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Chapter 1

THE USE OF FISH-SKIN AS A PRODUCT FOR LEATHER MANUFACTURING IS AN UNDER-DEVELOPED BUSINESS OPPORTUNITY IN MEXICO

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ABSTRACT

"The use of fish-skin as a product for leather manufacturing is an under-developed business opportunity in Mexico"

Depending on the natural structure of the fish-skin, once transformed to leather, the product is aesthetically elegant. The natural elegance is further accentuated in fish-hides which have medium to small scales. The finished fish leather product when combined with knowledgeable craftsmen has significant artistic potential.

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Presently, this potential leather source is under-utilized in Mexico, due to an inadequate supply chain, in part due the complex manufacturing process required to transform fish-skin into leather, requiring a high-level of tannery aptitude, as well as, familiarity with the organic compositions of fish-skin.

In this paper, we will discuss the current market and future potential opportunities for leather fish-skin products in Mexico. In addition, we will describe the standard tanning process for fish-skins, while citing examples of value added products.

INTRODUCTION

Production and Trade of Fish Skin in Mexico

The use of fish skin in México is not fully quantified; currently there is little market data regarding the production and foreign trade.

With a market of more than 100 different species[1], in Mexico, during the Christian religious observance of "Lent" which occurs over an eight-week period, culinary consumption of fish is estimated at 250,000.00 tons, with a variation of 100 different species. The species of highest consumption in Mexico is the Sardine which approximately 700,000 tons[2] are captured annually. Other significant species include: Shark at 36,000 tons[3], Squid at 30,000 tons and Tuna at 150,000 tons annually (2013 statistics)

Presently in Mexico, there are no statistics which differentiate the different uses for individual species, as fish-skin production is estimated, as having presenting a significant opportunity for further exploitation.

A summary of the production of fish species is described in the following table:

The most implemented species in Mexico is the Carp with an of 250 grams per unit and an average size of 20-25 cm, of which the skin is considered a waste product, with the bulk of the residues converted into flour

[1] CONAPESCA; http://www.conapesca.sagarpa.gob.mx/wb/cona/18_de_marzo_de_ 2014_ mexico_df

[2] *Dirección de Estadística y Registros Pesqueros*, Sagarpa, http://www. conapesca.sagarpa. gob.mx/wb/cona/seguimiento_mensual_de_la_produccion_de_sardina_20

[3] FAO; *Servicio Nacional de Información de Mercados*

The Carp immediately consumed can be frozen for up to 7 days[4]; but eventually the target is food and not exploitation of the rest of the sub-products or residues.

Table 1. Capture 2012

SPECIES	VOLUME (KG)	VALUE (PESOS)
DogFish	4.507.848	76.735.019
Tuna	97.512.600	1.108.075.543
CatFish	4.382.095	115.089.219
Shark	16.766.322	304.336.214
Mojarra	74.126.299	1.384.183.511
Carp	26.177.188	325.044.900

Source: CONAPESCA, RNPA, SAGARPA, MEXICO 2014.

Skins Market in Mexico

The demand for fish skins has been steadily increasing. There is a growing acceptance of fish-leather for the production of articles or items such as vases, cup holders, centerpieces, wallets, belts, boots, etc., of which these products are manufactured in countries like Peru and Costa Rica, Colombia, Mexico and Ecuador[5].

The species most commonly used for fish-skin leather include: Tilapia, Shark, Skate, Trout, Salmon, among others.

Brands like New Balance footwear (tennis), Adidas and Puma among others, are betting on using fish skins in some applications.

There is ever greater presence of fish skin used in the manufacture of clothing as jackets, shoes, and clothes made by designers.

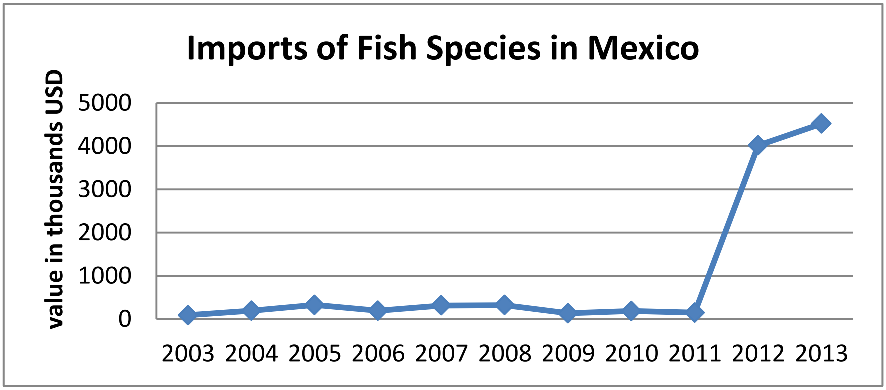
Tilapia Market in Mexico

On an international basis the fish species of Tilapia is the second most implemented in the production of aquaculture feed, over taking Salmon and Catfish.

4 “La carpa y su manejo”, SAGARPA, (colección Nacional de Manuales de Capacitación Pesquera), Delegación Tlaxcala, México. 1994.

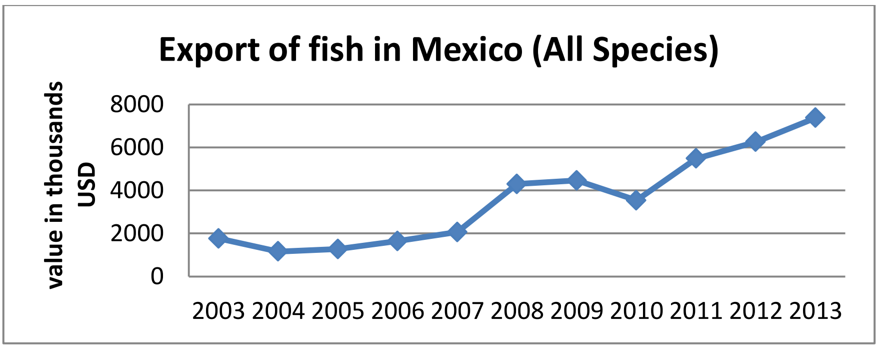
5 Moda y mar, “la piel de pescado” enero 2014. http://moda111.blogspot.mx/ search/label/leather.

Table 2. Imports of Fish Species in Mexico



Source: Secretaria de Economía, SIAVI 4; 2014.

Table 3. Export of Fish in Mexico



Source: Secretaria de Economía, SIAVI 4; 2014.

During the World Congress of Tilapia in 2013, the estimated data cited that 4 billion metric tons are annually manufactured, with China, Indonesia and Egypt as the leading manufactures and Mexico ranking within the top 10 producers of Tilapia.

Approximately 10% of tilapia is produced in fish farms (aquaculture).

The largest importers of Tilapia in 2013 were the United States, Mexico, Saharan Africa, Russia and the European Union.

According to a 2010 study conducted by the "Committee System Tilapia Production of Mexico, A.C." the domestic production of Tilapia ranked second with 71,018 tons manufactured.

One of the main purposes of the committee is to strengthen the supply chain by increasing productivity, which then will support the market growth objectives.

The study is a prospective analysis of 2020 on the tilapia market in México, highlighting some viability aspects, including the methodological process for integrating of a robust supply chain.

The analysis concerning the tilapia, for 2006, estimated that 30% of world fisheries were used for different purposes than food[6].

Internationally Mexico ranks as one of the top aquaculture manufacturers of shrimp, tilapia and oysters, with 25% of the market being Tilapia.

Almost 100% of domestic aquaculture production is intended for human consumption.

Aquaculture production in Mexico is almost 100% intended for use as food, the industrial production is not reported. In the case of tilapia in Mexico, is used 100% of the production for human consumption.

The domestic consumption of aquaculture products per capita increased by 28% between the years 2004 and 2008, with an average of 14 kg(s) per person.

At least 60 species of Tilapia have been documented; in 2009 international Tilapia production was estimated on 1.15 million tons with moderate growth increase.

Current market interests include the exportation of Tilapia to Latin American Countries, though in the case of Brazil, Mexico and Colombia, domestic production has satisfied market demand.

The largest Latin America producers of Tilapia are Brazil, Honduras and Colombia.

Ecuador is the leading producer of Tilapia for export to the United States with production ranging from 20,000 tons to 90,000 tons annually.

For Mexico, the Caribbean and the United States Tilapia farming is relatively new[7]. In Mexico Tilapia aquaculture was introduced during the 1960s. Tilapia production in Mexico has increased gradually; by 2003 a production of 61,500 tons was recorded, in 2008, 71 thousand tons[8], were produced.

Tilapia in Mexico is primarily from China, Taiwan and the United States, especially in the form of fish steaks for human consumption.

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[6] FAO, 2009.
[7] Tilapia 2020 "Prospectiva del Sistema – Producto Nacional de Tilapia en México". 2010.
[8] (CONAPESCA, 2008).

More than 36,000 tons of Tilapia is imported from China, whose aquaculture performance is 5 to 8 tons per hectare, over a period of 8-10 months of harvest.

In Mexico significant demand for Tilapia which has coincided with a modest increase in domestic production. The current trade balance is negative for Mexico; by the volume and value of exceeding 140 million USD, therefore highlighting an opportunity for increasing domestic growth to satisfy domestic demand.

The domestic market for Tilapia mainly consists of fresh, unfrozen fillets, sold in the major urban centers of Mexico City and Guadalajara, via intermediaries who import the fish from cultivation sites located in Michoacán, Veracruz and Tabasco.

In consideration of the increased demand for manufactured leather goods containing Tilapia skin, which remains underexploited and due to the cataloging of the fish hide as a waste material, the market opportunities for fish leather remains vast and undefined.

ADDED VALUE, DESIGN AND INNOVATION WITH FISH SKIN

One of the primary objectives should be the development of a production and supply-chain process that transforms the raw waste material into a value added product. Use of the recovered fish skin further expands the productive aquaculture chain.

The finished leather fish-skin is stylistically exotic comparable to the skin of other reptiles, the main aesthetic being the vacant cavities which on contained the scales. The size and richness of the texture depends on the species and manufacturing process applied to the leather. Its main feature is the natural aesthetic design of the cavities left by the scales of the fish. The variety of sizes and richness of texture reliefs depends on the type of scales species and the finishing process applied on the leather.

The size of the skin depends on the species and weight at the time when the fish is harvested. A 750 grams Tilapia fish usually will provide a square decimeter per-side. To maximize the yield of the skin during harvesting, a proportional cut must be taken from the entire material, thereby minimizing waste. The modular pieces of fish-leather are joined together with glue or stitching depending on the artistic outcome desired.

Figure 1. Dorado skin grain pattern.

Figure 2. Tilapia skin grain pattern.

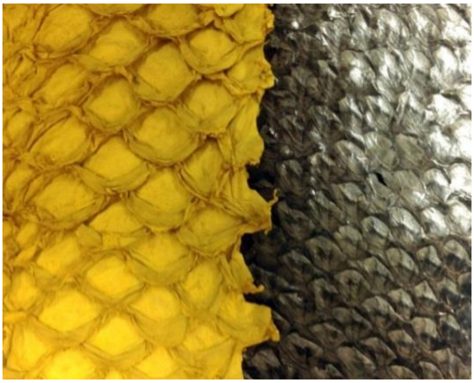

Figure 3. Snook Fish leather in crust and with glaze finish.

Figure 4. Carp Fish leather in crust and with glaze finish.

Figure 5. Shoulder bag made with Tilapia Leather. Design Elisa López; manufacturing development workshop, CIATEC, León, Guanajuato.

Figure 6. Cowboy boots made in patchwork, with Snook fish from the front to the heel. Made in Leon, Guanajuato, Mexico. By Rio Grande Boots.

Figure 7. Box of Tilapia Skin Panels with contrast stitching union.

Color is one of the most significant considerations leather design and with fish-skin there are no restrictions on colors which can be implemented, providing designers with ample design opportunity based on consumer preferences.

The color is seen differently depending on how the surface is textured, the more extensive the texture is, the richer and fuller the color will appear.

The strength of the fish skin is the result of the fibril entanglement and thickness. In physical testing, the tear strength, a 1.25 thick Snook skin has a resistance range from 12.6 to 7.1 kg and a 0.5 mm thick Tilapia skin has a resistance range from 3.2 to 2.1 kg., in both cases, the highest values occur longitudinally. For comparison, the Mexican Standard of Safety Shoes (NMX-S-051-1989) determines the materials used in the construction of shoes, a 10 Kg minimum and for the material used as lining 3.0 kg and fish leather is equally as tough as cowhide, pig or goat with equal thicknesses. However, it is recommended that in order increase the strength and shape of the skin, especially when worn in an adverse environment, the addition of an interlining is recommended.

Figure 8. Color Palette.

Figure 9. Slipper made of fish skin, by Alexander Wang, Spring 2012.

Presently, the major fashion houses focus their designs accessories. Due to increased media attention footwear companies now have greater exposure in the fashion industry, once only reserved for accessories.

Recently, fish leather has made appearances on the footwear and accessory collections of famous fashion designers.

Alexander Wang of New York was honored with the CFDA (Council of Fashion Designers of America, Inc.) as the Best Accessory Designer, which was subsequently followed by the launch of the Prêt-à-Porter collection where the fish leather had a leading role in the design of handbags, wallets and shoes.

But What Makes a Product Successful in the Market?

The implementation of fish leather into wearable fashion merchandise and accessories is increasing driven by incentive of the designers to produce modern and alluring compositions.

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Basic Fish Skin Composition and Process

Fish have a natural epithelial skin layer which is derived of cellular constitution without the presence of blood vessels. The epithelial layer contains a mucous lining of glandular origin which may have greater or less abundance depending on the fish species. The mucous lining serves as a protective shield serving protective functions uniquely found in fish species.

The mucosa acts as a shield, by preventing the penetration of pathogens agents (bacteria, parasites, fungus). Moreover, the mucosa protects the skin from abrasion caused by adverse water conditions (pH modify, salinity, temperature, etc.).

When the water conditions exceed the species metabolic level, the mucous is released and the organism responds producing an increased quantity, with greater density or viscosity as required, over time the mucous naturally.

Other functions of the mucus lining include: the capacity to regulate water permeability, the maintenance of a proper osmotic pressure, in the form of a filter between two different concentration levels (a diluted state to a concentrated state). When the lining is compromised the fish can become dehydrated or over-hydrated then the surrounding water.

The fish skin has two primary layers the epidermis which is derived from the embryonic ectoderm and the dermis (or corium) is derived from the mesoderm and neural crest.

The epidermis is composed of several layers of flattened cells. The thickest layer is the active growth and multiplication zone (germinal layer functioning as a boundary between the body and the environment, so it has a very important role as it provides protection, fluid exchange and sensitivity. The epidermis serves a significant function by minimizing the water skin flux in conjunction with specialized cells in the gills.

The dermis is unique and is composed mainly of extracellular components.

Interspersed between the flattened cells of the epidermis are numerous mucous glandular openings which extend into the dermis. These glands produce the mucus that covers the body of the fish. The mucus decreases the frictional resistance while swimming, while fish expelling microorganisms and irritants when accumulated become toxic. In some species, the mucus clots and triggers the expulsion of solids. The mucous cells also function as a source of chemical communication.

The neural crest cells reside in the epidermis and dermis interface and in the proximal layers of the epidermis. These cells are called melanocytes and produce brown, gray or black melanin granules. Other tones can be produced by overlapping the melanin structures: iridescences refract light, chromatophores provide color and vascularization of the skin where the blood provides tones of pink or scarlet colors. The pigment migrations within the chromatophores are responsible for the color changes as fluctuating feature of the fish which is regulated by nervous and hormonal metabolic mechanisms.

Other feature of the fish skin includes glandular complexes are which less common, including: poison glands, light organs. Luminescence in fish is provided by the presence of bacteria in the skin of fish or by self-luminescence. Some extension areas of the skin such antenna with specialized functions, serve a sensory purpose typically implemented to locate and identify food. While other skin extensions have protective or ornamental functions. One of the most proximate features of the skin of the fish is the presence of scales, though it is important to note that all fish species have them. Depending on the species there intermediate states can be found in which the scales only partially cover the body. Other fish do not have scales but alternatively have bony features. Structurally, there are three different types of fish scales: cycloid, ctenoid, placoid, and ganoid. The scales are the organic construction material for many other biological features of fish such as: spines, plates, surface of the skull-bone and the operculum.

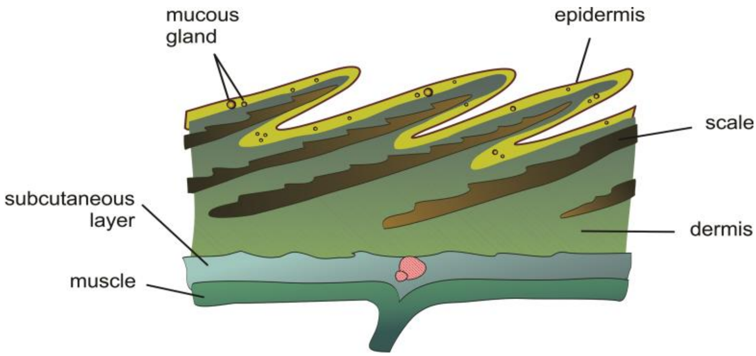

Figure 10. Transverse section of a fish skin.

Fish skin is comprised of the following layers:

a. Cuticle
b. Epidermis
c. Basal Membrane
d. Dermis
e. Hypodermis

a) Cuticle

It is the outermost layer consisting of mucopolysaccharides; this layer is extremely thin, only averaging a single micron thick. The physical consistency of the cuticle varies greatly from one species to species. The cuticle layer contains various defensive elements: specialized immunoglobulins, free fatty acids and a very important substance called lysozyme, all if which have anti-pathogenic properties. The cuticle is comprised of epithelial cells and mucous cells with cup-shaped shape.

b) Epidermis

The central component of the epidermis is the: “Malpighi” fiber cells. Unlike mammals, the epidermis is composed of cells capable of dividing by mitosis. The mucus excretory cells are found in the epidermis, with their density varying depending on the species and environment. In the epidermis are found other types granular cells. Furthermore in the epidermis layer appear cells such as lymphocytes and macrophages, both with immune defensive capacity. In the proximal region of the epidermis contains the germinative layer, which is a cell proliferation zone.

c) Basal Membrane

The Basal Membrane very thin layer and is basically a bonding layer located between the epidermis and the dermis, with no distinguishing feature.

d) Dermis

The dermis consists of two sub-layers: a spongy layer, which is formed by a sparse of collagen network, as this spongy layer contains pigment cells, leukocytes and scales. Below the dermis is the Compactum Stratum layer, which consists of a dense interwoven matrix of collagen, which is responsible for the strength of the skin. The pigment cells are called: “chromatophores” and are categorized by different types: (i) Melanophores are cells containing melanin having asteroid shaped features; (ii) Lipoforos contain soluble pigments, organic dissolvent´, of which there are two types: the Erythrophores (red pigments) and Xanthophores (yellow pigments), these two pigments cannot be synthesized by the fish, and must therefore be added to the diet; (iii) the Iridophores and (iv) the Leucophores, provide silver coloring, while Guanine, while the Leucophores which are located in the abdomen provide a whitish color.

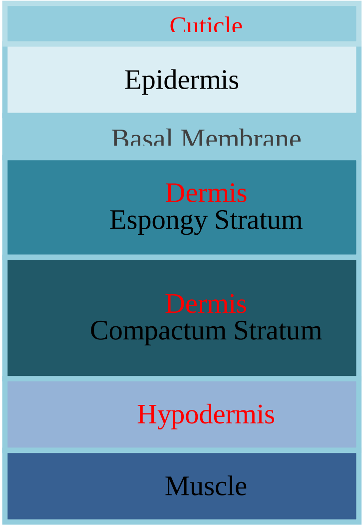

Figure 11. Layers of fish skin.

e) Hypodermis

The hypodermis layer is an enervated tissue, poorly vascularized and with adipose consistency. The hypodermis layer´s thickness is related to the species and the type of food consumed. This layer is often a place where infectious processes are started.

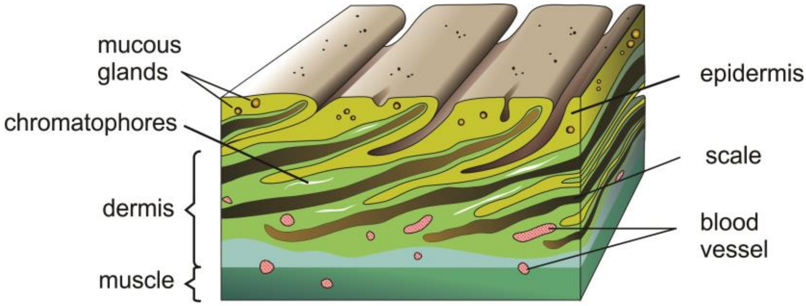

Figure 12. In this drawing we can see the sections of the fish skin and observe their characteristics.

Fish Skin

In general fish, dermis consists of a relatively thin upper layer of diffuse tissue area called compact layer. This area is rich in collagen fibers which are disposed in parallel form to the papillary layer and in a cross-linked form sheets, but not forming cross-linked networks as in the case of mammals.

Once deceased, the mucus is no longer offers effective protection and after a certain time, bacteria that consume the nitrogen of the mucus as a nutrient, leading to the degradation of the epidermis.

Figure 13. A big raw tilapia skin.

Figure 14. Raw snook skin.

The Collagen and Its Physicochemical

Collagen the main fibrous protein present in animals and are the primary connective tissue, constituting approximately one-third or more of the total body protein. The larger and heavier the animal is, greater the fraction of collagen is which contributes to the collective proteins in the body. It has been said that a cow retains its shape, mainly due to the collagen fibrils of the skin, tendons and other connective tissues. In cow skin, the collagen fibrils form a cross-linked network, with remaining portions in an almost perpendicular direction to the papillary layer.

The most abundant amino acid in fish skin is glycine. Glycine is collagen molecule formed by a chain consisting of 8 amino acids of glycine, plus 4 amino acids of proline, plus 2 amino acids hydroxyproline, plus 1 amino acid of arginine or lysine, plus 4 amino acid either tyrosine, aspartic acid, glutamic acid and histidine, and is structured repeatedly until it completes the polypeptide chain.

Although the collagens from different species vary in amino acid sequence, most contain about 35% glycine, 12% of proline and 9% of hydroxyproline, an amino acid that is rarely found in different collagen proteins. Proline and hydroxyproline differ from other amino acids because in its “R” group is a substituent in the amino group. The secondary structure is deduced to form a triple polypeptide chain which turns left, and is adhered by hydrogen bonds.

Figure 15. Side flesh of a tanned fish where the fibers are observed in a plane parallel to the surface and crossed almost 90 ° layers.

Figure 16. Fleshing machine.

The hydrogen bonds are formed from a carbonyl group consisting of a polypeptide chain and an amino group from an adjacent chain. The hydrogen bonds are common in the configuration of proteins and are the fundamental chemical basis for understanding the complex behavior of collagens reaction to pH, temperature and other physicochemical variables.

Furthermore, polypeptide chains of collagen contain a the hydroxyproline amino acid, permitting the formation of alternative of hydrogen bonds via a junction, such as a carbonyl group located in the pyrrole ring of hydroxyproline, providing further stability to the secondary structure by comparison to other proteins. It should be noted that with an increased number of hydrogen bonds, an increased temperature is required for complete denaturation.

Tanning Skin Fish

Fish skin has a smooth layer with moderate pigmentation, to which the scales are firmly adhered.

In comparison to bovine and swine hides, harvested fish-skins are very small, and, therefore, any fleshing process should concentrate minimizing waste.

The skin should be classified by species, size and pigmentation.

The desirable characteristics of the fleshed fish-hides prior to tanning should include:

1. The hides are clean and healthy
2. Flesh content is minimized
3. Irregularities due to poor fleshing techniques are minimized
4. The hides should be uniform in size

The tanning process occurs on 6 stages, which only the first stage occurs in the slaughter house, and the subsequent 5 stages occur within the tannery facility, these stages are included the: Beam House, Tanyard, Retan, Color, Fatliquor, and Finishing. Each stage is divided in 17 processes that are listed in Figure 17.

Figure 17. Stages of tanning process.

Conservation

a) Skinning and cleaning
b) Fleshing
c) Conservation (salting, freezing)

Skinning

Risk of contamination should be minimalized during filleting and transport to the conservation section.

It is recommended once the skin is removed from the animal; the hide is immediately placed into clean and suitable containers to prevent contamination with the residual flesh that found on the ground surface of the slaughter house.

Fleshing

Fleshing is critical step in ensuring proper preservation. The first step of the fleshing is to extend and lie flat the skins on a clean table with the flesh-side facing upward. This is then followed by removing the excess flesh with a knife or scraper, using care to prevent puncture holes and terminate marks on the hide, thereby decreasing the value. Tails, thorns and thick regions which the salt cannot penetrate should be removed and can adversely affect the preservation process.

Conservation of the Hide

Types of Conservation

1. Brine

Brining consists of soaking the skins in a container of salt saturated water for later use, or until the salt has been absorbed, reaching equilibrium, followed by draining and storing cool climate controlled environment

2. Dry Salt

After filleting and fleshing, the skins are washed in water, and allowed to drain for 10 minutes. After draining, the hide is placed flesh-side upward and coated in fine grain salt. The quantity of salt used is equal approximately 50% of the total weight of the skin, and distributed uniformly. Afterwards the hide is further drained on an inclined table for a minimum of two hours. Lastly, a smaller quantity of salt is applied and the hides are stowed in pairs with the flesh sides facing inward.

It is advisable to apply 50% or more by weight of salt on the skin. After that, let the skin drain in an inclinated table for 2 hours at least.

3. Freezing

The washed skins are drained and are stowed in pairs with the flesh sides facing inward. Then stored frozen at a temperature below 0^{0}C.

4. Storage

Dry salted preserved hides should be stored in a controlled cool and dry environment and, if possible, refrigerated until use. Warm and fluctuating temperatures facilitate degradation. Special attention should be paid that no putrefaction has occurred. Poorly fleshed hides cause improper chemical saturation in the subsequent processes.

Beam House Operations

a) Soaking
b) De-hairing and Liming
c) Deliming, Bating, Bleashing, Defating.

Soaking

All wet processes must be carried out in wooden, plastic or stainless steel drums, at the correct speed and with different equipment for each stage of the procedure. Alternatively, if specialized drums are unavailable, plastic buckets with sufficient stirring may be implemented. The purpose of the soaking is to clean the hide while removing salt and other impurities.

Abundant water quantities should be provided to ensure sufficient saturation of the hide. When implemented in conjunction with a surfactant and a bactericidal will further accelerate the process by removing the natural fat and other contaminates. In addition, a small quantity of sodium carbonate or salt can be added to assist with dissolving the globular proteins. The surfactant is a helper for soaking, accelerates the process and partially removes the natural fat that, in joint with bactericidal product, leaves the skins clean of dirt. The purpose of the rehydrating the hides is to reestablish flexibility. Should the hides still have scales, a rehydration process is necessary followed by a dry rolling. Depending load size typical dry rolling times are between 30 minutes and 2 hours. Care should be taken during the drying rolling process to ensure that the hides do not get heated or damaged.

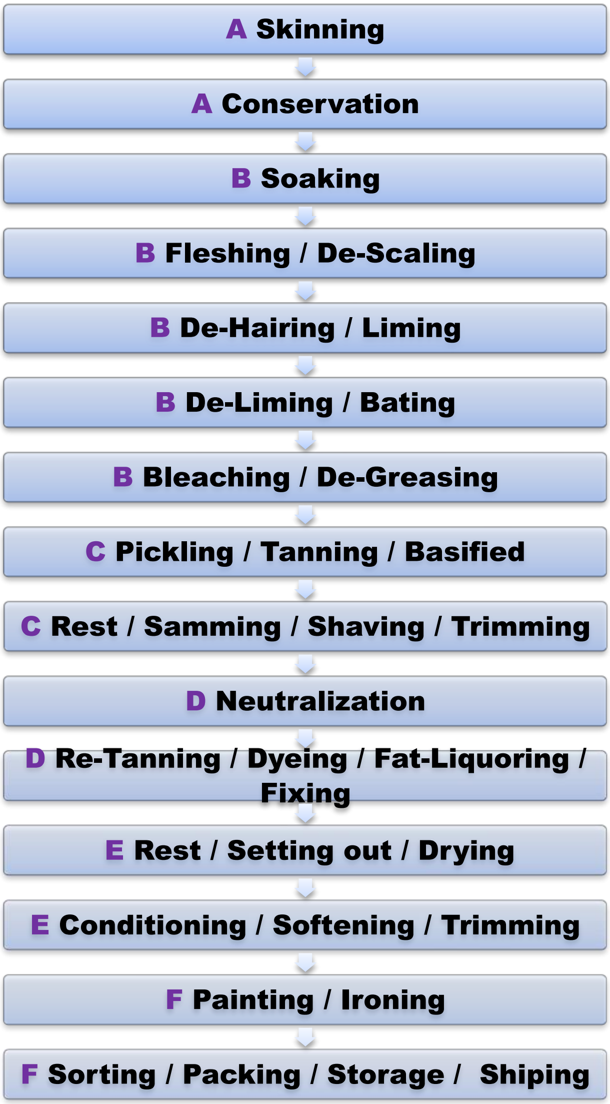

Figure 18. Diagram of tanning process.

Figure 19. Tanning pilot plant.

Figure 20. Tanning drum, made with stainless steel and clear acrylic face.

De-hairing (De-scaling) and Liming

The De-hairing process aims to remove the gelatinous pigmented layer along with any remaining scales. Combining sodium sulfide with a strong alkali (lime) triggers swelling, causing a charge repulsion between the protein molecules, allowing water to permeate.

Typically this process takes between 12 and 24 hours. To open the spacing between the fibers and achieve a uniform smoothness, depending on the species, the liming process can take place over a one to two day period. A proper liming process is essential for the remaining tanning and lubrication process

Figure 21. Pilot size wood tanning drum.

De-liming, Bating, Bleaching and De-greasing

The purpose of the de-liming process is to eliminate the lime absorbed by the hide, so that bating can take place. A swelling annulment is achieved when equilibrium between the liming bath and interior of the hide has been reached. In this process, sulfate salts or ammonium chloride, supplemented with some bisulfite are implemented. Phenolphthalein is used for process control, as a pH indicator which turns violet when a level higher than 8.5 is reached. The degreasing (rendering) action is achieved by the action of pancreating proteases and bacterial-type enzymes. After rendering the hides are washed once or twice with sodium bisulfite or for a stronger effect potassium permanganate, or other surfactants. This process usually takes over 1 to 2 hours using one of more baths, depending on species.

Tanning

a) Pickling
b) Tanning
c) Basified

Figure 22. Laboratory (Reactor) stainless steel tanning drum with opened door.

Pickling

The pickling process raises the pH to between 2.5 and 3.0 allowing the tan chroming to occur. It is important to note that the hides are sensitive to acids, so the implemented acids should be 10 times diluted in a saline medium, to prevent acid swelling and damage.

The addition of acid should be done while the drum is rotating and after the salt bath has achieved a density greater than 8^{a}Be. The drum should be rotating a low speed (10rpm) so that the hides receive a proper Consider explaining what “tapping” means achieving the wanted pH values, otherwise it may only achieve a: “dead tanning”, whereby tanning has only occurred on the surface of the skin, failing to penetrate the interior fibers.

Tanning

The tanning of hides prevents putrefaction, which is anaerobic decomposition. Tanning can be achieved using different compounds including: vegetable tannins, mineral salts, such as chromium, aluminum or zirconium and synthetic tanning agents such as phenol derivatives, naphthalene or modified by aldehydes. These reagents have tanning action either as filler for fibrillar skin structure or as direct reaction on collagen. The tanning method implemented is dependent on the desired leather characteristics For example, a chrome tanning process will create leather tear-resistant, voltage resistant and temperature resistant properties, while the other types of tanning have decreased resistant. Other tanning components provide excellent properties such as: fullness, sweat-resistance, compactness, the permitting of exotic colorings (dyeing or whiteness). However, internationally more than 80% of hides tanned are processed with chromium, due to its versatility and low-cost.

Basified

The tanning process should be complemented with a locking tanning material. In the case of tanning with chromium, a weak alkali combined with organic tannins and a weak acid such as formic acid. Both materials must be diluted 1 to 10 in water. In both cases, the resulting pH should be around 4.0.

Wet Finishing

a) Shaving and Trimming
b) Neutralization
c) Rechroming
d) Dyeing
e) Fat Liquoring

Shaving and Trimming

After tanning, the skins must be stowed, separately, for one or two days to reach peak adhesion and completion of the chromium molecule. The purpose of this process is to give the leather the required final thickness. Lastly, the leather is processed in a downgrade machine, which is 50 inches width, after the leather has been mechanically drained by pressure between two rollers wrapped in felt. If a samming machine is unavailable to drain the leather, it is recommended to place the skins outdoors, in a shaded area for a few minutes until they reach 50% moisture or in absence of a measurement tool, or until the leather has a consistency form permits machining. Shaving removes the remaining residual flesh,. Should the proper equipment be unavailable for this process, it possible to adjust thickness manually using moisture resistant sandpaper or with emery.

Neutralization

While curing, the chromium adheres to the collagen fibers causing a release of acid, decreasing the pH of the leather, so a neutralization process is necessary for the interior surface.

The complexity of the tanning process is largely dependent on the type of leather being manufactured. An exceeded neutralization of the pH will loosen the fibers, resulting, poor penetration of the re-tanning, anilines and oiling, leaving the leather with problems like stains, brittleness and with drying and finishing issues. This process is completed using smooth alkalis such as sodium or calcium formate and sodium bicarbonate or ammonium. At the conclusion it is necessary to soak the leather in a bath, for 20 to 30 minutes, at this point, the final pH should be between 4.5 and 5.0 for firm leather and greater than 6.0 to smooth leather. The pH control is monitored using a potentiometer in the bath.

Re-Tanning

In the re-tanning process the fullness of the leather is increased, manipulating this process can result soft or hard, elastic or rigid and smooth or rough leather. This is achieved by adding specific materials like vegetable tanning agents, minerals, organics, resins or polymers, which do not override the character of chrome tanning process. There is a great diversity of products that serve as tanning agents which are mostly of a synthetic origin.

Dyeing

While curing, the chromium adheres to the collagen fibers causing a release of acid, decreasing the pH of the leather, so a neutralization process is necessary for the interior surface. Anionic dyes are the most commonly used and are suitable for dyeing re-tanned leather. The composition of the dye is adjusted according to the depth of penetration required, based on the thickness of the leather. Some dyes are blended with metals to increase their hardness, while others blended with acids to intensify the color.

Fat-liquoring and Fixing

The fat-liquoring process can be aligned to the dyed leather or achieved separately in a new bath, after the anilines are fixed. The objective is to give the leather softness desired; to achieve a uniform lubrication a variety of oils should be used to achieve a symmetrical balance thereby providing a soft, delicate touch with a natural appearance. Fat-liquors are typically anion-active, suitable for the manufacturing of water-oil emulsions, but also for cationic surface effects. To prepare the fat liquoring bath, the emulsified oil must be at least 5 times its weight in water, at a temperature of 60^0C-70^0C. If the emulsion is prepared in the drug with cold water in oil and diluted, the emulsion will break causing the grease to be deposited on the surface, resulting in greasy leather. A wide variety of oils may be implemented, animal oils provide high softness (especially oil fish and neats-foot), Vegetable oils provides a dry, medium-firm texture, while mineral oils facilitate a more solid leather. Sulfitation administers a deeper oil penetration and stability even in a salty or acidic media. The sulfated and sulfonated oils have less stable emulsions but provide greater fullness and surface effect, while synthetic oils and phosphates provide increased stability and robustness. At the conclusion of the process, a greasing is required to insure an adequate adhesion of the materials, typically using small percentage of formic acid or another equivalent active material. Allowing coating to penetrate the leather 15 or 30 minutes and then afterwards washing out the access for 5 or 10 minutes to remove any unbound material, doing so prevents staining.

Drying (And Pre-finishing)

a) Drying
b) Softening

Drying

At the conclusion of wet finishing process, and prior to commencing the drying process the leather is allowed to cure for 12 hours to ensure the complete reaction of the materials. Drying process significant modifies the characteristics of the leather as dictated by the reduction in humidity and surface contraction. Less obvious changes, include: variation in the isoelectric points, changes in the formation of the inter-fiber bonds, the migration of soluble substances which were not properly adhered to the surface. Should the leather be dried outdoors, the leather will shrinks, shrivel and becomes rigid.

To insure the desired features remain intact drying the drying process the leather should be placed on a flat, clean, uniform surface. Fast drying causes a low-quality leather, while a slow, controlled drying, results in high-quality leather. Prior to commencing the drying process, best manufacturing processes recommend draining and stretching the leather, using roller. Doing so can eliminate 50% of the permeated water. In addition, measures should be taken to prevent excessive shrinking of the leather, for example, the drying temperature should never exceed 40^0C. The completion of entire drying process should take no longer than 12 hours. The objective is to have an approximate moisture content of 12% to 14%. The temperature to work with the leather should never exceed 40^{0}C to prevent leather from drying out and get hard during the entire process, which should not be more than 12 hours.

Softening

Once dried, the next process is the softening. This process adjusts the smoothness according to the desired traits. Doing so, may require an additional step where the leather is moisturized and covered for two hours before applying friction or tension, by mechanical means or friction. The moisture content of the leather, prior to the softening process, should be uniform and around 14% and 18%. Also is possible to soften the leather implementing a dry tumbling method, of which the duration will depend on the desired softness a typical tumbling drying times lasts between 2 to 8 hours. Most of the time, this method of softening should conclude with a tensioning step, lasting approximately 2 hours, against a flat surface to decrease skin elasticity while smoothing the surface.

Finishing

The softened fibers are ready for the finishing process which consists of the application of an aqueous and solvent borne resin applied by brush or sprayed, in a direction which maximizes uniform absorption. Normally, the leather received two uniform light applications with a drying process in between the two applications base. Once dried, the leather is ironed at a low temperature with minimal pressure, on a heated glass plate at 60^{0}C and 60 atm. After ironing, the leather receives a third layer of light base, once dried, the leather is further protected by applying a layer of an aqueous top or glossy lacquer solvent, if necessary the process is concluded with additional ironing. Fish leather is has a high intrinsic beauty, so the finishing process should be the minimal necessary to achieve acceptable protection without risking deterioration of its natural beauty. The most natural finishing process are based on casein and waxes, and only reinforced by small quantities of special resins (dry touch), without pigments or with small amounts of organic pigments.

Below are formulas to tanning the skins used in the products presented. Although it described in a generic formula, we have noted example materials, without implying that they are the only, or have better properties against similar products. The formulas cited have been used for a long time, however, preliminary testing is highly recommended to make the necessary adjustments to the raw materials, prior to producing the initial first batches.

RECIPES

ARTICLE	Fish Skin		PROCESS:		1 Beamhouse	
PROCESS	%	MATERIALS	Time Min.	Temp. º C	pH	Notes
Raw Material: Salted skins						
Pre-soaking	200	Water		t. a.		
	0.1	Bactericide				Busan 85 (Buckman)
	0.5	Surfactant				Borron JU (TFL)
Rest			60			
Move			60			
Drain						
Soaking	200	Water		t. a.		
	0.1	Bactericide				Busan 85 (Buckman)
	0.5	Surfactant	60			Borron JU (TFL)
Rest			30			
Move			60			
Rest overnight						
Control process						
Scaling and Fleshing						
Liming	200	Water		t. a.		
	1	Sodium Sulfide	45			
Rest			30			
	1.5	Sodium Sulfide				
	3	Calcium hydroxide	45			
Rest			30			
	3	Calcium hydroxide	45			
Rest			30			
Move			45			
Rest overnight						
Drain and Rinse						
Rinse	200	Water				
	0.5	Ammonium Sulfate	15			
Drain						
Deliming	200	Water				
	1.5	Ammonium Sulfate				
	1	Surfactant				Decaltal R (BASF)
	0.5	Sodium bisulfite				
	0.5	Surfactant	60			Borron JU (TFL)
Control Process						
Drain						
Degreasing	200	Water				
	0.5	Surfactant	30			Borron JU (TFL)
Drain						

Recipes (Continued)

ARTICLE	**Fish Skin**		**PROCESS:**		**1 Beamhouse**	
PROCESS	%	MATERIALS	Time Min.	Temp. º C	pH	Notes
Bleaching	200	Water				
	4	Salt				
	0.6	Potassium permanganate	10			
	100	Water				
	4	Salt	20			
Drain						
	200	Water				
	2	Sodium bisulfite	20			
	2	Sodium bisulfite				
	2	Salt	20			
Drain	200	Water				
	1	Sodium bisulfite	20			
Drain and Rinse						
Pickling	200	Water				
	15	Salt	15			
	0.5	Formic Acid	20			Diluted 1:10
	0.7	Sulfuric Acid	60		2.5	Add three parts every 15 minutes
Control process						Court
Rest overnight						
Tanning	6	Chrome Tann agent 33%B	60			Baycrom 33 (Lanxess)
Cutting Control						
Basification	0.45	Magnesium Oxide	8 hours		3.8-4.0	Cromeno FN-1 (TFL)
Control Tanning						
Drain and Stowed						
Rinse	200	Water		t. a.		
	0.3	Tensoactivo				Borron JU (TFL)
	0.2	Oxalic Acid	30			
Drenar						
Pretanning	150	Water		t. a.		
	2	Synthetic Chrome	40			Tanesco H (TFL)
Neutralized	1.5	Sodium formate		t. a.		
	1	Neutralizing agent	30			Tanigan Pakn (Lanxess)
	0.5	Sodium Bicarbonate	30			Control pH
Drain and Rinse						
Retanning	100	Agua		t.a.		
	2	Acrylic Retannage	30			Leukotan 1028
	6	Filler Retannage				Sellatan LV (TFL)
	6	Bleach Retannage				Sellatan FL Liq. (TFL)
Rinse	200	Water		t. a.		
	0.3	Tensoactivo				Borron JU (TFL)
	0.2	Oxalic Acid	30			

ARTICLE		**Fish Skin**	**PROCESS:**		**3 Wet Finishing**	
PROCESS	%	MATERIALS	Time Min.	Temp. º C	pH	Notes
Drenar						
Pretanning	150	Water		t. a.		
	2	Synthetic Chrome	40			Tanesco H (TFL)
Neutralized	1.5	Sodium formate		t. a.		
	1	Neutralizing agent	30			Tanigan Pakn (Lanxess)
	0.5	Sodium Bicarbonate	30			Control pH
Drain and Rinse						
Retanning	100	Agua		t.a.		
	2	Acrylic Retannage	30			Leukotan 1028
	6	Filler Retannage				Sellatan LV (TFL)
	6	Bleach Retannage				Sellatan FL Liq. (TFL)
	2	Rosin Retannage				Tergotan RD (Trumpler)
	2	Proteinaceous Retannage	90			Trupotan TFP (Trumpler)
Fatliquoring	5	Mixture Fatliquor				Leder soft SGA(ILCD)
	2	Sulfited Fatliquor	45	50		Leder Soft MK (ILCD)
Fixing	0.8	Formic acid	20			Diluted 1:5
Drain						
Rinse	200	Water	5			
Drain						
Dyeing	200	Water				
	2	Dispersant Retannage	20			Sellasol TD (TFL)
	3	Dye	45			
	1	Formic acid	30			Diluted 1:5
Drain and Rinse						
	300	Water				
Fixing	0.8	Fixing Agent	20			Sellafix WS (TFL)
Drain						
Drying Fixed, Staking						

ARTICLE	**Fish Skin**	**PROCESS:**	**4 Finishing**
MATERIALS	Preparation		PROCESS
	1st	2nd	
Wather	55	55	Apply 2 x Preparation 1, Dry
UR 1701 (Polyurethane Resin Dispersion (Stahl))	25	20	Iron 60°C, 120atm
FI 1950 (Wax Dispertion (Stahl))	5	5	Apply 2 x Preparation 2, Dry
LF-4247 (Proteinaceous Binder (Central Kimica))	15	20	Packing

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