Trends in leather processing: A Review

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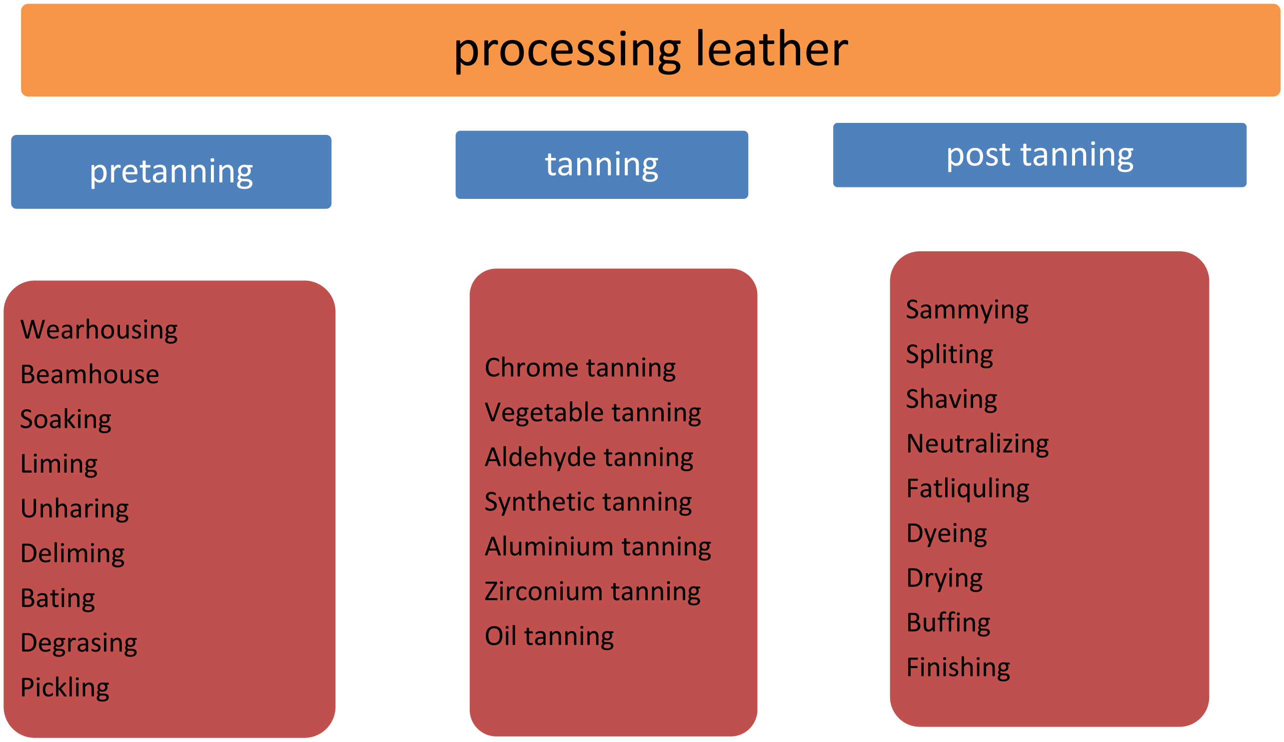
Abstract- Tanning is the process by which raw skins and hides are converted to a durable and flexible material which is non-putrescible. Leather has good hydrothermal stability, good mechanical properties, and its resistance to chemical and biological degradation helps it to be used in various applications. Leather can be used for various purposes such as making of handbags, belts, clothing, small accessories and shoes, furniture, interior decoration. The leather industry gets its raw materials form hides and skins of cattle, camel, sheep and goat and also from exotic sources such as ostrich, rabbit, crocodiles and fish. Kenya having a good strong base for fish industry there is need to pursue the production of fish leather. Leather processing involves three sub stages; pretanning, tanning and post tanning and finishing. There are different types of tannage available depending on the quality of the leather need by the consumer. The types include mineral tanning include (chromium, aluminum, iron, zinc)**,** vegetable tanning (mimosa, acacia, quebracho), aldehyde tanning (glutaldehyde, formaldehyde) and oil tanning. The range of physical properties determines the quality of product. Various physical, chemical and fastness properties are required from leather products depending on their field of use. New methods and technologies should be applied to reduce the ecological impact of leather production.

Index Terms- Tanning, Fish Leather, Hydrothermal Stability, Resistance, Properties

I. INTRODUCTION

Leather is a durable and a flexible material created by converting animal raw hide and skins [1]. It is created through a process known as tanning where the raw hide and skins are converted to non-putrescible material which resist bacterial attack, chemical degradation and resist mechanical deformation. The material gains hydrothermal stability, good breathability, durability, high strength among others characteristics[2]. The leather stability is attributed to the strong interlocking of the collagen fibers with the tanning agent which can either be organic or inorganic. The inorganic agent usually contains chromium salts which forms coordination complexes with the skin collagen enabling its biochemical stabilization[3]. Other inorganic salts used includes aluminium, zirconium, silicon and iron[4]. Organic tanning agents include vegetable tanning materials such as mimosa, different species of acacia, tara, oak quebracho among others. Vegetable tanning materials are considered less polluting than chromium but have a substantive high tensile and tearing strength, elongation, breathability and insulating properties and flexing endurance. Vegetable tanning involves treating the hide and skins with leaves and barks of trees containing tannins[5]. Other tanning agents include oil tanning[6], aldehyde tanning and synthetic tanning[7]. The processing of hide and skin involves different process and operations such as preservation stage, pretanning operations, tanning operations, post tanning and finishing to get the desired features of the leather [1].



Scheme.1 processing of leather

Preservation

Flayed skins and hides can be preserved through drying or salting. The aim is to dehydrate the skins to resistant putrefaction to allow their transport and storage. Preservation is done to destroy active bacteria, to prevent bacterial activity or to prevent bacterial contamination[8]. In sun-drying the interfibrillary substances coagulate and form some hard cementing substances which prevent the separation of fibres from each other, and thus make hide and skins difficult to soak back[9]. Sodium chloride curing system is the most popular animal skin preservation method adopted globally and this leads in the generation of large quantities of total dissolved solids. This has led tanners to search for better alternatives which are salt free and environmental friendly. The use of boric acid with little amount of sodium chloride salt is one of the altertanitives as suggested by[10]. They achieved more than 80% reduction in chlorides and total dissolved solids in the effluents. Silica gel has also been used to preserve as reported by[10].

Soaking

This is the first step in leather processing. It is an operation which can be carried out in pits, paddles or drum[2]. The aim of soaking is to rehydrate the skin proteins which results to opening up of the fibers, remove curing salt in case of salted skin, clean off surface filth such as dirt, dung and blood stains. Small residual concentration of sodium chloride is still desirable in the process bath, as it helps diffusion of water down the hierarchical structure of skin fibres for easier rehydration. The removed salt can be recovered for other uses after a series of purification[10]. When the skin open up there is removal of non-collagenous skin components: the hyaluronic acid and other glycosaminoglycans, the non-structural proteins, the fats and splitting the fibre structure at the level of the fibril bundles, to separate them[11].

Soaking operation should be done under certain conditions which include the float, temperature, pH, time and mechanical action. The soaking float is dependent on the condition of the skin in which the float can range from 200-300 % on the salted pelt. Green hides and skins are soft enough not require much soaking, but to remove the blood and dirt. Dried hides need more float for rehydration. Bactericidal agent can also be added to the float to prevent bacterial growth during the process. Since the raw material has a denaturation/ shrinkage temperature of about 65 ˚ C the temperatures should be limited to 30 ˚ C so as not to destroy the collagen. Soaking is carried out at PH values between 9 and 10 by addition of an alkaline which helps in the moderate swelling of the skins which in turn aids in rehydration[11]. In conventional batch soaking, salted hides usually require 6 hours or more to remove enough salt to ensure that the pelt is completely rehydrated in the center of the cross section and down the hierarchy of structure. Dried skins and hides require 24–48 hours or more. Increased mechanical action increases the rate of soaking of the material[12]. Controlled mechanical action is adopted since violent agitation destroys the fibres of the skin. Wetting agents aids in soaking and also enzymes have been adopted although make the final leather slightly empty therefore filling of leather is necessary in the post tanning process. A soaking method using proteolytic enzymes and carbohydrases in the pH range of 5.5 to 10 has been described by[13].

Liming and unhairing

The soaked skins are treated with milk of lime (calcium hydroxide) and additional sharpening agents like sulphides which aids in the removal of hairs, and other keratinous matter. Liming loosens the collagen fibres and improve the flexibility and fullness of the leather. This process helps to swell up the pelt which contributes to the opening up of the fibre structure. Liming raises the pH to 12-13 in which it’s a good environment for the hydrolysis of the amide side chains[14]. If the pH is lower, the unhairing chemistry does not work, because the equilibrium between the non-unhairing hydrosulfide ion and the unhairing sulfide ion is unfavorable. Liming also helps in the splitting of the fibre structure at the level of fibril bundles. This allows for better penetration of the chemicals and more effective reaction. Natural fats are partially saponified, most of the interfibrillar proteins such as albumins and globulins are eliminated, and mucoids are degraded[11].

The loosening of the hair is due the chemical action of the lime liquor on the hair root or base of the hair shaft. This weakening of the hair is dependent on the breakdown of the disulphide link of the amino acid, cystine, which is characteristic of the keratin class of proteins. Degradation reaction, which commences with sulfide attack at the disulfide bond, this is based on hydroxyl ion attack at the methylene group on the cystine side chain[11]. Hair saving method can also be adopted this process target the structure of the hair within the follicle, either the bulb or the prekeratinised zone. The effect is to ensure detachment of the hair from the base of the follicle. Use of enzymes in unhairing have been suggested with the aim of cleaner leather technology[15].

Fleshing

This is a mechanical operation which is done to the fresh side of the pelt to remove adhering fresh which was left after flaying. Fleshing is done manually for lighter pelts which a fleshing knife over the beam, for heavy pelts a fleshing machine is used to remove the fresh. Adequate fleshing allows the penetration of the chemicals in the subsequent processes. Green fleshing reduces the chemical uptake during liming and assists in achieving a uniform liming effect to enhance leather quality[15].

DE liming

The objective of this process is to remove from the limed pelt the lime and other alkalies, used in liming, either by repeated washing in water or by chemical treatment or by both**.** For surface lime it is removed by repeated washing with water but for combined lime it is removed with chemicals such as ammonium salts; ammonium chloride, ammonium sulphate, weak acids; boric acid, acetic acid. The reaction which takes place are as follows for ammonium chloride, ammonium sulphate and boric acid respectively[11].

1. $2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O$
2. $(NH_4)_2SO_4 + Ca(OH)_2 = CaSO_4 + 2NH_3 + 2H_2O$
3. $3Ca(OH)_2 + 2H_3BO_3 = Ca_3(BO_3)_2 + 6H_2O$

The use of carbon dioxide as a deliming agent has also been adopted in developed countries. The gas is sparingly soluble in water, producing acid that can neutralize the alkalinity of the limed pelt[16]. Completion of the deliming process is noted by cutting the pelt with a knife and using an indicator, usually phenolphthalein to determine the “lime streak” in the pelt in which absence of a pink color means complete deliming. Deliming adjusts pH from 12-12.5 to 8-9[11].

Bating

This process helps to make a finished leather which is smooth, flat, flexible, soft and stretchy[2]. It involves the addition of proteolytic enzymes. These proteolytic enzymes open the fibrous structure of the pelt to make it softer. Bating also removes the remaining lime in the pelt. Scuds are loosened and other unwanted proteins are removed and this increase the degree of stretch. Bating de-swells swollen pelts and prepares pelt for tanning. The process is performed at optimum temperatures for the enzymes 35-40 ˚C[11].

Degreasing

Degreasing process is carried out to eliminate the excess of natural fat substances from the skin. If the residue is not removed it can cause fatty acid spues, uneven dyeing and finishing, waxy patches in alum tanned leathers and pink stains in chrome tanned wet blue[17]. High amounts of fat can also cause hardness to touch and loss of physical strength. This process step is mainly part of sheepskin processing due to 30 to 40 % of fat substances output in respect to the raw weight. However, it is an essential operation in leather process to avoid quality loss. Organic solvents are employed as degreasing agents in the 2 to 3 hours lasting degreasing process. Palop and Marsal [18] studied the effectiveness of using lipase enzyme in the degreasing process. They observed that there is increase of the breakdown of the fats when the lipase was combined with protease in the process.

Pickling

The pickling process is primarily conducted to adjust the collagen to the conditions required by the tanning agent in tanning reaction. This process lowers the pH by addition of an acid and salt. The low pH end the bating process and improves the penetration of the subsequent tanning agent and prevents to prevent the rapid combination of the skin substrate with chromium compound [19]. The pickling agents normally used are 5- 10 % common salt or sodium sulphate, and O.6-1.5% acids (sulphuric acid, hydrochloric acid, acetic or formic acid or mixtures). The function of the salt is to prevent acid swelling. The function of the acid is to acidify the collagen, to protonate the carboxyl groups where the reactivity is modified, because the chrome tanning reaction only involves ionized carboxyl groups. The acidic treatment minimizes the negative charge of the carboxyl groups and maximizes the positive charge of the amino groups of the collagen peptides thus making the pelt positively charged[20]. After this process the skin can be shipped or stored for long period of time without deteriorating. Due to the environmental problems which the salts cause, salt free pickling process has been adopted to reduce the total dissolved solids. Recycling and reuse of pickle liquor for the subsequent batches have been studied[21]. Li, Chen [20] proposed a pickling process to reduce or eliminate the use of neutral salts thereby avoiding the shortcomings of the traditional pickling process.

Tanning

This is the process which converts protein collagen of the raw hide into a stable material which does not putrefy[2]. In this process additional crosslinks are introduced into the collagen combining the active groups of the tanning agents to the functional group of the protein. The tanning effect largely depend on the extent of the crosslinking between the collagen molecules and the thermodynamic stability of the crosslinking bonds. The stability is assessed by the determination of the shrinkage temperature of the leather. Satisfactory tanning effect is characterized by complete penetration and uniform distribution of the tanning materials[22]. There are several tanning methods and materials and the choice depends mainly on the properties required in the finished leather, the cost of the alternative materials, the plant available, and the type of raw material. Tanning may be done in many ways like mineral tanning (Chrome tanning, Alum tanning, Iron tanning, Zirconium tanning), Non-mineral tanning (Aldehyde tanning, vegetable tanning, Oil tanning, Resin tanning, Synthetic tanning, Combination tanning) which are discussed later in this paper. After tanning basification is done using sodium bicarbonate to increase the pH to favor the subsequent processes such as retanning dying and fatliquoring[23]. The basification process fixes the tanning material to the leather, and the more tanning material fixed, the higher the hydrothermal stability and increased shrinkage temperature resistance of the leather. The degree of tannage is determined by boil test or using shrinkage testing apparatus where each tannage has its shrinkage temperature. Chrome tanned leather have a shrinkage temperature above 100℃ of as reported by Covington. Vegetable tanning have a shrinkage temperature of 80-85 ℃ depending on the various species of tannins as reported byKuria, Ombui [5]. A research conducted by Shi, Li [24] indicated that wet white leather have a shrinkage temperature of 85 ℃. Combination tannage increases the shrinkage temperature as reported by Valeika, Sirvaityte [25]. Masking is also done using masking agents such as sodium formate, sodium acetate, and sodium oxalate. Masking is the modification of metal complexes, by replacing aquo ligands with other less labile ligands. The purpose is to render the complex less susceptible to additional complexing reactions, including precipitation[11].

Neutralization

Chrome tanned and semi chrome leathers are piled up after basification. Even in overnight piling, the pH drops, indicating the liberation of acid. The source of this acid may be from ionization of neutral carboxyl's, ionization of positively charged amino (-NH_3^+) groups and hydrolysis of chrome itself[26]. Neutralization is an important procedure in making leather, the process removes acidity in the leather aiding in thorough and uniform penetration of dyes. Most of the dyes and fatliqour used are anionic if these negatively charged materials have to penetrate into collagenous fabric, then the collagen should also bear a net negative charge Collagen becomes anionic when H+ of the carboxyl and also of the positively charged amino (i.e. –NH3+) groups are removed by treatment with an alkali. The choice of materials and the control of neutralization degree will have a direct influence on dyeing, fat liquoring and filling. Sodium carbonate, sodium bicarbonate are agents which are used to facilitate neutralization[27]. The leather is neutralized to abou**t** a pH **5.4-6.5** [26].

Retanning

The purpose of this process is to modify the properties and performance of the leather. In Order to make the finished leather level out, full and elastic and avoid the possibility of loose grain it is necessary to use retanning and filling agents[27]. The objectives are to fill the loose portions of the tanned leather, to achieve less shrinking during drying, to improve the penetration of anionic type fat liquors, dyestuffs and finish adhesion and to improve certain specific properties like perspiration resistance, fastness to washing, flammability. The retanning materials are taken into and interacting with the collagen matrix which constitutes the fibre structure in the leather. The interaction can be either chemical reaction, by coating the fibres or by filling the voids between the fibres[28]

The chemicals used are vegetable extracts, resins and syntans. Inorganic mineral substances (chrome, aluminium, zirconium salts) can also be used. Vegetable retanning improves the usable area and increases the thickness of the leather. Plants extracts such as acacia, quebracho, wattle, sumac, hemlock, oak, tara and commercially available mimosa are some of the vegetable extracts which are used in tanning[29]. Acrylic resins are widely used since they have a good selective filling property to improve the cutting value of the leather[30]. Different types of syntans which are used include Auxiliary syntans, Replacement syntans, Acrylic syntans, Whitening syntans, Bleaching syntans with each type of leather giving its own distinct characteristic. The amount of chemicals used is determined by the level of fullness required[11].

Fatliquoring

The leather is fatliqoured to prevent fibre sticking when the leather is dried after completion of the wet processes. This is due to the reaction with the fibrous structure of the collagen with the fatty material. In the wet state the leather is fully lubricated by the water which is held in between the fibre bundles and between smaller fibrils. Now when the water is removed the fibre approach each other and can stick together thus the need of applying fatliqour[31]. Secondary effect is to control the degree of softness and suppleness. One of the results of lubrication is an effect on the strength of the leather. This also helps to confer to the leather with the physical characteristics, such as tensile strength, extensibility, wetting properties, waterproofness and permeability to water vapour and air. The extent of penetration of the oils to the leather determines its properties. It is important to ensure adequate lubrication of the fine fibrils as well as for the coarser fibril bundles. This can be achieved by use of fatliqour emulsions of small particle size capable of penetrating down the hierarchy of the leather structure. If the fatliqour deposits oil primarily in the outer layers, the non-lubricated central core gives springy characteristics to the leather[31].

Fat liquoring is usually conducted with self-emulsifying, partially sulfated or sulfonated (sulfited) oils, which might be animal, vegetable, mineral or synthetic. The sulfated oils are chemically treated with sulfuric acid, which increases the affinity for the tanned fibers. The fatliqour is added inform of an emulsion. The sulfited oils have smaller particles and higher capacity of bonding. Crude oils can also be added to the fatliquoring bath. They are water insoluble, but they are emulsified by the sulfated and sulfited parts. Fleshings from the animal has been used to produce natural fatliqour for the use in the fat liquoring process. This helps to turn the fleshing waste into valuable product for the process and reducing the environmental impact of the otherwise discarded fats[32].

Dyeing

This is the coloring step. Almost any color can be struck on any type of leather, despite the background color, although the final effect is influenced by the previous processes.

Dyes can be classified in different ways such as the method of application where we have Acid dyes, direct dyes, Basic dyes, Pre-metalized or Metal complex dyes, Reactive dyes, Sulfur Dyes. They can also be classified as either natural or synthetic dyes[11]. All the early dyes were natural ones from either vegetable or animal sources. Colored substances from fruits, flowers, leaves, roots, seeds, barks, wood and also galls of plants were extracted and used. Applying dye in solution or pigment, to confer dense, opaque colour, can be performed in the drum or colouring agents may be sprayed or spread by hand (padding) onto the surface of the leather. With the increase of environmental concerns researchers have found many natural dyes thus leading to reduction use of the azo dyes which contain potential colon carcinogens, which is a possible hazard to humans when chronically exposed. Natural dyes are nontoxic and non-allergic to human[33].

Drying and Finishing

After wet processing, hides are usually dried to remove excess water and prepare the skin for final finishing. Drying is considered one of the most important mechanical operation in the leather processing. Drying helps the leather to gain its final texture and flexibility. Tensile strength increases with apparent density and decreases with drying rate. There are different drying methods which are used in the leather processing. The leather can be free hanged in the air in overhead dryers, vacuum drying, and toggle drying. Toggle drying results in improved area yield and better mechanical properties due to the moderate drying temperature[28].

The finishing process includes mechanical treatment followed by application of surface finishes. This is aimed at enhancing the natural qualities of the skin and to cover defects which might have been on the surface of the leather. The finishing of leather can bring different colors and pattern appearances to the surface of the leather which makes it more attractive to the customer. Finishing is done by various materials such as casein, nitrocellulose, polyurethane, acrylic, other components of resin and polymer which are mixed with natural substances like oils, waxes albumins, cellulose esters. The desired color is regulated by use of different dyes and pigments. Different techniques used to apply the finishes includes curtain coating, roller coating, padding and spraying[34].

Leather sector

Leather is one of the most widely traded commodities in the world[35]. Leather industry plays a prominent role in the world's economy with an estimated global trade value of approximately US$100 billion per year on average. The world trade in leather is currently growing the demand for leather and leather products is growing faster than supply.

According to World Bank report 2015, despite owning a fifth of the global livestock population, African countries account for 4% of world leather production and 3.3% of value addition in leather. In Kenya the leather sector contributes to estimated 4% to the agricultural gross domestic products. In 2013, leather exports from Kenya amounted to only US$140 million which accounts for 0.14 % of the world's export. Kenya is rich in leather raw material yet it cannot compete with globally. This can be attributed to inadequate leather processing capacity. Kenya tanning industry is developing and has been identified as one of the most important main earners compared to other east African countries. It is supported by influstructural entities that ensures the delivery and processing of the raw materials[36]. The industry has a high potential to make high quality products that can address social economic problems and create employment and wealth. Estimated 80% of the raw skins and hides are processed up to the wet blue stage and a small percent up to the finished leather. About 10% exported as raw materials. Kenya manufactures an estimated 4 million units of leather products, which is a meagre amount compared to the deficit of about 28 million, considering Kenya's population alone .The optimal growth of the leather industry is dependent on the value addition[37]. High value added leather products can be used for industries like footwear, fashion, furniture, automotive. There has been an increase in the tanneries from eleven to fifteen from 2010 and that's gives a sign of growth in Kenya's leather industry. Most of these tanneries are processing 88% of raw hides and skins up to wet blue and 2% finished leather. The remaining materials are exported as law[38].

As Kenya strives to become an industrialized, middle-income country by 2030, developing the leather and leather industry offers an opportunity for industrialization and diversification of leather products[39]. This can be achieved by expansion of export market for semi-processed, finished leather, leather goods and footwear. The implementation of the government policy of imposing exportation tax of raw materials by 80 % from 2012 has encouraged the value addition. Since there is higher exportation of semi processed leather there is need to upscale to higher value chains to encompass footwear and Leather goods stages to achieve optimal returns enjoyed in global leather markets. Sustained value addition chains are important because they provide attention to customers' needs while reducing the costs[40].

Sources of raw materials

The leather industry supply chain constitutes three stages: production of hides and skins which is a waste from the meat industry, conversion of hides and skins into finished leather and manufacture of foot-wear and other leather products from the finished leather. The raw materials used in the leather industry are hides and skins. The skins are external covering or integument of small animals such as goat, sheep and pig while hides are external covering or integument of large animals such as cow, buffalo, and horse[11]. Bovine contributes the largest source of raw materials[41]. The skins and hides of cattle, sheep, pigs and goats are the main source for the leather production with percentages 65%, 15%, 11% and 9%, respectively[42]. The remaining percentage accounts for the exotic leather. Various sources of leather production in Kenya are cattle, camel, sheep and goat and exotic sources such as ostrich, crocodiles and fish[38]. With an increase in the fish processing factories in Kenya there has been an increase in the production of fish skins as wastes in the fish industries[43]. This fish skins can be converted to leather which can be used to make various leather goods. Having a strong base for raw materials is a key factor for the development of the leather industry. Developing countries are the major producers of raw hides and skins due to climate and adequate husbandry for the livestock. This helps in producing raw materials of good grade which are free from surface defects and other structural deficiencies. This has resulted in the production of good quality leather and leather products. Livestock breeding, quality of flaying, transportation and preservation of the materials also affects the quality of the raw material with education on the flying and preservation methods being a contributor to getting quality raw materials[40].

The raw materials can be supplied to the tanneries as either flesh raw materials, wet salted or sun dried. Flesh raw materials are preferred since they do not require a lot of time to rehydrate as compared to the sun dried materials. Sorting of the raw materials before processing them is important since only quality raw materials are selected for processing thus producing high quality leather[11].

Fish skin

Fish leather are exotic leather types which are yet to gain general acceptance due to the limited literature available. Exploitation and application of fish leather is limited to lack of understanding of the properties of fish leather. The leather has an outstanding natural grain pattern formed by the pockets of the scales which makes it attractive and this has led to the increasing demand of the leather products made from fish leather. The uniqueness of the fish leather gives it a high market value[44]. There are many fish species which are available such as sturgeon, Nile perch, tilapia, salmon, carp, and stingray. Each species have a unique characteristic appearance. Some of these fish skins such as stingray has been used to produce soft leather[45]. In Kenya Nile perch fish is dominant thus it is the most traded and popular with the customers. It is abundant in Lake Victoria. Nile perch expansion has led to increased fishing activities along Lake Victoria. There is increase in the fish processing industries along the shores of Lake Victoria which leads to increased fish processing thus generating a lot of wastes[46]. Production of fish products leads to production of high volumes of byproducts. Disposing and managing wastes is a challenge facing the fishing sector in Kenya[46]. The solid fish wastes make up 30 - 40% of the total production, depending on the species processed. The solid waste is composed mostly of fish head and viscera, skin, scales, dorsal and ventral offcuts[3]. Reportedly, about 150,000 tonnes of fish waste is produced every year and 80% of it is dumped. These by-products are sources of pollution when disposed to the environment especially because they act as breeding grounds for mosquitos and other microorganisms, in addition they are sources of bad odour especially to people living in the surrounding places and also pollutes the environment due to decomposition. The waste generated can be processed into by products and sold to earn the industry money and reduce environmental pollution through dumping of wastes into the environment[47]. The fish skins can be used as raw materials for the leather industry to supplement the available bovine, goat and sheep skins as a new emerging source of raw material. To succeed as a new product fish skin leather must be presented in such a way that it provides a unique appeal to the customers as compared to the other materials. Reports of converting the Nile perch fish skins to leather has been reported in Kisumu but no scientific data has been reported on the characterization of the structural, physical and chemical properties of the fish leather.

Chemical composition of fish skin

Nile perch (Lates niloticus) is a warm water fish species. The length of the Nile perch increases with age with young (less than 80 days old) fish measuring as little as 6.4cm and the largest adult (13+ years old) measuring up to 160 cm long for males and 190 cm female[48]. As the fish grows, the skin proportionally thickens due to the increasing amount of collagen fibers, which will react with the tanning agents and give the characteristic resistance to the leather. The fish skin is composed of collagen fibers that forms alternating layers of right and left helices wrapped about the long axis of the animal. Collagen is a general extracellular structure protein involved in the formation of connection tissue. The fish skin has type I collagen. Collagen constitutes 25% of the total proteins[49]. The collagen differs with the amino acid sequence of the glycine, proline and hydroxyproline. The variation of the amino acids affects the stability of the collagen. Composition of the skin in relation to amino acids has a great influence during the processing of the fish skin and this gives the ability to change the properties of the collagen. Warm water fish species has high amount of amino acids and low content of hydroxyproline[48]. The crosslinking of the collagen is different in various ages since as the animal ages the crosslinking of their collagen increases and the type of cross link changes[48].

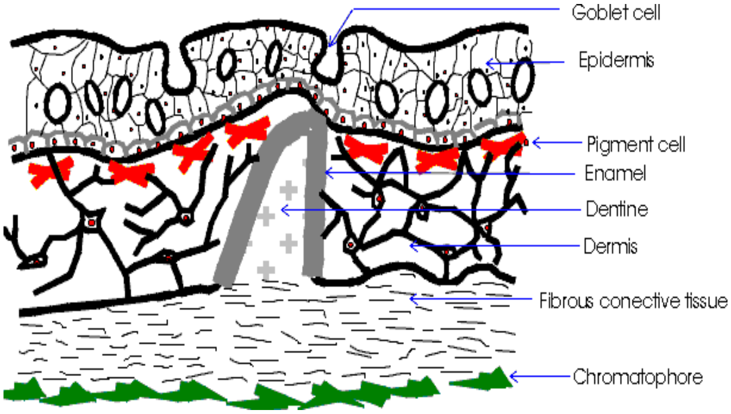


Figure 1. The structure of the fish skin

The Nile perch skin has scales in which the pockets of the scales gives an attractive appearance to the finished leather unlike Stingray which has denticles[45].

II. TYPES OF TANNAGES

Chrome tanning

Chrome tanning is the most widely used tannage in leather industry and it accounts for 85% of the world's leather production. It gives the leather comfortable feel, it's lighter, soft, and brighter and have high hydrothermal stability. Besides, chrome tanning is still the most important and most widely used tanning method in the leather industry due to its outstanding leather quality, good strength and competitive price[50]. But it's a controversial method from the view point of environmental protection due to the presence of the chromium and chloride content in wastewater as well as abundant waste chrome shavings. About 70 % of chromium salt penetrates and the rest remains in the liquor which is discharged for treatment. High chrome exhaustion or recycling of the chrome liquor is recommended to decrease chrome present in the liquor[23]. There are a range of factors which influences the chrome absorptivity. The process parameters largely affect the chrome absorptivity to the collagen. There are two main features of chromium salt which enable it to act as a tanning agent. Firstly, the complexes formed are of intermediate stability, and thus exchange of coordinating ligands can take place comparatively easily. Secondly, chromium has the ability to form polynuclear complexes in which Cr-O-Cr bridges are involved[1].

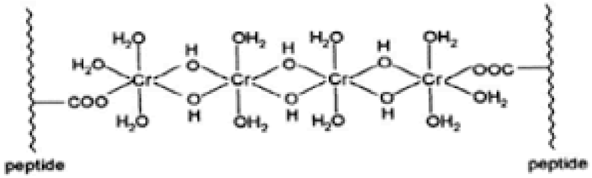


Fig 2. Chrome tanned cross linkages with collagen (protein) of the skin.

The mechanism involved is initial penetration of chromium (III) salt in solution into the pelt and down the hierarchy of the structure. Increasing the reactivity of the basic chromium (III) salt and carboxyl groups of the collagen by gradually increasing the pH of the solution. Creation of unipoint and finally multi point cross linkages, conferring a stable matrix collagen structure[11]. Tanning action increases as pH increases, and no tanning occurs at all when all carboxyl groups of the collagen molecules are protonated[11]. The practical measure of degree of chrome tannage is that of thermal stability (Covington, 1997). At the completion of any tannage the leather is tested to see what temperature, under wet conditions, it will stand. If it will resist 100˚C (boiling water) it is considered to be satisfactorily tanned.

Vegetable tanning

In 18th century before the introduction of chrome tanning method, the options available to the tanners were limited to vegetable tanning. Vegetable tannins are considered less polluting compared to chromium and the oldest known leather tanning agent. Vegetable tanning involve treating the hides and skins with leaves and barks containing tannins. Tannins are water soluble polyphenolic compounds having a molecular weight of 500-20,000 and ability to precipitate proteins and alkaloids[51]. There are two types of tannins based on their structure and properties. Pyrogallol tanning materials or hydrolzable tanning materials, include the tanning materials made from oak wood, chestnut, myrobalan, algarobilla, vallonia, divi divi, nut gall and sumac[52].

The hydrolzable tannins are subdivided on the basis of polyphenolic acid, or acid liberated or hydrolysis, those yielding gallic acid are referred to as gallo- tannins while those yielding ellagic acid are referred to as ellagitannins[1]. Pyrocatechol tanning materials or condensed tanning materials are the tanning materials made from quebracho wood, mimosa bark, pine bark and mangrove bark as well as gambier extract[52]. Their solutions having a pH of between 4.5 to 5. Condensed tannins on the other hand do not breakdown with acids, instead they give more complex compounds under the action of acids to yield tannin reds[53]. Both condensed and hydrolysable tannins have ability to crosslink with collagen to form a non-putrescible and hydrothermal stable leather. The interaction of the vegetable tanning material with the protein collagen can either be Hydrogen bonding of tannin to protein through the phenolic hydroxyl group of the tanning material or binding of tanning material to the protein through the more diffuse electrostatic bonds due to forces known as Vander Waals forces. Different sources of vegetable tanning materials gives leathers different physical properties. Vegetable tanned leathers offers benefits of high tensile and tearing strength , elongation, breathability and insulating properties, capacity to absorbs and transmit moisture, lasting molding ability and flexing endurance[54]. Vegetable tanned leather is used in making heavy leather such as furniture leather, garment leather and shoe upper leather[53].

Oil tannage

Oil has potential as a leather tanning agent for chamois leather. Chamois leather is a well-known product. It has specific uses, such as in high quality gasoline filtration, cleaning and drying optical equipment, spectacles, mirror, and vehicles. This is because of its softness and high water absorbance. The material has to be soft so that it does not scratch the surface to be cleaned[55]. Oil can be from different sources such as fish oil, rubber seed oil, cod liver oil among others. The traditional method of making chamois leather was to impregnate the skins with oil and then hung them in warm stoves to allow oxidation to occur. The excess oil was removed by hydraulic press then washed in warm alkaline water. The principle of modern oil tannage is to oxidize the oil already introduced into the pelt, with the help of atmospheric oxygen under controlled conditions[56]. Long oxidation periods required for making chamois leather places limits on large scale manufacture. Research is being carried out on use catalysts to reduce the oxidation time. The process using ozone to accelerate oxidation of the oil tannage, produced leathers with organoleptic properties comparable to those of conventional chamois leathers. In this approach it has been found that the use of ozone can reduce the oxidation time to 60 min from 10 – 12 days without any impairment in quality [56]. Tanning using fish oil faces an odour problem, caused by oxidized fish oil residues attached to the chamois leather. The odour cannot be removed completely from the leather. Reducing the use of fish oil in the chamois tanning would help to reduce the odour. Rubber seed oil is a vegetable oil which is expected to substitute for fish oil in tanning. The oil will not produce odour and might be able to cross-link with protein in the skin or hide to produce leather[6]. The formaldehyde pretannage helps to increase the penetration of fish oil and protects the pelt from putrefying during oxidation periods[57]. Oil tanning process takes about 12 days compared to chrome tanning which takes approximately 6 hours, and this explains why the technology is not commonly used. The shrinkage temperature which is a measure of degree of tannage, oil tanned leather has been reported to shrink as follows, for the rubber seed oil tanned leather 73 +/- 2°C and 71 +/- 2°C for the fish oil tanned leather[6].

III. ALDEHYDE TANNING

Aldehyde tannage system is used to produce chrome free leather by cross linking the amino groups of collagen with glutaraldehyde or formaldehyde to prevent purification. The crosslinks formed in collagen fiber through the reactions of glutaraldehyde are irreversible. Although it is a tanning method which produces chrome free leather the crosslink between aldehyde and collagen is weaker than the crosslink between collagen and chrome salt[58]. Natural polymers containing an aldehyde or a masked aldehyde group have also been employed for tanning[59]. Pretanning with aldehyde produces leather with a shrinkage temperature range of 70-80 ℃. Aldehyde tanning is often referred to as “wet white” due to the pale cream color it imparts to the skins. Formaldehyde is highly toxic to all animals and human’s ingestion of little solution containing 37% formaldehyde has been reported to cause death in an adult human and also carcinogen[60]. At concentrations below 2ppm it is an irritant to the eyes and has respiratory effects, repeated contact with solutions may cause eczematoid dermatitis. Maximum tolerance limit for formaldehyde in finished leather articles for adults is 150ppm and for children is 75 ppm Glutaraldehyde also has toxicity problems and may cause similar problems[61]. This this method is not normally often used but it can be used with other materials in the process of tanning[58].

IV. COMBINATION TANNAGE

This type of tanning is mainly done to reduce the environmental constrains caused by chromium salts. In this process there is use of less chromium combined with other tanning agent or other tanning materials can be combined to give leather with better properties. The alternative tanning system should not only match the properties of chrome but should also add more value to the leather in terms of special properties imparted by the chosen metal ions. A research conducted by Fathima, Kumar [62] about new system of combination tannage where they explored silica-aluminium-tetrakisphosphonium sulphate showed a significant reduction of emission loads in COD and TS by 41 and 67%, respectively. The shrinkage temperature was recorded to be 86℃ which is higher than that of silica alone[62]. Some of the vegetable combination systems studies include vegetable-oxazolidine[63], vegetable-aluminium[64], vegetable-zinc[65], vegetable-acrylic[66], vegetable-glutaldehyde[67]. Leathers tanned with these combinations resulted to shrinkage temperature values of near 100℃ and they had good physical-mechanical properties adequate for variety of applications.

V. CLEANER LEATHER TECHNOLOGY

With the increasing push by the international consumers and national governments to reduce the toxicity to the environment and limit harmful chemicals in the products lot of research is being done to find alternative processing methods. Cleaner technologies have been adopted in the recent past which have the benefit of saving chemicals, reduction of TDS, BOD, and COD to the effluent, low level of chromium in effluent and lower hazardous air emissions.

Leather processing is divided into three stages (i) pre-tanning or which clean the hides or skins; (ii) tanning, which permanently stabilizes the skin or hide matrix; and (iii) post-tanning and finishing operations, where aesthetic value is added[11].

Raw hides and skin are preserved before processed into leather. Salt preservation is the most used practice globally. This results in the generation of quantities of total dissolved solids (TDS) one of the pollutants that are very difficult to treat consequently. Possibilities of using other methods of preservations have been analyzed in order to reduce the pollution load in the soaking process of leather. Sivabalan and Jayanthi [68] studied the use of plant extracts as an alternative preservation method and concluded that it has the capacity to preserve skin by antimicrobial activity present in the plant extracts[68]. Use of less sodium chloride combined with either silica gel, boric acid, sodium meta-bisulphite showed a great potential as an alternative for sodium chloride preservation. Potassium chloride is a good substitute of sodium chloride without the environmental consequences associated with sodium chloride although it is expensive. Chilling, vacuum electric current and irradiation are some of the physical techniques which can be adopted to replace sodium chloride although they are limited to short term preservation[69].

Soaking is the first step in leather processing and use of enzymes is recommended since it has the advantages of reducing the soaking time, initiating the opening of the fibres. The enzymes used in soaking target broad-spectrum of reactions not specific reaction thus obtaining solubilization[15]. Soaking process alternatives based on counter-current method have been suggested. Use of flesh hides and skins also helps in reducing the total dissolved solids and also reduces the time needed for soaking. The conventional liming and un-hairing process uses calcium hydroxide and sodium sulphide. Due to high amounts of BOD, COD and TS caused by use of lime and sodium sulphide several process alternatives to lime and sulphide mixture have been considered and explored. Enzymatic treatment of leather using proteolytic enzymes which catalysis the breakdown of protein is an alternative method which aids in the reduction of the amount of lime and sulphide. The origin of the enzymes can be bacterial, animal, plant or fungi. The enzymes can be used in hair saving unhairing where enzymes attack the bond between the hair and derma thus lead to loose the hair. Recovering the hair eliminates the discharge load of COD and nitrogen. Immunization of the hair has also been proposed where sodium silicate was used to substitute lime and significant reduction in chemical oxygen demand (COD), biochemical oxygen demand and total Kjeldahl nitrogen were obtained in comparison with the comparative data for the conventional unhairing with hair burning[70]. Re use of the unhairing–liming liquids before discharging them to reduce the concentration of the chemicals was reported and the modified method reduced the environmental impact of the process by 24%, COD was reduced by 50% as well as sulfide which was reduced by 73% when the process water was recycled four times. The use of sodium aluminate as an alternative to calcium hydroxide was tested in the liming process and resulted to good opening up of the fibres and reduce pollution[71].

Conventional deliming agents are ammonium salts (ammonium sulphate and ammonium chloride). These chemicals release nitrogenous pollution to the environment and also release ammonia gas to the air. To reduce these emissions alternatives ways of deliming have been studied. Carbon dioxide deliming can be used as an alternative for the ammonium salts although it has low penetration rate and it is expensive since gas feeding systems have to be designed in the conventional drums[16]. Another alternative for non-ammonia deliming was suggested by Zeng, Lu [72] where they used sodium hexametaphosphate and boric acid to replace ammonium salts. The research concluded that boric acid and sodium hexametaphosphate gave the deliming liquor a pH range of 8-8.5 and thus prevent the risk of acid shock[72].

Conventional pickling process which is done to aid in the penetration of tanning agents uses salts such as sodium chloride[11]. The release of these salts results to environmental pollution thus alternative ways have been studies to prevent this. Salt-free and low-salt pickling as well as no-pickle tanning techniques have been developed to minimize chloride impact in the environment[73]. Application of non-swelling chemicals such as auxiliaries have been studied and treatment with 2% p-hydroxydiphenyl sulphonic acid is a valid alternative to reduce salinity. This auxiliary agent showed non swelling capacity. The residual bath of the pickling process with this chemical had the lowest conductivity and COD values. Also Naphthol 3-6-disulphonic acid reduced the conductivity and COD values of the pickling residual bath when compared with those of the conventional pickling process[18]. Leather tanning is dominated by chromium salts due to the unmatched properties that chromium gives to the leather. Chrome tanned leather has high thermal stability, physical-mechanical property, excellent soft touch and good anticorrosive property[74]. Discharge of chrome can lead to accumulation of heavy metals and this can be toxic to plants, fish and human beings. If chrome (iii) is oxidation to chrome (vi) it causes cancer if human beings are exposed to it. A lot of research has been done either to totally eliminate chrome in the tanning process or reduce the chrome that is drained to the effluent[75]. Vegetable tanning is one of the alternative to eliminating the chrome salts in the tanning process. Many researchers have identified various plants extracts which can be used as tanning extracts[1, 5, 51, 53]. High chrome exhaustion is another alternative which increases the absorption of the chrome into the leather and thus reducing the content of chrome in the effluent. Some of the high chrome exhaustion methods which have been studied include tanning without the addition of float to the leathers, diminishing the amount of added salt and obtaining greater amounts of chrome fixed to the hide. There various aids which helps in chrome exhaustion such as Long chain carboxylic acids, Aromatic polycarboxylates, Silicates of Mg or Al, Polyacrylic acids,Polyamides,Mannich bases,Protein hydrolysates[76]. The recovery of chromium from spent tanning and re-tanning baths provides a significant economic advantage in terms of both its reuse and the simplification of the processing of global wastewaters[77]. Combination tannage where there is use of small amount of chrome salt and other tanning agent can also be used to reduce the amounts of chrome salts in the waste[78].

VI. PHYSICAL CHARACTERIZATION OF FISH LEATHER

Among other things that are used to assess the quality of the leather, physical properties are the most important. The properties are affected by factors such as species, age, weight, sex, skin orientation, source of the material and mainly tanning process[3]. The range of physical properties determines the quality of product. Various physical, chemical and fastness properties are required from leather products depending on their field of use. Some of the parameters used to test the physical properties of leather includes the tensile strength, tear strength, elongation, flex resistance and burst strength. Tensile strength helps to calculate the elongation and percentage elongation which indicates how long the material is stretched before break. The samples for tensile strength are sampled parallel and perpendicular to the back bone. This is because of how the fibers of the leather are aligned, the tensile strength is dependent on the fibre direction. From literature the different fish species have different tensile strengths. Focking, Simoes [3] who processed Nile Tilapia (scale fish) skins with chromium salts obtaining 13.06 N/mm^2, Karthikeyan, Babu [45] also processed stingray fish skin and obtained a tensile strength of 28.05 N/MM^{2,} Taotao, Qiaoqiao [27] who processed sturgeon fish skin and obtained a tensile strength of 19.60 N/mm^2 and according to Pessoa da Silva, Bertoldi [44] who processed cat fish skin and obtained 23.40 N/mm$^{2.}$ The variation of the tensile strength is due to the composition of the collagen and also the different species of skins have different skin structure. The variation can also be affected by the tanning agent used in the stabilization of the material with chromium tanned materials having a higher strength than the vegetable tanned leather. The Nile perch fish leather tensile strength has not yet been reported and that's got to the attention to investigate its strength. Tear strength is a physical property where the leather is exposed to highly concentrated stresses under a specified load. The main aim is to find the amount of force used to break the test piece material. This property is important as it is associated with softness, tensile strength and dome plasticity and helps to evaluate these materials more comprehensively[50]. It is also dependent on the species since from the literature it has been reported that the different species of fish skins have different tearing strengths. Burst strength is also a result of leather deformation under the impact of force. It is usually concerned with the behavior of shoe upper on the durability and lasting of shoe making. Four parameters are measured distention at grain crack, load at grain crack, distension at burst and load at burst. Flex resistance is used to asses durability of the leather used for shoe upper. The material is subjected to a specified amount of flexes and observed for any change. Good flexibility of leather prevents emergence of cracks and deterioration of surface finish after repetitive flexing during a leather items life cycle (IULTC/IUP 20, 2001). Shrinkage temperature determines the thermal stability of leather which can be determined by using shrinkage temperature apparatus or by use of differential scanning calorimetry. Shrinkage temperature varies with different tanning agents. A good leather should have a minimum shrinkage temperature of 75 °C[11].

VII. CONCLUSION

With the largest source of raw materials for leather industry in Kenya being from hides and skins of cattle, goats and ships there is need for diversification. Exotic leather supplements the raw materials although there has not been any commercialization of production of the exotic leather in Kenya. Due to the increased consumption of fish in Kenya there is increased production of fish skins which are normally discarded as wastes. The Nile perch is the most commonly consumed fish species therefore its skin is available. The raw material should be explored to produce fish leather and determine the physical properties which can help predict the final use of the leather

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