RECYCLING OF UNHAIRING-LIMING SOLUTION

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Dedication

To my mother, father, brothers, sisters

and my friends
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It is my pleasure also to acknowledge with gratitude the grant received from the German Academic Exchange Service (DAAD).
ABSTRACT

This work has been undertaken to utilize the used sulphide-lime unhairing liquor in order to reduce these caustic chemicals in the effluent, save the fresh water and minimize the cost of the liming processes. The chemical analyses of the used liquor indicated that a considerable amount of sulphide of 2100 mg/l was present. And as the lime has a limited solubility of 0.125%, undissolved lime always remains in solution; this undissolved lime will dissolve when its equilibrium solubility is disturbed by recycling. It has been observed that the unhairing power of the old lime liquor was more effective than the fresh liquor; this is due to the fact that the disulphide link of the hair is broken and dissolved during the liming process and consequently the sulphide content will build-up through recycling.

Wet salted sheepskins were processed with the normal recipe and the once-used lime solution was analyzed for lime and sulphide content, its composition was leveled by a make-up fresh lime-sulphide liquor and recycled. The same was repeated for seven cycles, each time the recycling flow rate was leveled with a fresh make-up. The average savings were 65% sodium sulphide, 33% lime and 90% water. The limed-unhaired pelts from each cycle were further processed through tannage, retannage, drying, and finishing. The physical and chemical properties were satisfactory. The leather produced is normal, soft, of good tensile strength, full and of good quality.

This process is recommended to be applied in all tanneries. Its application is simple. It requires a collection pit, a filter, a pump and a pipe line to and from the drums.
البحث

يكم نحن في حاجة لتصريف المادة العازلة لتمكينها من مراحل التعامل، وتعتبر هذه المراحل مهمة، وهي تشمل إزالة المواد غير المرغوبة. وتشمل هذه المواد المواد الغير صالحة، والمواد الكبيرة، والمواد البيولوجية.

إعادة القدرة على الفحص لغرض الدراسة، هذه إجراءات، إعادة القدرة على التحسين، وتحسن البيئة على الأماء، هذه في المسرعة.

في هذا السياق، يمكن أن نلاحظ أن الكفاءة في المواد مالية ويعود إلى الكفاءة في المواد الكيماوية والمواد الداعمة.

ويتم ذلك بواسطة تكييف المواد، وتبني الطريقة في ذلك، بواسطة المواد التي يتم استخدامها.

ويتم ذلك بطريقة طبيعية، متماسكة، وتنوعة، وواستبدال قوة ذاتها.

ويتم ذلك عن طريق

العديد من الأمائ، لائحة كفاءة

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المواد، والمواد الكيميائية، والمواد الطبيعية، وواستبدال قوة ذاتها.
CHAPTER ONE

INTRODUCTION

Hides and skins of the principal species of domesticated animals such as cattle, buffalo, goat and sheep are the main sources of raw material for conversion into various types of leather. The above types of hides and skins are obtained regularly in commercial quantities. As meat is a daily food requirement in all of the world, hides and skins become available as a byproduct of the meat industry and it has become a necessity to preserve and utilize them properly for social and economic benefits, and to avoid public health and pollution problems.

Sudan has very large resources of hides and skins. This is due to the huge live stock population, which is estimated to be 124.7 million, heads in the year 2000 (Table 1).

Approximately 4.7 million cattle hides, 11.0 million sheepskins, 10.4 million goatskins, and 100 thousand camel hides were produced in 1999 (Table 2).

Leather is a unique natural material, which is superior to the modern synthetic leather. It has special properties; it is ancient and modern at the same time. Since prehistoric time, man used leather in crude form for clothing, carrying water, as containers, covering material for himself; his hut and food. But raw hides and skins have three main
defects: (i) They are damp, (ii) when left in a wet, warm climate they soon start to putrify, the hair falls off and they stank, (iii) dried skins lose their flexibility and softness and become hard, brittle, and quite unsuitable for clothing and other uses. Moreover, if it becomes wet again putrefaction recommences.

Hides and skins are turned into leather by tanning. There are many ways of tanning but all of them cause the following changes into the raw hides and skins: (i) the tanned skin does not putrefy even after drying and wetting, (ii) on drying the tanned skin does not become hard, brittle but remains flexible and workable (Sharphouse 1983).

The early civilizations practiced the tanning of raw hides and skins, over more than 5000 years ago. The Romans tanned their animal skins with olive oil, alum and with Oak bark (Nelson and Brown1950). During the early and middle stages of the industrial revolution, rapidly increasing quantities of leather were required for factories and transportation to supply the exploding population spawned by this upheaval (Hergert 1989). By beginning of the 20\textsuperscript{Th} century, leather tanning was one of the major industries in all over the world.

Now the location of leather production is moving away from highly industrialized countries towards the agricultural and newly developed areas of the world. It is obviously sound economical for those countries, which possess large livestock populations, to tan and dress the hides and
skins into leather themselves, and ultimately these areas will become leather and footwear exporters (Tuck, 1981).

The practice of leather manufacture varies considerably from one tannery to another, and from country to country, so that there is no single universally applied process. The main sequences of operations and their aim are the same, but there are wide differences in the state of the art. (Tuck, 1981).

The chrome tanning method is most widely used in all leather sectors. However, the vegetable tanning method and combination of chrome and vegetable tanning is also applied. The process includes different steps during which, large quantities of water and chemicals are applied to skins and hides. A lot of different chemicals are used in leather processing depending on the type of raw material used and type of finished product. Most of these chemicals are very pollutant and cause problems to environment when disposed to the drain.
Till the 1880’s, only hair-save methods (straight lime or sweating) were used for unhauling. These methods required subsequent mechanical unhauling. Originally this was done by hand on a beam; unhauling machines were introduced at a later stage. From the 1880’s onwards, hair-destroying unhauling processes using lime and sulphide were used in tanneries; a practice that has since been generally adopted in most countries. This method of unhauling saves both labour and time. It also ensures a clean pelt and opens up the skin substance to a satisfactory degree (Frendrup, 2000).

The above method of hair destruction results in high organic pollution in the waste water. With increasingly stringent environmental regulations, it has become necessary to reduce the pollution load in waste water to a minimum (Frendrup, 2000).

Thianikaielan et al., (2001) showed in table (3) the content of untreated lime-sulphide effluent.
Table (3): content of untreated lime-sulphide effluent

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Spent lime-sulphide</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^2$</td>
<td>588 (ppm)</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>2960 (ppm)</td>
</tr>
<tr>
<td>*COD</td>
<td>31010 (ppm)</td>
</tr>
<tr>
<td>Total Solids</td>
<td>32160 (ppm)</td>
</tr>
<tr>
<td>Volume of effluent</td>
<td>4000 (l/ton of raw skins**)</td>
</tr>
<tr>
<td>Emission load</td>
<td>(kg/ton of raw skins**)</td>
</tr>
<tr>
<td>$S^2$</td>
<td>2.4</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>11.8</td>
</tr>
<tr>
<td>COD</td>
<td>124</td>
</tr>
<tr>
<td>Total Solids</td>
<td>127</td>
</tr>
</tbody>
</table>

* Chemical Oxygen Demand

** Weight of skins before soaking.
The unhairing-liming operation is the largest contributor to the net pollution in tanneries. Conventionally, mixing the hides with lime and sodium sulphide leads to residual floats containing 55% of suspended solids, 55% of COD, 70% of BOD₅ (Biochemical oxygen demand), 40% of nitrogen giving 76% of the toxicity of tannery effluent (Aloy, 1993).

Recycling of materials has become one of the better methods of pollution control (Money, and Adminis 1974). Slabbert (1981) mentioned that there are three main reasons for carrying out recycling operations in tannery; (i) to utilize excess chemicals in a process which if not recycled would have been discharged; (ii) to reduce the pollution load in the effluent, and (iii) recycling as a means of water saving.

The direct recycling of lime-sulphide liquors has been widely examined. These processes lead to reduction of the total sulphide consumption and also to reduction of the total amount of organic pollution in tannery effluents caused by unhairing and liming processes (Winters, 1983, Ludvik, 1991, Rydin and Frendup, 1992 and Buljan, 1995).

The objective of this research is to investigate the possibility of recycling lime-sulphide unhairing liquors to utilize excess chemicals in the used (old) unhairing solutions in order to:

(1) Eliminate the pollution load of the unhairing-liming effluent.

(2) Reduce the manufacture cost by maximizing utilization of chemicals and water save, through blending the used lime solution with a fresh make-up sulphide and lime.
2.1 Hides and skins

Hides and skins are defined according to the British standards that, the hide is the raw skin of mature or fully-grown animal of large kinds such as cattle, horses and camels. And the Skin is raw skin of mature or fully-grown animal of smaller kinds, such as sheep, goat, reptiles, birds and fishes, or the immature animals of larger species, e.g. calves and colts (Sharphouse 1983).

Hides and skins are raw material of leather. They are tissues of animals body made up of living cells and their products. The production of leather involves the removal of those tissues, which can’t be converted into leather, and treatment of other in such a way that the final product has the desired properties (Lotta and Dag 1998).

2.1.1 Chemistry of Hides and Skins:

2.1.1.1 Chemical constituents:

Fresh hides and skins consist of water, protein, fatty materials and some mineral salts. Of these the most important for leather making is protein. It consists of many types. The important ones are collagen, which, on tanning, gives leather, and keratin, which is the chief
constituent of hair, wool, horn and the epidermis structures. The approximate composition of fresh hide is as follow:

**TABLE 4 COMPOSITION OF HIDE/SKIN**

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Protein</th>
<th>Fats</th>
<th>Mineral Salts</th>
<th>Other substances</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>64%</td>
<td>33%</td>
<td>2%</td>
<td>0.5%</td>
<td>(Pigments etc.) 0.5%</td>
</tr>
</tbody>
</table>

Structural Protein

- **Elastin**
  - Yellow fibre woven in collagen fibre
  - 0.3%

- **Collagen**
  - this tans to give leather
  - 29%

- **Keratin**
  - protein of the hair and epidermis contains sulphur
  - 2%

Non-structural Protein

- **Albumins**
  - Globulins soluble, non fibrous proteins, often removed in liming, etc.
  - 1%

- **Mucins, Mucoids**
  - material associated with fibres
  - 0.7%

All skins are made up of the above constituents, but the figure of keratin varies widely depending on the amount of hair present, and the figure of fat is also vary. The division between albumin and mucins is debatable (Sharphouse, 1983).
The fat content of the most of skins is relatively low. Skins of certain animals (e.g. sheep) at certain times in their live, contain quantities of fat in globular cells amounting to 25% of their weight. The fat cells of corium and adipose tissue contain mainly triglycerides (true fat). The fat glands of epidermis contain mainly waxes, which are esters of fatty acids and alcohols.

The small percentage of mineral matter presents include sulphides, sodium chlorides, potassium, magnesium and calcium.

Hides and skins also contain carbohydrates like glycogen, sugar, amino-sugar, etc (Sharphouse, 1983).

2.1.1.2 proteins of animals skins

The main constituent of hides and skins is protein which is the leather forming substance, there are two types of protein:-

(i) Globular protein as albumins, globulins, and various protein mucins and melamine (Removed in beamhouse operation).

(ii) Fibrous protein as keratin (epidermis, Hair), collagen, elastin, and reticulins. (Structural protein substance for leather-making) (Sarkar, 1981).

The above-mentioned Proteins other than collagen are mostly taken from hides and skin, so only collagen remains for conversion into leather. The properties of other proteins are of interest only for understanding the mechanism of their removal by the various materials used for the
purpose. Thus, albumins, which are soluble in water, are removed by washing. Diluted salt solution dissolves globulin, which are removed when salted hides and skins are soaked and washed with water. The mucoids are soluble in diluted alkalis and are removed by lime solution in liming process. The softer keratins of epidermis are dissolved by lime liquor and thereby the hair and the entire epidermal structure are loosened by liming and are subsequently removed from hide and skins by mechanical scraping. The treatment with other sodium sulphide dissolves even the harder keratins like hair. The elastin is partially removed by enzymatic treatment in bating operation. Reticulin is attacked by strong alkaline treatment and removed by sodium sulphide (Sarkar, 1981).

2.1.1.3 Keratins

These are the fibrous proteins of the outer layer of the skins and its appendages. The amount of keratin in the skins varies with species and age. Rosenthal (1916) reported that 19.91 % to 36.15 % of the dry matter of calf skin to be keratin.

Keratins are insoluble in water, ether and alcohol but soluble in concentrated alkalis and acids. They are very sensitive to reducing agents such as sodium and calcium sulphides. They are slightly swollen by acids and alkalis. Keratin is characterized by its high content of sulphur, due to the presence of sulphur-containing amino-acids (cystine and methionine).
The presence of high amount of cystine (fig.1) in keratin is greatly responsible for its characteristic properties.

Keratin is established through disulphide bond (\(-s-s-\)). The fully developed keratin in hair, nails, and the upper part of the epidermis layer is resistant to chemical or biological attack, except for sulphide, which breaks down the di-sulphide bonds. The immature keratin found in hair roots, hair sheaths, and the lower layer of epidermis is easily degraded and dissolved (Frendrup, 2000).

2.1.2 Anatomical structure of hide and skin:-

The cross-section of skin (fig. 2) reveals its structure stating on the hair side.

(a) The hair, embedded in skin, each in a sheath of epidermis known as hair follicle and each of hair root at its end, fed by tiny blood vessel. Chemically the hair consists of protein keratin in a form dead and resistant at the tip and living and easily destroyed at the root.

(b) The epidermis, a protective hardwearing layer of keratinous cells. Those on the outside are dead, on drying and shrinking, fall off the skin as scurf or dandruff. On the underside, next to skin proper, they consist of soft jell-like living cells, which have little resistance and are readily attacked by bacterial action or unhairing enzyme. They are easily disintegrated by alkalis, such as caustic soda, lime.
and especially sodium sulphide or hydrosulphide. This action is the basis of the common unhairing process in the lime yard when the lime and sulphide used destroy the hair roots and soft underside of epidermis.

(c) The sweat glands (sudoriferous gland), which are also lined with epidermis and discharge sweat from the skin through the pores in grain surface.

(d) The sebaceous glands located at the side of hair follicles and discharge into them an oily, wax substance, which protects the hair. Muscles, the erector pili, which cause the hair stand upright, operate the gland; this happens when the animal is cold or frightened.

(e) The skin proper or corium consisting of the network of collagen fibres, very intimately woven and joined together. In the grain layer these fibres become very thin. Towards the centre of corium the fibres are coarser and stronger. The predominant angle as they are woven indicates the properties of the resultant leather. If the fibres are more upright and tightly –woven, one expects a firm, hard leather with little stretch, whereas if they are more horizontal and loosely woven, one expects a soft, stretchier leather. The corium is generally the strongest part of the skin.
The flesh side of corium, next to the “meat” where the fibres have more horizontal angle of weave, and fatty (or adipose) tissue may also present.

The corium fibres are composed of rope-like bundles of smaller fibrils, which consist of bundle of sub-microscopic micelles. These in turn are made of very long, thread-like molecules of collagen twisted together. This gives a very strong, tough, flexible structure.

The non-structural proteins “inter-fibrillary”, or pro-collagen, are essential for growth of skin and also render the fibre structure non-porous. When the skin is dried, they dry to hard, glue-like material, which cement together all the corium fibres and make the skin hard and horny. In making leather to be soft or supple, it’s most important to remove these inter-fibrillar proteins.

The skin also contains small arteries and veins conveying blood to live tissue, and nerve structures necessary for sense of touch (Sharphouse, 1983).

The space from the epidermis to begging of the corium, equal to full length of hair follicle, is referred to as “grain area”, while the corium surface on which epidermis rest is referred to as grain surface. (O’ Flaherty, 1961).

The epidermis, hair, sebaceous and sweat glands and to some degree the inter-fibrillar proteins are removed from the skin during
beamhouse operations. It’s therefore understandable that the upper
korium or grain layer consisting of a number of cavities after liming will
make the grain particularly sensitive to the tanning and finishing
operations. The flesh layer is removed by cutting off the flesh by a
fleshing machine (Sarakar, 1981).

2.2 Preservation of hides and skins

The preservation or curing of raw stock must be done quickly and
efficiently after flaying. Curing involves the protection of the hides and
skins from the attack of microorganisms, rats, beetles, larvae, etc. The
cured stock must be capable of being stored and transported without
significant deterioration. The preservation process must not bring about
any undesirable irreversible effects in the stock, and most of changes
must be capable of being reversed by tanner, so allowing full dehydration
of stock to it’s normal level. The first symptoms of bacterial attack are
loosening of hair or wool, i.e. hair slip, followed by discoloration of flesh
side and smell of ammonia (Tuck 1981).

The following curing methods are used to prevent putrefaction or
damage before tanning:

2.2.1 Wet-salting

The cold flayed skin is spread out, flesh side up, on concrete floor
and well sprinkled with salt (sodium chloride). A second skin is placed on
the first one also sprinkled with salt. This is repeated until stock 5 – 8 feet
high are formed, the top hide being well covered with salt. The stock is left for some days when the salt dissolves in the moisture in the skin and the brine permeates the pile. The amount of salt used should be 25 – 30 % of raw hide or skin weight (Shaphouse 1983).

2.2.2 Brining

Brining is more efficient method, practiced in the big American abattoirs. The hides are cleaned by washing with water and are then placed in pit or run in large paddles in very strong salt solution (brine). This gives very good and uniform salt penetration in 12 – 14 hours for heavy hides. The hides are then drained and piled, and may have a further sprinkle of salt, as in wet-salting process. Care must be taken to check the purity and strength of the brine liquor before re-use, as it may become contaminated with halopholic bacteria (Shaphouse 1983).

2.2.3 Dry salting

The flayed skin is salted by either, or both of the above methods and is then hung up to dry. This reduces the weight and cost of transport.

2.2.4 Air-drying

As bacteria must have certain amount of free water or moisture to survive, putrefaction can be stopped by removal of water so that the hide contains only 10 – 14 % moisture. Their activity then ceases, and some types are killed, whilst others dry up into spore form, in which they can
remain a long time until there is enough water for them to be active again. Curing by drying requires care, especially with thick hide because:

(i) If drying is too slow, putrefaction may occur before the moisture content is low enough to stop bacterial action.

(ii) If drying is too fast and the temperature is too high, part of the wet skin will start to gelatinize to glue-like material. This makes the skin hard and brittle and prevents drying of the inner layers. It is difficult to see this fault in dried hides until they are soaked back in water, when holes appear or the smooth grain is lost or has a blistered appearance, owing to gelatinized part of skin dissolved in water.

Drying is practiced in countries with hot, dry climates (Sharphouse 1983).

The old method of ground or flint drying, i.e. laying the stock on the ground in the sun, causes shrinkage and loss of shape, gelatinization surfaces, trapping pockets of water in the corium, which can not escape. In the wet pockets the growth of anaerobic bacteria commences, causing liquefaction of collagen and complete breakdown of fibres structure. Hides and skins damaged in this way are not suitable for tanning and should be used for gelatin and glue manufacture (Tuck 1981).
2.2.5 Short-term curing

2.2.5.1 Cooling and light refrigeration

The removal of heat energy is to inhibit the activity of proteolytic bacteria. For this method to employ, cooling chambers, refrigerated storage facilities are required. Cooling below 10°C will preserve hides and skins in good condition for three to five days, while refrigeration to –1°C to –3°C is required for long storage period.

2.2.5.2 Treatment with antibiotics

The treatment of hides and skins by spraying, immersing or drumming in either dilute solutions of proprietary antiseptic, or in standard antiseptics, such as chlorine – containing oxidizing agent, has become established. The strength of solution used lie in the range 0.5 – 2 % w/v and while they inhibit bacterial action, they must not bring about permanent changes in the skin proteins (Tuck 1983).

2.3 Pre-tanning processing

Before the raw hide or skin can be converted into leather, certain pre-tanning operations are essential: pre-tanning consists of sorting and trimming the skins, liming, unhairing, fleshing, bating and pickling (Gustavason 1965).

2.3.1 Soaking
The initial process of leather manufacture commences with soaking, which has two functions. The first is to remove dirt, dung and curing salts, and the second is to reverse the dehydration of curing and to restore the water content of the pelt to level closely similar to that in fresh skin (Tuck, 1981). Van Oss (1972) stated that soaking is a process in which hide and skin are restored to its original condition, as removed from the animal, but free from blood, manure, dirt and salt. Soaking may be done in a pit, paddle, or drum. Soaking should commence with pure water at 20° C and mechanical action started as soon as the stock is soft enough to withstand movement without physical damage. (Tuck, 1981). When skins are unusually dry, it is customary to add softening agents such as alkali in form of sodium sulphide, sodium polysulphide or soda ash to soaking water. Since the skin or hide is bound to be contaminated with many species of bacteria, it is often necessary to destroy the latter by the addition of a disinfectant to the soaking water (O’ Flaherty 1961). In the first washing a portion of the curing salt is removed, but it’s presence in the soaking operation is desirable, as salt solution has the ability to dissolve some of the cementing substances (globular proteins) formed between the fibres and permits their separation, and improve the physical characteristics of the leather (O’ Flaherty 1961). Brine-cured skins require less soaking, but it is necessary to remove the salt to a degree where it will not interfere with the subsequent unhairing. Fresh skins are
processed by treatment in a salt bath for 3 to 4 hours, and then the brine-
cured or fresh hide can enter the lime solution and processed in the same 
way as green salted hides or skins (O’ Flaherty 1962).

2.3.2 Unhairing:

The aim of unhairing (depilation) and liming is to remove the hair, 
epidermis and to some degree the inter-fibrillar proteins, and to prepare 
the hide for removal of loose flesh and fat by the fleshing process 
(Sharphouse 1983).

The removal of the epidermis system, ie the hair, wool, or bristles, 
and pigmentry matter, is achieved with the aid of depilatory agent. The 
epidermal system consists mainly of protein keratin, which is different 
from collagen of the fibre structure in many important aspects. The most 
important is that it includes sulphur-containing amino acid cystine and 
strong cross-link are formed by sulphur. Oxidizing and reducing agents 
readily attack this link and thus form the main depilatory agents. It is also 
known that certain proteolytic enzymes attack keratin, and other enzymes 
attack the substrate in which keratin is found. The process of depilation 
can be carried either as a separate process prior to liming, or the 
depilation and liming effects are combined into a single simultaneous 
operation (Tuck 1981).

Methods of hair removing can be divided into two groups:
(i) methods based on destruction or modification of the epidermis tissue surrounding the hair, so that it can be loosened and removed, and
(ii) methods in which the hair itself is attacked and its structure is destroyed (use of alkali Ca(OH)$_2$ or NaOH and Na$_2$S).

2.3.2.1 Enzyme unhairing:

Enzyme preparations that preferentially attack the keratin cells at base of hair roots or epidermis are available. Enzymes are specific in their action and are active within a narrow range of temperature and pH. Since optimum temperature for unhairing enzymes are close to those for bacterial growth, it is essential to use some disinfectant to prevent bacterial putrefaction. Enzyme unhairing has been used commercially for many years on goatskins and is now being seriously considered as other types of unhairing material, in order to eliminate the nuisance of sulphide in tannery effluent disposal. Enzyme preparations are available which preferentially attack the young keratin cells at the base of hair roots or epidermis. They give very clean flat grain. The soaked skins are paddled or drained in a water float 28-30°C with 1-2 % (base on skin weight) of specific enzyme preparation at pH 8-9 for 4 hours. Adding 0.2 % sodium chlorite may prevent bacterial contamination (Sharphouse, 1983).

2.3.2.2 Paint unhairing:

The washed or soaked skins are piled to drain off the surplus water and then painted, or sprayed on the flesh side with a "paint" which may
be made from approximately 50 parts hydrated lime, 50 parts water and 5-2- parts sodium sulphide (fused). The sodium sulphide and lime dissolve in the water and penetrate through the corium and dissolve the keratin cells, which enclose the hair roots. The process may take 5-12 hours depending on thickness of the skin, tightness of fiber structure, and amount of fat and flesh left on the skin. Green fleshing before painting can be good. After washing and further treatment in lime liquor, the skins are sorted into group according to weight and size prior to tanning. Mechanical unhairing and re-liming are necessary (Van Oss, 1972).

2.3.2.3 Pulping techniques:

An alternative method of depilation is complete immersion of the stock in sulphide solution, with or without addition of lime. The sodium sulphide treatment may be incorporated into the general liming procedure; alternatively it may be short sharp pretreatment followed by washing and further plumping in alkaline liquors. For calf and wet salted hides the best method is to apply the sodium sulphide during liming, but for sun-dried hide and goatskins sharp pretreatment is preferable. For calf and wet salted hides, between 3% and 4% of sulphide (62%) on the weight of stock is used for a period of 24 – 48 hours. With total float 400% water on pelt weight, the effective concentration of sodium sulphide is 0.75 – 1 % by volume. In sun dried hides and goat skins it may be increased to
2.5% by volume to similar periods, or increased up to 5% for solution treatments of one or two hours duration. (Tuck, 1981)

2.3.2.4 Oxidation unhairing:

As has been previously stated, the cystine cross link in keratin can be broken by oxidizing agents, and the use of sodium chlorite plus hydrogen peroxide has been investigated in Germany. The advantages are an alkali sulphide free effluent and firm clear white pelt (Tuck, 1981)

2.3.3 Liming

Liming is a process in which the hide or skin are immersed in solutions of lime, to which sodium sulphide and some enzymes maybe added. The aim of liming is primary to loosen the hair, and destroy epidermis; at the same time the fibrous structure becomes swollen plumped with a partial separation of the fibres (Van Oss 1972). Methods of liming vary both in the chemicals used and in procedures. Unhairing and liming can be carried out simultaneously by immersing the skins in the lime and water mixture, often with the addition of other chemicals known as sharpeners, e.g., sodium sulphide.

The objectives of lime as reported by Sarkar (1981) are as follow:

(i) Liming removes the epidermis together with the hair and are thus separated from the corium or true skin.
(ii) Dissolution of the cementing substance of the corium. This removal of cementing substance makes the final leather pliable and soft.

(iii) Splitting up of the fibre bundles into individual fibres and also splitting up of individual fibres into fibrils: this is necessary for satisfactory tannage. By splitting up and consequent separation of the individual fibres and fibrils their surface all round them is exposed to the action of the tan liquor from which the fibres and fibrils absorb tannin and become converted into leather. The opening up of the fibres is also due partially to rupture of the elastin bands holding them together.

(iv) Saponification of grease: Hide and skins contain natural fat. This fat is saponified and is converted into lime soap by action of lime. The lime soap is not removed by washing the limed hides. It is mechanically removed by scudding. Unless this natural fat is removed the final leather will have patches of fat (known as fat spue) in grain and a light and uniform finished surface will not be obtained.

(v) Swelling and plumping

2.3.3.1 Straight lime liquors:
Water dissolves a relatively small amount of lime. Approximately 1/8 parts lime per 100 parts water gives a clear solution. And lime is unusual because it dissolves less with increasing temperature. The alkali solution causes the collagen fiber of the corium to swell by absorbing more water. The hair and epidermis swell to a lesser extent, and the interfibrillar proteins become more soluble and are loosened from the fibre structure. These effects occur with all soluble alkalis and the stronger the alkalinity, the greater the effect. As lime has a limited solubility compared with other alkalis, it is considered safe for hides and skins.

The alkali modifies and breaks down the collagen fibre of the skin, but much more slowly than the keratin. Therefore, if skins are limed too long they suffer from thinness, looseness and weakness.

For skins that have already been unhaired; straight lime liquors of 2 parts lime per 100 parts water are used. The skins are immersed in about 5-6 times their weight of this liquor, for 12-60 hours at 13-18º C.

This quantity of lime is in excess of that needed to get the necessary alkalinity (pH 12-13), plus the lime, which it’s chemically fixed to the hide. The surplus may be spent by adsorption on grease, loose protein or by carbonation. It also makes handling of the hides slippery. However this excess lime often requires expensive effluent treatment.
2.3.3.2 Paddles liming

The use of paddles for liming is wildly practiced, it gives well overall results. A shallow running paddle is preferred and it should be turned for only one or two minutes hourly, this method is more rapid than pit liming and labour costs are lower (Duck 1981)

2.3.3.4 Drum Unhairing:

When the hair is of little value and the hides are of a quality which will not suffer from the process, they may be drummed in a relatively strong sodium sulphide solution, such as 300 % water on hide wt. at 16 °C, 2-5 % sodium sulphide (flake). After 6 hours the hair and epidermis are reduced to a pulp, which can be washed off, and the hides are well swollen. A small amount of salts may limit the swelling, which may also be reduced by replacing part of sodium sulphide with sodium hydrosulphide. Mechanical action should be gentle to avoid pebbling.

2.3.3.5 No lime systems

Are favored for thinner skins e.g. hair sheep and goat. Advantages are absence of lime soap formation, which may cause uneven tanning and dyeing. Hair or wool may be previously removed by a "lime free" sulphide paint. Usually sulphide or hydrosulphide is used to adjust the pH 12.6 - 13 at a liquor concentration of about 0.2 % caustic soda. As the temperature increases to 28-30°C less swelling occurs giving a finer
flatter grain, and although hydrolysis of the skin occurs, this is slower and can be controlled by time (6-8 hours).

2.4 The efficiency of old lime liquors for unhairing

Sharphouse (1983) indicated that old lime liquors are more effective for unhairing, because under very alkali conditions, some of the young keratin decompose to produce sulphur compounds, these, in conjunction with lime, accelerate the break-down of further keratin. Thus, the lime causes unhairing and the more keratin break-down impurities it contains, the more rapidly it unhairs. All these reactions are accelerated by increase in time, temperature and high alkalinity.

2.5 Uses of old lime liquors

The used liquor may be drained away but as it has become stronger in unhairing power and less alkaline, it has good properties for starting the liming of the next pack of hides.

A technique of how to mix the fresh and old lime liquors was investigated long ago. In fresh liquor swelling is stronger and opening up is weaker, old liquors are better hair looseners. A similar effect may be obtained by adding methylamine to lime liquor.

2.6 Recycling of lime – sulphide unhairing liquors

The possibility of direct recycling of lime/sulphide liquors has been widely examined. These processes lead to reduction of the total sulphide consumption and also to reduction of the total amount of organic

Blazej et al. (1971) re-used lime liquor after removal of solids, acid precipitation of soluble proteins and conversion of hydrogen sulphide to sodium sulphide for re-use. It was decided that this method would not be economical at present but that alternative methods of removal of sulphide and the proteins should be investigated, however during trials comparing several methods of protein removal, it was found that satisfactory unhairing can be achieved when lime liquors are recycled without removal of either the soluble or the solid; it is only necessary to replenish with lime, sodium sulphide and water. While further work was carried out re-using lime liquor both with and without solids removal.

Simoncini et al., (1972) published some work describing similar lime liquor recycling investigation. In their trails lime liquors strengthened with lime and sulphide were re-used 20 times in succession without any treatment to remove soluble proteins or solids.

Money and Adminis (1973) have shown that lime-sulphide unhairing liquors can be recycled more than 20 times, perhaps indefinitely. Recycling of lime liquors has no apparent effect on leather quality or yield. This method could be developed as no-effluent system of unhairing if liquors can be cycled indefinitely. Even the liquors can be discharged after 20 uses there can be overall a 20-fold reduction in water
consumption and effluent sulphide, and a seven-fold reduction in effluent lime and protein.

Aloy (1993) reported that in Direct recycling of liming floats, the aim is maximum recovery of the residual float. Solid waste, in excess of a certain gauge (currently 1 mm) is separated, and the chemical content of the float is restored to its initial composition before being reused in another unhairing-liming operation. Several large tanneries, for shoe upper leather, use this recycling technology. Its implementation requires the solution of a variety of technical problems. The enrichment of dissolved organic matter is not higher than 3 times the conventional concentration, owing to the clean water intake at each cycle, resulting from swelling of hides and rate of recovery of float in drums. The lower scudding effect observed at the end of the liming phase may be compensated by modifications in the process.

This technology, used for over 12 years in tanneries, holds much interest, as, in practice, it can save 35 to 40% of the involved sodium sulfide, and almost 45 to 50% of the conventional lime consumption.

Fine screening of the residual float reduces a substantial amount of organic matter. On the whole, 30 to 40% of the COD and 35% of the nitrogen may be eliminated from the mixed effluents. The principal limiting factors are: the quantity of hides to be processed and the reliability of the laboratory analyses, which are indispensable for a quality
control of recycling. The quality of the leather produced might be affected negatively with this process, unless unhairing and opening up processes are used in two phases.

Ludvik, (1991) mentioned that a new recycling process based on separate unhairing and liming has been developed. The unhairing liquor is filtered and, after blending with chemicals and water, is reused. The hides are then thoroughly washed. The washing bath is recovered and used for soaking. The pelt is then limed in lime liquor with an addition of NaOH to control the degree of swelling. The liming liquor is also recovered and blended with chemicals and water for the next cycle. The efficiency of this recycling method depends on the number of recycles. With 20 days of recycling, sulphide content in the waste water from liming is reduced by 80%, lime content by 93%, COD by 17% and BOD by 15% in comparison with the conventional method.
CHAPTER THREE
MATERIALS AND METHODS

3.1 Raw materials

Wet salted Sheepskins of average weight 2 kg were used in all trials.

The reagents, added to unhairing lime liquors are the following:

Lime (65% calcium hydroxide).

Sodium sulphide (60% flake).

3.2 Experimental works

3.2.1 Micro scale trials:

Wet salted Sheepskins were used in all trials. The skins were cut into 10 cm squares each; they were treated in 0.2 m diameter drums operating at 6 revolutions per minutes. They were soaked in 500% water, stand for 30 minutes, and drumming for one hour, drained, washed in running water for 15 minutes, then a float of 300%, 0.2 % antiseptic agent were added, and run for 5 hours, drained and run into a fresh unhairing liquors contained 4% sodium sulphide, 3% lime and 300% water. Drumming was continuous for the first hour and 15 minutes every hour for the following 4 hours, after being left over-night, the drums were turned on for 30 minutes giving a total liming time of 21 hours.
The degree of unhairing was assessed, skin pieces were weighed and samples of liquor were analyzed to determine the sulphide and lime content.

Solids were removed from used liquors by passing them through filter (stainless steel screen), which retained the greater parts of the hair debris and fat but not the lime.

Before each recycle, the liquor replenished with 2 % lime and enough sodium sulphide to raise the concentration to 4% and a float to 300%. The liquor was recycled seven times.

3.2.2 Semi production scale trials

Forty-eight wet salted sheepskins were used in eight trials, six skins in each; they were treated in 1.5 m diameter wooden drum operating at 8 revolutions per minute. All processes were carried out as in micro scale trial except cycle 7, which was treated with 0.75% caustic soda. Degree of unhairing and swelling were assessed and after completion of tanning operations, the produced leathers were subjected to both chemicals and physical tests.
3.3 Method of Sulphide determination. (Idometreic Method)

Reagents:

(i) Hydrochloride acid HCL, 6N.

(ii) Standard iodine solution 0.0250 N. 20-25 g KI was dissolved in a small amount of water and 3.2 g Iodine was added after Iodine has been dissolved, and then diluted to 1000 ml.

(iii) Standard Sodium Thiosulphate solution 0.0250 N. Dissolve 6.205 g Na$_2$S$_2$O$_3$.5H$_2$O in distilled water. Add 1.5 ml 6 N NaOH or 0.4 g solid NaOH and dilute to 1000 ml.

(iv) Starch solution.

Use either an aqueous solution or soluble powder mixture. To prepare an aqueous solution, dissolve 2 g laboratory grade solution starch and 0.2 g salicylic acid as preservative in 100 ml water.

Procedure:

Measure from a buret into 500 ml flask an amount of Iodine solution estimated to be an excess over the amount of sulphide present. Add distilled water, if necessary to bring the volume to 20 ml. Add 2 ml 6N HCL and piped 5 ml sample into flask. Discharge sample under solution surface. If Iodine colour disappears, add more Iodine solution, so that colour remains back. Titrate with Na$_2$S$_2$SO$_3$ solution, add few drops of starch solution as end point is approached, and continuing until blue colour disappears (Clesceri et al; 1989)
Calculation

One ml, 0.0250 N Iodine solution reacts with 0.4 mg S^-

\[ \text{Mg s}^-/l = \frac{(A \times b) - (C \times d) \times 1600}{\text{ml sample}} \]

Where:

- \( A = \text{ml Iodine solution} \)
- \( B = \text{normality of iodine solution} \)
- \( C = \text{ml Na}_2\text{S}_2\text{SO}_3 \) solution
- \( D = \text{normality of Na}_2\text{S}_2\text{SO}_3 \)

3.4 Method for the total available strong alkali

This method is used to determine the total available strong alkali (sodium hydroxide, dissolved lime and suspended lime).

The outline of the method:

A representative sample of liquor with its suspended solids was treated with a solution of sucrose to bring the calcium hydroxide into solution. A suitable liquor was then filtered and titrated with 0.1N hydrochloric acid.

Reagents:-

- 10% sucrose solution.
- 0.1N Hydrochloric acid.
- Thymol violet indicator 0.2 g. in 100 ml. ethanol.

Procedure.
1. If the sample contains much hair, it is passed through a wire gauze. The suspension was well agitated and approximately 20 ml transferred to a 25 ml cylinder.

2. The volume was noted and the contents of the cylinder washed rapidly into a 500 ml graduated flask with sucrose solution. The flask is shaken for two hours, and the volume was completed to 500 ml with distilled water.

3. About 110 ml were filtered rapidly through a 18.5 cm fluted no. 54 whatman paper, the first 10 ml being discarded. A hundred ml sample is titrated at once with 0.1N Hydrochloric acid.

Results expressed as CaO per 100 ml liquor.

1 ml 0.1N alkali = 2.8 mg CaO or 3.7 mg Ca (OH)$_2$. (Official Methods of analysis, SLTC 1965).
3.5 Chemical analysis

3.5.1 Sampling location for skins.

The pieces for chemical analysis were cut from official sampling position (fig. 3) (SLTC 1996).

3.5.2 Preparation of sample

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

3.5.3 Determination of moisture

A sample of 3 g was weighed, and then dried to constant weight at 102 ± 2°C in a normal oven for five hours. After cooling in a desiccator for half an hour it was reweighed. Check weigh after further one-hour drying and half hour cooling. If, after re-drying, there is a further reduction in weight of more than 3 mg., drying should be continued but not for longer than eight hours in all.

Calculation

\[
\text{Moisture \%} = \frac{G_1 - G_2}{G_1} \times 100
\]

where:

\( G_1 \equiv \) weight of sample before drying

\( G_2 \equiv \) weight of sample after drying
3.5.4 Determination of ash content

Portions of prepared sample (5 g) were placed in porcelain crucible of a determined constant weight. Firstly, the sample was carbonized on hot plate under a fume cupboard, and then placed in a furnace at about 800 °C until a constant weight was reached.

Calculation

\[
\text{Ash } \% = 100 \times \frac{t_2}{t_1}
\]

Where:

\[t_1 \equiv \text{sample weight}\]

\[t_2 \equiv \text{ash weight}\]

3.5.5 Determination of Fat content

A portion of sample (10 g) was placed in a Soxhlet apparatus tube extracted by petroleum ether (boiling point 40 – 60 °C) for 5 hours, at least 30 siphons. After extraction, the solvent was concentrated under vacuum to thick syrup in a tared round bottom flask and then dried in oven at 103 ± 3 °C.

Calculations

\[
\text{Fat content, } \% = 100 \times \frac{a}{b}
\]

Where:

\[a \equiv \text{combined fat weight, g}\]

\[b \equiv \text{weight of leather sample, g}\]
3.5.6 Determination of Chromic oxide in Leather by wet oxidation

1 g of full chrome leather was weighed into a 500 ml conical flask. 5 ml of concentrated nitric acid followed by 20 ml of oxidizing mixture (perchloric acid + sulfuric acid, 2:1) were added. The mixture was heated in fume cupboard with the fan on until it turned orange and the heating was continued for 1 minute more. After cooling, approximately 150 ml of cold distilled water and few anti bumping granules were added, then the solution was heated to boiling for 10 minutes, to remove any free chlorine. The solution was allowed to cool and diluted to 250 ml with distilled water in volumetric flask. 100 ml of the solution were pipetted in two conical flasks and 10 ml of 10 % potassium iodide solution was added to each flask, using measuring cylinder. Then the flasks were carefully closed and placed into the dark for 10 minutes. Starch indicator, (1 ml) was added to each flask, then titrated with 0.1 mol dm⁻³ sodium thiosulphate solution until a pale violet colour is reached (SLTC 1996).

Calculation

\[
\text{Chromic oxide (Cr}_2\text{O}_3\text{), } \% = \frac{T_1 \times 0.000235 \times 100}{M_0}
\]

Where:

\(T_1\) = volume of sodium thiosulphate used in the titration.

1 ml 0.1 N titran \(\equiv\) 0.00253 g Cr₂O₃

\(M_0\) = mass of dry sample of chromium leather.
3.5.7 Determination of Skin Substance by Total Kjeldahl Nitrogen Analysis

One g was taken and placed into a dry 250 ml Kjeldhal flask with 15 – 20 ml of concentrated sulphuric acid, as well as some glass beads. The flask was heated gently in an inclined position. The flask was equipped with a small funnel to prevent loss of acid during hide destruction. Five gram of potassium sulphate plus 5 g of copper sulphate was added to the flask. They were heated up to boiling where the solution became clear and the colour stopped changing. This procedure took about 30 minutes. After cooling, the solution was quantatively transferred in to an ammonia distillator. Through a dropping funnel, sodium hydroxide solution (0.05 M) was added until the solution colour became black.

During distillation, the quantity of ammonia was reduced to one third. The ammonia was distilled using 100 ml of sulphuric acid (0.05 M) in the presence of methyl orange as indicator. Usually, It is considered that all ammonia has been distilled when obtaining about 150 ml distillate. The procedure took about 40 minutes. The access acid was titrated back with 0.05 M NaOH.

Calculation

Percentage of hide substance should be calculated according to following formula:
Hide substance, $\% = \frac{A \times 100}{B}$

where,

$A \equiv \text{hide substance weight (g)}$

$B \equiv \text{leather sample weight (g)}$
3.6 PHYSICAL ANALYSIS

3.6.1 Preparation of sample

The pieces for physical tests were cut from the official sampling position (HGJK) and from shoulder (fig. 4) (SLTC 1996).

Condition

The specimens for physical testing were kept in standard atmosphere of temperature 20 ± 2° C and relative humidity 65 % ± 2% during 48 hours immediately preceding its use in a test.

3.6.2 Measurement of Thickness

The specimens were placed in the standard dial micrometer gauge with grain side up with applied loading 500 g/cm² at the presser foot. The thickness of the leather was measured in four positions at least 1 cm from the edge, and the time of dwell was 5 seconds before taking reading. The mean value of thickness was calculated (SLTC 1996).

The diameter was measured in two positions at right angles using Vernier calipers on the flesh and grain sides. The mean diameter (cm) was calculated (SLTC 1996).

3.6.3 Measurement of Tensile Strength and Percentage Elongation

(I) Tensile Strength

The tests are indented to be used with all kinds of leather. The same specimen may be used to carry out any or all of the tests. The
samples were cut parallel and perpendicular to the backbone using a
dumbble shape as shown in fig. (4).

The thickness and width of the specimen were measured in the
same position using standard thickness gauge and Vernier calipers
respectively i.e. measured one at the mid point E and the other two
midway between E and the line AB and CD. The width must be measured
on the flesh and grain side, and then the mean thickness (mm) and width
(cm) were calculated.

The cross-sectional area of each specimen was calculated by
multiplying its width by thickness (SLTC, 1996).

The jaws of the tensile strength machine were set at 50 mm a part,
and then the sample was clamped in the jaws, so that the edges of the
jaws lie along the lines AB, CD.

The machine was run until the specimen was broken and the
highest load reached, was taken as broken load (SLTC. 1996).

**Calculation**

\[
\text{Tensile strength} = \frac{\text{maximum breaking load}}{\text{Cross-sectional area}}
\]

Units Nm\(^2\) or Kg cm\(^2\)

**(ii) Percentage Elongation at Break**

The initial free length between the clamps before and after final free
length was set at 5 cm and the elongation calculated (SLTC 1996).
Calculation

\[ \text{Elongation \%} = \frac{\text{Final free length} - \text{Initial free length}}{\text{Initial free length}} \]

3.6.4 Measurement of Distension and Strength of Grain by Ball Burst Test.

A Lastometer was used. It is provided with:
(i) A clamp for holding securely the rim of circular flat disc of leather, while leaving the central portion of the disc free to move. The clamp holds the clamped area of disc, stationary when any load up to 80 kg. is applied to its centre. The diameter of free area is 0.25 mm.
(ii) A mechanism for thrusting a steel ball, with rotation, against the center of the flesh side of leather disc, and means for measuring the load applied. The ball diameter 6.25 mm., and the accuracy of load measuring mechanism shall be such that the load at grain crack and burst of the specimen is measured with an error not exceeding 3%.

Preparation of specimens

Cut the specimens to the dimensions required for clamping them in the apparatus.

Procedure.

1. Clamp the specimen in the instrument with its flesh surface adjacent to the ball, and its grain surface flat.
2. Increase the distention, and watch the grain surface for the occurrence of crack, and corresponding values at the burst if the leather disc bursts before the maximum load is reached. (JSLTC, 1960).

3.7 Statistical Analysis

The data were analyzed using (SPSS) computer program (version 10.05), while Duncan Multiple Range Test (DMRT) used in means separation.
CHAPTER FOUR
RESULTS AND DISCUSSIONS

Chemical analyses of both fresh and used liquors are given in table (5). The analysis showed that about 65% and 33% from the total amount of sulphide and lime respectively remained in the used liquor.

The amount of sodium sulphide found in the used liquor is due to the amount in excess, in addition to the fact that pulping reaction induced by sodium sulphide had produced sludge containing keratin sulphide reaction products.

As lime has a limited solubility of 0.125 %, undissolved lime remains in solution, the amount of lime chemically fixed to the skin is 2% of soaked weight (Sorkar, 1981). However, it is customary to use a quantity of lime in excess of that suspended in liquor to maintain the strength of the liquor regardless of the soluble lime absorbed by the skin, the quantity in excess of that chemically fixed to the skin remains in used liquor.

Table (6) shows that the amount of sulphide and lime in recycled liquors remains approximately constant from one cycle to another, due to the addition of make-up of each compound. The consistency of the amounts of chemicals after each cycle indicates that the liquor may be recycled indefinitely.
The amount of water, sodium sulphide and lime added to the conventional and recycled liquors are given as a percentage based on soaked skins in table (7).

A 300% float was used in all trials because similar floats are used in most tanneries, but Simncini et al; (1972) used 400% water and higher percentages of lime and sodium sulphide based on skins weight while Money and Adiminis (1973) used 200% float based on hide weight. However, the float must be enough to enhance the mechanical action of the drum and should not be too high to affect the diffusion rate.

The adjustment of used liquors with 30% water based on soaked weight, agrees with the fact that the conventional swelling requires 20-40% water absorbed by skin to open up fibre bundles (Thanikaivelan et al., 2001). These amounts to only one tenth of the amount of water employed during the conventional unhairing method.

The average replenishment with 1.4% sodium sulphide and 2% lime based on the soaked weight is applied to increase the concentration similar to those in fresh liquors.
The efficiency of unhairing and degree of swelling of conventional and recycled unhairing methods are shown in table (8).

From visual observation during unhairing, it is possible to make conclusion that the extent of hair removal is 100% for both control and recycled pelts. The statistical analysis revealed that there is no significant different in the swelling between conventional unhairing and cycle 1, 2 and 7 ($p > 0.05$), but there is significant difference between conventional and cycles 3, 4, 5 and 6 ($p < 0.05$). The increase in weight (swelling) of skins during unhairing was greater in the fresh unhairing liquor than the various recycled liquors. This decrease of swelling was significant after the second use and was almost constant for other cycles except cycle 7, which was treated by caustic soda.

The decreased of swelling in the recycled liquors was in agreement with the findings reported for cattle hide by Money and Adiminis (1973). They attributed that to the increasing concentration of sodium chloride in the used liquor during recycling. The addition of caustic soda in cycle 7 had improved the swelling to a degree similar to that obtained in conventional method and this was due to the strong alkali action of caustic soda.
The chemical analyses of the leathers produced by conventional and recycling unhairing methods are shown in table (9).

There were no significant difference ($p > 0.05$) between the two methods in the percentages of moisture, ash, fat and chromic oxide content, where skin substance is significantly higher ($P<0.05$) in the leathers produced with recycling after the third cycle. This was due to that the skin during unhairing takes the degraded protein in the used liquors, but no difference has been detected in the final leathers.

The thickness and the strength properties such as tensile strength, elongation, load at grain crack and load at grain burst values were obtained by standard physical testing methods and are presented in table (10).

The results revealed no significant differences in thickness and strength properties between the leathers produced with conventional and recycling methods, these results agreed with that of Money and Adiminis (1973).

The consumption of the chemicals and water for both conventional and recycling unhairing methods are shown in table (11).

The average consumption of recycling unhairing liquors based on soaked weight was 30% water, 1.4% sodium sulphide and 2% lime. That saving was about 90% water, 65% sulphide and 33% lime compared with
conventional method. This will make a reduction in the total cost of unhairing and liming process.

Even if the unhairing liquors were discharged after eight cycles there could an overall a 7-fold reduction in unhairing effluent pollution. However, the recycling process could be applied indefinitely with some tight control of filtration and make-up addition.
CONCLUSION

According to the present study the recycling of unhairing lime solution, can solve the environmental problem from the unhairing-lime effluent. The process could contribute in creation of clean technology and environment.

The save in chemicals and water is considerable and reflected in the reduction of the total cost of the unhairing and liming operations. The quality of the leather processed through recycling is acceptable as shown by the chemical and physical analysis as well as the visual assessment.

The decrease of swelling during recycling did not affect the final product and could be easy eliminated by addition of caustic soda.

The treatments necessary before re-use are solids removal, and replenishment with 2% lime, 1.4 sodium sulphide and 30% water based on soaked skins weight.

The equipments required for the process are a collection pit, a pump, a filter and pipe line to and from the drums, but it may be possible to pump the liquor directly from one drum to another.
Table (5): Chemical Analyses of fresh and used lime-sulphide liquors

<table>
<thead>
<tr>
<th></th>
<th>Sulphide (S⁻) (mg/L)</th>
<th>Ca(OH)₂ (mg/L)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>3200</td>
<td>6500</td>
<td>13</td>
</tr>
<tr>
<td>Used</td>
<td>2100</td>
<td>2500</td>
<td>12.4</td>
</tr>
</tbody>
</table>
### Table (6): Total amount of the sulphide, lime and pH of recycled liquors

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Sulphide (S⁻)</th>
<th>Ca(OH)₂</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2100</td>
<td>2500</td>
<td>12.4</td>
</tr>
<tr>
<td>2</td>
<td>2100</td>
<td>2350</td>
<td>12.3</td>
</tr>
<tr>
<td>3</td>
<td>2000</td>
<td>2400</td>
<td>12.3</td>
</tr>
<tr>
<td>4</td>
<td>1900</td>
<td>2500</td>
<td>12.3</td>
</tr>
<tr>
<td>5</td>
<td>2000</td>
<td>2400</td>
<td>12.3</td>
</tr>
<tr>
<td>6</td>
<td>2000</td>
<td>2450</td>
<td>12.3</td>
</tr>
<tr>
<td>7</td>
<td>2000</td>
<td>2400</td>
<td>12.3</td>
</tr>
</tbody>
</table>
Table (7): Comparison of recycling and conventional methods

<table>
<thead>
<tr>
<th></th>
<th>Water %</th>
<th>Sulphide %</th>
<th>Lime %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional (control)</td>
<td>300</td>
<td>4.0</td>
<td>3</td>
</tr>
<tr>
<td>Cycle 1</td>
<td>30</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>32</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>30</td>
<td>1.3</td>
<td>2</td>
</tr>
<tr>
<td>Cycle 4</td>
<td>29</td>
<td>1.4</td>
<td>2</td>
</tr>
<tr>
<td>Cycle 5</td>
<td>29</td>
<td>1.3</td>
<td>2</td>
</tr>
<tr>
<td>Cycle 6</td>
<td>30</td>
<td>1.4</td>
<td>2</td>
</tr>
<tr>
<td>Cycle 7</td>
<td>30</td>
<td>1.4</td>
<td>2</td>
</tr>
</tbody>
</table>
Table (8): Degree of swelling and efficiency of unhairing

<table>
<thead>
<tr>
<th>Total time</th>
<th>Degree of swelling</th>
<th>Unhairing</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Hour)</td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Conventional (control)</td>
<td>21</td>
<td>35&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cycle 1</td>
<td>21</td>
<td>34&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>21</td>
<td>33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>21</td>
<td>33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cycle 4</td>
<td>21</td>
<td>33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cycle 5</td>
<td>21</td>
<td>33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cycle 6</td>
<td>21</td>
<td>33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cycle 7</td>
<td>21</td>
<td>35&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Degree of significance - * -

In this and subsequent tables, N.S stand for not significant.

* p<0.05

** p<0.001

a, b, means on the same column with different superscripts differ significantly
Table (9) Chemical analyses of leathers

<table>
<thead>
<tr>
<th>Conventional (control)</th>
<th>Moisture %</th>
<th>Ash %</th>
<th>Skin Substance %</th>
<th>Fat %</th>
<th>Cr₂O₃ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle 1</td>
<td>9.5</td>
<td>7.5</td>
<td>65.40&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11.0</td>
<td>3.92</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>8.5</td>
<td>8.0</td>
<td>66.40&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>9.5</td>
<td>3.96</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>9.0</td>
<td>7.0</td>
<td>67.90&lt;sup&gt;b&lt;/sup&gt;</td>
<td>10.0</td>
<td>3.92</td>
</tr>
<tr>
<td>Cycle 4</td>
<td>9.2</td>
<td>7.0</td>
<td>67.95&lt;sup&gt;b&lt;/sup&gt;</td>
<td>12.0</td>
<td>3.92</td>
</tr>
<tr>
<td>Cycle 5</td>
<td>9.0</td>
<td>7.0</td>
<td>67.40&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9.5</td>
<td>3.90</td>
</tr>
<tr>
<td>Cycle 6</td>
<td>9.1</td>
<td>7.0</td>
<td>67.20&lt;sup&gt;b&lt;/sup&gt;</td>
<td>11.0</td>
<td>3.93</td>
</tr>
<tr>
<td>Cycle 7</td>
<td>9.0</td>
<td>7.0</td>
<td>68.00&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9.0</td>
<td>3.93</td>
</tr>
</tbody>
</table>

Degree of significance: N.S N.S * N.S N.S
Table (10): Physical properties of leathers

<table>
<thead>
<tr>
<th></th>
<th>Thickness</th>
<th>Tensile strength</th>
<th>Elongation</th>
<th>Load at grain crack</th>
<th>Load at grain burst</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Control)</td>
<td>1.00</td>
<td>160</td>
<td>39</td>
<td>27.5</td>
<td>32.5</td>
</tr>
<tr>
<td>Cycle 1</td>
<td>1.10</td>
<td>155</td>
<td>45</td>
<td>30.0</td>
<td>37.0</td>
</tr>
<tr>
<td>Cycle 2</td>
<td>1.10</td>
<td>159</td>
<td>37</td>
<td>37.0</td>
<td>39.0</td>
</tr>
<tr>
<td>Cycle 3</td>
<td>1.15</td>
<td>195</td>
<td>35</td>
<td>28.0</td>
<td>37.0</td>
</tr>
<tr>
<td>Cycle 4</td>
<td>1.05</td>
<td>166</td>
<td>45</td>
<td>25.0</td>
<td>33.0</td>
</tr>
<tr>
<td>Cycle 5</td>
<td>1.00</td>
<td>150</td>
<td>44</td>
<td>25.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Cycle 6</td>
<td>0.85</td>
<td>180</td>
<td>32</td>
<td>27.0</td>
<td>31.0</td>
</tr>
<tr>
<td>Cycle 7</td>
<td>1.10</td>
<td>195</td>
<td>37</td>
<td>28.0</td>
<td>35.0</td>
</tr>
<tr>
<td>Degree of significance</td>
<td>N.S</td>
<td>N.S</td>
<td>N.S</td>
<td>N.S</td>
<td>N.S</td>
</tr>
</tbody>
</table>


Table (11): Conventional unhairing method versus recycling method

<table>
<thead>
<tr>
<th></th>
<th>Consumption with out recycling %</th>
<th>Net consumption with recycling %</th>
<th>Saving %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>300</td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td>Sodium sulphide</td>
<td>4</td>
<td>1.4</td>
<td>65</td>
</tr>
<tr>
<td>Lime</td>
<td>3</td>
<td>2</td>
<td>33</td>
</tr>
</tbody>
</table>
Fig (1) Cystine structure (Sarkar, 1981).
Figure (3) Cross section of skin
Physical tests

Chemical analysis

Figure (3) official sampling method 1996
Figure (4) Dumbbell shape for tensile strength
### Appendix

Out line Recipes for upper leather

<table>
<thead>
<tr>
<th>Process</th>
<th>%</th>
<th>Material</th>
<th>Time Min.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Presoaking</td>
<td>300</td>
<td>water rest run</td>
<td>30 rest</td>
<td></td>
</tr>
<tr>
<td>Rinse soak</td>
<td>300</td>
<td>water run</td>
<td>30 run</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+ 0.2</td>
<td>BAYMOL AN run total duration:</td>
<td>15 run 5 hrs</td>
<td></td>
</tr>
<tr>
<td>Rinse Liming</td>
<td>300</td>
<td>water stand overnight total duration:</td>
<td>120 stand overnight 21hrs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>sodium sulphide (62)</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>lime (65)</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>Flesh, split if desired, weight. % based on limed weight</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>wash deliming</td>
<td>150</td>
<td>water drain</td>
<td>15 drain</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>water pH 8-8.5 pp. color less drain</td>
<td>30 pH 8-8.5 pp. color less drain</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>ammonium sulphate bating agent</td>
<td>30 pH 8-8.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>bating agent pH 8-8.5</td>
<td>30 pH 8-8.5</td>
<td></td>
</tr>
<tr>
<td>wash Pickle</td>
<td>200</td>
<td>water drain</td>
<td>30 drain</td>
<td></td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>water °Be 6-7</td>
<td>15 °Be 6-7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>commonsalt pH 2.8-3</td>
<td>60 pH 2.8-3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>formic acid (1:5)</td>
<td>15 pH 2.8-3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>sulphuric acid (1:10)</td>
<td>60 pH 2.8-3</td>
<td></td>
</tr>
<tr>
<td>Chrome tannage</td>
<td>2.0</td>
<td>Chromosal B Leave overnight</td>
<td>120 pH 3.6-3.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.5</td>
<td>Baychrom A</td>
<td>180 pH 3.6-3.8</td>
<td></td>
</tr>
</tbody>
</table>

Horse up
<table>
<thead>
<tr>
<th>Process</th>
<th>%</th>
<th>Material</th>
<th>Time Min.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wash</td>
<td>300</td>
<td>water</td>
<td>20</td>
<td>drain</td>
</tr>
<tr>
<td>Chrom retan</td>
<td>100</td>
<td>water</td>
<td>60</td>
<td>pH 3.6</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>chromosol B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+</td>
<td>2.0</td>
<td>sodium formate</td>
<td>60</td>
<td>pH 3.6</td>
</tr>
<tr>
<td>Nutralization</td>
<td>100</td>
<td>water</td>
<td>60</td>
<td>drain</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>sodium formate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td>sodium bicarbonate</td>
<td>60</td>
<td>pH 4.8</td>
</tr>
<tr>
<td>Retannage</td>
<td>50</td>
<td>water 30°C</td>
<td>120</td>
<td>drain</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>Tanigan OS</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>Retinigan R7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>Garad</td>
<td>120</td>
<td>drain</td>
</tr>
<tr>
<td>wash</td>
<td>200</td>
<td>water</td>
<td>10</td>
<td>drain</td>
</tr>
<tr>
<td>Fatilquir</td>
<td>150</td>
<td>water 50°C</td>
<td>120</td>
<td>drain</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>sulphonated oil</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Dry, condition, finish as required.
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<table>
<thead>
<tr>
<th></th>
<th>Vegetable tannage</th>
<th>Chrume tannage</th>
<th>Alum tannage</th>
<th>Oil tannage</th>
<th>Aldehyde tannage</th>
<th>Synthatic tannage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tanning material</strong></td>
<td>Water extracts of barks, woods, leaves, fruit and roots of plant or trees</td>
<td>Chromium sulphide or chlorides</td>
<td>Alum or aluminium sulphides or chlorides</td>
<td>Cod live oil</td>
<td>Formaldehyde Glutaraldehyde</td>
<td>Synthatic tanning materials</td>
</tr>
<tr>
<td><strong>Quantity as a percentage on</strong></td>
<td><strong>drained weight of skin prior to tannage</strong></td>
<td>6% to 12% typical chrome powder</td>
<td>3% to 8% of alum</td>
<td>30% to 40% cod liver oil</td>
<td>1% to 2% formalin</td>
<td>Very variable, e.g. 10% to 20%</td>
</tr>
<tr>
<td><strong>Effect of pH of tan liquor</strong></td>
<td>Low pH gives faster and greater fixation</td>
<td>Low pH reduces speed and degree</td>
<td>Low pH reduces speed and degree of tan fixation</td>
<td>Not very sensitive</td>
<td>Low pH reduces fixation soft leather</td>
<td>Low pH gives faster and greater tan fixation</td>
</tr>
<tr>
<td></td>
<td>Relatively dense, firm or soft leather</td>
<td>of tan fixation</td>
<td></td>
<td></td>
<td>Very soft stretchy leather</td>
<td>As required usually like vegetable tan</td>
</tr>
<tr>
<td><strong>Handle produced</strong></td>
<td>Give a high weight of leather per unit raw hide</td>
<td>Low yield</td>
<td>Low yield</td>
<td>Low yield</td>
<td>Low yield</td>
<td>Low yield generally</td>
</tr>
<tr>
<td><strong>Weight yield of leather</strong></td>
<td>Pale brown generally darkness in daylight</td>
<td>Pale green or blue, little change in daylight</td>
<td>White, little change in daylight</td>
<td>Dull yellow bleach in daylight</td>
<td>White, goes whiter in sunlight</td>
<td>Generally pale than veg. tans, mat darker in daylight</td>
</tr>
<tr>
<td><strong>Colour after tanning</strong></td>
<td>Depends on finishing treatment, washes out very slowly</td>
<td>Does not wash out</td>
<td>Tan can washed out</td>
<td>Nil, very water absorbent, tan does not wash out</td>
<td>Nil, very water absorbent, tan does not wash out</td>
<td>Usually similar to veg. tan, but does not wash out</td>
</tr>
<tr>
<td><strong>Removal of tan by water</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Characteristic uses</td>
<td>Shoe sole leather, upholstery and bags, shoe lining leathers, belts, straps</td>
<td>Shoe upper leather, gloving and clothing leather, some sole and belting leather</td>
<td>Gloves, fur skins</td>
<td>Wash leathers, washable gloves</td>
<td>Washable gloves and clothing</td>
<td>White leathers, specially leather</td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------</td>
<td>-----------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
<td>-------------------------------</td>
</tr>
</tbody>
</table>

Shaphouse 1983
Figure (4) Dumbbell shape for tensile strength