neutral salt would only add to the salt load of the waste water. If the amount of ammonium salts in the effluent needs to be reduced, as much as possible, the use of ammonium-free bating will be necessary [15].

Calcium salts (mainly sulphates), sulphide residues, degraded proteins (collagen and hair) and residual proteolytic enzymatic agents and the lime constitute the main pollution load of delimiting and bating effluents [36].

2.6.4 Pickling and chrome tanning

Chromium (III) has been used widely in tanning for the excellent properties that it gives to the leather and simplicity of operation. But due to the toxicity of chromium compounds and the poor uptake of chromium during tanning process the continued use of this matter has been challenged[39].

Minimization of chrome offer and rate of pH and temperature change and maximization of mechanical action end temperature final pH and reaction time will increase chrome uptake substantially[40].

The salt used in the pickling process is the second biggest contributor of the total salt freight in the waste water. Common salt is the source for the chlorides, while sulfuric acid is the major source for sulfates and sulfate masked chrome as the second source.[41]

About 35% of TDS generated from tannery effluents are from the pickling process. Even though treatment methodologies such as membrane separation (ultra-filtration), or reverse-osmosis and electro-dialysis have been employed, they have the inherent problem of generation of solid wastes in the form of salts which must be separated from the effluent. About 800 l of water and 80 kg of salt are used in the pickling process for every tone of

hides/skins. About 50-60% of the salt and acid used are usually sent to the waste stream.[41]

There are two fundamentally different methods of reusing the unused chromium remaining after tanning. Chromium can be reused by either recycling the spent solutions directly or after recovering the unused chromium as chromic hydroxide and regenerating as BCS for reuse.[2]

Recycling spent floats direct from chrome tanning back into processing is the simplest means of reusing chrome. Several recycling techniques are employed industrially. All these techniques consist of recovery of the spent chrome tanning liquor, screening, replenished with sulphuric acid and reuse of this liquor as the next pickle liquor. Then the bated stock should be run in the pickle solution. After a period of time, the remaining chrome tanning material is to be introduced and the tanning should proceed for approximately 24 hours, after which the basification took place [2].

2.6.5 Vegetable tanning

The main problem associated with the recycling of vegetable tanning solution is the possibility of a build-up of non-tans and neutral salts in the closed system, to levels which would interfere with the uptake of vegetable tannins [35].

The ratio of tans to non- tans should be 1:6, ensuring that the tannin particles can penetrate and colour the pelt. The salts limit the degree of swelling produced by the acids present. As tannage proceeds, the acidity of the liquor and the ratio of the tans to non -tans increases. The increased acidity reduces the rate of penetration by tans, and results in an increase in the size of tan particles and in the amount of tan fixed [14].

2.7 Planning a rural tannery

The tanner can establish his tannery alone or with cooperate with other tanners. Choosing a suitable location for a tannery needs a careful thought.[1]

2.7.1 Site

Ideally, a tannery should have a copious supply of suitable water and allow easy disposal of water (effluent) it should be readily accessible by road or rail; it should be situated as closely as possible to permanent source of raw materials such as hides, skins tannins and lime in an area where skilled labour is available and near leather consuming area. It is unlikely that one site will offer all these advantages, various factors, therefore, must be considered.[1]

A new tannery should be constructed that it allows adequate space for the planned output. It should be on high ground to allow for easy drainage and waste disposal; it should be sanitary and provide good working conditions for the laborers; it should allow the continuous flow for materials; it should ensure that hides and skins are so handled through the tannery that all unnecessary movement is avoided. Finally it should be easy to enlarge the tannery, if the volume of trade increases.[1]

2.7.2 Size

The size of the tannery depends on the output and types of leathers to be produced, the method of tanning and the financial means of the owner. When planning a tannery, allowance should be made for enlarging the premises, if when required, rather than starting with a building which only just large enough. The leaching pits, for instance, should be located close to the suspenders, and provision for the crushing of barks, etc. should be made.[1]

2.7.3 Basic sections

Whether the tannery is to be small or large, provision for the following assets is essential:

a. Store for hides and skins

The store should be large enough for a two- month production of hides and skins to be tanned. It should be weather and vermin-proof and well ventilated. It should be fitted with a slatted platform on which the hides and skins are stored and it should be provided with a platform scale.[1]

b. Store for tannins

The store should be large enough to store large quantities of tannin- bearing materials and full protected from the rain. It should be provided with a slatted platform to keep tannin- containing materials on it and well ventilated to prevent the growth of moulds. Lime should be separated from tanning materials.[1]

c. Leaching shed

It must have a stone or cement floor sloped inwards, towards the walls of the tannery; it should discharge into the main tannery drain, but not in the effluent drain. Provision should be made for possible expansion accommodation.[1]

d. Beamhouse

There should be enough space for each operation. The floor should be made of cement, brick or stone. There must be provision for an adequate and quick water supply. Vats should be erected above ground level and not built completely into the ground; otherwise draining is difficult. [1]

e. The tannery proper

The part of the building where the hides and skins are tanned, must be separated from the beamhouse. The size of the tannery proper depends on

the amount and on the nature of the material to be treated and also on the number of the hides and skins to be taken for each soak. If the tannery is handle skins as well as cattle hides, eight suspenders and handlers, each 1.5m long 0.9m wide and 1.5m deep and three lay away tanks of the same dimensions are required. There must also be enough space for leaching the park. The eight suspenders and handlers are interconnected by staggered drain ways, which are about 15cm in diameter, at the top of the dividing walls. These drains allow the tan liquor, which is always added to the last suspender, to over flow from vat to vat. They strengthen each vat in turn by an equal volume of mellow liquor, while an equal volume of used liquor is rejected from the first vat, either by flowing or by draining. The number of hides which enter the first vat is indicated to the number which leaves the last. Thus a continuous and steady flow of goods is maintained. When tanning skins it is better to install paddles, and not hand- driven drums. One or two large enough tables are needed for scouring, fatliquoring, oiling and stuffing. [1]

f. Drying sheds

Any shed built of wood or adobe, however will be adequate. It must protect the leather from rain, direct sunlight, heat and dust. The sides of the shed should be built in such a way that parts of it can be opened to increase circulation of the air. The beams of the roof should be provided with hooks made of brass or stainless steel, from which leather can be hung. This part of the tannery does not need a permanent floor.[1]

g. Finishing room

Staking, dyeing, glazing, buffing and compressor and hand rolling for sole leather and sorting are done in the finishing room. Here it is necessary to have Shelves, cupboards for dyes and chemicals Tables and “horses”. It is

also desirable to have a box 1.2m long, 1.2m wide and 0.3m deep for clean sawdust.[1]

h. A store for finished leather

Finished leather must be kept on racks in a well ventilated and dry store. A measuring table and a weighing scale should be provided. This store should also be the tanner's office, where he keeps all his records, invoices and books.[1]

2.7.4 Machinery

In the design of rural tanneries, no provision has been made for machinery. When, however, expansion occurs, when labor becomes more expensive and increased funds are available, a gradual replacement of manual labor by machinery may follow [1].

2.7.5 Drums

To increase the rate of penetration of different chemicals into the hides and skins certain degree of relative motion between the liquor and the hides is always required. For this purpose drums are used and the heat generated due to mechanical action is also utilized to aid quick penetration. Any type of mechanical action, of course, reduces the natural quality of hides and skins even though tanner's aim is to preserve them to the maximum possible extent. Like all other machines, drums are also, therefore designed in such a way that the mechanical action on leather is neither too high nor too low but optimum [6].

The drums are constructed by fitting 5 to 6 inches wide and 3 inches thick wooden blanks on two circular wooden end discs separated by a distance equal to the width of the drum. The sides of the wooden blanks are shaved correctly so that they fit to each other nicely. Both the side ends of the blanks are nicely grooved so that the drum may be made leak proof by

introducing a common long wooden tongue through the grooves of the adjacent two planks. The drum is then tightened on two ends by two or more even number adjacent iron rings. Inside the drum pegs or shelves in two or more series are provided for lifting the stock out of the solution. For feeding the chemicals hollow axle is provided at the centre of one end disc. Suitable arrangements are made for quick closing and opening the wooden door provided at the centre of the curved surface of the drum. Care is taken to see that no iron part comes in contact with chemicals inside the drum.[6]

Driving arrangements are usually provided according to the purpose for which the drum has to be used. For heavier liming drums low speed gear box may be used. When belt drive arrangement is made, fixed and loose pulleys are provided to stop or run the drum without disturbing the main drive of the factory. The drive being transmitted to the drum through a pinion with machine-cut teeth and cast iron gear-ring fitted to the drum end itself [6].

Thus, the capacity of a drum can be increased either by increasing its diameter or its width, but the increase of the capacity will be more due to increase of diameter than the width by the same unit. If the capacity is increased by increasing the width, the torque on the driving motor will unnecessarily increase because the drum is driven from one of its ends. Moreover, the chemicals added through the hollow axle will take longer time to get mixed with the liquor of the drum resulting uneven distribution of chemicals in the leather. Tanners therefore prefer to increase the capacity of the drum by increasing its diameter. But such increase in drum diameter increase the mechanical effect on the leather which cannot be completely compensate by reducing the revolution of the drum especially when the diameter becomes very high. So in tanneries standard size drums are generally used. According to diameter and process the r.p.m of a drum

varies. With standard drums the r.p.m varies with a range, depending on the process carried out [6].

Good quality, well seasoned timber, free from knots and other irregularities should be used for drum construction. The wood should also have the following qualities: (1) it should have moderately high density (2) it should be hard (3) it should not be too heavy and must not give off colour at different chemical conditions (4) it should be easily available (5) it should retain its shape in spite of atmospheric changes during different seasons of the year. (6) It should be inert to dilute acids and alkalies. (7) The wood should be non- absorbing type and. (8) it should be durable [6].

Alternative materials for tannery drum construction have frequently been investigated with varying degree of success. Stainless steel drums are primarily used for dyeing, milling and laboratory work but in some forms also for the liming and tanning processes. Theoretically there is no limiting factor in size but because of economic and design aspects the generally do not go beyond the 3m diameter \times 2.5m length mark, although a few manufactures list 4m \times 3m drums in their catalogues [42].

Fiberglass built drum bodies in small and medium sizes are in service. Their endurance over long periods is questioned. Polypropylene has been adopted as a constructional material, particularly for large bodies, as a substitute for wood and appear to offer advantages over it. A smoother interior is unarguable and resistance to the action of chemicals is claimed to be excellent. From a construction point of view polypropylene is moldable and thus offers greater flexibility in design. Circulation system ducting can be manufactured with greater precision and with optimal dimensions to suit the flow of liquid. Reinforced hoops and ties, door frames and door sealing can

all be integrally engineered without the limitation imposed by wooden components.[42]

A drum with equivalent exterior dimensions built in this material will have a 10% to 15% greater volume capacity than the wooden drum. Thermal conductivity is shown to be only slightly higher than with the timber built drum. Research carried out up to the year 2000 indicates that deterioration due to wear is less than that experienced with wood. Drives follow the pinion and gear ring arrangement as adopted by wooden drums. Dimensions wise so far bodies 3m diameter × 3m length are being offered [42].

2.7.6 Paddles

Now – a – days paddles are largely used in place of drums. The advantage of paddle over drum is that the stock is visible in paddle and so it is easy to control the process. Moreover, the mechanical beating is less in paddle than in drum. But unfortunately large volume of liquor is required in the paddle to ensure easy floating and opening of the stock during the operation and so, unless the same solution is reused paddle system becomes uneconomical.

Paddle is consists of a semi-cylindrical wooden or masonry vat fitted with a wooden paddle – wheel agitator. The size of the paddle drum varies widely, but a big size paddle may have 8' length 6' 7" width and 5' 7" depth with an agitator wheel of diameter 4'. [42]

The paddle has usually 4 vanes and the paddle blades dip a few inches into the liquor. If the liquor level is too high, the skins may tend to be carried over by the blades and wrapped around the axle. General practice has established that the best movement of skins is obtained when the paddle blades dip uniformly into the liquor to a depth 10 to 12 inches. The number of blades in the wheel is also very important. The greater the number of blades in the wheel, the smoother the action is on the skins. If less number of

blades (less than 4) is used, the skins get an increased hitting action rather than a push. This hitting action may have some detrimental effect upon the skins especially when the skins are in swollen condition. For easy working and smooth movement of the stock, the paddle wheel is generally set slightly back, of center, and the speed which varies from 5 to 20 r.p.m. is controlled by a suitable reduction gear. The object of paddling is to move the material in the solution to assist the diffusion process and to prevent goods from piling up. If the wheel turns too slowly, the hide will form a long roll at the bottom of the vat [6].

2.8 Sudanese rural tanning

The information given bellow was collected by interviewing 10 tanners in the villages of Baroka, and Algamair in Khartoum state using a structured questionnaire from 5th to 11th of June 2013. Data were also collected by direct observation, Photographs and films were captured from the site. The collected data included data on gender, age, education, and experience of the respondents. Furthermore, information on types and quality of raw materials, tanning vessels, tanning agents used and their effectiveness, the tests carried out during the different tanning stages, mechanical operations and the tools used, types and uses of the tanned leathers, management and marketing were noted. Moreover, notes on services offered by local authorities, hazards and safety equipments used, training programs they attended, waste disposal facilities and their acceptance of the modern tanning technologies were taken.

2.8.1 Raw materials (types and quality)

The rural tanners purchase their raw materials from the local market. The most species of raw materials used by rural tanners are sheep, goat skins, and cattle hides (**Figure 2.3.**).

Camel hides are scarcely processed. Tanning of Reptile skins declined since the secession of South Sudan. The most dominant types tanned are wet and dry salted followed by air dried hide and skins. Green or fresh hides and skins are not available. Most of raw materials processed are of low quality because it is cheap and easily obtainable. The number of pieces processed ranges between 75-100 pieces of sheep and goat skins and 30-50 pieces cattle hides per a week.



Figure 2.3: Raw hides and skins

The addition of water and materials for the different tanning processes depends on the number of skins or hides processed in the batch which they called it Tariha. In modern tanning methods the quantities of chemicals to be added are based on percentage skin weight. The batch consists of 75-100 pieces of sheep and goat skins and 30-50 pieces of cattle hides.

2.8.2 Soaking

Soaking process is done in underground pit (2m×1m×1.5m) dug in the ground and lined with red bricks and cement to prevent absorbance of the soak water by the ground (**Figure 2.4.**).

For every 100 pieces of sheep and goat skins they add 4 barrels (800 litres) of water. Soaking period varies according to the type of skin and hide from 3-6 hrs for wet salted to 1 day for dry salted and air dried hide and skins.



Figure 2.4 Soaking pit

The hides and skins are not washed before soaking, hence the soak water becomes very dirty and bloody and, the goods are greatly subjected to putrefaction. This is accentuated by the fact that, the soak water is reused many times before it finally thrown away and the rural tanners do not use biocides in soaking liquor to prevent bacterial attack. Another possible problem with the use of salted hides when soaking liquors are reused is that the concentration of salt in the liquor will increase to a level which will affect the diffusion of water into hides and skins. Moreover it is observed that the capacity of the pit is not sufficient for the number of skins processed. Therefore, the skins on the top have not adequate water for satisfactory soaking. Soaking is carried out under the direct sun light, the temperature of the soak water would be higher especially in summer season. However, the temperature of the soak water should be kept at 16°C to 21°C. If temperature exceeds 38°C, the protein fibers will tend to shrink, the skin lose area and become thicker, and protein fibers gelatinize, giving thick

inflexible leather. In addition, the putrefaction accelerates with increasing temperature resulting in loose empty leather, damage grain or even holes

2.8.3 Liming and unhairing

Liming is done in pits dig in the ground (**figure 2.5**) with the same dimensions of soaking pits.



Figure 2.5 liming pit

For liming, the rural tanner adds 4 barrels of water and 2 tints of burnt lime. The burnt lime is slaked first to avoid damage and burns to the skins during the slaking process.

Sometimes they use *trona* especially in winter season to accelerate loosening of hair. Liming process takes 4-8 days in case of sheep and goat skins and 10-15 days in case of cattle hides.

After liming, the hair is loose and the rural tanner scraps it with especially made tools called Dassa and Warjia as shown in (**figure 2.6**). For cattle hides the loose hair is removed using a knife with two handles and a wooden board called Kalwata (**figure 2.7**).

After removal of hair from the grain side, the flesh and fats are also removed from the flesh side using the same tools.



Figure 2.6: Dassa and Warjia



Figure 2.7: Knife and Kalwata

2.8.4 Bating

The fleshed hides and skins are transferred into other pits with the same dimension of soaking and liming pits where bating process takes place (**figure 2.8**).



Figure 2.8: Bating pit

Bating is done by treating the pelts with an infusion of hen or pigeon dung. For every 100 pieces of sheep and goat pelts, 2 barrels (400 liters) of water and 1 sack of pigeons or hens dung are added. The bating process takes from 15 to 30 minutes. The completion of the process is ascertained by the softness, fallen of the pelts and darkening of the pelt colour. Some tanners said that they know the completion of the process by the removal of lime smell.

The rural tanners do not carry out deliming process, because they believe that bating can remove the lime from the pelts and this view was proved to be incorrect. Under condition in which bating is carried out in tanneries, bating enzymes have no action on the collagen, elastine and lime. For pulling down the pelt the action of enzyme is not necessary and the removal of lime which is mostly combined with collagen is chemical and not enzymetical [6].

The removal of alkali from pelt before tanning is important and essential for the production of good quality leather. If limed pelts are put straight into vegetable tan liquor, without going through the deliming process, the lime present on the grain and flesh sides will quickly darken the colour of vegetable tannins. The colour of the leather also will be extremely dark due to the oxidation of tannin. On the other hand, calcium tannate is insoluble in water and therefore large amount of tannate in the interfibrillary spaces of the grain layer will cause roughness and crackiness to the leather [6]. Whether the removal is partial or complete depends on the type of leather to be produced. Unless the lime is removed, the finished leather will be hard; the grain will be brittle and discolored [1].

2.8.5 Fleshing

Fleshing is the removal of the hypodermis from the flesh side of hide or skin. Sheep and goat pelts are fleshed using Dassa and Warjia while cattle hides are fleshed by using a sharp Knife with two handles and a board. Rural tanners of Baroka perform fleshing operation after Bating and not after liming. It is better to carry out fleshing process after liming, because lime causes a plumping of hypodermis and makes it thick and flabby and can easily be cut off. While, after bating the skins are rendered soft and fallen due to the removal of plumping caused by liming process.

2.8.6 Tanning

Tanning process takes place in a cone-shaped hole (**figure 2.9**), dig in the ground.



Figure 2.9: Tanning pit

For every 100 pieces of sheep or goat skins, they add 4 barrels of water and 3-4 sacks of ground acacia nilotica pods (Garad). Garad powder is added in portions and the hides are trampled during each addition. In these holes sheep and goat skins remain for 1 day and cattle hides remain for 7 -10 days. The process is completed by adding 1 tint of common salts in case of sheep and goat skins and no salt is added in case of cattle hides. Some tanners said that they know the completion of the process by the appearance of small pebbles on the grain surface also by the leathers being apart from each other. In fact, pebbling and wrinkling of the skin surface may be caused by astringency effect. Astringent tannins draw together the grain of the pelt and produce hard leather. Moreover, immersing hides directly into strong solutions of vegetable tannins causes the surface to tan so hard and the pores are contracted too rapidly that the tannin cannot penetrate into the center producing leather which is untanned inside or “casehardened”. Furthermore, excess vegetable tannage may cause difficulties in dyeing and finishing thus must to be avoided. So that it is essential first to start tannage in mellow tan liquors and to follow them by using astringent tannins. In some modern

methods of tannage good sole or light leather is made by adjustment of the pH of the pelts which are then immediately immersed in strong liquors of 70-90° Bkr without causing casehardening of the surface [1].

Although Sudan has many indigenous tannin bearing trees, the most tanning material commonly used by rural tanning is *acacia nilotica* pods (Garad) because it is abundant and widely distributed in the country. Other tanning materials should be introduced to rural tanning and blends of these materials should be investigated to obtain better results. Also imported vegetable tanning materials such as mimosa which are not used by rural tanners may be introduced for their good properties they render to the leather.

2.8.7 Oiling

The rural tanners of Baroka apply oil only on cattle hides. The oil is prepared by immersing the exhausted sesame seeds, obtained from traditional oil mills, in water. Then the oily water is sprayed on the flesh side of leather. This method of oiling is not effective and the amount of oil prepared by this method is seems to be not sufficient for softening the leather. This is ascertained by the hardness of the produced leather. This method may be suitable for producing sole leather which has to be firm, hence requires little oil. Leather for shoe uppers and light leather, however, must be pliable and soft; therefore, much oil is required. The more pliable the leather has to be the more oil should be incorporated. Oil used alone can only penetrate the leather with difficulty. To facilitate penetration of oils into the leather, the oil should be used as an emulsion which can be made with the help of emulsifying agent such as soap or egg yolk. Sulphonated oils; these are oils which have been treated with sulphuric acid, and have become water- miscible, are commercially available. Therefore, it is important to

train the rural tanners how to prepare emulsifying and sulphonated oils using locally produced oils and to use them as fatliquors.

2.8.8 Drying and staking

Drying of sheep and goat tanned leathers carried out by hanging them over robes to dry by air, while calf and cattle leathers are spread out on the ground (figure 2.10)



Figure 2.10: Drying cattle hides

Before complete drying, sheep and goat leathers are pulled and stretched in all directions so as to reduce creases and to increase the area of the leather while, cattle hides and calfskins are folded grain side in, across the backbone. Cattle and calfskins are softened by working over with a tool called “*Moharra*” shown in (figure 2.11).



Figure 2.11: Moharra

In spite of all these efforts, it is observed that the tanned leathers are still hard and have many wrinkles and creases. These drying methods are carried

out under the direct sunlight. However, drying should be done in a semi-dark and well ventilated shed away from the sun, rain and excessive wind.

The rapid drying of leather by exposure to the sun or to very hot air is injurious; for it causes shrinkage, hardening, cracks and discoloration [1].

2.8.9 Uses of tanned leathers

None of the rural tanners interviewed had a workshop to turn his leathers into leather products. The tanned leathers were sold in the local market for shoes makers. According to the tanners the tanned leathers were used for making shoe uppers, lining and insole leathers. Other traditional products such as leather cases for cooling water and whips were also made. Hair removed from skins is used for making billows for donkeys (**figure 2.12**).



Figure 2.12: Making hair billows

2.8.10 Services

Water is not readily available for rural tanners of Khartoum state. They purchase water for tanning processes. Also, electricity and waste disposal facilities are not available. The tannery waste such as trimmings and the residues getting out from the pits and holes of the different processes are thrown away around the tannery (**figure 2.13**).



Figure 2.13: waste disposal

2.8.11 Hazards and safety equipments

According to the responders no occupational diseases or any hazards caused by tanning materials have been detected. Although some of the materials used by rural tanners have harmful effect such as lime, the rural tanners do not use any safety equipments to protect them from these materials. In addition, there is possible infection with bacteria when dealing with hides and skin or with pigeon and hens dung. Some tanners said that they only used gloves when they dealt with lime. Some tanners mentioned that some patients suffer from inflammatory bowel diseases were cured by immersing them for some time in tanning liquor (Garad solution).

2.8.12 Training

All of the respondents have never participated in any training program they said that they have never been called in to participate in such programs. It is very important for rural tanners to be trained on modern tanning technologies in order to be able to produce leathers of better quality.

2.8.13 Acceptance for new techniques

The rural tanners were interviewed whether they will accept the adoption of the proposed modern tanning technique, they said that they will accept the new techniques if it is shown to be better than their traditional methods, and

the produced leather is cheaper and of better quality than the leather produced by their method.

2.8.14 Problems facing rural tanners

One of the major problems facing the rural tanners of Khartoum state is the lack of water and other services such as electricity and waste disposal facilities. Water and electricity are the backbone for any industry. Therefore, a water supply and electricity source should be provided for rural tanneries. Moreover, shortage and high cost of raw materials due to the competition of modern tanneries and the foreigners such as Chinese and Nigerians who they offer high prices for the raw materials. Furthermore it is observed that tanning processes are carried out in an opened area, they have no shelters to protect them from exposure to direct sun light, rain and strong wind, this is due to poverty and. Therefore, financial assistance is very important to enable rural tanners to build up their tanneries and equipped them with the necessary tools and machines and to be able to purchase raw materials and chemicals. To enable rural tanners to produce leathers of good quality, they must be trained on modern tanning methods. Also they should be aware of the importance of safety precautions and first aids. Further studies should be conducted in other parts of the country to document the tanning methods practiced in those parts and to explore the possibilities for development.

Materials and Methods

3.1 Raw materials

Freshly flayed sheep skins, obtained from local market were used for optimizing chrome offer operations to be used for rural tanneries as a pre-tanning agent.

Wet salted goat skins of large sizes were used in the matched- sides trials for recycling the process liquors from soaking up to re-tanning.

3.2 Tools, instruments, machines and apparatuses

- A hand- operated drum especially designed for the study was used to carry out the beamhouse, tanning and retanning operations.
- A traditional shrinkage tester (prolific shrinkage tester sr No 1340.1.2) was used for determining the shrinkage temperatures of pre-tanned and retanned leathers.
- A standard dial micrometer gauge was used for measuring the thickness of crust leathers.
- A tensile machine was used for determining the tensile and tear strength of crust leathers.
- Lastometer tester was used for determination of the load and distension at grain crack of crust leathers.
- Furnace was used for determining the ash and insoluble ash content of crust leathers.
- Air oven was used for drying the samples used for determining the moisture, fat and oil, total ash, insoluble ash, total soluble of crust leathers.

- Digital balance was used for weight measurement of samples and chemical reagents. Electric heater was used for boiling and heating processes.
- pH papers were used for determining the pH of the liquors and pelts in different tanning processes.
- Glassware (beakers, volumetric flasks, burettes, pipettes, funnels etc.) were used in chemical analysis of crust leathers and used liquors.

3.3 Chemicals

3.3.1 Chemical used for tanning operations

All the chemicals used for beamhouse, pre-tanning and retanning processes were of commercial grade and these include: bactericide, sodium sulphide (60% pure), lime (62% $\text{Ca}(\text{OH})_2$), delimiting agent (Ammonium sulphate), bating agent (Orpon), common salt, sulphuric acid, Basic chromium sulphate (26% Cr_2O_3 , 33% basicity) used as pre-tanning agent, *Acacia nilotica* sp *tomentosa* pods (garad) were used as re-tanning agent. Garad pods were ground in a mill and used in the powder form, Fatliquor.

3.3.2 Reagents used for chemical analysis of crust leathers

Reagents used for chemical analysis of crust leathers were of analytical grade and these include:

Light petroleum ether, HClO_4 , conc. H_2SO_4 , conc. HNO_3 , KI solution, $\text{Na}_2\text{S}_2\text{O}_3$, starch indicator.

3.3.3 Chemicals used for analysis of spent liquors

Reagents used for chemical analysis of spent liquors were of analytical grade and these include the following:

HClO_4 , conc. HNO_3 , KI, sodium thiosulphate, starch indicator, phenolphthalein, glycerol, Zinc carbonate, Na_2CO_3 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, Lead acetate, HCHO , NH_4Cl , NH_4OH , Ammonium oxalate, potassium

permanganate , Silver Nitrate, potassium thiocyanate , Ferric ammonium sulphate

3.4 Design of a hand – operated drum

A stainless steel drum was especially designed to carry out all the wet processes from soaking through retanning. Six shelves were fitted perpendicularly to the inside of the drum wall to lift the goods during the process and to promote turbulence and interaction between goods and float. Two flanges were fitted to the ends of the drum tightened to the drum ends by four plastic- coated bolts fixed with nuts from the outside. The stub axles were inserted into two ball bearings and the housing were mounted on two iron support stands. On the driven side a handle was fitted to enable the tanner to revolve the drum easily while a funnel was joined to the other side to allow chemicals and liquids to be poured into the drum through it while the drum is rotating. For loading and unloading the drum, a removable door sealed with rubber to prevent leakage was made by cutting a rectangular piece from the body of the drum. The door was fitted with a clamp to keep it in place while the drum is rotating. The drum was design using TopSolid programme as illustrated in **Figure 3.1**.

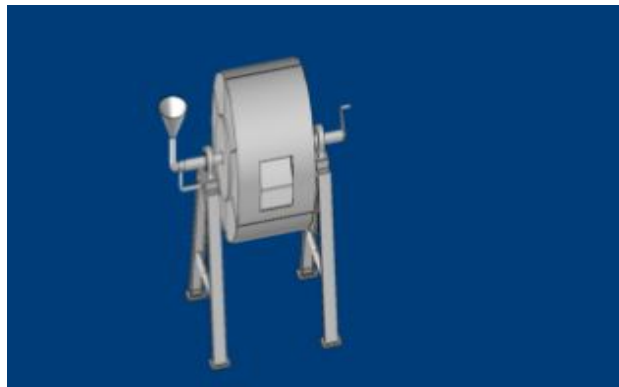


Figure 3.1: A hand- operated drum

3.5 Developing an optimum recipe to be used for rural tanneries

Wet –salted sheep skins, of fairly similar size and free from physical defects (18 skins) were trimmed, divided into nine batches (two skins per batch). Each batch was converted into pickled pelts by traditional Beam house operations (Soaking, Liming –Unhairing, Deliming- Bating and Pickling processes) using the hand – operated drum designed above.

To optimize the amount of chrome offer to be used as a pre-tanning agent in rural tanneries, eight proportions of chrome powder (26% Cr₂O₃, 33% basicity) offer were used varied from 0.5% to 4% along with a fixed amount (20%) of a vegetable retanning agent (Garad) and other chemicals. The formulation of pre-tanning, tanning and retanning operations are given in **Table 3.1**.

The values of corresponding shrinkage temperatures for both pre-tanned and retanned leathers of experiments and control leathers were determined. The crust leathers obtained were also subjected to various physical tests and chemical analysis to check their applicability to the manufacture of footwear articles. The shrinkage temperatures and physical properties values of various tanned leathers were benchmarked against the standard for selecting the optimum amount of chromium suitable for rural tanning. In the experiments carried out eight experiments of chrome – Garad combination tannage processes were carried out. In each experiment two pieces of pickled sheep skins were used. Another two pieces of pickled sheep skins were tanned using only vegetable tanning agent (garad) in order to use them as control. Fatliquoring process was carried out common to all combination processes and control. The formulations used in these combination experiments and control are shown in **Table3.1**.

Table 3.1: Formulation of beamhouse, tanning and retanning operations for experimental and control processes

Process/products	% *	Time	pH	Remarks
Dirt soak				
Water	200	2hrs		
Main soak				
Water	200	2hrs		leave O/N
Bactericide	0.1			
Unhairing and Liming				
water	200			
Na ₂ S (60% pure)	2.5	2hre		
lime (62% pure)	2.5	4hrs		
Leave Overnight, flesh, wash, take fleshed weight				
Deliming and Bating				
Water	100			
ammonium sulphate	2	2hrs	8-8.5	Colorless to phenolphthalein
bating agent(Oropon)	0.5	2hrs		check air flow
drain and wash				
Pickling and pre- tanning				
water	100			
common salt	10	10min		check Baume
sulphuric acid	1.5	2hrs	2.8-3	
Chrome(26% Cr ₂ O ₃ ,33% basicity)	x	6hrs		x=0.5, 1, 1.5, 2, 2.5, 3, 3.5 or 4% check penetration
Basification				
Sodium bicarbonate (dissolve 1:20)	0.8	2hrs	4-4.2	add slowly until the desired pH is achieved
Leave Overnight, check T_s, drain and pile				
Retanning				
water	200			
Garad powder(30% tan)	10	4hrs		
Garad powder(30% tan)	10	4hrs		
leave overnight, drain and wash				
Fatliquoring				
water	100			
Fatliquor (Rockol Atlas)	5	2hrs		
Formic acid(1:10)	0.3	15min	3.5	
Drain and wash, pile O/N, check T_s, toggle dry, stake and trim				

*Percentages are based on wet salted weight for soaking, soaked weight for liming, fleshed weight for deliming, bating, pickling and tanning, and wet blue weight for retanning and fatliquoring.

3.6 Physical testing of leathers

Tensile, and load at grain crack of crust leathers were performed according to the official methods of analysis.[43] Tear strength was determined as per standard procedure. [44].

3.6.1 Sample preparation

The specimens for physical testing were obtained from experimental and control crust leathers, cut from official position (**Figure 3.2**)

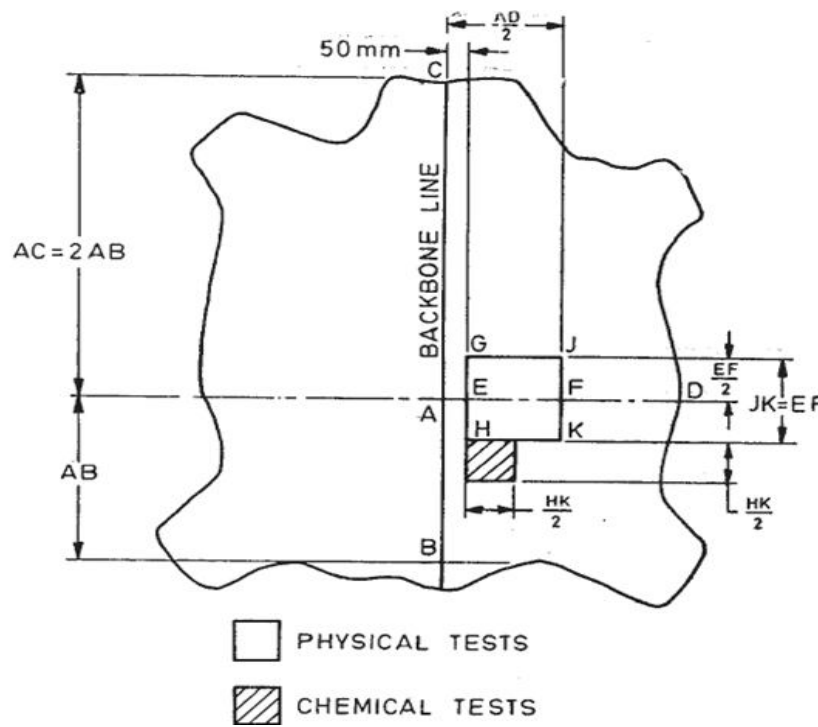


Figure 3.2: location for cutting out test pieces in a whole hide, skin and side Specimens for tensile and tear strength were cut parallel and perpendicular to the backbone and the thickness of each specimen was measured using a standard thickness gauge at three positions on the grain side and three positions on the flesh side, and then the mean of the six measurements was calculated. Each value for tensile and tear strength represents the average of four samples (2 values along the backbone and 2 values across the

backbone). Each value for grain crack strength is the average of three samples.

Figures 3.2 represents a skin or hide with the head removed. B is the root of the tail. A is a point on the backbone such that $AC = 2AB$. AD is a line perpendicular to BC. F is the midpoint of AD, and AE is of length 50mm. the lines GH and JK, whose midpoints are E and F respectively, are parallel to BC and each of length equal to EF. The pieces for physical tests were cut from the square HKJG, and as close to the line EF as possible.[43]

3.6.2 Conditioning

During the 48 hours immediately preceding its use in a test, each specimen for physical testing were kept in a standard atmosphere of temperature $20^{\circ} \pm 2^{\circ}\text{C}$ and relative humidity $65 \pm 2\%$. [43]

3.6.3 Measurement of thickness

After the specimens were conditioned in accordance with the method for conditioning, the specimens were placed in the gauge with the grain side up. The load is applied gently and the reading is taken five seconds after the full load is reached. Three measurements were taken at three positions; at the point E and midway between E and the lines AB, CD and the mean of the three thickness measurements was taken as the thickness of the specimen. The area of cross section of each specimen was calculated by multiplying its width by its thickness. [43]

3.6.4 Measurement of tensile strength and percentage

Four specimens were cut, (two parallel and two perpendicular to the backbone) with the press knife having the shape and dimensions of the internal surfaces shown in **figure 3.3**.

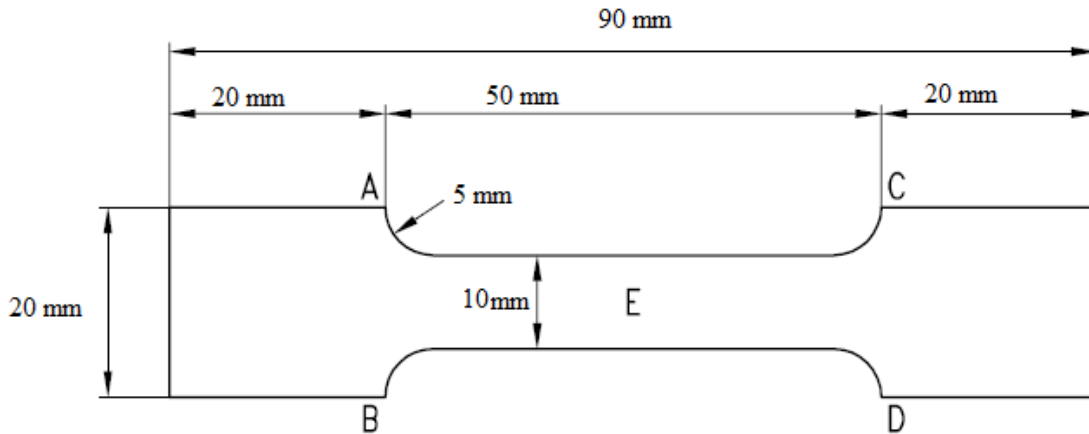


Figure 3.3: Shape and dimensions of tensile strength specimen

The specimens were conditioned according to the method of conditioning. The thickness of each specimen is measured to the nearest tenth of a millimeter at three positions on the grain and at the three positions on the flesh side; in each group of three, three measurements were made one at the midpoint E of the waist of the specimen and the other two at positions approximately midway between E and the lines AB, CD. The arithmetic mean of the six measurements is taken as the width of the specimen. The thickness of each specimen is measured in accordance with the method of measurement of thickness. The area of cross section of each specimen was calculated by multiplying its width by its thickness. The jaws of the tensile strength machine were set 100mm apart and the specimen was clamped in the jaws so that the edges of the jaws lie along the lines AB, CD and the grain surface of the specimen lead in one plain. The machine was run until the specimen broken and the highest load reached was taken as the breaking load. The tensile strength was calculated in kg/cm^2 by dividing the breaking load by the area of cross- section of the specimen.

The distance between the pair of the jaws at the instant when rupture of the specimen occurred was noted and the elongation at break was calculated by taking the difference between the initial length and the length at break. This difference was expressed as a percentage of the initial length.[43]

3.6.5 Measurement of tearing load

Tongue tearing is a simpler tear test where the tearing takes place through the weakest region of the leather specimen. A 5mm diameter hole was punched at a point one- third of the length of the specimen, 75×25mm from one end and on the central line of the specimen as shown in **figure 3.4**

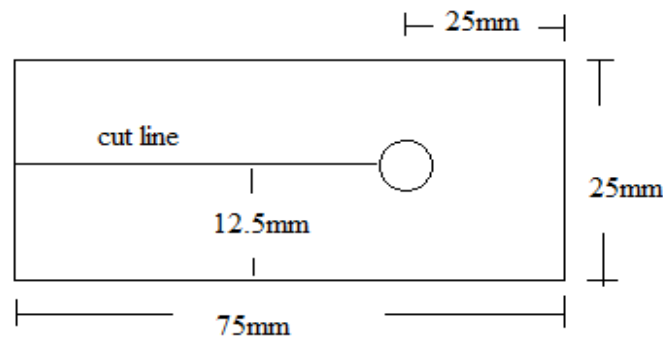


Figure 3.4: Tear specimen dimensions

The leather specimen was then cut into two tongues at right angle to the grain surface for two third of its length. The ends of the two tongues thus formed were clamped to the two jaws respectively of the tensile strength tester. The load required to continue the tear is recorded from the dial of the machine.[44]

$$\text{tearing strength kg/cm} = \frac{\text{tearing load (kg)}}{\text{leather thickness (cm)}}$$

3.6.6 Measurement of distension and load at grain crack

The specimens were cut and conditioned in accordance with method SLP.3. The conditioned specimen was clamped in the instrument with its flesh surface adjacent to the ball, and its grain surface flat. The distension was increased until the grain cracked then the load and distension were noted. The loading continued with a little delay as possible, when the disc burst the load and distension were noted. The means of three tests were taken for the load and distension at grain crack and the corresponding values at burst were reported. [43]

3.6.7 Measurement of shrinkage temperature

If a strip of leather is slowly heated in water, a sudden shrinkage occurs at a temperature which is characteristic of the tannage. This temperature is called the shrinkage temperature.

Shrinkage temperatures of both tanned and retanned leathers as well as for control leathers were determined for each tannage using a traditional shrinkage tester (prolific shrinkage tester sr No 1340.1.2). The specimens were cut from the official sampling position as strips of length and breadth 50mm and 3mm and two small holes were punched at positions 5mm from the ends and on a line parallel and equidistant from the sides of the rectangle. The specimen was supported from the hooks and immersed into water put in a glass beaker at room temperature. The water was slowly heated at 2°C/min and continuously stirred using magnetic stirrer attached to the tester. The temperature of the water was gradually increased and the temperature of the water at which the strip shrunk was taken as the shrinkage temperature of the leather. The mean of three measurements was taken. [43]

3.7 Chemical analysis of leathers

moisture content, chromic oxide content, oil and fats content, total ash content, water soluble matter, insoluble ash, hide substance and degree of tannage of both combined tanned leathers and control were determined by the official methods of analysis.[45]

3.7.1 Sampling

The items envisaged for chemical examination are first divided in accordance with the sampling direction for physical tests see (**figure 3.2**). The designations given in the figures in SLP.2 also apply on to the present directions. Slight defects in the grain or flesh side are of no significance.

A square piece of leather adjacent to line HK see (**figure 3.2**) in the direction of the root of the tail, is taken from point H and with the side length equal to the half line HK. If necessary, the section can also be taken from the corresponding place in the opposite half of the skin.[45]

3.7.2 Determination of moisture content in leather

Sample was cut into small pieces and 5gms of the sample were taken and dried at $102\pm 2^{\circ}\text{C}$ in a normal oven for 5 hours. After cooling in the desiccators, the sample was weighed. After a further one hour drying and half hour cooling, the weight was checked again and the process of drying and cooling was repeated until a constant weight was obtained. [45]

$$\text{moisture \%} = \frac{w_1 - w_2}{w_1} \times 100$$

w_1 = weight of sample before drying

w_2 = weight of sample after drying

3.7.3 Determination of oils and fats

5gm of the sample was placed in a Soxhlet apparatus attached to a weighed flask to be extracted with light petroleum ether B.P below 60°C for 5 hours.

After extraction, the solvent was decanted from the fatty residue. Then the extract was dried at 100 °C in an oven for 4 hours, cooled and weighed.[45]

$$\text{fat content \%} = \frac{\text{g extract}}{\text{g original sample}} \times 100$$

3.7.4 Determination of water soluble matter

Water soluble is defined as the quantities of all those substances, which under certain conditions, are dissolved out of the leather by water. These are principally organic tannins, non-tannins and mineral salts. After the extraction of fats, the sample of the leather was shaken at 50±10 revolution per minute for two hours with 500 ml distilled water at 22.5 ± 2.5°C in a wide necked flask. Then, the content of the flask was filtered until clear and the first 50ml of the filtrate was discarded. A further 50ml of the filtrate was evaporated on the water bath until dry on a previously weighed dish heated at 800°C, dried at 102 ± 2°C for two hours, cooled in the desiccators and weighed quickly. The drying was repeated until the reduction in weight amounts to less than 2 mg.[52]

$$\text{total water solubles in \%} = \frac{\text{g dry residue} \times 10}{\text{g original weight of leather}} \times 100$$

3.7.5 Determination of insoluble ash

. The leather after extraction of water soluble matter was air dried, separated from the filter paper, and transferred to a tared dish. The leather was heated gently at first until decomposed. Then, the ashing was completed in a muffle furnace, at 800°C until all carbon was consumed, cooled in a desiccator and weighed. [45]

$$\text{insoluble ash in \%} = \frac{\text{g ash}}{\text{g original sample}} \times 100$$

3.7.6 Determination of chromium in leather

Aim: The chromic oxide content of a leather is defined by the quantity of chromium compounds found in it, calculated as chromic Cr_2O_3

Principle: The trivalent chromium present in the leather is converted into hexavalent state using strong oxidizing agent like the acid mixture. In this process the organic matter on the leather is also thoroughly digested. Consequent liberation of iodine by the addition of potassium iodide and titration with standard sodium thiosulphate leads to the estimation of chromium.

Reagents: acid mixture (11.5ml HClO_4 + 3.5ml conc. H_2SO_4 and 5ml conc. HNO_3), 10% KI solution, 0.1N sodium thiosulphate solution and starch indicator.

Procedure: 1g of leather sample, cut into small pieces was weighed accurately and transferred into a 250 ml conical flask. 20ml of acid mixture was added and the flask was covered with a funnel so that water can evaporate without loss by splashing and the contents were heated to boiling. After the colour was completely changed to orange, the contents were cooled immediately and 100ml of distilled water and a few porous bits were added to eliminate chlorine created and the contents were boiled for 10 min. After cooling, 15ml of pure phosphoric acid and 10ml 10% potassium iodide solution was added to mask any iron present. The contents were left to stand 10 min in the dark, then titrated to light green using 5 ml of a 1% starch solution as indicator, with 0.1N sodium thiosulphate. 1ml 0.1N thiosulphate solution corresponds to 0.002534 g Cr_2O_3 . [45]

$$\%Cr_2O_3 \text{ in leather} = \frac{\text{ml 0.1N thiosulphate solution}}{\text{g leather taken}} \times 0.002534 \times 100$$

3.7.7 Determination of total ash

5 g of the prepared sample was put into a previously weighed tared crucible, heated gently at first until the leather completely decomposed then, the ashing was continued in a muffle furnace at 800°C until all the carbon is consumed. Then the crucible was cooled in a desiccator and weighed. Re-ignited, cooled and weighed until constant weight was obtained.[45]

$$\text{total ash in \%} = \frac{\text{g ash}}{\text{g original sample}} \times 100$$

3.8 Recycling operations

Seven wet salted goat skins were trimmed and each of them was cut across the backbone in two symmetrical halves. The right halves were used as control and the left halves were used as experiments. The control halves were soaked, limed, delimed and bated, pre-tanned and retanned using the method presented in **Table 3.1**. The pre-tanning was performed using 3% chrome offer. The re-tanning was carried out using 20% ground *Acacia nilotica ssp tementosa* pods (Garad).

The spent liquors at the end of each process was collected, filtered, sampled and reused in the next operation. Seven cycles were carried out using the spent liquor from the previous cycle of each process after being analyzed and replenished with the calculated amounts of chemicals and topped up to the required float.

The liquors for analysis were filtered as rapidly as possible in polythene bottles which were completely filled with the filtered liquors and tightly

stoppered, leaving no air space to reduce the oxidation of sulphide and the absorption of carbon dioxide to a minimum.[45]

3.8.1 Estimation of sodium sulphide in used lime liquor

To estimate the amount of Na_2S in the given sample of used lime liquor

Reagents: 0.1N Zinc sulphate solution (1.435g of ZnSO_4 dissolved in 100ml of dist. Water), Buffer solution pH 10 (17.5g of NH_4Cl + 140ml of NH_4OH dissolved in 250 ml water)

Procedure: The lime liquor was filtered to remove the suspended matter 20ml of buffer solution was taken in a conical flask. 25 ml of the filtered lime liquor was added to it. The contents were titrated against zinc sulphate solution using 10% lead acetate solution as external indicator. The end point was ascertained by spotting into a dry filtered paper along with 10% lead acetate solution till no more brown color or stains were developed immediately.[45]

Calculations: 1 ml of 0.1N ZnSO_4 = 0.0039g of Na_2S

3.8.2 Analysis of used lime liquor

Aim: To estimate the amount of lime in the used lime liquor

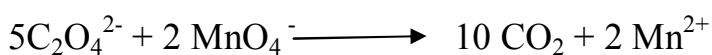
Principle: The calcium in the used lime liquor is precipitated as calcium oxalate and dissolved in hot sulphuric acid. It is then titrated against standard potassium permanganate.

Reagents: Saturated solution of ammonium chloride (10%), Ammonium oxalate 10% solution and 0.1N solution of potassium permanganate

Procedure: 50ml of filtered lime liquor was pipette out into a beaker. It was diluted to about 250ml with dist. Water. 25 ml of ammonium chloride was added and boiled. Hot solution of ammonium oxalate was added to precipitate calcium. The beaker was allowed to stand on a water bath for 2 hrs. the precipitate was then filtered and washed with dilute ammonia

solution till it was free of oxalate. This was ascertained by taking 25 ml of filtrate acidified with dil. H₂SO₄ did not decolorize 1 drop of 0.1N KMnO₄. The calcium oxalate precipitated on the filter paper was dissolved into a 500ml beaker using hot H₂SO₄ and this hot solution was titrated against standard permanganate. The end point was the appearance of permanent pale pink colour.[46]

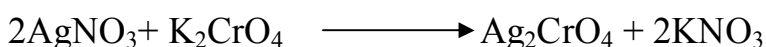
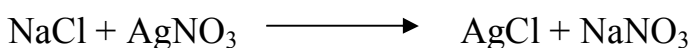
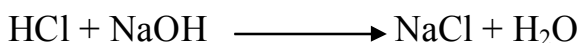
Calculations: Lime present in 50 ml of used lime liquor as calcium =
 $V_{\text{KMnO}_4} \times N_{\text{KMnO}_4} \times 0.02$



3.8.3 Analysis of pickle liquor (NaCl – HCl system)

Aim: The aim is to estimate the amount of the amount NaCl and HCl in the given sample of pickle liquor.

Principle: The pickle liquor was titrated against standard NaOH to find out the acid content and the neutralized pickle liquor is titrated against standard AgNO₃ to find out the salt content.



Reagent: 0.1N NaOH and 0.1N AgNO₃

Procedure: 10 ml of diluted pickle liquor was taken in a conical flask and titrated against 0.1N NaOH using phenolphthalein indicator. The end point was the appearance of pale pink colour.

In another flask, 10 ml of pickle liquor was pipetted out and the acid present was neutralized by adding the same amount of alkali consumed in the previous experiment. Then it was titrated against standard AgNO₃ using potassium chromate indicator. The end point was the appearance of brick red color precipitate.[46]

Calculation:

Pickle liquor Vs NaOH = a cc

Pickle liquor Vs NaOH = b cc

1 cc of 0.1 NaOH = 0.00365g HCl

1 cc of 0.1N AgNO₃ = 0.005845g NaCl

a cc of the of N NaOH = 0.00365 × a × N NaOH /0.1 = g HCl in 10 cc of sample.

Salt content = total chloride – chloride in reaction with AgNO₃

Mill equivalents of total chlorides = V_{AgNO₃} × N_{AgNO₃}A

M eq. of HCl = V_{NaOH} × N_{NaOH}B

Amount of NaCl in 10 ml = (A-B) × 0.005845/0.1

3.8.4 Determination of chromium in used liquor

Aim: This method is used for the determination of chromium in used liquors.

Reagents:

- Pure concentrated nitric acid
- A mixture of 230 ml perchloric acid 60% and 70% ml pure concentrated sulphuric acid
- 10% potassium iodide solution
- 0.1N sodium thiosulphate solution
- 2% soluble starch solution.

Procedure: A measured volume of the chrome liquor containing approximately 0.05g Cr, was transferred to a 500 ml conical flask provided with a funnel in the mouth to act as a trap. 20 ml concentrated nitric acid were added followed by 20 ml of the perchloric/sulphuric acid mixture. The flask and its contents were gently heated at the boil until the mixture became

a pure orange- red colour. The boiling continued for further one min after this point had been reached. The flask was removed from the source of heat and cooled rapidly as soon as ebullition had ceased by swirling the flask in a bath of cold water. 100 ml distilled water, a few glass beads or anti – bump granules were added and boiled for 10 min to remove free chlorine. The solution was cooled using sodium thiosulphate solution.

The solution was cooled to 20°C and transferred to an iodine flask. 10 ml 10% potassium iodide solution were added and the stopper moistened with the same reagent and replaced. The flask was allowed to stand for 10 min in the dark. The stopper and the neck of the flask were washed with distilled water into the solution and titrate with 0.1N sodium thiosulphate solution adding the starch indicator when the titration was almost completed.[45]

Calculations:

The chromium content should be calculated using the factor

1 ml 0.1N titrant \equiv 0.00173 g Cr or 0.00253 g Cr₂O₃

3.8.5 Tannin analysis

The presense of the salts and non tans in the used lime liquor will influence the Bk reading. This means that a used liquor of 20° Bk may contain only 0.3% tans, which account for 2°Bk, the other 18 ° Bk being due to the salts and non tans. In order to obtain a more precise idea of the tan content any liquor can be analyzed in the laboratory by the “shake” method. [14]

A sample of the liquor to be analyzed was taken from the tan liquor which has been well plunged. A definite quantity of this liquor was taken so that on diluting it to 1 liter with distilled water, a solution of 0.4% tan strength was obtained.

50 ml of this liquor was pipetted into an evaporation basin, evaporated to dryness and the residue weighed. This measures all the soluble and insoluble tans and non- tans.

To determine the soluble, the prepared solution was filtered by filtered paper, the insoluble tans and non tans settling out on the paper. 50 ml of the optically clear filtrate was pipetted into an evaporation basin, evaporated to dryness and the residue weighed to give soluble tans and non -tans.

Another aliquot was shaken with hide powder, which has been treated with chrome alum solution in order to accelerate the fixation. The hide powder abstracted the tans, Left in the solution are the non tans e.g. acids, salts and sugar, which are filtered off from the tanned hide powder , evaporated to dryness and weighed to give soluble non- tans

The preparation of chrome tanned hide powder: 3.125g of hide powder was digested with 31.25ml distilled water for one hour. 3.125ml of 3%chrome alum solution were added and stirred frequently for several hours and allowed to stand overnight. The powder was transferred to a filter cloth, drained and squeezed. The cloth was put in a porcelain dish, opened and 46.9ml of water were added. The powder and water were mixed and digested for 15min, drained and squeezed to approximately 75% moisture content. The digestion was repeated three more times in the same manner with distilled water and finally squeezed to about 75% moisture. The cake of the powder was mixed uniformly and weighed. The quantity (Q) of chromed powder was added to a shake bottle containing 50ml of the unfiltered tannin liquor plus (13.125- Q) ml distilled water and shaken with hand for 15sec and then with a rotary shaker at 50 rpm for 10min. the powder and the solution were poured into a filter cloth supported by a funnel, drained and squeezed. 1g of kaolin was added to the filtrate, mixed and filtered through a

filter paper and repeated until clear. 25ml of the filtrate was evaporated and dried to a constant weight. Tannin matter was defined by subtracting non tannins from total solubles. [45]

Results and discussion

4.1 Developing an optimum recipe to be used for rural tanneries

To optimize the amount of chrome offer to be used for pre-tanning in rural tanneries, different proportions of chrome offer were used. The effect of chrome offer on chromic oxide content in leather was studied and the results of corresponding shrinkage temperatures values for both pre-tanned and retanned leathers of experiments and control leathers were determined. The crust leathers obtained were also subjected to various physical tests to check their applicability to the manufacture of footwear articles. Considering the shrinkage temperature and the properties of the tanned leathers as well as the cost suitable for a rural tanner, the optimum chrome offer was selected.

4.1.1 Effect of chrome offer on chromic oxide content in leather

The effect of chrome offer on Cr_2O_3 content in leather was presented in **Figure 4.1**.

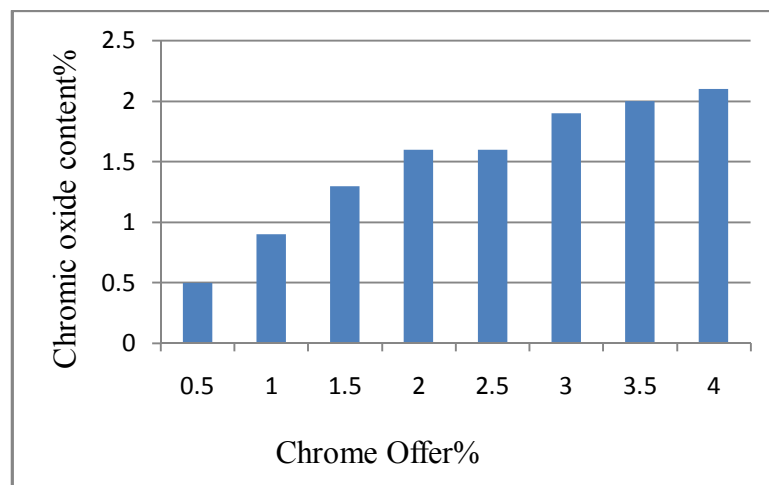


Figure 4.1: Effect of chrome offer on chromic oxide content in leather

The final chromic oxide content in the experimental crust leathers was found to range between 0.5- 2.1% resulting from initial chromium powder offers in

the processing bath ranging from 0.5% through to 4% chrome powder. From the figure it is observed that the chromic oxide content in leather increased as the chrome offer increased.

4.1.2 Effect of chromic oxide content in leather on shrinkage temperature

The effect of chromic oxide content in leather on shrinkage temperature was presented in **Figure 4.2**

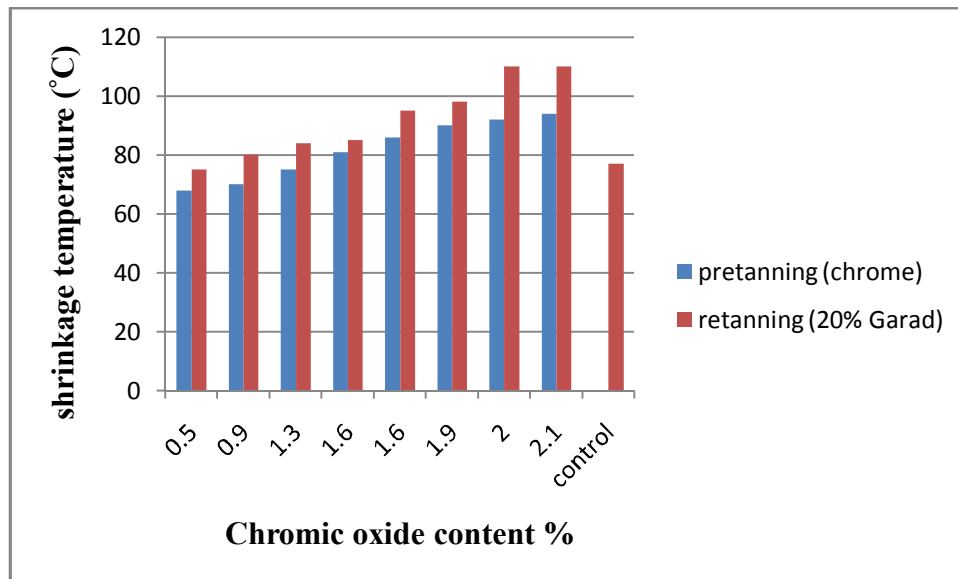


Figure 4.2: Effect of chromic oxide content in leather on shrinkage temperature

From the above figure it is obvious that the shrinkage temperature increased with the increase of chrome content in leather. However, all of the chrome offers applied could not be able to achieve a shrinkage temperature of 100°C before re-tanning; this affected the boil fastness of the leathers produced. After re-tanning a shrinkage temperature of approximately 100°C was achieved with 3% chrome offer. The control sample tanned with 20% Garad has gained only a shrinkage temperature of 77°C which does not fulfill the

requirements for foot ware leathers. However, most end-uses of leather require high hydro-thermal stability.

For example, shoe upper leather must withstand hot lasting and heat setting, while garment leather must withstand steam pressing [26]. So that the hydrothermal stability must be raised higher than the value quoted above in order to meet the desired requirement. This was achieved by introducing chromium as a pre-tanning agent.

4.1.3 Effect of chromic oxide content on physical properties of crust leathers

The values for physical tests for experimental and control leathers were presented in **Table 4.1**

Table 4.1: Physical properties of crust leathers from experimental and control processes

Parameter	Experimental (Chromic oxide in leather %)							Control (20%Garad)
	0.9	1.3	1.6	1.6	1.9	2.0	2.1	
Tensile strength (kg/cm²)	191.8	190.5	216.5	203.4	250	204	215.8	219.8
Elongation at break (%)	64.5	56	68	60.5	61	55.5	66	49.5
Tongue tear strength (kg/cm)	26.6	37.7	34	41.4	31.2	40.1	28.6	34.5
Load at grain crack (kg)	6.5	8.3	9.5	8.5	7.8	7.1	8.2	7.1
Distention at grain crack(mm)	11.5	9	11.7	11.5	10.7	11	12	11.3

Values for tensile strength, elongation and tear strength are the average values of four readings; two are parallel and two are perpendicular to the backbone. Values for load at grain crack are the average of three separate determinations.

The leathers tanned with 1% and 1.5% chrome; contained 0.9% and 1.3% respectively have the lowest tensile strength among all other leathers (<200kg/cm²). This low tensile strength was not due to less lubricants of the fibre surfaces i.e. low sliding effect because their percentages elongation were high, but may be due to the weak and less number of fibres in these leathers and this was shown by the low tear strength of these leathers.

The leathers tanned with 3% and 4% chrome powder; contained 1.9% and 2.1% respectively, show high tensile strengths but low tongue tear strengths. Low tongue tear strength may be due to poor fibre strength of the original raw skin or the fibre strength reduced during pre-tanning operations. And the high tensile strength, inspite of poor fibre strength, indicates that the number of fibres per unit cross sectional area of the leather was high i.e. the leathers had a good substance. There was no significant difference in percentage elongation at break between the experimental leathers. This indicates that the interfibrillary material were the same for all experimental leather. But the percentage elongation of control leather was less than the experimental leathers and this may be due to the effect of chromium which increased the extensibility of the experimental leathers or the total lubricants were more in experimental leathers than in control leathers.

4.1.4 Chemical analysis of crust leathers

The chemical analysis of crust leathers were given in **Table 4.2**. The chemical characteristics of the experimental and control leathers were found to be quite normal. The low values of total matter soluble in water for experimental leathers indicate good resistance to water, while the control leather showed the highest value of water soluble indicating that it has less resistance to water.

Table 4.2: Chemical analysis results of experimental and control crust leathers

Parameter	Experimental (Chrome Powder offer%)								Control(Garad)
	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	
Moisture %	8.6	7.8	8	7.4	9.6	9.6	9.9	12.4	9.4
Total ash content%	4.9	3	5.4	3	5.8	6	5.1	3.1	9.3
Cr ₂ O ₃ content%	0.5	0.9	1.3	2.6	2.6	2.9	3.2	4.5	-
Water soluble matter%	0.98	0.4	1.02	0.6	1.12	1.2	1.0	0.54	1.84
Insoluble ash %	0.96	1.1	1.6	1.4	2	2.4	2.1	3.4	0.8

4.1.5 Recommended recipe

From the above discussion, considering the shrinkage temperatures and the properties of the crust leathers obtained as well as the cost suitable for a rural tanner, a chrome powder offer of 3% (based on the fleshed weight) has been found to be the optimum offer to be used by rural tanneries as a pre-tanning agent. Beamhouse, retanning and fatliquoring operations can be carried out as indicated in **Table 3.1**.

4.2 Recycling of spent liquors

4.2.1 Recycling of soaking liquors

The analytical results of soaking liquor for dirt and main soak of cycle 1 and cycle 7 of were presented in **Table 4.3**.

Table 4.3: Salt concentration (g/l) of dirt and main soak

Cycle No	Dirt soak	Main soak
1	7.5985	1.1690
7	9.3520	2.1627

Recycling of soaking liquors greatly depends on the amount of salt, dirt, dung and blood carried over by salted hides and skins. The accumulation of salt in recycled soaking liquor may reach to a level which may affect soaking process. Also, the accumulation of organic matters in this liquor will lead to putrefaction. So it is risky to recycle the dirt soak liquor, instead this liquor may be used in pickling operation due to high concentration of salt.

4.2.2 Recycling of unhairing and liming liquors

The analytical results of the spent solution after each cycle reported to the nearest milligram were given in **Tables 4.4**.

Table 4.4: Analytical results of spent lime-sulphide liquors used for each cycle

Cycle No	pH	Na ₂ S (g/l)	Ca(OH) ₂ (g/l)
1	13	3.900	0.481
2	12	4.290	0.377
3	13	2.870	0.474
4	12	2.652	0.423
5	12	2.184	0.423
6	13	2.262	0.444
7	13	2.324	0.370

Although there was a reduction in unhairing- liming liquor due to losses on recovery, screening and uptake by the skins, an average of about 43% recovery of unhairing- liming liquor was obtained. The chemical savings amounted to about 40% in sodium sulphide, 34% in lime and 60% in water. The average consumptions based on the soaked weight were 3% Na₂S, 3.3% lime and 160% water. The removal of hair, scud and plumpness of the pelts were satisfactory in all cycles.

4.2.3 Recycling of deliming liquors

The analytical results of spent de-liming-bating liquors reported to the nearest milligram were given in **Table 4.5**.

Table 4.5: Analytical results of spent deliming liquors used for each cycle

Cycle No	(NH ₄) ₂ SO ₄ g/l	pH
1	9.504	8.5
2	8.026	8.5
3	7.656	8.0
4	7.867	8.5
5	10.085	8.0
6	8.501	8.5
7	9.504	8.0

The average savings were 45% and 82% (NH₄)₂SO₄ and water respectively. The average replenishments based on fleshed weight of the pelt were 1.1% (NH₄)₂SO₄ and 18% water.

4.2.4 Recycling of pickle – chrome liquors

The analytical results of spent tanning liquors were presented in **Table 4.6**.

Table 4.6: Analytical results of spent chrome – pickle liquors used for each cycle

Cycle No	HCl (g/l)	NaCl(g/l)	Cr ₂ O ₃ (g/l)
1	2.8	30.0	2.0
2	3.9	36.5	2.4
3	3.5	42.4	2.9
4	3.3	40.0	2.1
5	2.9	45.2	2.0
6	3.4	46.0	2.7
7	3.1	44.0	2.5

Considerable savings in water and basic chemicals were achieved. Water, chromium, Salt and acids were only given to make up the solution as needed, instead of a full amount being added for each fresh float as in the conventional process. Impressive savings of 84% in water, 41% in salt, 20% in acid and 27% in chromium have been achieved. The average consumptions based on the fleshed weight of the pelt were 2.2% chrome, 5.9% NaCl, 1.6% H₂SO₄, and 15% water.

4.2.5 Recycling of retanning liquors

The analytical results of spent Garad solutions used for each cycle were given in **Table 4.7**

Table 4.7: Analytical results of retanning spent liquors used for each cycle

Cycle No	Tannin (Garad) (g/l)	pH
1	1.9080	4.5
2	2.0264	4.2
3	2.896	4.0
4	2.980	4.0
5	1.937	3.8
6	1.285	3.8
7	1.4633	3.8

In the recycling of Garad solution, it is observed that, the acidity of the liquor and the ratio of tans to non- tans (T/NT) tend to increase progressively as the tannage proceeds. This may come to a level which would reduce the rate of penetration by tans, and results in an increase in the size of tan particles and in the amount of tan fixed. The uptake of tannin by the leather is very high and savings in Garad powder and water were found to be 7% and 58% respectively.

4.2.6 Physical and chemical characteristics of recycled leathers

The physical and chemical results were given in **Table 4.8** and **Table 4.9** respectively.

Table 4.8: Physical tests of experimental and control crust leathers (Garad)

Parameter	Batch 7	
	Experimental	Control
Tensile strength (kg/cm ²)	278.4	276.3
Elongation at break (%)	63	64
tear strength (kg/cm)	36.3	35.1
Load at grain crack (kg)	21	20
Distention at grain crack (mm)	11	10

Table 4.9: Chemical analysis of experimental and control crust leathers (Garad)

Parameter	Batch 7	
	Experimental	Control
Moisture %	9.8	9.5
Total ash content%	3.8	3.7
Cr ₂ O ₃ content%	2.6	2.8
Fat and oil %	5.6	6.4
Water soluble matter%	0.2	0.2
Insoluble ash %	1.8	1.9

The results of physical and chemical analysis of crust leathers obtained by recycling of spent liquors as well as by control process do not show any differences in color or appearance between the control and experimental leathers.

4.2.7 Summary of recycling operations

An impressive savings of chemicals and water can be achieved by recycling of spent liquors from different tanning stages. Consumptions and savings on chemicals were summarized in **Table 4.10**.

Table 4.10: Summary of percentages of chemicals and savings of recycling processes

Chemicals	Cycle No								Average	used for replenishment	saving %
	fresh	1	2	3	4	5	6	7			
Na ₂ S%	2.5%	1.3	1.45	0.95	0.9	0.75	0.75	0.75	0.99	1.5	40
lime%	2.5%	0.95	0.75	0.95	0.85	0.85	0.9	0.75	0.85	1.65	34
(NH ₄)SO ₄ %	2%	1.0	0.8	0.8	0.8	1.0	0.9	0.8	0.9	1.1	45
NaCl%	10%	3.0	3.7	4.2	4.0	4.5	4.6	4.4	4.1	5.9	41
H ₂ SO ₄ %	1.5%	0.4	0.5	0.5	0.4	0.4	0.5	0.4	0.4	1.6	20
Chrome%	3%	0.8	0.9	1.1	0.8	0.8	1.0	1.0	0.8	2.2	27
Garad %	20%	1.3	1.4	1.9	2	1.3	0.9	1.0	1.4	18.6	7

Percentages are based on wet salted weight for soaking, soaked weight for liming, fleshed weight for deliming, bating, pickling and tanning, and wet blue weight for retanning and fatliquoring

Conclusion and recommendations

5.1 Conclusion

Rural tanneries can be mechanized to some extent by constructing hand operated drums to speed up the process and to take out some of the hard physical work. Hand – operated drums can be introduced in areas where electricity is not available to carry out successfully all wet processes from soaking up to retanning. The drums are relatively simple machines and can be constructed locally using timber, stainless steel or plastic.

By the introduction of modern tanning materials such as biocides, lime, sodium sulphide, deliming agents, bating agents, acids and little quantity of chromium as a pre-tanning agent, the resultant leathers have a better quality and higher thermal stability compared to rural tanned leathers.

Comparing the leathers obtained by experimental processes using chrome powder offers ranged from 0.5% to 4.0% and the leathers obtained by control process using 20% Garad powder, no differences were found in strength properties. But the hydrothermal stability and handling properties of experimental leathers were better than that of control leathers. Regarding the thermal stability and the cost of production suitable for rural tanners, it is consider that 3% chrome powder offer is the optimum dose for rural tanning. The results show that, recycling of the spent liquors from the different wet processes could reduce the environmental impact and the cost of production.

5.2 Recommendations

Water and electricity are the backbone for any industry. Therefore, a water supply and electricity source should be provided for rural tanneries. Financial assistance is very important to enable rural tanners to build up their tanneries and equipped them with the necessary tools and machines and

to be able to purchase raw materials and chemicals. Moreover, rural tanners must be trained on modern tanning methods to be able to produce leathers of good quality. Also they should be aware of the importance of safety precautions and first aids. Further studies should be conducted to investigate the possibility of using eco-friendly pre-tanning agents other than chromium which have a less environmental impact such as aluminium.

Fleshing is the hardest process of the whole tanning operations and requires a lot of time and hard physical work. Therefore, it should be mechanized by introducing a fleshing machine. Toggle and paste drying techniques should be introduced to rural tanneries in order to increase the area and to eliminate the creases and wrinkles of the produced leathers. Softening of the leather after drying can be done easily by introducing a staking machine. Only one fleshing and staking machine is sufficient to carry out the work of the whole rural tanning complex.

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