Sudan University of Science and Technology

College of Graduate Studies

Application of New Techniques by using local Tannage Material (Acacia nilotica Garad)

تطبيقات تقانة حديثة باستخدام مواد دباغة محلية

(السنط النيلي، قرض)

A thesisSubmitted in Fulfillment for the Requirements
of the Degree of PhD in Leather Technology (Animal Production)

By

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Dedication

This thesis is dedicated to my parents, my brothers and my sisters,

To all of my friends,

To all of my teachers,

Acknowledgment

Firstly I want to thank DAAD for funding this research my thanks are also extended to prof. Mohamed Tageldin Ibrahim who had spent efforts and time in supervising this work.

My appreciation is extended to Sudan University of Science and Technology (Leather Industrial Incubator) for allowing me to carry out the process from soaking to fatliquoring.

My special appreciation is to the staff of the National Center of Leather Technology Khartoum- Sudan for allowing physical and chemical testes in their laboratory.

Abstract

The aim of this research was to enhance the Sudanese leather process using local tanning agent, to apply the ideas of cleaner technology in Sudan, to reduce environmental pollution generated by chromium and to produce a new type of leather with a specific identity that can compete easily in the international market.

After the process of tannage, almost 25% by weight of input raw material are wasted. The occurrence of such a large amount of waste presents economic and mainly ecologic problem for this industry; thus substantial global effort is given to development of improved technologies for the disposal of chromium tanned waste. (*Acacia nilotica*) Garad used with a mineral chromium and aluminum to limit the consumption of undesirable chromium.

In the experimental work 24 pieces pickled cattle hides were processed in eight trials, in each trial three pieces pickled cattle hides were treated in pilot drum with speed of 8 rpm. Four trials were treated with 30% garad as tannage and different percentages chromium of (1,2,3,4%) as retannage, other four trials were treated with 30% garad as tannage and different percentages aluminium of (1, 2, 3, 4%) as retannage.

The leather produced was analysed for physical testing, including thickness, tensile strength, percentage elongation at break, load at grain crack, load at grain burst and shrinkage temperature. And chemical analysis including moisture content, ash content, fat and chrome contents. The results were compared with the standard specification and found to be satisfactory.

خلاصة البحث

أهمية هذا البحث كانت زيادة القيمة المصنعة للجلود السودانية بدباغة محلية، دخول أفكار تكنولوجيا نظيفة في السودان، تقليل التلوث البيئي المولد بالكروم، وتصنيع نوع جديد من الجلود ذي مواصفة تستطيع بسهولة أن تنافس في السوق العالمي.

بعد عملية دباغة الجلود تقريبا 25% من مدخل المادة الخام من عائدات الكروم تفقد في الدباغة،هذا الحدث يمثل هدرا اقتصاديا ومشكلة بيئية لهذه الصناعة مما أدي لبذل مجهود عالمي ضخم لتنمية وتحسين تقنيات لتخلص من فاقد الدباغة بالكروم، استخدام القرض مع معدني الكروم والألمونيوم هذه الطريقة تحد من استهلاك الكروم.

في هذه التجربة 24 قطعة جلد بقري محنطة قسمت الي ثمان تجارب في كل تجربة ثلاث قطع جلد بقري محنطة عولجت في برميل سرعته 8 دورة في الدقيقة اربع تجارب عولجت ب 30% قرض كمادة دابغة ونسب مختلفة من الكروم (4،3،2،1%) في اعادة الدباغة الاربعة الاخري عولجت ب 30% قرض كمادة دابغة ونسب مختلفة من الالمونيوم (4،3،2،1%) في اعادة الدباغة.

الجلود المنتجة أجريت لها الاختبارات الفيزيائية وشملت السمك، قوة الشد، الاستطالة، قوة الاختراق، ودرجة الانكماش وأجريت لها الاختبارات الكيمائية نسبة الرطوبة، نسبة الرماد، نسبة الدهن، نسبة الكروم تمت مقارنة النتائج مع الحدود العالمية وقد كانت مطابقة للمواصفات.

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1. Chapter one

1. Introduction

The Sudan is the largest country in Africa and it is rich in livestock population. It is estimated to 103570493 heads of cattle, sheep, goat and camels (Ministry of Animal Resources and Fisheries 2011**).** Estimated of hides and skins production No in (1000) pieces cattle 4596.0, 4611.0, sheep 14888.0, 15228.0, and goat 14681.0, 14894.0 2009, 2010 respectively (Ministry of Animal Production and Fisheries). Values of livestock from hides and skins (million $) 16.584, 13.974 in 2009, 2010 respectively (Sudan Bank).And full capacity of tanneries in Sudan pieces from cattle 3400,sheep and goat 99000 and production capacity from cattle 1000, sheep and goat 57500 daily production (Report year of tanneries2009).

The Sudanese have been familiar with processing of hides and skins in the rural tanneries using local tanning materials from ancient times to satisfy their requirements from leather goods such as shoes, leather bags for carrying water and personal commodities as well as leather for making their covers and homes, and other requirements.

Leather is a direct industrial product of a natural fabric, skin. The architectural marvel of skin is yet unmatched by man-made synthetics. The comfort and personal hygiene of leather products have remained unique. Leather processing technology has evolved naturally from a traditional practice to an industrial activity. The leather industry contributes substantially to pollution of the environment. Environmental challenges from leather processing arise from both of nature and the quantum of wastes discharged (Veeger, 1993; Ramasami, *et al.*1998 and Gaidau, *et al.* 2009).

Stringent environmental regulations on the discharge of pollutants from various industries have prompted researchers to seek the development of eco-benign technologies and process innovations aimed at low-waste and high exhaust chrome tanning systems. However, an effective biotechnological solution for reducing chromium pollution that is cost effective, commercially adaptable high exhaustion chrome tanning process has not been explored (Venba, *et al*. 2008).

Heavy metals represent a major environmental problem in many industries and they may cause potential danger to human health when they are present in/on leather and textile and exposed long term contact with them in sweaty condition (Lalueza, *et al*. 2010).

Growing concerns over the toxicity of chromium and its influence on the health of customers using chromium tanned garment leathers has forced the leather industry to search for alternative tanning agents (Sreeram, *et al.* 2010).

As a result of the huge environmental impacts chromium (III) salt, other solutions are put into serious consideration. Tanning is the process of transforming animal skin to leather. Over the past 30 years global demand for leather and related products has increased by about 55% (Rivela, *et al.* 2004).

The current state of leather science (not leather technology) in the global leather industry is reviewed. The review focuses on the following questions. Is leather science still required by the leather industry: if so, to what purpose? What remaining problems should be addressed? Recent trends in leather science research are analysed in terms of the published topics over the last twenty-five years and the sources of the publications in JSLTC and JALCA, as representative of the global research programme. The current state of knowledge is compared to the understanding of leather science in recent decades, where appropriate. Predictions of industrial and technical requirements made in the past are discussed with regard to the progress made to the present day by leather scientists. The final question is leather science a luxury the leather industry cannot afford? And, if leather scientists should be needed, from where can they be found? (*C*ovington, 2012)

The origins of vegetable tannin are lost in prehistoric time primitive people in all parts of the globe and from all ages of the past have developed vegetable tannin systems based on material available locally The vegetable tannins come from a wide variety of plants, and may be found in wood, leaves, nut, twigs and bark. The extract of a particular plant consists of a wide variety of substance, and there is no such thing as single tannin from a particular plant source (Thorstensen, 1993) .

Vegetable tannin extracts are used as tannin agents to convert skin into leather in aqueous solution. To ensure full penetration and reaction of tannin with collagen, an excess of vegetable tannin extracts is usually used in tanneries (Madhan, *et al.* 2005 and Gao, *et al.* 2001).

Semi- metal tannage (Covington, 1997) was tried using different types of vegetable tannins. But it was not tried with the garad. In Sudan the majority of tanners use Acacia nilotica fruit (garad) as the main agent of retannage. The reversing of the method initially gave appreciated results with a mineral, chromium, aluminum, would limit to the consumption of undesirable tannin agents ability of garad tanned to produce good leather, could make it possible for Sudan to compete in the international market.

The objectives of this research

1- To establish new recipes for leather production.

2- To identify the chromium and aluminum used for retannage, that would provide the best type of leather.

3- To test the chemical, physical and fastness properties of the produced leather.

1. Chapter Two

2. Literature Review

2.1. Pre-tannage operation:

These are also known as the beam house operations. The term ‘beam house’ ’refers to the process in the tannery between removal of the skins or hides from storage and their preparation for tanning. The term is dated back to the time when the hair was removed from the skins by means of a hand beam; which was carried out on sloping curved table or large log; knew beam and using a two handled curved knife. These operations include soaking, trimming, fleshing, unhairing, liming, de liming and bating. Even in the modern and sophisticated facilities, some handwork on the beam is needed occasionally for quality improvements. The beam house operations have the distinction of being the most disagreeable step in leather manufacture. It involves the use of the bad smelling concoctions, which have been responsible of poor names of leather industry in its community reaction. Nevertheless, the beam house operations are of tremendous importance in ultimate quality of the leather. Indeed, in the opinion of most practical tanner’s, “leather is made in the beam house”. Beam house operations also employ principles of biochemistry and inorganic chemistry (Thorstensen, 1993).

Practical beam operations, however, can be reduced to relatively simple steps, and good quality leather can be made close attention to detail and empirical observations of cause and effect. The main protein in skin is collagen. Some proteins, which are found in native skin, such as myosin, mycoids, albumins and globulins, are removed during the early stages of leather making process, together with other non- collage nous components, such as glycosaminoglycans, especially hyaluronic acid and proteoglycans, especially derma tan sulfate, and triglyceride fats. Removal of non-collagenous protein is essential to produce soft leather (Covington, 1997).

Tanning stabilizes the skin matrix permanently and is considered the heart of leather processing. In commercial practice, vegetable and chrome tanning methods are widely employed. Between these two methods, chrome tanning is the most commonly used tanning method. Hence, the relationship between the chromium content and drape related properties of garment leathers. The bending length and drape parameters were measured for goat suede leathers with different chromium contents and analyzed. The goat suede leathers were prepared in three different ways; namely full chrome (FC), semi chrome (SC) and full vegetable (FV) methods. Whereas FC and FV goat suede leathers had increasing drape coefficient values, the drape coefficient for SC goat suede leathers was the lowest in the range of 35.1±7.2. Further, softness, bending length and number of nodes for SC goat suede leathers were statistically superior in the stand point of drape ability compared to FC and FV goat suede leathers. Hence, it is validated that the semi chrome goat suede leathers possess better drape ability compared to full chrome as well as full vegetable goat suede leathers. Consequently, the presence of chromium in the leathers plays a major role in the draping ability of goat suede apparel leathers; however, it is also inferred that more amount of chromium in the leathers (FC) did not yield better drape ability (Krishnaraj, *et al*. 2010).

There are three major steps involved in beam operation: soaking, unhairing, and bating. These steps common to all type of leather produced, although there are significant variations depending upon the type of skin used and the leather be made. All three steps are closely related and intedependent (Thostensen, 1993).

2.2 Tannage operation:

2.2.1 Theory of tannage:

The tanning process converts the protein of the raw hide or skin into a stable material, which will not putrefy and is suitable for a wide variety of purposes. The main purpose of tanning is to convert skin into leather. The tanning operation would (BASF, 2003):

-Stabilize it against enzymatic degrading and increase its resistance to chemicals.
-Raise its shrinking temperature and increase its resistance to hot water.
-Enhance its strength properties.
-Lower its density by isolating the fibers.
-Reduce deformability.
-Reduce its shrinkage in volume, area and thickness.
-Enhance the porosity of its fiber texture.

The chemical nature of collagen allows it to react with a variety of agents often resulting in its conversion to leather changes in appearance and properties that are the consequence of tanning. One of the most important is the increase in hydrothermal stability (Covington, 1997).

The nature of cross-link or cooperating units is not clear. A cross-link may function through the natural covalent cross-links and additional hydrogen structure elements in collagen, supplemented or modified by the tanning effects of hydrogen bonding or covalent cross-linking at polar groups on the amino acid side chains or through multiple interactions at peptide link itself. Thus, the tanning reaction may be highly complex on the molecular level, to the extent that there is no clear model of its effect on hydrothermal stability. The effect of the tannage may be related in part to the chemistry that is the particular reaction sites within the protein that are involved.

The ultraviolet-visible and near-infrared diffuse reflection (UV-Vis-NIR DR) spectroscopy was employed for further understanding of the mechanisms of three kinds of classical tannages, including aldehyde tanning, vegetable tanning and mineral tanning. The NIR DR spectra of glutaraldehyde tanned leather exhibited a decreased peak intensity of amino group at 1475 nm, suggesting that the main reaction groups of collagen in aldehyde tanning are amino groups. Comparing the NIR DR spectra of pickled pelt and vegetable tamed leather, it was proved that the vegetable tanning is based on the mechanism of multiple hydrogen binding interaction, where the amino groups, carboxyl groups and peptide chains are involved in. As for mineral tannages, the tanning mechanisms of chromium sulfate, zirconium sulfate, ferric sulfate, titanium sulfate and aluminum sulfate were investigated. Based on UV-Vis-NIR DR analysis in the wavelength range of 200 to 2070 nm, it was confirmed that the main reactions involved in mineral tanning are the chelating interactions of metal ions with both the carboxyl groups and the amino groups of collagen, although the reactivity of metal salts toward carboxyl groups is higher than toward amino groups. The reactivity of metal salts toward carboxyl groups of collagen follows the sequence of chromium salt > zirconium salt > ferric salt > titanium salt > aluminum salt. However, the reactivity of metal salts to amino groups of collagen is in the sequence of zirconium salt > chromium salt > ferric salt >

titanium salt > aluminum salt. Meanwhile, the peptide chain of collagen was also found to play an important role in fixation of metal ions during tanning process (Junling, *et al.* 2011).

Recently, increasing interests have been directed towards incorporating nanotechnologies into leather manufacturing, which offer cost-effective improvements in leather performances, as well as enabling the industry to meet stricter legislation regarding environmental safety. In order to guide the leather technologists and chemists worldwide, this article reviews state of the art related to existing nanotechnologies in leather manufacturing processes, including tanning, finishing and effluent treatment, over the past decade. The emphasis is placed on the mechanism by which nanotechnologies improve conventional processes, impressive performances of the resultant leather and possible obstacles that cloud technical development, potential health and environment risks associated with the incorporation of nanotechnologies, which are particularly important for daily necessities such as leather but have been basically overlooked by many researchers involved, are also addressed (Yi Chen, and Bi chi. 2011).

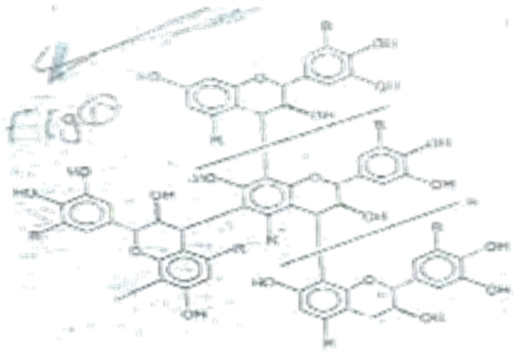
There is an abundance of hydrophilic groups in the collagen fibers in leathers. Because the affinity between these hydrophilic groups and water molecules varies with changes in temperature and relative humidity, leathers will adsorb or de-adsorb water as these factors change; affecting strength, permeability, and thermal stability. Retanning is a key operation in leather making with the purpose of retanning is to obtain leathers with some special characteristics. The water content in leathers, often 15-20 wt%, is an amount that cannot be neglected. However, few reports are found on the interactions between collagen and water, particularly the influence of retanning on the interaction between water and collagen fibers. The state that water molecules exist in collagen fibers, the mechanism for collagen fibers to absorb water, the de-adsorption kinetics for water molecules to escape from collagen fibers, and the influence of retanning on the adsorption of water on collagen fibers need to be studied to improve the leather making technology for controlling the structure and behaviors of leathers. After being chrome tanned, collagen fibers were retanned with chrome, glutaraldehyde, TGR retanning agent (proprietary acrylic based), and wattle extract, respectively, to obtain different retanned samples. The water adsorption isotherms of the samples were determined by using a gravimetric method, by which the influence of retanning on the equilibrium water adsorption capacity and the influencing mechanism were evaluated. Different retanned samples varied in water adsorption characterization and equilibrium adsorption capacity. The TGR retanning increased the equilibrium adsorption capacity, while glutaraldehyde retanning decreased it; likely related to differences in retanning mechanisms. For different relative humidity environments, leathers should be retanned with different retanning agents to get an optimum property. (Keyong, *et al*. 2009).

Some tannages, like vegetable tanning, aldehyde tanning and metal tanning, have been used by tanners for several thousand years. The chemical principles of these tannages have been clearly revealed in the last decades and have greatly improved technologies of leather processing. At the same time, the scientific essences involved in these principles are enlightening our inspirations of diversified applications of tanning methods to create a series of novel functional materials based on skin collagen. Herein, some ingenious applications of the tanning principles were reported, which might inspire more scientific ideas and imaginations of leather chemists. 1. Based on the principle of vegetable tanning, a novel adsorbent which can selectively remove tannins from natural beverages and medicinal plant extracts was devised. It was prepared by processing skin into collagen fibers with the proper size. This new adsorbent was shown to be more effective for this purpose in comparison with commonly used polyamides and macroreticular resins. 2. According to the principle of vegetable-aldehyde combination tanning, tannins which are able to complex with metal ions were immobilized onto collagen matrix. As a result, the tannin-immobilized adsorbent and membrane materials were prepared. Both of them presented high adsorption capacity for heavy metal ions, such as Hg2+, Pd2+, Au3+, UO22+ and Cu2+, in aqueous solutions and therefore, are expected to be used for removing toxic metal ions from wastewaters or separating precious metals from mixed solutions. 3. By utilizing the principle of metal tanning, a series of functional materials were prepared by loading metal ions, such as Zr4+, Fe3+ and Pt4+, onto collagen fiber. The Zr4+ and Fe3+ loaded materials exhibited strong adsorption to inorganic anions, such as F-, PO43-, AsO43-, CrO42- and V2O74-, in aqueous solutions, showing potential to be used in environmental protection. At the same time, Fe3+ and Pt4+ loaded materials have been experimentally proven to be the heterogeneous catalysts with high catalytic activity. Meanwhile, as a special kind of metal-loaded collagen fiber, the adsorption behaviors of chrome-containing leather waste to organic compounds in waste water were also investigated. It presented high adsorption capacity to dyes, surfactants and aromatic acids. 4. In terms of the principles of versatile metal-organic combination tannages, a series of novel carbon fiber and metal fiber materials with controllable mesoporous structures were prepared by using collagen fiber as the template. They are believed to have great potentialities in selective adsorption, chemical sensor and catalyst support (Bi Shi, 2008).

2-2-2 Vegetable tanning:

Many plant materials contain polyphenols which can be used in tanning. To be effective, the molecular mass must be 500-3000; lower molecular mass fractions in tannin are referred to as non tans and higher molecular mass species are gums. Tanning products may be powdered plant parts or aqueous extracts of those parts; the properties they confer to the leather are as varied as the many sources from which they are obtained. Tannins are classified as follows: hydrolysable or pyrogallol tannins, sub-classified as gallotannins (example are Chinese gallotannin or tanic acid, sumac, Tara) or ellagitannins (examples are myrobalan, chestnut, oak), and condensed or catehol tannins (examples are mimosa, quebaracho, and gambier).Hydrolysable tannins are sugar derivatives, based on glucose, but may be larger polysaccharides; plant extracts may contain tetrasaccharides as less useful gums. Gallotannins are characterised by glucose esterified by gallic acid; esterification may occur directly with the glucose ring or as depside esterification of bound gallic acid(Bailey, 1992). Ellagitannins have sugar cores, esterified not only with gallic acid, but also with ellagic acid (Heidemann, 1982) and chebulic acid (Brown, *et al.* 1996). Examples of structures hydrolysable tannins are chebulinic acid (Kadler, 1994) from myrobalan, chebulagic acid (Weir, 1949) and vescalagin (Covington, *et al.* 1989) and casatalafin (Ramachandran, 1968) of chesnut.

Condensed tannins are based on the flavonoid ring system, shown in fig (1-1)

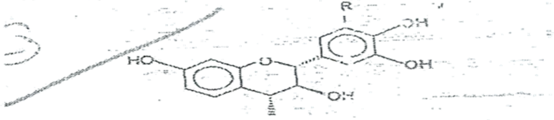


The A ring usually contains phenolic hydroxyl groups and the presence of the C ring makes both rings reactive to forming carbon- carbon bonds; the B ring does not exhibit the same reactivity, it often contains the catehol group, hence the alternative name for this group of compounds. The condensed tannins are illustrated in the generalised structure (Haslam, 1993) and the monomeric units of mimosa (Haslam, 1988) and quebracho (Haslam, and Cai 1994)

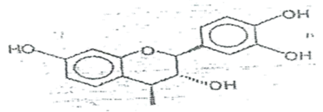
The condensed tannins do not undergo hydrolysis instead they may deposit a precipitate, an aggregate of polyphenol molecules, called ‘reds’ or phlobaphenes. Unlike the hydrolysable tannins, which are relatively light fast, the condensed tannins redden markedly upon exposure to light; this is understandable in terms of their linked ring structure and ability to undergo oxidative crosslinking. Condensed tannin typically raises the shrinkage temperature of collagen to 80-85°C. Vegetable tannins react with collagen primarily via hydrogen bonding, as indicated in the model presented in fig (1-2).

R = H, procyanidin
R = OH, prodelphinidin

Condensed tannins 8



mimosa 9



quebracho 10

This type of interaction is inferred from studies of reaction with polyamides. Also, is it known that polyphenols fix to amino side chains by electrostatic salt links with carboxylate or hydrogen with carboxylic acid groups (depending on PH). It is known that condensed tannins have an additional mechanism for reaction, because they are more resistant to removal by hydrogen bond breakers. For example, treating leather tanned with myrobalan (hydrolysable tannin) with 8 M urea removed 80% of the bound tanning, reducing the shrinkage temperature by 10-20 °C, but mimosa (condensed tannin) tanned leather treated under the same conditions lost only 50% tannin and shrinkage temperature fell by 4-5 °C. It has been suggested that this additional interaction is covalent reaction between the protein and aromatic carbon in the tannin molecules via quinoid structures. (Covington,1997).

The traditional way to tan with vegetable tannins in pits, where the slow penetration of large reactive molecules can take place over a prolonged period of time; when leather quality was overseen by the Gluids, hide had to stay in the pits for a year, a form of quality assurance. Today, that tanning period has been reduced to a few weeks. A feature of pit tanning with hydrolysable tannins is that they deposit `bloom`; natural fermentation breaks down the tannin into sugar acids and precipitates components such as ellagic acid. The bloom has a filling effect within the fibre structure, useful because sole leather is sold by weight, and the organic acid salts provide a buffer against the detanning effects of sulfur oxides and nitrogen oxides in the atmosphere. This latter reaction is known as ‘red rot’, familiar as the cracking and disintegration of bookbinding leathers, a phenomenon once investigated by Michael Faraday. Hydrolysable tannins typically raise the shrinkage temperature of collagen to 75-80°C (Covington,1997).

Implementation and improvement of a system that applies ultrasound technology to vegetable the system is versatile and requires no major modifications or investment expense for tanneries. Particular investigated grain fineness and fixation of tannins in relation to several mechanical approaches, which included: no mechanical effect (pits), drum, ultrasound, and ultrasound plus drum. A comparative study of energy expenses on the basis of the mechanical effect being used was also carried out (Morera, *et al.* 2010).

Genipin, a naturally occurring protein crosslinking agent, isolated from the fruit of Gardenia jasmindides Ellis, is beginning to replace glutaraldehyde as a fixative for biological tissues. Earlier research in this laboratory demonstrated that the apparent shrinkage temperature of hide powder could be increased from 60°C to 79°C by treating the powdered hide with 5% genipin at pH ~ 7 and 35°C for 24 hr, a significant improvement, but not enough for most leather uses. Typical tannages proposed to reduce the use of chromium are combinations of vegetable tannins or aldehydes with each other or with minerals. The tanning effect on bovine hide powder of genipin in combination with aluminum or vegetable tannins has been investigated. In terms of thermal stability, vegetable tannins in combinations with genipin appear to offer little advantage over either component alone, suggesting little if any synergy. Likewise, aluminum tanning over a genipin pretannage appears to provide little advantage. However, when hide powder was first tanned with 8% aluminum and then retanned with genipin the thermal stability increased linearly with increasing concentrations of genipin (2% to

10%). The apparent shrinkage temperature was > 100°C for aluminum post-tanned with 8%-10% genipin, suggesting the possibility that a practical combination tannage based on genipin could be designed *(*Ding, *et al*. 2007). Tanning of animal hides produces leather, flexible material that is stabilized against putrefaction. Chrome-tanned wet blue, aldehyde crosslinked wet white, and vegetable tanned hides are major contributors to current leather production. Although the chemistries involved are significantly different, the product in each case is leather. Vegetable tanning, the oldest of these technologies is, from a mechanistic perspective, the least well understood. To explore possible vegetable tanning mechanisms, we have applied molecular modeling techniques to the study of interactions of gallotannin, a component of chestnut tannins, with the collagen microfibril. A model gallotannin molecule was constructed and energy minimized. This model was docked into several energetically favorable positions on a fragment of the ERRC collagen microfibril model, generally with a good fit at a proline or hydroxyproline residue. The alpha carbon backbone of collagen was kept immobile during molecular dynamics simulations at 400 - 800K with and without an added layer of water for solvation to identify possibly more favorable interactions sites for the gallotannin molecules. Both inter and intra chain interactions were possible, and several potential sites for hydrogen bonding via arginine residues or hydrophobic interactions with alanine or isoleucine residues were identified. The information gained from this model study is an early step in the development of a vegetable tanning model (Eleanor, *et al*. 2011).

We have demonstrated the effectiveness of enzymatic and chemical modification of waste protein from leather, used alone or in combination with protein from the dairy industry, in preparation of fillers for leather treatment. We are continuing to build on these techniques to make products from sustainable resources that can enhance retanned leather. Vegetable tanning, utilizing polyphenols extracted from plant materials, is used primarily for production of heavy leathers for saddles, belts and shoe soles. Recently, the polyphenolic acids involved in vegetable tannage have been investigated extensively for their ability to modify gelatin. We explored whether gelatin, when modified using polyphenols, could give products with properties that might have application in leather processing. Before we investigated individual polyphenolic acids, we tested tannins, e.g. quebracho, to see if indeed these vegetable tannins themselves could be used in crosslinking. Quebracho can be employed to improve crust leather products in the retanning, coloring and fatliquoring process (Taylor, *et al.* 2012).

The fruit of the tara tree (Caesalpinia spinosa) as a sustainable source for tanning agents and proposes alternatives to the commercial mineral salts and vegetable extracts to comply with an increasing demand that concerns low carbon footprint raw materials and health safety although tara tannins have been used in the leather industry and its properties being well known, using tara as wet-white pre-tanning agent. Combinations with naphthalene sulphonic and phenol condensation syntans will be used for wet white. Tests are evaluated determining shrinkage temperature, tensile strength, elongation, tear resistance and light fastness (Castell, *et al. 2011).*

Modern vegetable tanning, especially for sole leather, is still conducted in pits and the procedure retains some of the traditional elements. For example, the high affinity of polyphenols for protein means that tannage must start in weak liquors and the hides are progressively moved through a series of pits containing increasing concentrations of the vegetable tannins; depleted liquors are strengthened by toping up with stronger liquors and in this way the hides go one way through the system and the liquors go in the opposite direction, the counter current method of pit tanning. The use of extracts, rather than the plant material itself, allows highly concentrated solution to be employed and by warming the pits, hot pitting, the whole process takes only a few weeks. Vegetable tanning can also be conducted in rotating drums, but there is a need to make the hide less reactive, to allow the tannins to penetrate into the thick hide (Covington, 1997).

The study of plant polyphenols is an active field, not only because of application to tanning technology, but also (interalia) because it is a fruitful area for a wide range of products, either isolated compounds or chemically modified polyphenols: that range includes adhesives, inhibitors to fungal, bacterial and viral growth and antitumour activity (Hemingway, *et al.* 1992 and Haslam, 1994).

Vegetable tanning is one of the more versatile tanning methodologies involving natural materials. The problem associated with this tanning method is that it takes longer time for diffusion of vegetable tanning agents (VTA) though the pelt matrix. Therefore, there is a pressing need to transform this traditional eco-friendly tanning process into a tanner friendly efficient methodology by way of augmentation techniques such as the use of ultrasound influence of ultrasound on vegetable tanning process has been studied. The influence of important process parameters such as process time, ultrasonic power, pre-tanning on VTA uptake has been investigated. The effect of ultrasonic power on shrinkage temperature of tanned leather has also been studied. The results indicate that there is a significant enhancement in vegetable tanning process due to the use of ultrasound. There is about 30-40% increase in %uptake of VTA due to the use of ultrasound for 120 – 210 watts. In order to find out the possible mechanism for the enhancement with ultrasound, effect of pre-sonication of substrate (pelt matrix) as well as substance (VTA) has been studied. There is an appreciable reduction in the particle-size of VTA due to sonication prior to tanning process aiding penetration. Therefore, ultrasound application in vegetable tanning process could improve the diffusion rate leading to significant savings in process time and enhancement in quality of the tanned leather. This methodology can be easily adopted in existing paddle or tanning pit systems for large scale production. Hence, this novel technique is a viable option for tanners in near future (Sivakumar, *et al.* 2008).

Quebracho a vegetable tannin can be used to modify gelatin to produce a product that has been applied effectively as a filler in leather processing, another vegetable tannin, tara is examined for its possible application in protein modification the tara tanning substance is a gallotannin, comprised mainly of gallic acid, and is extracted from the pods of the small tara tree (caesalpinia spinosa); it is a native plant species of Peru, advantages for using tara are that it not only gives an almost colorless product, which would be desirable in production of light colored leather, it also imparts light-fastness to the resultant leather and is a truly sustainable resource. The possibility of using both Tara and its main component, the polyphenolic gallic acid, as crosslinking agents for gelatin and whey protein concentrate (WPC). Protein modification parameters were developed and the results of product characterization using physicochemical analyses showed that products had improved physical properties. The molecular weight distribution indicated that the bands indicative of gelatin and whey had been altered suggesting higher molecular weight moieties. Thus, by-products from the leather and dairy industry, modified by using a sustainable resource, have the potential to be used in leather processing, specifically as fillers (Taylor, *et al.* 2012).

The effect of three different offers of both vegetable retanning agent (0, 5 and 10 %) and a sulphated fatty alcohol (0, 2 and 4 %) on the physical properties of goatskins was assessed. A standard process was applied to the left halves of goatskins from Nigeria, whereas the right halves were subjected to the corresponding variables.. Most of the studied leather properties exhibited the highest values with the lowest offer (0 %) of the vegetable retanning agent. However, a 5 % offer of the vegetable retanning agent was required to obtain the highest values of tear resistance for both parallel/perpendicular to the backbone test samples whereas the highest offer (10 %) provided the best values of grain firmness. The best results of softness and physical resistances were obtained with the highest offer (4 %) of the sulphated fatty alcohol, whereas a 0% offer provided the best results of color intensity and grain firmness (Palop, *et al.* 2007).

2-2-2-1Vegetable tans:

Vegetable tans which are water extracted from plant leaves, barks etc., consist of large polyphenol with some acidic groups and high secondary valency potentials (dipole H. Bonds).The acidic groups may combine with basic groups of the protein displacing the hydrated water, and the numerous secondary valencies dipole or hydrogen bond, to the peptide groups, 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 tan molecules (Sharphouse, 1979).

The increased rate of fixation may result in excessive deposition on the surface of the skin. Practical tanning by the vegetable processes will depend not only on the nature of the vegetable tanning material and the condition of hide, but also on a skill balance of PH, temperature and concentration (Thomas, 1969).

The quantity of vegetable tanning material necessary to bring about proper tannage is much greater than one would expect from a purely chemical point of view. The vegetable tanning material molecule is very large, and in spite of its possibility of multipoint attachment it cannot reach the available sites in the protein –the large size also prevents fixation of a second vegetable tannin molecule to an available site. The tannage become effective.

1- By the chemical reaction between the vegetable tanning material and the hide protein.

2- By coating of the fibers and isolation of the reactive groups, and

3- By filling of the physical voids in the leather (Thomas, 1969).

4- The characteristic of the various vegetable tanning materials with respect to their case of dispersion, degree of penetration, and degree of filling properties are related more to their colloidal character than chemical nature of the tannins involved. In the vegetable tannage of light leather, particularly in a drum, the chemical aspect is most important. Here the tanner is trying to obtain a full, soft tannage with a minimum amount of material (Thomas, 1969).

The speed of penetration is of limited importance, and the tannage is controlled by control of the liquor ratio, temperature, and PH of the solution (Thomas, 1969).

Tannins are bitter substances present in barks, fruits pods, leaves, roots 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 origins, however, and they differ in strength and in character, color, 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 (Mann, 1966).

To rural tanner of tropical and sub tropical Africa and Asia, the acacia are one of the most important tannin- bearing trees. Several species such as Acacia Senegal, A.nilotica, and A.adamsomia, have supplied pods and barks since immemorial time, the acacia pods and bark are known variously in the countries where they grow as babul (Hindustan, babar (sindj), garad or sunt (Sudan), babla (Africa), neb-neb (west Africa) and gabarua (Nigeria).The pods used for tanning from 10 to 20 centimeters long and 1 centimeter broad, and they have 8 to 10 seeds. Contrary to common belief, the seeds do not contain tannin, which is present only in the pods. The pods should be collected when they are rippe; for their tannin- content reaches them highest level just they are falling from the trees; according to the condition of soil and the climate, their tannin- content varies from 20 to 30 percent (Mann, 1966).

Valonea is one of the well-known vegetable tannins, used for tannage and retanning processes in leather making. Although it is used very extensively in the leather industry, its main components and chemical structure are only gradually being identified. In order to investigate the chemical structure of valonea with novel techniques, MALDI-TOF (Matrix-Assisted Laser Desorption/Ionisation Time-of-Flight) and FTIR (Fourier Transform Infrared) Spectroscopy were used. The MALDI-TOF spectrum showed the presence of low molecular weight fraction of hydrolysable tannins such as nonahydroxytriphnoic, flavogallonic acid, ellagic and gallic acid, pentagalloylglucose and all sorts of degradation and oxidation products which are thought to be major components of valonea tannin. Moreover, castalagin/vescalagin and those added by a few residual structures/atoms, thus creating larger molecule and greater mass than castalagin/vescalagin, derived by internal rearrangements of a larger molecule constitute major components of valonea (Ozguny, *et al.* 2007).

Tannin occurs in varying degrees in nearly all from plant life. Plant sources are used commercially where amount of tan present is high and large quantities of the material can be collected economically other consideration are color and particular properties of the tan extracted. The part of plant containing the required tan, whether bark, fruit, wood, leaves or roots, is immersed in water and tan is allowed to "leach" out into water. This occurs quite readily if the material is thin or finely divided, as in case of leaves. The "mashing" of tea leaves with hot water is an everyday example of leaching the tan out of leaves. To hell the water penetrate more quickly, the materials such as barks, woods and fruit are usually chopped up ground into smaller pieces. Hot water will always extract the tan more quickly than cold water. The chemist would analyze this water extract into tans and non tans, tans being those parts which will combine with, of fix on to hide or skin under usual condition and remainder being non-tans (Sharphouse, 1975).

Presently, there is rising demand for the manufacture of chrome-free leathers. An attempt has been made to manufacture chrome-free garment leathers using a combination tannage based on Tara tannin and co-tanning adjuncts viz., aluminum and gluteraldehyde. The shrinkage temperature of leathers using different combinations Tara and aluminum/ gluteraldehyde were found to be around 90°C. Tara-aluminum combination tanning system resulted in leathers with less softness and grain smoothness compared to tara-gluteraldehyde combination tanning system. The order of addition of gluteraldehyde had a significant influence on the organoleptic properties of the leathers. Gluteraldehyde pretreatment of Tara tanned leathers gave better results when compared to post treatment. Tara at the 8% level was found to be optimum for combination tanning using 2% gluteraldehyde pretreatment. The gluteraldehyde-tara tanning system resulted in white leathers compared to the undyed chrome tanned crust leathers. The physical, organoleptic, dyeability and finishing characteristics of the crust leathers from both control and gluteraldehyde-tara tanning were comparable (Madhan, *et al.* 2007).

2-2-2-2 Basic principle of vegetable tanning:

The principle of vegetable tanning is that when tannins come into contact with hide protein, they combine and react together to from leather; and this completely new produced is resistant to putrefaction.

Immersing hides directly into strong solution of vegetable tannins causes the surface tan so hard that tannin cannot penetrate into center. This can be compared to putting bread into a very hot oven, where it rapidly from a crust, while the inside remains uncooked.

To be successful, therefore, vegetable tanning has to start with weak liquor and gradually to progress to stronger liquors. This may be achieve 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 (Mann,1966).

2-2-2-3 Dyeing:

The vegetable tanning process, common to practically all primitive leathers, imparted a natural brown color, the shade of which depended upon the extract and the type of tanning process employed. The quantities of oil were dark brown and saddle leathers containing less oil were a lighter brown. The color of vegetable tanning materials was of great importance, and the lighter – colored tannins were premium. The leather industry still is affected by traditions of the past that natural vegetable tanned colors (the browns and tans) are most popular shades (Thomas, 1969).

Tanned and colored at the same time in single drum operation and thereby produced with a colored and fat liquored base, ready to finish (Fredo, *et al.* 1962).

The color changes of bovine leathers, tanned with commonly used hydrolysable and condensed vegetable tannins, were measured colorimetrically as a function of prolonged irradiation with Xenon test light. The results showed that hydrolysable and condensed tannins exhibited differences in their light fastnesses. The color change of hydrolysable tannins under the effect of light was considerably low when compared to the condensed tannins. Gambier and quebracho tannins, among the condensed tannins, exhibited a rapid color change in the direction of red and yellow, while mimosa showed a slower color shift. Tara, among the hydrolysable tannins, exhibited a slower color shift than the others. At the end of 24 hours, the color changes, observed as darkening in all the tannin groups reached a maximum point after which color lightening was observed with extended time (Ozgunay, 2008).

Polyphenols are the basic building blocks of natural skin and hair pigments: they can be polymerised to create versions of natural black, brown and orange melanins. These reactions can be catalysed by laccase: not only do they create color, but also, if they are conducted in the presence of collagen, the resulting pigment is bound to the leather in a covalent tanning manner. Therefore, the leather becomes colored by a lightfast pigment, which is firmly fixed. It has been not proved possible to create a pure black, but earth shades from green to brown/black are easily produced. It appears to be a feature of this type of stabilising mechanism for collagen, the reaction of a polyphenol matrix around the triple helix, that it has the added benefit of actually strengthening the leather. Since every traditional process step effectively weakens collagen, especially tanning, this is the first chemical reaction that has been shown to reverse that effect (Covington, *et al.* 2005).

2-2-3 Mineral tannages:

Leather processing is one of earliest industrial activities carried out by humans weakens due to protection of their feet from harsh environment. Ancient Egyptians were the first who were applying mineral tanning of leather processing. There are different methods of leather tanning (Josep, *et al*. 2008 and Agrawal, *et al*. 2008).

The basic salts of chromium, zirconium and aluminum behave in a rather different way .Their initial fixation is on the acid groups of the protein where they displace some of the bound water, but they may from cross-links between adjacent acid groups, which will stabilize the wet hydrated skin structure. The dehydration effect of these tannage and the quality fixed is less than with vegetable tannages and therefore the shrinkage and hardening on drying is more pronounced. Invariably some type of oil is applied to wet fibers before drying. Its effect on softening the dried leather should be more pronounced on chrome leather than on vegetable tanned leather. The color of mineral tanned leather is white from aluminum and zirconium but pale greenish-blue from chromium tannage. They are fast in day light chromium tannage does not wash out but aluminum can be washed out. Some typical uses for chrome leather are: shoe upper leather, gloving, clothing leather, some sole and belting Leather .The uses for alum leather are gloves, fur-skins. A review across the Periodic Table of the tanning effects of simple inorganic compounds reveals that many elements are capable of being used to make leather. (Chakravorty, *et al.*1958).

But, if the practical criteria of effectiveness, availability, toxicity and cost are applied, the number of useful options is much reduced. In all cases, the benchmark for comparison is tannage with chromium (III): Ts > 100°C is easily achieved, it is readily available, with large reserves in Southern Africa, it is relatively cheap and has minimum health hazards or environmental impact.From the Periodic Table: Groups 1, 2, 6, 7, 8 do not tan. Groups 3, 4, 5: elements of the first period do not tan. The remainder have weak tanning powers but only elements of the second period are of practical interest; of those, aluminium (III) has the best effect, silicates and polyphosphates have auxiliary functions in tanning. Transition elements: only titanium, zirconium, chromium and iron have practical possibilities. Lanthanides: individual elements or mixtures have moderate tanning properties. The tanning agent must be able of cross-linking the molecules of collagen (should be multifunctional). The degree of cross-linking is careful considered. If is too much crosslink, than the product is harsh and brittle (mobility of fibrils are restricted). Apart from introducing a limited number of cross-links, a tanning agent should not at the same time of lead to undue fibril modification (reduction in fibril length or solution of protein material). In addition to number of cross-links introduced by tanning, their general character is great importance. It could be: H-bonds, ionic bonds or covalent bonds. A high Ts is achieved either by the precise effects of chromium (III) complexes or by controlled multiple interaction between tanning species and collagen. Current tanning technology is dominated by chromium (III); it was introduced about 130 years ago and by the turn of century, it had begun to replace the traditional tannages, which were based on plant polyphenols (so called vegetable tannins).Today, 90% of the world’s leather production is chrome tanned; the remainder is tanned with vegetable tannins, mostly for leather goods or shoe soles. Typically, chrome tanning alone is insufficient to provide the visual requirements for the wide range of leather types produced by industry, so the main or prime tannages is complemented with other tannages, which are applied after chrome. The full range options available to the modern tanner will constitute the body of this review (Covington, 1997).

2-2-3-1 Chromium tannage

There is a fortuitous coincidence of reactivities in chrome tanning. The reaction occurs at ionized carboxys groups; aspartic and glutamic acid side chain carboxys have pKa values 3.8 and 4.2 respectively, providing a reaction range at pH 2-6. Chromium (III) forms basic salts in the range pH 2-5, although in practice the useful range is pH2.7-4.2, where the basicity ranges from 33 to 67%. Note, Schorlemmer basicity is defined by the number of hydroxyl groups associated with the metal ion, relative the maximum number allowed by the valency. In that useful range, the number of chromium atoms in the molecular ion increases from 2-3 to > 3 and the availability of ionized collagen carboxys increases from 6 to 47% of the total number.

Hide is prepared for tanning by pickling with sulfuric acid in a solution of sodium chloride; the neutral electrolyte is necessary to prevent osmotic swelling of the collagen. Chrome tanning is usually initiated at pH 2.5- 3.0, using 33% basic chromium (III) sulfate in the form of spray dried powder, obtained from sulfur dioxide reduced chromic acid. During the course of the tanning process, the pH is raised to 3.5-4.0, causing the number of reaction sites on collagen to increase and the chrome species to increase in size. Starting the process under conditions of low reactivity of both collagen and chrome favours fast penetration of chrome into substrate, bit slow reaction/n; increasing the pH increases the reactivity of both components if the reaction, resulting in reduced penetration rate. To obtain a continuing balance between reaction rate is the part of tanner's art; this is not simple especially if the skin is thick and is not uncommon for heavier hides to more than 1 cm thick in places (Covington, 1997).

Chrome Tanning, being still the most used tanning method, has been challenged more and more in the recent past. The main reasons were questions of sustainability and the fact that chromium VI can be formed in leathers tanned with chromium III compounds. From a technical point of view, many solutions exist for using the chrome tanning agent in a most economic and ecological way. Another way is shown for maximizing the distribution of chromium in the cross section of the hide as well as the exhaustion of chromium from tanning float, thus reducing the total chromium emission into the environment. Also the leaching of chrome from wet blue during retanning operations will be considered. The type of chemicals used and the process conditions play an important role in this regard, as well as the type of chrome tannage used to manufacture the wet blue. Various measures and solutions will be discussed. The role of chromium VI in tanning is looked at with special attention to the real risks associated with it. Finally the formation of chromium VI will be discussed as well as methods to prevent its formation. A new additive (anti oxidant), which is able to eliminate existing chromium VI and reduce the likelihood of reformation, will be introduced (Christner*, et al.* 2012*)*.

Chromium is a common pollutant introduced into natural waters due to the discharge of variety of industrial wastewaters. On the other hand, chromium based catalysts are also usually employed in various chemical processes, including selective oxidation of hydrocarbons. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is 0,05 mg1… (Mojdeh, *et al.* 2009).

Chromium is a chemical element in the periodic table that has the symbol Cr and atomic number 24. It is steel-gray, lustrous, hard metal takes a high polish and has a high melting point. Chromium is present in the environment in several different forms. The most common forms are chromium (0), chromium (III), chromium (VI) (Mojdeh, *et al.* 2009).

The metal chromium, which is the chromium (0) form, is used for making steel. Chromium (VI) and Chromium (III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving (Mojdeh, *et al.* 2009).

Cr (VI) is mobile in the environment and highly toxic. Cr (VI) can easily penetrate the cell wall and exert its noxious influence in the cell itself, being also a source of various cancer diseases (Barnowski, *et al.*1997 and Gil, *et al.* 2006). At short-term exposure levels above the maximum contaminant level, Cr (VI) causes skin and stomach irritation or ulceration. Long-term exposure at levels above maximum contaminant can cause dermatitis, damage to liver, kidney circulation, nerve tissue damage, and death in large doses (Katz, *et al.* 1994 and Kotas, *et al.* 2000).

Cr (III), on the other hand, is less toxic than Cr (VI) and is nearly insoluble at neutral Ph (Venitt and Levy 1974). Cr (III) is listed as an essential element, as micronutrient, to maintain good health and helps in maintaining to normal metabolism of glucose, cholesterol, and fat in human bodies (Kimbrough, *et al.* 1999). It is poisonous only at high concentration.

Chrome tanning is the most common type of tanning in the world. Chrome tanned leather are characterized by top handling quality, high hydro-thermal stability, user-specific properties and versatile applicability. Waste chrome form leather manufacturing, however, poses a significant disposal problem.

Waste chrome is contained in:

Liquid waste: Spent floats from tanning and re-tanning, as well as waste from sammying and draining.

Sludge: Dewatered slurry resulting from sedimentation of suspended solids during

Tanned (solid) Shaving: buffing dust and unusable (mostly wet blue).

Waste: spilt, as well as crust and finished leather trimmings.

Throughout the world, chrome discharge from tanneries is subject to strict regulations. That not withstanding, chrome is a component that has to be strictly monitored.

The environmental impact of chrome discharged from tanneries has been a subject of extensive scientific and technical dispute. Although the legislative limits on the disposal of solid chrome-containing waste have been relaxed in some countries, liquid emissions remain strictly regulated throughout the world.

Limits on total chrome discharge in effluent vary widely between 0,05 and 10mg/1 for discharges into water bodies (direct discharge) and 1-50 mg/1 on discharge into sewage systems (indirect discharge). (Bosnic, *et al.* 1998).

Chrome- containing sludge is mostly disposed of in landfill which has to be provided with a leachate collection and treatment system. The use of sludge in land applications is governed by very strict regulation in most European countries (Poncet, 1998).

Some tanned wastes are partly used in by- products, but most are deposited in landfill. Blue shaving and trimmings are used in manufacture of leather board; they also undergo chemical and/or hydrolysis, pyrolysis, and incineration (Environment commission of I.U.L.T.C.S. 1997).

The main findings of the investigations carried out at LGR, Germany (Hauber, and Germanx.2000) on a possible formation and avoidance of chromate in leather were as follows:

1. /a close connection between the pH-values of the neutralization float and the Cr (VI) content of the leather could not be established.
2. The use of a wetting auxiliary with reducing abilities prior to the dyeing could not avoid in some the Cr (VI) formation under drastic conditions like heating at 80°C.
3. Vegetable tanning agents like wattle, quebracho, chestnut and tara play a very important role in avoiding chromate in leather. Especially tara was very effective even using very low offer.
4. Polymers or synthetic retanning agents had neither a negative nor or a positive effect.
5. Cr (VI) formation in leather is heavily influenced by fat liquors, especially natural products such as fish oils.
6. Mechanical processes like vacuum drying or buffing of the leather seem not to contribute to the formation of Cr (VI) in leather.

The result of some investigations in Italy (Sammarco, 1998) was that no Cr (VI) could be detected after correctly performing the conventional chrome tanning processes, analysed after each processing stage. After thermal treatment and UV radiations high amounts of Cr (VI) were found in the sane crust leathers. Experiments using single chemical substances showed that fat liquoring with sulphited fish oils resulted in high Cr (VI) values. Retannage with natural tannins did not support Cr (VI) formation.

An interesting factor, also observed at LGR, was raised by D. Graf in his article dealing with the influence of the relative humidity of air during storage on Cr(VI) can be formed only if the leather is in contact with atmospheric oxygen, if it is fat liquored with fat liquors containing unsaturated fatty acids and / or natural fat, if these fat liquors are free from anti oxidants, if less than 4% vegetable retanning agent is used and if the relative humidity of air is under 35%. People often say that Cr (VI) is developing under storage conditions(Graf, 2000).

Heavy metals in waste waters and sludge may cause significant environmental problems, and it is known that conventional recovery technologies cannot always achieve satusfactort treatment. For example, they are inappropriate to completely recover the chromium in the case of waste waters from the tanning process. Chromium can be recovered (by precipitation) from effluents that contain high concentrations of this metal. However, effluents from the later stages in present day tanning process often have a low concentration of chromium that cannot be recovered and is found in the sludge of the waste water treatment plant (WWTP).Is to recover and reuse the chromium (III) from post-tanning effluents by means of a biotechnological sequestering method using acidophilic fungi. When the post-tanning process was carried out on a pilot plant scale in which conventional rechroming and neutralization stages were undertaken and the use of additional chemicals was avoided, chromium (III) sequestration values of above 95% were obtained. As these results are so promising, further studies will focus on searching for more resistant fungal strains and determining which of the chemicals used in the post-tanning process can be avoided or replaced by alternatives (Lalueza, *et al.* 2010).

An established body of evidence has associated the chromium –based leather tanning industry with environmental and occupational health concerns, which has been reviewed by several investigators (Losi, *et al.* 1994; Battista, *et al.* 1995; Chattopadhyay, *et al.* 1999; Chandra, *et al.* 2004; Meric, *et al.* 2005; Mwinyhija, *et al.* 2006; Taghiari, *et al.* 2004 and Zhou, *et al* 2005).

Leather making is a very long process and consists many different chemical and mechanical process steps. The most important tanning method is chrome tanning (Approximately 85% of world heavy leather making). There are many factors governing the tanning effect: the type of the compound; its basicity, concentration, pH value and neutral salt content; the temperature of tanning bath; and the time of interaction, which is long. The previous history of the skin material is also important. Many of these factors are intedependent and difficult to consider separately. The basic chrome tanning chemistry is well explained by (Gustavson, 1956. and Mintysalo, et *al.* 1997.)

Most attempts to find suitable alternative for chrome tanning have been undertaken primarily in order to reduce the pollution due to tannery effluents. In certain cases, such efforts were aimed at cost-reduction (Adewoye, *et al.* 2000).

Large quantities of solid waste containing chromium are generated by the leather industry. In recent years the specialized literature has described protein and chromium recovery processes. The molecular weight spectrum of the recovered protein shows that for retanning purposes the average molecular weight is too low. Obtain an environmentally friendly protein modification process to generate high molecular weight protein to be used in the retanning step of leather wet processing. The aim was to test potential modifications to hydrolyzed protein using different tanning agents to generate retanning products. The retanning agents developed were applied in experiments on leather wet processing, where the influence of the addition of vegetable tannin was also evaluated. The controlled variables were molecular weight of the tanning preparations, leather characteristics (compressibility, density, physical-mechanical resistance, grain firmness, and color) and the COD of the wastewater. The results obtained indicated the possibility to use hydrolyzed protein combined with glutaraldehyde as a retanning agent to obtain good quality leather (Mariliz, *et al*. 2010).

In recent years, considerable research has been done to replace chrome tanning with alternative tanning systems. But there are very few methods that are environmentally friendly and cost effective that give leather with performance as good as chrome tanned leather. A novel eco-friendly approach for the production of upholstery leather is given that avoids pickling. The leather is pretanned after Bating at pH 7.5-8.5 with 2% oxazolidine E (1-aza-3,7-dioxabicyclo-5-ethyl (3,3,0) octane) to obtain shrinkage temperature around 75-80°C for hides and 80-85°C for skins. These pelts are simultaneously or after treated with 2-3% replacement syntan. These pretanned hides and skins may be split and/or shaved at this stage, without any difficulty, to the required thickness. This provides opportunities for a tanner to either chrome tan with 4-5% chrome powder 25/33 (25% Cr_2O_3 content / 33% basicity). The splitting and shaving at this stage has the added advantage of lowering the amount of chrome use, very low chrome in effluent, flatter grain, higher area yield of the final leather, and biodegradable chrome-free shavings. This would considerably minimize the disposal problem for a tannery. *(DasGupta, 2009)*.

The retanning process is a very important step in the leather manufacturing wet processing operations because it can overcome some of the disadvantages of chrome tannage. For this purpose, two different nano-emulsions of styrene/acrylate copolymers were prepared, using seed emulsion polymerization technique, for use as retanning agents. The main difference in characteristics of the two nano - copolymers was studied. The nano-particle size of the two prepared co-polymers was determined by transmission electron microscope (TEM) and the influence of the two prepared copolymers on chrome tanned leather as retanning agents was studied. The properties of the retanned leather, namely, tensile strength, elongation at break and tear strength, were measured. Thermal stability and texture of grain surface and fibers were examined using thermal gravimetric analysis (TGA) and scanning electron microscope (SEM), respectively. Evaluate the applicability of the copolymers as efficient retanning agents. The retannage leather showed an improvement of mechanical properties, levelness of dying, softness, and firmness of grain as well as enhancement of thermal stability (Nashy, *et al.* 2011).

2-2-3-2 Aluminium tannage:

The use of potash alum in leather making is almost as old as leather making itself; it is known that the Egyptians used it 4000 years ago, because written recipes survive. Throughout tanning history, alum was often used in conjunction with vegetable tannins (see below); for example, in medieval times, Cordovan leather (from Cordoba in Spain, hence the name cordwainer, (meaning shoemaker) was in widespread use in Europe, made by vegetable tanning then dyeing with cochineal

Used by itself, alum (solution pH 2) interacts weakly with collagen, scarcely raising the shrinkage temperature and having little leathering effect. However, in a mixture of water, salt, flour (to mask the aluminum ion and fill the fibre structure) and egg yolk (the lecithin content is an effective lubricant), skin can be turned into soft, white, leathery product, traditionally used in past for gloving. But even in this case, the shrinkage temperature is not raised (hence, it possible to discriminate between leathering and tanning) and the aluminum salt can be washed out of the leather if it gets wet; for these reasons, this process is called 'tawing' to distinguish it from tanning (Covington, 1997).

The reaction site for aluminum (III) are the collagen carboxys, but unlike chromium (III) to which it bears superficial resemblance in a tanning context, aluminum (III) does not form defined basic species nor does it form stable covalent complexes with carboxyl groups; that interaction is predominantly electrovalent, accounting for the ease of hydrolysis. The reaction can be optimised for tanning by modifying aluminum sulfate with masking salts, such as formate or citrate, and basifying the tannage to pH 4, close to the precipitation point. (There is a rule of thumb in tanning technology, that any metal salt has its greatest tanning effect just before it precipitates). In this way, reversibility of tannage is minimised and shrinkage temperature as high as 90°C can be achieved. Basic ALiii chlorides are also known in leather making and several commercial tanning formulations are available as solo tanning agents. They are slightly superior to salt based on the sulfate. However, the leathering effect of aluminum (III) is inadequate, producing firm leather, which may dry translucent due to the fibre structure resticking. Therefore, as tanning agents, aluminum (III) salts have limited value (Covington, 1997).

Aluminum salts are not much used in the tanning industry because of regulatory pressure and the perception of toxicity; the leather influence is fuelled by the (continuing but misinformed) association with Alzheimer's disease and accidental poisoning, such as the recent experience at Camelford, UK. (Covington,1997).

Alum- derived water treatment sludge is a material deposited in large quantities in waste disposal areas in many parts of the world (Babatunde, *et al.* 2007). Indeed, alum (Al2 (SO4)3) is the most widely used coagulant in drinking water treatment (Faust, *et al.* 1998). When added to water it flocculates as hydroxyl-Al species and results in coagulation of colloidal materials such as soluble organic matter and fine soil particles. During flocculation, sedimentation and filtration, colloids in the raw water remain entrapped in, or adsorbed to, the Al gel and after dewatering the water treatment sludge is transferred to disposal sites. Beneficial reuse of the material would reduce both the cost and need for disposal. Water treatment sludge has recently been used as an effective adsorbent for anions such as phosphate (Zhao, *et al.* 2009 and Babatunde, *et al.* 2009).

Current studies on the use of aluminum in the leather industry were motivated by demands for a white leather as substrate for dyeing, to reduce environmental impact by replacing chrome and also strategic concern over chrome supplies (Covington, *et al*. 1984).

The research and development work since the latter half of his century was oriented towards developing a tanning agent based on aluminum that stable in solution and will form cross-link with collagen in such a way that real leather, resistant to water and adequate hydrothermal stability is produced. Once such stable aluminum tanning agent is the basic aluminum sulphate wherein the aluminum is complexes with citrate anions (Adewoye, *et al*. 2000).

Development of cleaner technologies for leather manufacture is imperative for the sustenance of the tanning industry. A combination tanning system based on a henna-aluminum tannage for the production of upper leathers as a cleaner alternative is presented. Extract from the leaves of widely distributed Lawsonia inerims (Henna) from Sudan has been evaluated for its tanning characteristics in a combination tanning system based on henna and aluminum sulfate. Aluminum-henna (Al-henna) leathers tanned using 2% Al2O3; followed by 20% henna resulted in shrinkage temperature above 95°C. The uptake of henna in henna-Al tanning system with henna (20%) followed by aluminum (2% Al2O3) has been found to be better than the tanning system of Al-henna. These leathers showed compact fiber structure, indicating that the tanning process did not bring about any major change or destruction on the fiber structure of the leathers. Surface color values of henna-Al leathers resulted in darker shades with less red and more yellow components in the crust leathers. The combination tanning system provides significant reduction in the discharge of total dissolved solids in the wastewater. Henna-Al combination tanning system resulted in leathers with good organoleptic and strength properties. Established the use of henna and aluminum combination tanning system as an effective alternative cleaner tanning methodology (Musa*, et al.* 2011).

Using the basic aluminum sulphate, in combination with vegetable tannins, other mineral tanning agents, and syntans, almost all types of leathers, which were previously tanned with chrome combination systems, could be produced (Adewoye, *et al.* 2000).

A new Tetrakis hydroxymethyl phosphonium sulphate (THPS)-aluminum combination tanning system has been developed. The optimum dosage of THPS was 2.0%. The amount of THPS and basic aluminum chloride was optimized at 2.0% and 3.0% (basing on the weight of pelt). The influence of ligands on the shrinkage temperature (Ts) of leathers was also studied and the Ts of THPS-aluminum combination tanned leathers were above 88°C. Color fastness to dry/wet rub of THPS-aluminum combination tanned leathers was much better than the relevant color fastness to dry/wet rub of leathers tanned with THPS alone. Scanning electron microscopic studies showed that the fiber weave of THPS-aluminum combination tanned leather was much closer than leathers tanned with THPS alone and the fiber weave of THPS-aluminum combination tanned leather was closer (tighter) with an increase of amount of basic aluminum chloride. Hence, with the increase of the amount of basic aluminum chloride, the reactive ability of basic aluminum chloride with collagen fiber was stronger and the softness became worse. Degradation rate of soiling for the THPS-aluminum combination tanning leather was much quicker than that of chrome tanning leather.

Through SEM analysis, the surface structure of leather which was not degraded was more regular than the leather degraded for 30 days. Meantime, the of THPS-aluminum combination tanning leather degradated much more easily than the chrome leather, which suggested a benefit for the sustainable development of the leather industry in future (Ren, *et al.* 2009).

Earlier theoretical assumptions were that, in tanning solutions, aluminum formed linear polymeric complexes similar to chromium with a maximum of four Al3+ nuclei in a complex. The sizes of aluminum complexes, composition distribution and coordination of organic acid anions with Al3+ nuclei were determined by ferron assay, gel filtration chromatography (GFC) and low-pressure ion chromatography (LPIC). The results were as follows: (1) In the pH range of aluminum tanning process (pH=2.5-5.0), two types of organic acid masked aluminum complexes were found: Ala, mononuclear complexes, and Alb, polymeric complexes (small polymeric complexes containing 2~4 Al3+ nuclei, as well as larger "Al13 like" complexes). The percentage of Alb increased dramatically when pH was increased from 3.0 to 4.0, with more than 80% of the total Al3+ in this state at pH ≥3.5. (2) In organic acid masked aluminum salt solutions, most of the added organic acid anions were in "free" state, i.e., they were not coordinated with Al3+ nuclei. (3) In solutions of citrate masked aluminum sulfate, whatever the dose of citrate, the first elution fractions had unusually large values of [Al3+]/[Cit], some greater than 30. These results suggest that there might be something about the structure of aluminum complexes in tanning solutions that earlier theoretical assumptions did not consider. May provide some theoretical and practical guidance for a better understanding of the mechanism of aluminum tanning or aluminum combination tanning with other tannins (Keyi, *et al,* 2006).

27Al NMR was applied to gain the information about the composition distributions and the structures of organic acid masked aluminum complexes in tanning solutions. The result indicated that in the pH range of aluminum tanning condition, three classes of organic acid masked aluminum complexes were found, i.e.: mononuclear complexes, linear polymeric complexes containing 2 - 4 Al3+ and “Al13 like” complexes. The predominated species was the “Al13 like” complexes, with more than 70% of the Al3+ when the solution pH was ≥3.5. “Al13 like” complexes have a stiff spherically symmetrical structure (ε-Keggin structure), consisting of one central [AlO4]5- tetrahedron, and surrounded with 9 - 30 octahedral aluminum complexes sharing edges. The diameter of a “Al13 like” complex is about 8 - 16 Å. The understanding about the special structure of “Al13 like” complexes give a rational explanation as to why in organic acid masked aluminum complex solutions, most of the added organic acid anions were in “free” state. Provide a basis for better understanding of the mechanism of aluminum tannage or aluminum combination tannage with other tanning agents (Keyi, *et al.* 2006).

2-2-3-3 Titanium (IV) salts:

In the tanning terms, the chemistry of titanium (IV) salts lies somewhere between AL111 andCr111. Empirically, the chemistry is dominated by the titanyl ion $TiO+_2$ but the species are chains of titanium ions bridged by hydroxyl and sulfato ligands, like Cr111. However, the coordinating power is weak with respect to carboxyl complexation, so the interaction is more electrostatic than covalent.

The traditional use for titanium (IV) in tanning was in the form of potassium titanyl oxalate, to retan vegetable tanned leather for hatbanding, a product for which demand has reduced in the latter half of the 20th century. Titanium solo tanning is only moderately effective, because large quantities are required to achieve the highest shrinkage temperature, > 95°C, but this causes the leather to be overfilled, although remaining soft. In addition, high hydrothermal stability is only achieved when the collagen is pretreated with phthalate, possibly resulting in interaction of the following type:

$\text{Collagen-NH}_3\text{+}\ldots\text{-O}_2\text{C.C}_6\text{H}_5\text{.CO}_2\text{H}\ldots\text{-SO}_4\ (\text{Ti}\ (\text{OH}_2 2)\ n\ \text{SO}_4\text{-}$

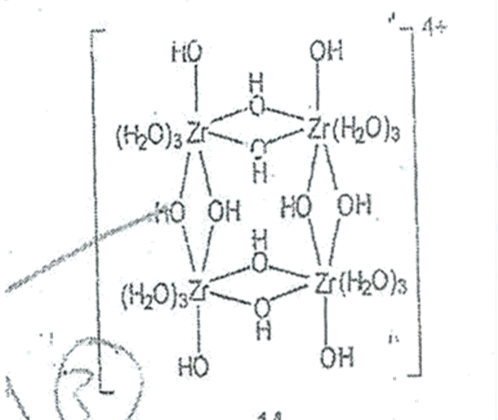
Also, Russian work has shown that the tannage is best basified with a mixture of hexamethylenetetramine and sodium sulfate; the mechanism is not understood. An advantage of tanning with titanium (IV) is that it is a colorless tannage and therefore makes white leather. Hence, it has found application in tanning sheepskins with the wool on; this is a problem area, firstly because the use of chromium (III) produces a discoloration by reaction with the partially degraded keratin at the weathered wool trips and secondly because the reaction must be conducted using high solution to skin ratios, to avoid tangling (felting) the wool (Covington, 1997).

A key objective for improving titanium tanning power is increasing titanium solution stability and adjusting both the states and behaviors of the Ti(IV) species in aqueous solution so that titanium tanning can be carried out at a suitable (high) pH. The influence of 35 organic ligands, including mono and multiple carboxylates, amino-ligands and hydroxyl-carboxylates, on the stability and tanning power of titanium sulfate liquors were investigated. Results show that only some hydroxylcarboxylates, such as lactate, tartrate, citrate, sulfosalicylate etc., can effectively improve titanium sulfate solution stability. Only these ligands form stable chelate-type coordination compounds with Ti4+, as shown by potentiometic titration, FTIR spectroscopy and elemental analysis of the coordination complexes. Among these hydroxylcarboxylates, the lactate-masked titanium sulfate system at 0.40-0.5:1 mole ratio of lactate to Ti4+ has the best tanning power. Lactate has a relatively small molecular volume as well as a moderately high formation constant with Ti4+. Leather tanned by lactate-masked titanium sulfate liquor had the highest titanium content, the best titanium distribution uniformity, a shrinkage temperature, Ts, of 97°C with pleasing softness (Peng, *et al.*2007).

2-2-3-4 Zirconium (IV) salts:

The development of zirconium tannage is relatively recent but it soon gained industrial acceptance. Form its position in the Periodic Table, Zr (IV) Might be expected to display similar tanning properties to Ti (IV). A comparison of those properties is set out in Table 2. It can be seen that the tanning power exceeds that of Al (III), but in a way matches Cr (III). Whilst the tanning effects of Zr (IV) and Ti (IV) are similar, the chemistries of their salts are different. Zirconium (IV) salts are characterised by eight coordination and high affinity for oxygen, resulting in a tetrameric core structure; the basic unit structure is four Zr ions at the corners of square, linked by diol bridges, above and below the plane of square (Irving, 1974).

By hydrolysis or basification, the tetrameric units can polymerise, by forming more diol or sulfate bridges. In this fig (1.3) Way, Zirconium species may be cationic, neutral or anionic and large ions can form. So, tanning may involve all the polar sidechains of collagen, those bearing carboxyl, amino or hydroxyl groups. Hydrogen bonding via the hydroxyl groups in the Zr (IV). Species is an important feature of the tanning reaction; together with filling effect by the big molecules, the overall tanning effect is somewhat similar to tanning with plant polyphenols hence zirconium tanning has been referred to as the inorganic equivalent of vegetable tanning.



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Zirconium (IV) is not often used as a solo tannage, partly because of its indifferent effectiveness at raising the shrinkage temperature and partly because the acidity of the salt and the vulnerability to hydrolysis mean they must be applied at high concentration and at pH < 1, therefore running the risk of osmotic swelling in the hide; its main use is for retanning, to fill and firm (tighten) the grain or to make better suede (Covington, 1997).

2-2-4 Oil tanning:

The familiar wash leather (chamois or chammy') is tanned with unsaturated oil, the preferred agent is cod liver oil. Useful oils contain fatty acids, either free or as glycerides, which are polyunsaturated; the degree of unsaturation is critical, because if there is too little unsaturation the oil will not oxidise readily and therefore function only as a lubricant, if there is too much unsaturation, like linseed oil (Sharphouse 1985).

In this tannage, sheepskins are processed in the normal way to the pickled state, when they are then swollen by osmotic effect in water, so they can be spilt more easily. Usually the skins used for chamois have inferior or damaged grain surfaces and this portion of the skin is discarded. The flesh splits are then treated with the cod oil; a traditional method of forcing the oil into the wet pelt was to use 'fulling stocks' or 'kickers', in which the oil was literally hammered into skin by wooden mallets, nowadays rotating drums are sufficient. Blowing warm air into the vessel serves two functions: the skins are dried a little, to aid oil penetration and autoxidation of the oil is initiated, which is the basis of the process.

The actual nature of the tannage is not known, except for the following observations:

The unsaturation decreases.

(i) Peroxy derivatives are formed.

(ii) Hydroxyl function appears.

(iii) Acrolein, $CH_2=CH.CHO$, is produced.

It is thought that the tannage may be due in part to an aldehyde reaction and to polymerisation of the oil; the presence of the latter effect could account for the differences between the characteristics of oil and aldehyde tanned leathers. The situation is further complicated by the observation that oil tanning hardly raises the shrinkage temperature of collagen; so this is a leathering process rather than a tanning process, based on the accepted criteria of tanning.

Oil tanned leather exhibits the interesting Ewald effect: if the leather is heat shrunk in water at 70°C, but immediately placed in cold water, it rapidly relaxes to regain ca.90% of its original area and this is replace. (Normally, heat shrinking is an irreversible phenomenon). Furthermore, if the wet leather is held under tension whilst it is being heat shrunk, the dried leather remains soft and flexible, unlike other leathers which may come hard and brittle. This process, known as ‘tucking’, is used to mould leather to a desired shape, but keeping its feel.

The most remarkable feature of oil tanned leather is its hydrophilicity, surprising considering its tanning process. Well tanned chamois leather is expected to take up at least 600% water on its dry mass and to be hand wrung to 180%. Also, this must be repeatable after drying. In use, no grease must be exuded to cause smearing.

2-2-5 Aldehyde tanning:

2-2-5-1 Formaldehyde tanning:

The archetypal aldehyde tannage is with formaldehyde, probably most familiar in preserving biological specimens or in embalming. Reaction occurs primarily at a amino groups: Collagen- NH_2+ HCHO----- Collagen-NH-CH_2OH

The N-hydr0xymethyI group is highly reactive and cross linking can occur at a second amino group:

Collagen-NH-CH_2OH+H_2N-Collagen-----

Collagen-NH-CH_2-NH-Collagen

In this way, the shrinkage temperature can typically be raised to 80-85°C. However, the crosslinking is relatively inefficient probably because the formaldehyde species are not monomeric.

Amongst the species formed in solution is par formaldehyde, $HOCH_2$ (CHOH) n CHO. The presence of polyhyroxy species and their reaction with skin produces a white, spongy, hydrophilic leather, although the absorptive property of oil tanned leather is not matched.

The health and safety implications associated with formaldehyde mean that its use as a tanning agent is effectively banned. The only remaining common functions are for fixing casein, which is fused to the grain surface in glazing operations, or to impose permanent straightening to the wool of rug skins or sheepskin clothing leathers, by reacting with the keratin under conditions of wet heat tension (Covington, 1997).

2-2-5-2 Glutaraldehyde tanning:

Of the many mono-and multi-functional aldehydes which might be used for tanning (and all can be made to work), only glutaraldehyde and its derivatives have found commercial acceptance, with the possible exception of the more expensive starch dialdehyde. The crosslinking options are wider than for simple aldehydes, but the result is the same, a shrinkage temperature of 85°C maximum. In the same way that formaldehyde is not a simple species in solution. The terminal hydroxyl groups of the polymer are active and capable of reacting with amino groups. The polymer itself can interact with the collagen peptide links by hydrogen bonding via the alicyclic oxygen's and so the leather is given its spongy, hydrophilic character. Tanning with glutaraldehyde itself confers a yellow- orange colour to the leather, which is undesirable. Several attempts have been made to modify the chemistry, to prevent colour development, including making the monobisulfite addition compound or hemiacetals, but none has been totally successful. Glutaraldehyde is coming under scrutiny with regard to health and safety implications, so it too may have to be phased out of the tanner's options (Covington, 1997).

2-2-5-3 Oxazolidine tanning:

An alternative to aldehyde tanning, but which retains the essential reactions, is to use oxazolidine, developed less than 20 years ago (Dasgupta, 1977). These compounds are alicyclic derivatives of an amino alcohol and formaldehyde (Gotsis, *et al.* 1992; Russell, and Shuttleworth, 1965); under hydrolytic conditions, the rings can open, to form an N-hydroxymethyI compound (Sykes, 1956), which can react with one or more amino sites, in an effectives though aridly odiferous tannage.

2-2-5-4 Active hydroxyl compounds:

The reactivity of the carbon in N-hydroxymethyl compounds is not the only example of an active hydroxyl. Similar reactivity has been observed in the following compounds:

$(P\ (CH2OH)_4)+ (SO_4$—or CL-)	$(HOCH_2)_3CNO_2$
Tetrakis-hydroxymethyl	tris- hydroxymethyl
Phosphonium sulfate or chloride	nitrmethane

The phosphonium salts are available as bactericides (because they tan the bacteria), but they are not available in sufficient quantities to be industrial tanning agent. So far, the nitro methane derivative is only a chemical curiosity (Covington, 1997).

2-2-6 Syntans:

The term syntan means synthetic tanning agent. This class of tanning agents was introduced early this century, with the purpose of aiding vegetable tanning, although the range of reactivities currently available means that they may serve several different functions. They are classified into three types, according to their primary properties (Covington, 1997).

(1) Auxiliary syntans

(2) Retanning syntan

(3) Replacement syntans.

(4)

2-2-7 Organic tanning:

In the modern leather industry, the preferred method of tanning is to use chromium (III) salts, because they are versatile, effective and easy to apply and have low environmental impact. Despite the evidence to the contrary, the latter aspect of chromium (III) is not wholly accepted by regulatory authorities (with the exception of the USA) and consent limits for discharge of chromium are increasingly stringent limits of <5ppm Cr (< 10-4 m) are typical. Consequently, although there is a commitment to continuing to use chrome, the industry is constantly searching for a viable alternative.

The ideal tannage to rival chrome tanning should importance the following features:

(i) High hydrothermal stability, Ts > 105 °C.

(ii) No metal salts.

(iii) White or pale coloured leather.

(iv) Lightfast.

(v) Low environmental impact.

(vi) Comparable cost.

The most difficult criterion to achieve is that specifying shrinkage temperature, which has hitherto been impossible to achieve with organic compounds alone. However, recent developments have indicated that the target is achievable (Covington, 1997).

2-2-8 Semi metal tanning:

The only established organic tannage capable of producing leather with high hydrothermal stability is that in which the collagen is the first stand with vegetable tannin, then retanned with a metal salt, preferably aluminium (III); semi alum leathers made with condensed tannins typically have shrinkage temperatures ca. 90°C (mimosa is exceptionally higher, possessing pyrogallol groups), whilst semsi alum leathers made with hydrolysable tannins have shrinkage temperature of 115-120°C.

There is a correlation between shrinkage temperature and the presence of the pyrogallol group. This effect can be seen even by treating collagen with catechol or pyrogallol themselves, then retanning with aluminum (III); resulting shrinkage temperature are 71 and 98°C respectively and the same pattern is obtained for more complex polyphenols.

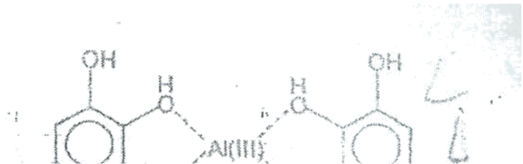
The synergistic interaction between the polyphenol and the aluminium (III) may arise from one of the following options:

Collagen-Al-veg- Al- Collagen

Collagen- veg- AL- veg Collagen

Collagen-veg- Al-Collagen

It is known that applying the aluminum salt before the vegetable tannin produce only moderate shrinkage temperature, characteristic of aluminum alone. Therefore, the first and third options are unlikely. The most probable mechanism is for the aluminum (III) to crosslink the vegetable tannin (Hemandez and Kallenberger, 1984). In effect, the crosslinking polyphenol on collagen is itself crosslinked, to form a matrix within the collagen matrix,



to stabilise the collagen by a multiplicity of connected hydrogen bonds in the new macromolecule (Covington, 1991).fig (1-4)

Because of the importance of the presence of pyrogallol groups, semi metal tannages are confined to the hydrolysable tannins and the condensed tannin mimosa many metal can perform this function, depending on the affinity for phenolic hydroxyl, but aluminium (III) is the best. It is probable that this tannage is thousands of years old, because of the availability of native potash alum, which must have been used together with vegetable tannins, if only for the purposes of mordanting for dyeing.

Growing concerns over the toxicity of chromium and its influence on the health of customers using chromium tanned garment leathers has forced the leather industry to search for alternative tanning agents. Semi-metal tanning agents, aldehyde based systems, etc. Have been considered but the toxicity issues are lingering. Hence, attempt has been made to develop vegetable tanned garment leathers. The indiscriminate use of vegetable tannins and subsequent stripping prior to retanning and fatliquoring has been evaluated. It has been found that an 8% offer of wattle for tanning provides better physical and organoleptic properties. A polyamide based retanning system was found to offer better perspiration and organoleptic properties. Amongst the various fatliquoring compositions, a 50:50 combination of synthetic and natural fatliquors was found to offer higher softness. The optimized tanning – retanning – fatliquoring combination was found to be comparable to chrome tanned garment leathers and superior to semi-chrome garment leathers (*Sreeram*, *et al* 2010).

Genipin, a naturally occurring protein crosslinking agent, isolated from the fruit of Gardenia jasminoides Ellis, is beginning to replace glutaraldehyde as a fixative for biological tissues. Earlier research in this laboratory demonstrated that when hide powder was first tanned with 8% aluminum and retanned with (2% to 10%) genipin the thermal stability increased linearly with increasing concentrations of genipin, suggesting the possibility that a practical combination tannage based on genipin could be designed. When pieces of bated hide were pretanned with 6% aluminum, then split and tanned with 6% genipin based on the weight of the split wet-white pelt, the hydrothermal stability was about 89°C as determined from the onset of the melting curve in a differential scanning calorimetry (DSC) experiment, or Ts = 92°C by a traditional shrinkage temperature measurement. Values for the physical-mechanical properties were similar to those measured for aluminum-glutaraldehyde and mimosa-aluminum leathers prepared, as controls, under equivalent conditions. By subjective evaluation, the appearance of aluminum-genipin tanned leather was rated 4 on a scale of 1 (poor) to 5 (very good), and the leather was more stable to washing than were control leathers. These results suggest the potential for development of practical genipin-based tannages (Ding, *et al* 2008).

Conventionally, leather manufacture involves mutli-step processing viz., beam house operations, tanning, post tanning and finishing. Even though this multi-step processing followed for centuries is logical, it will be highly beneficial if there is a possibility of integrating any of these steps. Hence in the current work, integration of tanning and post tanning operations in processing of upper leathers from pickled goatskins has been tried. For this integrated process, vegetable based tanning system in combination with aluminum, zinc, acrylics and oxozolidine has been assessed. Vegetable - aluminum based tanning system has been found to be more suitable for the integrated one step upper leather processing as it has resulted in leathers with shrinkage temperature of 94°C, good physical strength and organoleptic properties (Madhan *et al.,* 2005).

Semi metal tanning system is gaining importance in recent times as an alternative for chrome tanning. Many reports are available regarding vegetable-aluminum combination tanning systems, but the mechanism of interaction between the aluminum and the vegetable tanning molecules has not been elucidated in detail. Involves the determination of the complexation behavior of aluminum with the hydrolysable tannin, myrobalan and with the molecular species viz., gallic and tannic acid of hydrolysable tannin. Stoichiometry and binding constant of the polyphenolics-aluminum complex have been studied. It is observed that aluminum exhibits strong binding with hydrolysable tannin polyphenols. Externally prepared myrobalan-aluminum complex has been employed for the tanning studies, which showed a 10°C increase in shrinkage temperature compared to the self-tanning of the combination system (Madhan *et al.,* 2006).

In our earlier work Vegetable-Aluminum (Veg-Al) combination tanning system was found to be suitable for the manufacture of integrated chrome free upper leather processing. The physical strength properties, techno economic feasibility and environment impact assessment studies of integrated process in comparison with conventional upper leather processing from chrome tanning have also been carried out. The offer of post tanning auxiliaries viz., syntans and fatliquors is optimized based on the organoleptic properties of the leathers obtained. The integrated process and the leathers thereof were compared with upper leather processing and leathers from conventional chrome tanning respectively. The integrated process resulted in more than 60% saving of water compared to the conventional upper leather processing from chrome tanning. The experimental process has benefits in terms of improved productivity and decrease in production cost due reduced water, time, power and labor utilization resulting from the integration of process (Madhan *et al.,* 2005).

2. Chapter three

3. Material and methods

3-1 Method:

The tannage and retannage were carried out during the period March 2010 – January 2011 at Sudan University of Science and Technology (Leather Industrial Incubator). The physical testing and chemical analysis of leathers were carried out at the National Center of Leather Technology Khartoum-Sudan.

3-2 Raw materials:

Dry salted cattle hides, 24 pieces average weight 7Kg a hide from local market used in all experiments. The raw hides were subjected to a series of processes such as: soaking, liming, deliming, bating, pickling, degreasing, depickling, tannage, retannage and fatliquoring. All percentages were based on the initial dry salted hide weight.

3-2-1 Soaking:

This was carried out in a pit, 12 cattle hide dry salted average weight 84Kg soaked in 700% water, temperature 25- 30°C, addition 0.1-0.5% sodium sulphide, wetting agent 1- 2 parts per 1000 parts water on the weight of dry salted, left in a pit over night.

3-2-2 Unhairing and liming:

After soaking hides put in a paddle, 300% water on hide weight, temperature 25- 30°C, added 4% sodium sulphide run for 3 hours, added 4% lime run over night. In second day added 1% lime, leave hides in paddle over night, pH in this stage 12-13. After unhairing and liming process, mechanical operations fleshing which is removal of the hypodermis by fleshing machine, in this stage hides were cut in half pieces.

3-2-3 Deliming and bating:

They are done in one bath, put the hides in a drum and washed with continuous flow of cold clean water is fed in. After that drained water, then added clean water 100%, of hide weight in temperature 25-35°C, added 2% ammonium sulphite run for 45 minutes. Added 0.5% bating agent run for 1 hour. Take small piece from hides, to check complete of deliming by using phenolphthalein, a piece colourless that mean complete deliming, also adjust pH by using pH paper, pH 8.5.

3-2-4 Pickling:

Put the hides in a drum and washed them with continuous flow of cold clean water is fed in. after that drained water, then added clean water 70%, of hide weight in temperature 25-35°C, hides are drummed in the 10% salt (sodium chloride) for 15 minutes. Added 1.5% sulphuric acid drummed for 15 minutes. Then added 0.5% formic acid drummed for 2 hours, leave hides in the solution over night, after that adjust pH 1-2.

3-2-5 Process:

Processes:

The following processes were carried out in this research for leather manufacturing. All percentages were based on the initial pickled weight.

3-2-5 -1 Degreasing:

This was carried out in a drum after pickling to remove the natural fat in pelts. In the first day, the pelts were put in drum contain 5% of common salt (sodium chloride) and 3% degreasing agents (SUPRLAN 80), drummed for 30 minutes. During that period, the float of 100% water was added to wash the pelts; it was repeated again for 60 minutes. Then, 5% of common salt (sodium chloride) was added and 3% of degreasing agents (SUPRLAN 80) were added, drummed for 30 minutes. The pelts were drained, horsed up, and leave overnight.

3-2-5-2 Depickling:

In the following day, depickling was carried out in a drum after the degreasing, to prepare the pelts for tannage operation. The pelts were wetted back and washed in 150% float of 6.7°Be drummed for 20 minutes. The pelts were drained, repeated wetted back in 150% float of 6.7°Be drummed for 20 minutes. During that period 30% float of water at 35°C and 4% salt (sodium chloride)of 6.7°Be were added. And 0.8% of sodium bicarbonate was added and drummed for 60 minutes. This raised the pH 3.8, then added .4% sodium bicarbonate, added 300% water and drummed for 30 minutes. This raised the pH 4.5 for tannage process.

3-2-5-3 Tannage operations:

Immediately after depickling, the tannage was carried out in a drum in the same day.300% water, garad powder (vegetable tannins) (30% pickled hides) was added in three portions. The first portion, 10% of garad powder, was added and drummed for 45 minutes. Then second portion, 10% of garad powder was added, drummed for 45 minutes, and third portion of 10% of garad powder was added an drummed for 45 minutes. After tannage process 0.6% formic acid was added in two portions for fixation. The first portion 0.3% formic acid was added and drummed for 15 minutes. The second portion 0.3% formic acid added, and drummed for 15 minutes, added 0.3% preservative agent, drummed for 30 minutes then adjust pH by using pH paper, pH 3.5. After this period the pelts drained, horsing up, leave overnight.

3-2-5-4 Retannage:

Before this period the pelts were shaved by shaving machine. The retannage was carried out in a drum. Pelts were wetted back in water, then they were thrown in a drum contain 6.7°Be salt, pH 3.5 drummed for 30 minutes, then added 0.9% sulphuric acid drummed for 90 minutes. Then deferent percentage from chromium or aluminium were added and drummed for 90 minutes, after that added 0.25% magnesium oxide drummed for 40 minutes, then adjust the pH 3.8, added 1% sodium bicarbonate drummed for 30 minutes, then adjust the pH 4.5 after that 10% garad was added drummed for 45 minutes. Added 0.3% formic acid drummed for 15 minutes. Then 0.01% anti mould agent and 1% sodium bicarbonate were added drummed for 30 minutes. There raising of the pH from 5.5 to 6 drummed over night.

3-2-5-5 Fatliquoring:

Fatliquoring is carried out in a drum after retannage. Added 100% hot water (45-50°C) to liquors of retannage, 4% of sulphonate oils (PELLASTOL XO) was added in two portions, the first portion 3% of sulphonate oils (PELLASTOL XO) was added and drummed for 45 minutes. Then second portion, 1% of sulphonate oils (PELLASTO OX) was added, drummed for

45 minutes. Then added 1.5% formic acid in two portions, the first portion 0.75% formic acid was added drummed for 15 minutes, 0.75% formic acid was added. The pelts were drained and rewashed, after wash the pelts horsing up, left over night, set out by staking machine and drying.

3-3 Experimental work:

Pickled hides were processed in eight trials, in each trial three pieces cattle were treated in pilot drum with speed of 8 rpm. Four trials were treated with 30% garad as tannage and different percentages chromium of (1,2,3,4%) as retannage with 10% garad, and other four trials were treated with 30% garad as tannage and different percentages aluminium of (1, 2, 3, 4%) as retannage with 10% garad.

3-3-1 Experiment 1 chromium as retannage agent:

Pickled hides were processed in four trials in each trial three pieces hides were treated in pilot drum at speed of 8 rpm. Average weight pickled 3.5- 5 Kg, for half piece. All trials were treated with 30% garad as tannage and deferent percentages (1, 2, 3, 4%) chromium as retannage with 10% garad.

3-3-1-1 Degreasing:

Degreasing: drum pelts for 30 minutes with

5% common salt

3% degreasing agents (SUPRLAN 80) at 35°C

Then add: 100% water at 35°C

Running for 60 minutes,

Then add: 5% common salt

3% degreasing agents (SUPRLAN 80) at 35°C

Running for 30 minutes

Horse up, overnight.

3-3-1-2 Depickling:

Pelts washing in 150% solution have 6.7°Be, drummed for 20 minutes, repeated washing150% solution have 6.7°Be, drummed for 20 minutes drained.

Then add: 30% water at 35°C

4% salt of 6.7° Be

0.8% of sodium bicarbonate drummed for 60 minutes this raised pH 3.8

0.4% sodium bicarbonate drummed for 30 minutes this raised pH 4.5 for tannage process.

3-3-1-3Tannage operations:

Add: 300% water

Then add: 10% of garad powder, drummed for 45 minutes

10% of garad powder, drummed for 45 minutes

10% of garad powder, drummed for 45 minutes

Then fixation: 0.3% formic acid was added and drummed for 15 minutes

0.3% formic acid was added and drummed for 15 minutes

0.3% preservative agent, drummed for 30 minutes then check pH 3.5

Horse up overnight,

3-3-1-4 Retannage:

Drum pelts for 30 minutes with

70% water at 35°C

6.7°Be salt, pH 3.5

Then add: 0.9% sulphuric acid drummed for 90 minutes

Then add: the different chrome offers (1%, 2%, 3%, 4%) and drummed for 90 minutes

Then add: 0.25% MgO drummed for 40 minutes, then check pH 3.8

Then add: 1% sodium bicarbonate drummed for 30 minutes then cheek pH 4.5

Then add: 10% garad drummed for 45 minutes

Then add: 0.3% formic acid drummed for 15 minutes

Then add: 0.01% anti mould agent and 1% sodium bicarbonate drummed for 30 minutes rising pH from 5.5 to 6

Drummed overnight.

3-3-1-5 Fatliquoring:

Drum pelts for 45 minutes with

100% of hot water (45-50°C)

3% of sulphonate oils (PELLASTOL OX)

Then add: 1% of sulphonate oils (PELLASTO OX) drummed for 45 minutes

Then add: 0.75% formic acid drummed for 15 minutes

Then add: 0.75% formic acid pelts were drained and rewashed

Horse up left overnight, set out and drying.

3-3-2 Experiment 2 aluminum as retannage agent:

Pickled hides were processed in four trials in each trial three pieces cattle were treated in pilot drum with speed of 8 rpm. Average weight pickled 3.3-4.5 Kg, for half piece. All trials were treated with 30% garad as tannage and different percentages (1, 2, 3, and 4%) aluminum as retannage with 10% garad.

3-3-2-1 Degreasing:

Degreasing: drum pelts for 30 minutes with

5% common salt

3% degreasing agents (SUPRLAN 80) at 35°C

Then add: 100% water at 35°C

Running for 60 minutes,

Then add: 5% common salt

3% degreasing agents (SUPRLAN 80) at 35°C

Running for 30 minutes

Horse up overnight,

3-3-2-2 Depickling:

Pelts washing in 150% solution have 6.7°Be, drummed for 20 minutes, repeated washing150% solution have 6.7°Be, drummed for 20 minutes drained.

Then add: 30% water at 35°C

4% salt of 6.7° Be

0.8% of sodium bicarbonate drummed for 60 minutes this raised pH 3.8

0.4% sodium bicarbonate drummed for 30 minutes this raised pH 4.5 for tannage process.

3-3-2-3 Tannage operations:

Add: 300% water

Then add: 10% of garad powder, drummed for 45 minutes

10% of garad powder, drummed for 45 minutes

10% of garad powder, drummed for 45 minutes

Then fixation: 0.3% formic acid was added and drummed for 15 minutes

0.3% formic acid was added and drummed for 15 minutes

0.3% preservative agent, drummed for 30 minutes then check pH 3.5

Horse up overnight,

3-3-2-4 Retannage:

Drum pelts for 30 minutes with

300 water at 35°C

6.7°Be salt, pH 3.5

Then add: 0.9% sulphuric acid drummed for 90 minutes

Then add: the different aluminum offers (1%, 2%, 3%, 4%) and drummed for 90 minutes

Then add: 0.25% MgO drummed for 40 minutes, then check pH 3.8

Then add: 1% sodium bicarbonate drummed for 30 minutes then cheek pH 4.5

Then add: 10% garad drummed for 45 minutes

Then add: 0.3% formic acid drummed for 15 minutes

Then add: 0.01% anti mould agent and 1% sodium bicarbonate drummed for 30 minutes rising pH from 5.5 to 6

Drummed overnight

3-3-2-5 Fatliquoring:

Drum pelts for 45 minutes with

100% of hot water (45-50°C)

3% of sulphonate oils (PELLASTOL OX)

Then add: 1% of sulphonate oils (PELLASTO OX) drummed for 45 minutes

Then add: 0.75% formic acid drummed for 15 minutes

Then add: 0.75% formic acid pelts were drained and rewashed

Horse up left overnight, set out and drying.

3-4 Physical testing:

All Physical tests were carried out according to the Official Methods (SLTC, 1996).

3-4-1 Positions of sampling:

Cut the pieces for physical tests from the square HKJG, and as close to the line EF as possible (fig 3- 1).

For all physical tests half of the test pieces are to be taken along the backbone and other half along the direction parallel to the backbone but all pieces should be within the sampling location.

3-4-2 Condition:

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

3-4-3 Measurement of thickness:

The specimens were placed in the standard micrometer gauge with grain side up and the thickness of leather was measured in four positions and the time of dwell was 5 seconds before taking the reading.

The mean value of the thickness was calculated (SLTC, 1996).

3-4-5 Measurement of tensile strength and percentage elongation:

I- Tensile strength:

The tests are carried out usually with all kinds of leather. The specimen may be used for any of the tests. Samples were cut parallel and perpendicular to the back bone, as already explained, using a dumbbell shape.

The thickness and width of the specimen were measured in the same position using standard thickness gauge and verries callipers respectively ie one at the mid point E and the other two measures midway between E and line ABCD. The width must be measured on flesh and grain side, and then the mean thickness (mm) and width in (cm) were calculated.

The cross-section 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 apart and then the sample was clamped in the jaw, so that the edges of jaws lie along the line AB, CD. The machine was run until the specimen broken and the highest load reached as breaking local. The tensile strength was calculated by diving the breaking load by the area of the cross section of specimen in kilograms per square centimetre.

Tensile strength= Maximum breaking load in kgs

Cross-section area in Cm^2

II-Percentage elongation at break:

The distance between the jaws was measured and taken as

The initial length of the specimen for purpose of the test machine started to run and the distance was watched closely until the load at the break.

Calculation of the elongation at the load at break was taken as the break and calculated as follows:

$$\text{Elongation} = \frac{\text{final free length- initial free length}}{\text{Initial length}}$$

3-4-5 Measurement of grain crack properties of leather lastometer determination:

A standard thickness was carried out. The specimens were cut was used cut two samples from backbone of leather. The thickness was measured by standard thickness. Then the average of thickness was calculated, the lastometer was used to determine the load. The specimen flesh side down in the lastometer and clamp securely used special toll. The distension was increase at a rate 1 mm per 10 seconds whilst watching the grain surface for appearance of grain crack/ burst.

3-4-6 Measurement of bally flexometer:

Samples were cut 7.0 x 4.5 cm. similar samples to those used for the Satra test may cut for direct comparison. The flexometer machine was used. The bottom edge of the upper clamp was adjusted in a horizontal position clamp the leather, grain to grain, the machine was started (100 flexes min-1) which causes a running folds in the leather passing through an angle of 22.5.Then after each 100, 500, 1,000, 5,000, 10,000 and 16,000 flexes and after 1 hour, 2 hour, 3 hour, reported to condition of the leather at these points with the a of an illuminated lens (10x mag) to observe and report any of the followings:

1-Change shade in grey scale

2-Crazing of flesh with small to large surface cracks

3-Loss of finish adhesion

4-Flaking off

3-4-7 Measurement of shrinkage temperature:

The shrinkage temperatures of leathers were determined by boiling fastness test (SLTC, 1996). The method was intended for use with any type of leather whose shrinkage temperature lies below 100°C.

Shrinkage temperature is determined by suspending a strip of pelt or leather about 1.7cm in water which was heated and observing the temperature at which just cover the strip, is raised at rate of 30 to 100°C in 40 minutes.

3-5 Leather chemical analysis:

3-5-1 Principles:

The directions cover the chemical determinations by which to ascertain the composition of leather. Comments made at the end of some methods are not to be regarded as part of methods. They indicate devices, apparatus and accessories with which to facilitate the work. They also contain, however, directions for the preparation of special reagents for determining the strength of special solutions and working methods, which must be applied in special cases. This is mainly to save, as far as possible, the search for and testing of suitable methods. (SLTC 1996).

3-5-2 Sampling Position for chemical analysis of leather:

The items envisaged for chemical examination (hides, buts bends, shoulder, or bellies) are first divided in accordance with the sampling directions for physical tests.

3-5-3 Number of pieces to be analysed:

Usually, three pieces (skins, sides, bends, shoulders or bellies) are to be sampled and at least a duplicate analysis carried out on an average sample. If this is not the case, it should be noted in report of the test with details of the number of items investigated (SLTC 1996).

3-5-4 Minimum weight of material to be taken from each piece:

The flowing minimum weight of material is necessary for a chemical analysis of leather:

3-5-4-1 In the investigation of vegetable and combination tanned leather 100 g.

3-5-4-2 In the investigation of mineral tanned leather 60 g.

3-5-5 Preparation of test material by grinding:

For chemical analysis, leather of all kinds must be ground in a cutter mill. The ground material obtained from the mill called “ground leather” or “leather powder” (SLTC 1996).

3-5-6 Determination of volatile matter in leather (Moisture):

3-5-6-1 Fundamentals:

An exact determination of the moisture contained in leather by drying is not possible, as at elevated temperature other volatile substances escape and tannins and fats can be oxidised. Some adsorbed water may be left in the leather after drying.

3-5-6-2 Determination of moisture:

A sample of 2.5 gm was weighed and then dried into a constant weight at 102+ or – 2°C in a normal oven five hours. Weigh after cooling in the desiccator for half hour, drying should be continued until constant weight is reached but no longer than 4 hours in all.

Calculation: (3-1)

$$\text{Moisture \%}\ \frac{G1 - G2}{G1}$$

G1= weight of sample before drying.

G2= weight of sample after drying.

3-5-7 Determination of total ash:

Weigh 2.5 gm, of the original leather sample to an accuracy of 0.001 g and carefully carbonise it over a low flame in a crucible that has previously been heated to 800°C, cooled and weighed, so that the leather burns with small flame. Carbonise fatliquored leather particularly carefully so that the grease burns only slowly. Then thoroughly moisten with 2N sulphuric acid and heat over a low flame until sulphuric acid fumes are no longer visible. Then heat more vigorously, or better still ignite in the furnace at approx 800°C until completely ashed, cool in the desiccator and weigh. Repeat the addition of acid heating, cooling and weighing until the weight of the residue is constant.

Calculation: (3-2)

$$\text{Ash } \% = \frac{t2}{t1} \times 1oo$$

t1= sample weight

t2 = ash weight

3-5-8 Determination of substance fats:

3-5-8-1 Apparatus and reagents:

1- Soxhlet extraction apparatus (extraction flask of suitable size).
2- Filter paper thimbles of suitable size and manufacture or suitable glass filter bells.
3- Dichloromethane**, boiling point 38/ 40°C, freshly distilled, kept in a dark flask over CaO.
4- Laboratory scales with a sensitivity of 0.05 g.
5- Analytical balance.
6- Oven set to 102 ± 2°C.
7- Suitable desiccators.

3-5-8-2 Method:

1-Weigh 10 g leather and press evenly into filter paper thimble or into the glass bell. Cover the leather with a thin layer of cotton wool (grease free).

2-Dry the extraction flask with two glass beads in it by heating for half an hour at 102± 2°C; weigh after cooling in the desiccators.

3-After at least 30 changes of solvent, distil the dichloromethane from the flask containing the extract. Dry the extract in the oven for four hours at 102± 2°C.

Calculation: (3-3)

$$\text{Extractable substance in \%} = \frac{\text{g extract}}{\text{g original sample}} \times 100$$

3-5-9 Determination of chromic oxide (Cr2 O3):

3-5-9-1 Reagents, solutions and apparatus:

3-5-9-1-1For the perchloric acid method:

1- Con. Sulphuric acid.

2- 60-70% perchloric acid.

3- 85% phosphoric acid.

4- 10% potassium iodide solution or 1 g tablets.

5- 1% starch solution (freshly prepared or made to keep for several months by addition of a little mercuric iodide) or soluble starch powder.

6- 0.1 N sodium thiosulphate solution.

7- 300 ml heat resistant Erlenmeyer flask, or Kjedahal flask, with ground glass stopper.

8- Glass funnel, glass beads, earthenware pebbles.

9- Burette with appropriate scale.

3-5-9-2 Method:

3-5-9-2-1 According to the perchloric acid method:

Put the ash of 1-5 g leather in heat resistant 300 ml Erlenmeyer or Kjedahal flask.

Add 5 ml conc. Sulphuric acid and 10 ml 60-70% perchloric acid, and heat to boiling on the wire gauze with a moderate flame. Cover the Erlenmeyer flask with a funnel so that the water can evaporate without loss by splashing. As soon the reaction mixture begins to turn to orange, lower the flame. After complete change of colour, heat slowly for a further two minutes. Cool of a short time in air, and then rapidly in cold water, and dilute the contents to approx. 200 ml. To eliminate the chlorine thus created, boil for approx. 10 minutes using earthenware pebbles (glass beads are not sufficient to prevent bumping). After renewed cooling, add 15 ml 85% pure phosphoric acid to mask any iron present and 20 ml. 10% potassium iodide solutions or an appropriate quantity of tablets. Leave to stand for 10 minutes in the dark. Then titrate to light green using 5 ml of a 1% starch solution or starch powder as indicator, with 0.1 N sodium thiosulphate.

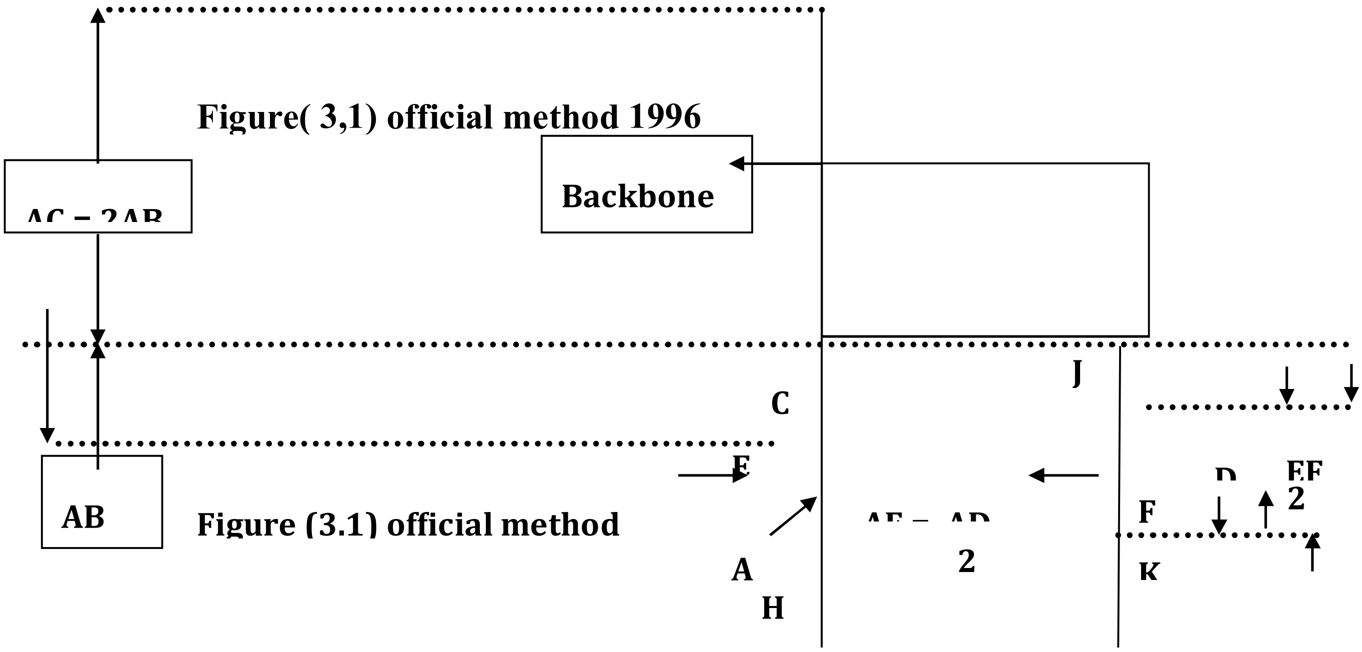
Calculations: (3-4)

1ml 0.1 N thiosulphate solution corresponds to 0.002534 g Cr_2 O_3

<u>Ml 0.1 N thiosulphate solution</u> . o.002534= % Cr_2O_3 in leather.

g leather take

3.1 Physical analysis:



Figure(3,1) official method 1996

Figure (3.1) official method

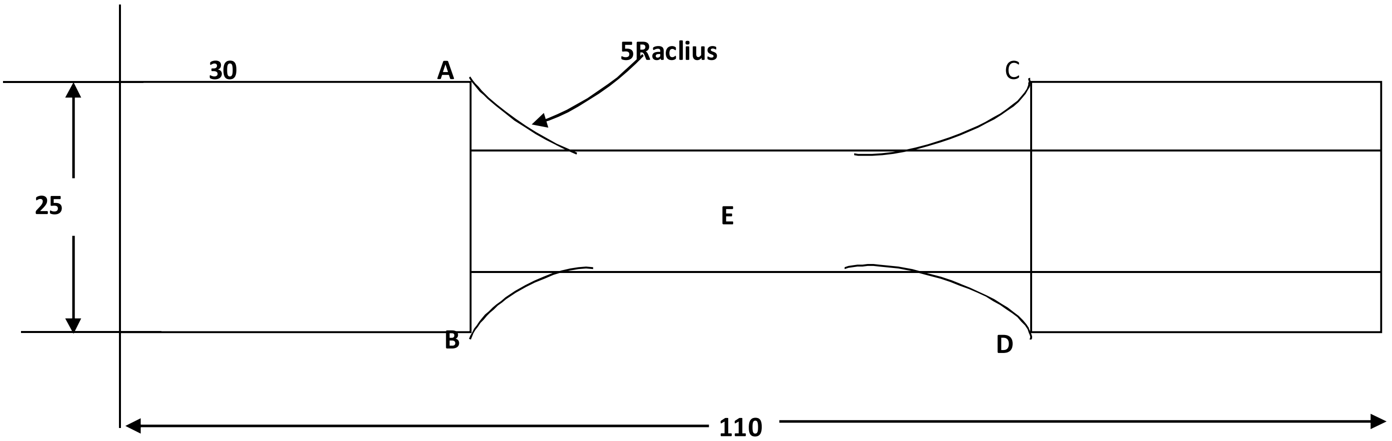


Figure (3-2) dumbbell shape for tensile strength

3. Chapter Four

4. Results and Discussion

4-1 Results:

4-1-1 Results of experiment 1, chromium as retaining agent:

In this study *Acacia nilotica* (garad) was used as tanning agent at constant concentration (30%). Different chrome offers (1%, 2%, 3%, 4%) were used for retanning. All raw hides processed were converted into normal leather with good softness, fullness, smoothness, general appearance and dye uniformity.

Some physical analysis used 30% Acacia nilotica (garad) as retannage and low level chromium of (1, 2, 3, 4%) were carried out for experimental crust leather and the data was given in table (4-1-1) characteristics of the leather produced in this study were determined so as to describe the effect of tanning. The thickness of the leather produced higher values in chromium of 3% as retannage agent 1.96mm, lower value in chromium of 4% as retannage agent 1.5mm, but in chromium of 1% and 2% as retannage agent 1.68- 1.63mm respectively are significantly different between leather produced. The physical strength measurement includes tensile strength, elongation, load at grain crack and load at grain break. The tensile strength of the leather produced range from 103- 185.75 kg/cm2 was increased when increasing level of chromium as retannage agent, leather produced chromium of 1% as retannage agent was significantly low than that produced from all other when used chromium of (2, 3, 4%) as retannage agent. The elongation of the leather produced gave higher value in chromium of 4% as retannage agent 39.3%, low value in chromium of 3% as retannage agent 30.6%, but in chromium of 1% and 2% as retannage agent 33.6- 31.6% respectively are significantly different between leather produced. The grain crack of the leather produced higher value in Chromium of 1% as retannage agent 8.28 kg, lower value in chromium of 3% as retannage agent 5.78 kg, but in chromium of (2, 4%) as retannage agent 6.18- 7.85 kg respectively are significantly different between leather produced. The grain at break of leather produced in different percentage chromium of (1, 2, 3, 4%) as retannage 9.50, 8.60, 8.75, 9.35 respectively are not significantly different between leather produced.

Chemical analysis used 30% Acacia nilotica (garad) as retannage and low level chromium of (1, 2, 3, 4%) were carried out for experimental crust leather and the data is given in table (4- 2-1) characteristics of the leather produced in this study were determined so as to describe the effect of tanning. The moisture of the leather produced increased when increasing levels of chromium as retannage agent (1, 2, 3%) 5.88, 6.1, 6.67% respectively but low in level 4% of chromium as retannage agent 4.00% are significantly different between leather produced. The ash content of the leather produced gave higher value in chromium of (1, 2%) as retannage agent 3.43, 3.63% and low level in chromium of (3, 4%) as retannage agent 1.86% 2.66% respectively are significantly different between leather produced. The fat percentage of the leather produced chromium of (1, 2, 3, 4%) as retannage agent 4.23, 3.87, 4.67, 4.70% respectively are significantly different between leather produced. The chromium oxide content of the leather produced was of higher value in chromium of (2, 4%) as retannage agent 2.90- 2.50% low value in chromium of (1, 3%) as retannage agent

1.38- 2.10% respectively are significantly different between leather produced.

The shrinkage temperature data when used 30% Acacia nilotica (garad) as retannage and low level chromium of (1, 2, 3, 4%) are given in table (4- 3 1). It was seen that leather produced in different percentage chromium of (1, 2, 3, 4%) as retannage shrinkage temperature increased when increasing level of chromium as retannage 85.4, 86, 86.4, 87°C.

Table (4-1-1): Effect of chrome retannage on physical characteristics of hide crust leather

Parameter *Chrome conc.*	*Thickness mm*	*Tensile strength kg/cm2)*	*Elongation %*	*Grain crack (kg)*	*Grain break (kg)*
1%	1.68 ± 0.16^{b}	103.00 ± 18.4^{c}	33.6 ± 4.8^{ab}	8.28 ± 0.4^{a}	9.50±0.1
2%	1.63 ± 0.16^{bc}	159.00 ± 11.96^{b}	31.3 ± 1.4^{b}	6.18 ± 0.8^{b}	8.60±1.5
3%	1.96 ± 0.00^{a}	171.00 ± 40.4^{a}	30.6 ± 1.8^{b}	5.78 ± 0.9^{b}	8.75±0.5
4%	1.50 ± 0.00^{c}	185.75 ± 76.4^{ab}	39.3 ± 7.2^{a}	7.85 ± 0.5^{a}	9.35±0.2
Significanc	**	**	*	**	NS

e

a,b: Means within columns followed by different superscripts are significantly (P<0.05) different

**: significant at (P<0.01)

*: significant at (P<0.05)

NS: Not significant.

Table (4-1-2): Effect of chrome retannage on chemical characteristics of hide crust leather

Parameter *Chrome conc.*	*Moisture (%)*	*Ash (%)*	*Fat (%)*	*Chromium oxide content (%)*
1%	5.88±0.1^{c}	3.43±0.2^{a}	4.23±0.2^{b}	1.38±0.0^{d}
2%	6.10±0.1^{c}	3.63±0.1^{a}	3.87±0.2^{c}	2.90±0.1^{a}
3%	6.67±0.2^{a}	1.86±0.2^{c}	4.67±0.2^{a}	2.10±0.1^{c}
4%	4.00±02^{b}	2.66±0.^{l}	4.70±0.2^{a}	2.50±0.0^{b}
Significance	**	**	**	**

a,b: Means within columns followed by different superscripts are significantly (P<0.05) different

**: significant at (P<0.01)

Table (4-1-3): shrinkage temperature chromium as retannage of hide crust leather:

Chromium conc	shrinkage temperature
1%	85.4 °C.
2%	86.0 °C.
3%	86.4°C.
4%	87.0 °C.

4-1-2 Results of experiment 2, aluminum retanning agents:

In this study *Acacia nilotica* (garad) was used as tanning agent at constant concentration (30%). Different aluminum offers (1%, 2%, 3%, 4%) were used for retanning. All raw hides processed were converted into normal leather with good softness, fullness, smoothness, general appearance and dye uniformity.

Some physical analysis used 30% Acacia nilotica (garad) as retannage and low level aluminum of (1, 2, 3, 4%) were carried out for experimental crust leather and the data was given in table (4-2-1) characteristics of the leather produced in this study were determined so as to describe the effect of tanning. The thickness of the leather produced higher values in aluminum of (1, 3, 4)%) as retannage agent 2.13, 2.26, 2.09 mm respectively, lower value in aluminum of 2% as retannage agent 1.66 mm, are significantly different between leather produced. The physical strength measurement includes tensile strength, elongation, load at grain crack and load at grain break. The tensile strength of the leather produced aluminum of (1, 2, 3, 4%) of as retannage 227.39, 279.68, 279.17, 215.06 kg/cm2 respectively, are not significantly different between leather produced. The elongation of the leather produced aluminum of (1, 2, 3, 4%) as retannage 35.4, 27.3, 30.6, 38.3% respectively were not significantly different between leather produced. The grain crack of the leather produced (1, 2, 3, 4%) of aluminum as retannage 7.70, 7.78, 8.30, 8.10 kg respectively are significantly different between leather produced. The grain at break of leather produced in different percentage aluminum of (1, 2, 3, 4%) as retannage 9.13, 8.95, 9.80, 9.40 respectively were significantly different between leather produced.

Some chemical analysis used 30% Acacia nilotica (garad) as retannage and low level from aluminum (1, 2, 3, 4%) were carried out for experimental crust leather and the data is given in table (4-2-2) characteristics of the leather produced in this Study were determined so as to describe the effect of tanning. The moisture of the leather produced higher value in aluminum of (2, 3, 4%) as retannage agent 6.72, 6.98, 6.43%, low value in aluminum of 1% as retannage agent 3.98%, leather produced aluminum of 1% as retannage agent was significantly low than the produced. The ash content of the leather produced was higher value in aluminum of (2, 3%) as retannage agent 3.53, 3.00% and low value in of aluminum of (1, 4%) as retannage agent 1.64% 2.70% respectively were significantly different between leather produced. The fat percentage of the leather produced higher value in aluminum of 2 % as retannage agent 6.98% low value in aluminum of (1, 3, 4%) as retannage agent 4.27, 4.10, 4.27 respectively were significantly different between leather produced.

The shrinkage temperature data when used 30% Acacia nilotica (garad) as retannage and low level from aluminum of (1, 2, 3, 4%) are given in table

(4-2-3). It was seen in leather produced in different percentage from aluminum of (1, 2, 3, 4%) as retannage shrinkage temperature increased when increasing level of aluminum as retannage 70, 71, 73, 80.1°C.

Table (4-2-1): Effect of Aluminum retannage on physical characteristics of hide crust leather

Parameter *Aluminum conc.*	*Thickness (mm)*	*Tensile strength (kg/cm2)*	*Elongation (%)*	*Grain crack kg)*	*Grain break(kKg)*
1%	2.13±0.0^{c}	227.39±35.9	35.4±1.8	7.70±0.4^{b}	9.13±0.3^{bc}
2%	1.66±0.0^{b}	279.68±75.1	27.3±1.0	7.78±0.4^{b}	8.95±0.2^{c}
3%	2.26±0.1^{a}	279.17±181.9	30.6±2.4	8.30±0.2^{a}	9.80±0.1^{a}
4%	2.09±0.1^{c}	215.06±37.2	38.3±14.6	8.10±0.3^{ab}	9.40±0.2^{b}
Significance	**	NS	NS	*	**

a,b: Means within columns followed by different superscripts are significantly ($P<0.05$) different

**: significant at ($P<0.01$)

*: significant at ($P<0.05$)

NS: Not significant

Table (4-2-2): Effect of Aluminum retannage on chemical characteristics of hide crust leather

Parameter *Aluminum conc.*	*Moisture (%)*	*Ash (%)*	*Fat (%)*
1%	3.89 ± 0.7^{b}	1.64 ± 0.0^{d}	4.27 ± 0.3^{b}
2%	6.72 ± 0.3^{a}	3.53 ± 0.2^{c}	6.98 ± 0.1^{a}
3%	6.98 ± 0.1^{a}	3.00 ± 0.0^{a}	14.10 ± 0.1^{b}
4%	6.43 ± 0.1^{a}	2.70 ± 0.2^{b}	4.27 ± 0.3^{b}
Significance	**	**	**

a,b: Means within columns followed by different superscripts are significantly ($P<0.05$) different

**: significant at ($P<0.01$)

*: significant at ($P<0.05$)

NS: Not significant

Table (4-2-3): shrinkage temperature aluminum as retannage of hide crust leather:

Aluminum conc	shrinkage temperature
1%	70°C.
2%	71°C
3%	73°C.
4%	8o ° C.

4-2 Discussion:

Tanning is a chemical process that converts animal skins and hides into leather by introducing additional cross-links to collagen. The efficiency of tanning depends on the binding activity of the tanning agents to the functional groups. It also depends on the thickness of the animal skins or hides. Complete penetration of tanning agents to the skin or hide lead to uniform distribution of these agents which will lead to satisfactory tanning.

In this study Acacia nilotica (garad) was used as pretannage agent at constant concentration (30%) with chromium as retannage in different percentage (1, 2, 3 and 4%) and Acacia nilotica (garad) was used as pretannage agent at constant concentration (30%) with aluminum as retannage in different percentage (1, 2, 3 and 4%). All raw hides used are converted into normal leather with good softness, fullness, smoothness, general appearance and dye uniformity.

The use of mechanical effect (drum) in tanning operation in the current study resulted in reduction of tanning time (few hours) compared to very long time in traditional vegetable tannage in pits. This is due to the slow penetration of large reactive molecules (Covington, 1997 and Morera *et al.,*2010).

Some physicals table (4-1-1, 4-2-1), the thickness of the leather produced of chromium (1, 2, 3, 4%) as retannage, and aluminum (1, 2, 3, 4%) as retannage, concentrations used range between 1.50-2.26 mm. Animal hides are not uniform which means there are big differences in thickness and type of fibril weaving existing in different areas of a hide (Krysztof,1983). All other physical characteristics determined in this study (tensile strength, elongation, grain crack, grain break and shrinkage temperature) showed high values. The chromium as retannage and aluminum as retannage improve the strength properties of the leather. The tensile strength is the force required to rupture a leather specimen of unit cross sectional area. The tensile strength was thus the combined breaking strength of all the fibers which are taking part to fight against the applied load. The tensile strength of this semi metal gave competitive results, to produce different type of leathers (Dutta, 1999).

The percentage elongation at break load properties of vegetable tanned garad with different percentage chromium of (1, 2, 3, 4 %) as retannage were 33.6, 31.3, 30.6, 39.3 and with different percentage aluminum of (1, 2, 3, 4 %) as retannage were 35.4, 27.3, 30.6 and 38.3 % respectively. The obtained values are quite normal. The obtained values of the grain crack and grain break in this study are normal and indicate good strength of the leather produced.

The flexibility after 100,000 flexes for the experimental leathers compared with the grey scale indicates good flexibility and the semi metal leathers produced could be accepted for shoe upper leather manufacture. The resistance to flexural fatigue plays an important role among the elasticity properties.

Some chemicals result in table (4-1-2, 4-2-2) characteristics of the leather produced in this study were determined so as to describe the effect of tanning. The moisture (3.89-6.98%), ash (1.64-3.63%) and fat (3.87-6.98) of the produced leather fall within the normal values. The moisture content was significantly affected by the concentration of chromium and aluminum it tended to increased with the increasing of chromium and aluminum concentration. However, the moisture content of the leather obtained from retanning with 1% aluminum lower, than that obtained from retanning with all other aluminum was significantly. The moisture content of the leather obtained from retanning with 4% chromium was lower, than that obtained from retanning with all other chromium concentrations was significant.

Results of this study showed significant different percentage in moisture chromium and aluminum as retannage. Indicate chromium and aluminum as retannage ensure better water resistance. There is an abundance of hydrophilic groups in the collagen fibers in leathers. Because the affinity between these hydrophilic groups and water molecules varies with changes in temperature and relative humidity, leathers will adsorb or de-adsorb water as these factors change; affecting strength, permeability, and thermal stability. Retanning is a key operation in leather making with the purpose of retanning is to obtain leathers with some special characteristics (Keyong *et al.*, 2009).

The ash content in the current study (1.64-3.63) was significantly affected by the concentration of chromium and aluminum. However, all values obtained are comparable to those reported by Musa and Gasmelseed (2012). A very wide range of ash content (0.9-70%) was obtained by Haroun *et al.* (2008). The fat % in this study (4.10-6.98) was also significantly affected by concentration.

Results, in this study shown in table (4-1-3, 4-2-3) the shrinkage temperature when used vegetable garad (Acacia nilotica) as tannage offer 30% with low level chromium of (1, 2, 3, 4%) followed 10% garad, Collagen- veg- Cr- veg Collagen the shrinkage temperature were found 85.4, 86, 86.4, 87°C. respectively, this indicated that the chromium increased the shrinkage temperature and this is enough for most leather uses. The full range options available to the modern tanner will constitute the body of this review. And when using vegetable, garad (Acacia nilotica) as tannage offer 30% with low level aluminum of (1, 2, 3, 4%) followed by 10% garad, Collagen- veg- Al- veg Collagen the shrinkage temperature were found as 70, 71, 73, 80.1°C. respectively indicted could be introduced this review in tanneries and alternatives to chromium tannage, regarding environmental safety. Vegetable - aluminum based tanning system has been found to be more suitable for the integrated one step upper leather processing. This same with chemical nature of collagen allows it to react with a variety of agents often resulting in its conversion to leather changes in appearance and properties that are the consequences of tanning. One of the most important is the increase in hydrothermal stability (Covington, 1997). This can be measured by observing the point at which a specimen shrinks, when it is held in continuously heated water (at a rate of 2°C per minute). This is the conventionally measured shrinkage temperature, (Ts). It is necessary to specify the conditions, because shrinking is a kinetic process and, as such can be treated thermodynamically. The relationship between Ts and change in heat indicates that breakdown of the tanning interaction is not the cause of shrinkage. It is thought that even the weak, hydrolysable aluminum tannage is not reversed during shrinkage. The reaction, which is visible as heat shrinkage is a breakdown of the hydrogen bonding in collagen or leather; that regardless of the tanning process, the shrinkage reaction is the same. The hydrogen bonding is the structure component that is broken down during shrinkage. That is, if tanning process only modifies the shrinkage temperature, without changing the shrinkage mechanism it raised if the size of the cooperating unit in the shrinkage process is larger the unit as the kinetics become slower and i.e the higher is the shrinkage temperature. Ts appears to be related to the size of the artificial cross link, which may be related to the size of unit involved in the shrinkage reaction. From measurements of rate shrinkage and entropy of activation, it was found that size of the cooperating unit in raw collagen, with shrinkage temperature 60 °C is 25 residues, but aluminum and chromium tanned collagens with shrinkage temperature 73 and 107°C have cooperating unit containing 71 and 206 amino acid residues respectively (Covington, 1998). In all cases, the benchmark for comparison is tannage with chromium (III): Ts > 100°C In addition to number of cross-links introduced by tanning, their general character is of great importance. It could be: H-bonds, ionic bonds or covalent bonds. A high Ts is achieved either by the precise effects of chromium (III) complexes or by controlled multiple interaction between tanning species and collagen. Current tanning technology is dominated by chromium (III); it was introduced about 130 years ago and by the turn of the century, it had begun to replace the traditional tannages, which were based on plant polyphenols (so called vegetable tannins).Today, 90% of the world's leather production is chrome tanned; the remainder is tanned with vegetable tannins, mostly for leather goods or shoe soles. Typically, chrome tanning alone is insufficient to provide the visual requirements for the wide range of leather types produced by industry, so the main or prime tannage is complemented with other tannages, which are applied after chrome. The full range options available to the modern tanner will constitute the body of this review. Condensed tannin typically raise the shrinkage temperature of collagen to 80-85°C but Hydrolysable tannins typically raise the shrinkage temperature of collagen to 75-80°C (Covington, 1997). There is an abundance of hydrophilic groups in the collagen fibers in leathers. Because the affinity between these hydrophilic groups and water molecules varies with changes in temperature and relative humidity, leathers will adsorb or de-adsorb water as these factors change; affecting thermal stability (Tang *et al.*, 2009). Genipin, a naturally occurring protein crosslinking agent, the apparent shrinkage temperature of hide powder could be increased from 60°C to 79°C by treating the powdered hide with 5% genipin at pH ~ 7 and 35°C for 24 hr, a significant improvement, but not enough for most leather uses. Typical tannages proposed to reduce the use of chromium are combinations of vegetable tannins or aldehydes with each other minerals. Genipin in combination with aluminum In terms of thermal stability, vegetable tannins in combinations with genipin appear to offer little advantage over either component alone, suggesting little if any synergy. Likewise, aluminum tanning over a genipin pretannage appears to provide little advantage. However, when hide powder was first tanned with 8% aluminum and then retanned with genipin the thermal stability increased linearly with increasing concentrations of genipin (2% to 10%). The apparent shrinkage temperature was > 100°C for aluminum post-tanned with 8%-10% genipin (Ding *et al.*, 2007). A combination tannage based on Tara tannin and co-tanning adjuncts viz., aluminum and gluteraldehyde. The shrinkage temperature of leathers using different combinations of tara and aluminum/ gluteraldehyde were found to be around 90°C (Madhan *et al.*, 2007). Chrome tanning is the most common type of tanning in the world. Chrome tanned leather is characterized by top handling quality, high hydro-thermal stability (Bosnic *et al.*, 1998). A tanning agent based on aluminum that stable in solution and will form cross-link with collagen in such a way that real leather, resistant to water and adequate hydrothermal stability is produced (Adewoye *et al.*, 2000). Aluminum-henna (Al-henna) leathers tanned using 2% Al_2O_3; followed by 20% henna resulted in shrinkage temperature above 95°C (Musa *et al.*, 2011). The only established organic tannage capable of producing leather with high hydrothermal stability is that in which the collagen is the first tanned with vegetable tannin, then retanned with a metal salt, preferably aluminium (III); semi alum leathers made with condensed tannins typically have shrinkage temperatures ca. 90°C (mimosa is exceptionally higher, possessing pyrogallol groups), whilst semi alum leathers made with hydrolysable tannins have shrinkage temperature of 115-120°C. treating collagen with catechol or pyrogallol themselves, then retanning with aluminum (III); resulting shrinkage temperature are 71 and 98°C respectively and the same pattern is obtained for more complex polyphenols. The synergistic interaction between the polyphenol and the aluminium (III) may arise from one of the following options:

Collagen-Al-veg- Al- Collagen

Collagen- veg- AL- veg Collagen

Collagen-veg- Al-Collagen

It is known that applying the aluminum salt before the vegetable tannin produce only moderate shrinkage temperature, characteristic of aluminum alone. Therefore, the first and third options are unlikely. The most probable mechanism is for the aluminum (III) to crosslink the vegetable tannin (Hemandez and Kallerberser 1984). In effect, the crosslinking polyphenol on collagen is itself crosslinked, to form a matrix within the collagen matrix, to stabilise the collagen by a multiplicity of connected hydrogen bonds in the new macromolecule (Covington, 1991). When pieces of bated hide were pretanned with 6% aluminum, then split and tanned with 6% genipin based on the weight of the split wet-white pelt, the hydrothermal stability was about 89°C as determined from the onset of the melting curve in a differential scanning calorimetry (DSC) experiment, or Ts = 92°C by a traditional shrinkage temperature measurement (Ding *et al.*, 2008). Vegetable - aluminum based tanning system has been found to be more suitable for the integrated one step upper leather processing as it has resulted in leathers with shrinkage temperature of 94 °C (Madhan *et al.*, 2005).

The provided evidence that garad with low level of chromium, and garad with low level of aluminum based leather tanning may be regarded as amore environmental friendly technology compared with chromium based leather industry.

5 Chapter five

5. Conclusions and Recommendations

5-1 Conclusions:

In this study, we have shown that a combination tannage involving vegetable tan (garad) and chromium cross links collagens, producing leather high shrinkage temperature around 87°C. On the other side when was using garad as tannage and aluminum as retannage producing leather with shrinkage temperature around 80°C.

All results of crust leather produced to be quite normal and this study for tannage by using garad with mineral chromium and aluminum reduced pollutions from use chromium tannage and introduced new cleaner technology for tanneries. It concluded that the leather produced using garad as tannage agent retannage with mineral chromium, aluminum was quite successful. It was full, soft with good physical and chemical properties. On the other side the natural color of the crust is biscuit and can be used successfully for shoe upper of natural color. It is very acceptable, and can easily compete in local and international market.

5-2 Recommendations:

1- Garad could be used as alternative for chromium in tannage operation to reduce environmental hazard resulting from chromium.

2- More study relation between vegetable tannage garad and Fatliquoring.

3- It will be necessary to carry out more studies to compare economic effectiveness between this study and tannage by using chromium.

5. Chapter six

6. References

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