Training Toolkit: Courses and Exercises.
Unit 2: Modern Production Tehnologies for Leather

WP 2.1.

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1. Introduction

INNOLEA project aims to fill an apparent gap in the area of specialized services for the leather sector with the establishment of four leather centres in local Universities, two in Jordan and two in Egypt, utilizing the experience and expertise of EU partners in the area of services for the leather sector.

Through the creation of these centres and the further tasks that will be implemented in this project, the leather sectors in Jordan and Egypt will be offered access to business development services, such as quality testing, product certification, training, fashion trends, production organization, BtoB and funding opportunities, and subsequently the Jordanian and Egyptian leathers sector will have a valuable ally for its further development.

The project also aims to create and maintain a link between Universities and businesses of the leather sector that will foster innovation and the manufacturing of high value quality products, as well as further cooperation between EU and Jordan and Egypt Universities and leather businesses.

The project also aims to help encourage the Egyptian and Jordanian governments to favour the establishment of leather centres within universities and to promote research and projects between EU and Egypt and Jordan universities in the leather sector, by creating a research innovation and training network, which will continue to operate after the end of the current project.

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2. UNIT 2: Modern Production Technologies for Leather

2.1. Objectives

1. To acquire technical competences and skills on tanning process development
2. To acquire key skills and competences
3. To acquire knowledge on the different types of leather, their properties and applications
4. To be able to implement properly all different steps in the leather processing
5. To know in details all tools, machines and instruments used for treating and processing leather

2.2. Lesson 1: Raw hides and skins – slaughterhouse and curing operations

Author: Joaquim GAIÃO - CTIC

- Raw skin preservation methods
- Slaughterhouse operations
- Curing operations

2.2.1. Leather: History and Origin

A tanner is someone who transforms animal hides or skins into leather. Tanners exist since ancient times and will continue to bring their contribution to Society as long as meat will constitute the basis of our diets.

The sacrifice of animals for meat production yields as a by-product a hide or a skin. The dermal envelope is taken off the carcass through flaying shortly after the stunning and giving death to the animal. Without tanners, the hides or skins would have to be disposed off with considerable costs for the Society. They are instead recovered from destruction for serving as the fundamental raw material for the production of leather.

Hides and skins are fascinating natural structures of organic material. Collagen fibres are naturally woven into a tissue with properties that man has not been able to reproduce artificially. A cross-section of a hide or skin reveals bundles of fibres increasing their density towards the top. This structure is what gives the leather its breathability, strength and flexibility. The tanner simply ensures that this wonderful material that nature has created is preserved from decay and put at the service of man for the production of shoes, garments, gloves, belts, leather goods, furniture, car and airplane interiors and many other applications.

Processes for converting animal skins into leather have been known to man for at least 100 000 years. Our Stone Age ancestors used smoke, oils and fats to preserve skins. Later, it was found that the bark and fruit of certain plants were very effective tannins.

In the Middle Ages, two distinct processes came to predominate: vegetable tanning in pits with vegetable materials; and tawing with alum, a naturally occurring mineral form of aluminium sulphate. It was not until a hundred years ago that the chrome-tanning process was discovered. This breakthrough offered the first rational, cost-effective means of manufacturing leather on a industrial scale.

The advantages of chrome-tanned leather, such as its versatility and its resistance to shrinkage at high temperatures, opened up new areas of application for leather and made it possible to mass-produce leather shoes and garments for the first time. Full vegetable tannages became restricted to special applications such as sole leather, and aluminium tanning processes fell into disuse for many years.

In the past few years, the increasing environmental awareness of the public at large has resulted in a controversial, emotional discussion on the use of heavy metals such as chromium in the manufacture of leather. Legislation concerning the dumping of solid waste has been tightened up, and the costs of treating tannery effluent and exhaust air have begun to make their mark in the balance sheets of leather manufacturers. The avoidance and recycling of waste become important topics of discussion for leather industry and its suppliers in the chemical industry, and the development of new, environmentally friendly products and processes has become a priority in research and development.

The purpose of these more environmentally friendly products and processes is to reduce the levels of potential pollutants contained in tannery effluent, exhaust air and solid waste, and to allow savings in water, energy and man hours to be made without impairing the quality of the leather.

2.2.2. The relation between Leather and Meat Production

The leather industry may be regarded as a bridge between production of the hide or skin as a by-product of the food industry and its manufacture into shoes and other leather goods, for which it provides a basic raw material. The technologies and skills involved in the production of meat and those required in the production of usable goods from leather are widely different.

The hide or skin is in immediate need of some form of preservation from decay. Once this is accomplished it can be shipped great distances or stored until used. The cured hide and skin, regardless of source, is an article of international commerce. The demand for a particular type of hide may have no relation to the supply. The amount and type of meat in the diet of the people determines the supply of hides.

2.2.3. Slaughterhouse and curing operations

Flaying

Flaying is normally carried out in abattoirs with the main objective of separating hides or skins from the carcass of the animal. Flaying has an important impact on leather production that is not often taken into consideration at the abattoir. A poorly flayed hide or skin may result in a downgrading in leather production with important economic impact.

Flaying is done after ripping. This operation must be performed with symmetrical cut patterns along the lines shown on the figure.

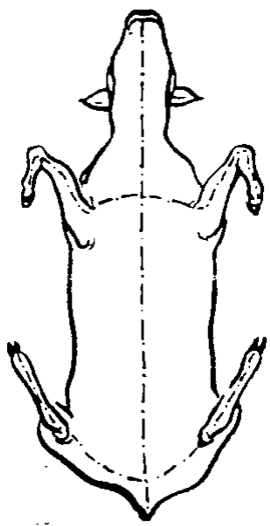

Figure 2.1. Flaying ripping cuts

Ripping is generally followed by a series of cuts in order to separate the skin from the carcass in just the amount necessary to allow the hide to be pulled by mechanical means (standard procedure in Europe).

Modern mechanical flaying prevents flaying cuts and damage to skins commonly found in hand flaying procedures. In the case of small animals using compressed air can facilitate flaying. This compressed air is blown between the skin and the carcass helping the required separation.

Trimming

Trimming is performed to eliminate parts of the hide or skin that have no commercial value for the tanner. Another reason to eliminate undesirable parts such as nostrils and shanks is because of these parts are usually highly contaminated with bacteria that can cause and spread putrefaction throughout the hide/skin.

More recently the BSE crises and other epidemiological diseases have imposed a special treatment for hide/skin trimmings. If these parts of the hide are not trimmed at the abattoir then the tanner must face the burden of ensuring specific methods of disposal for these residues.

The most convenient situation would be for trimmings to be disposed of by the abattoir since this is not the only residue in the same class that needs to be eliminated (the abattoir must account for e.g. elimination of inner organs of the animal). However commercial reasons often interfere with this process leaving a situation that is not favourable for the tanner (the elimination of the hide trimmings has a cost and a trimmed hide has a lower weight – therefore a lower value).

To add up to this situation two standards are usually referred to when trimming is concerned. There is an ISO standard (ISO 2820) and a British Standard (BS 3935). Both of these standards make different interpretations of the correct pattern of trimming. The British Standard trim pattern is similar to the one used by the North American leather industry. These patterns are represented below:

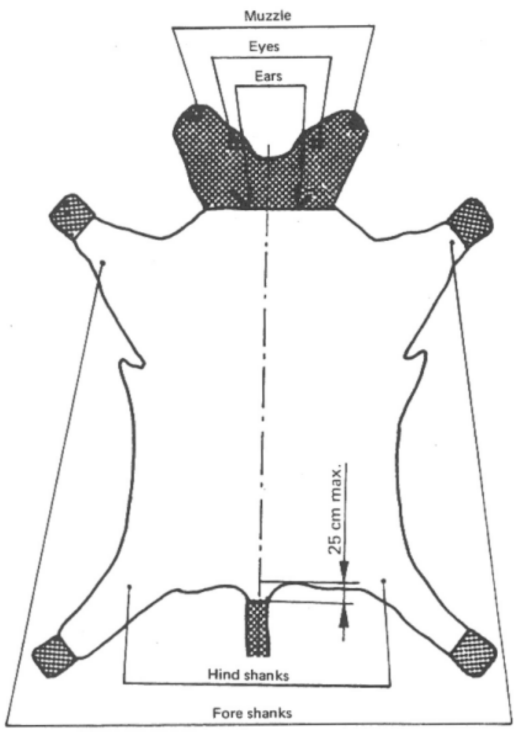

Figure 2.2. Pattern of trimming according BS 3935

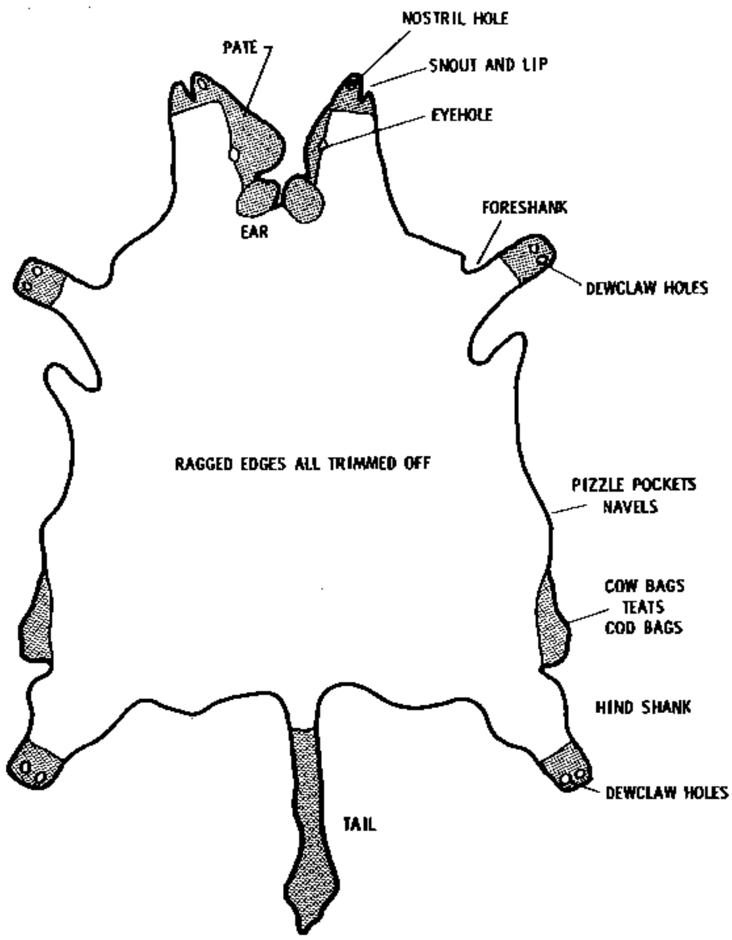

Figure 2.3. Pattern of trimming according ISO 2820

The ISO standard differs from the British Standards mainly on the trim pattern of the head.

The final decision on the trim pattern to be adopted must be negotiated by the tanner taking in consideration his production requirements.

2.2.4. Raw hides and skins

Parts of hides and skins

Hides and skins characteristics vary also according to the animal type. Apart from these differences we can represent the average shape of a mammal hide/skin in the following drawing. The shaded areas represent the parts of a hide/skin that have no commercial value for the tanners. The highlighted area represents the usual shape that can be found in the earlier stages of leather manufacturing.

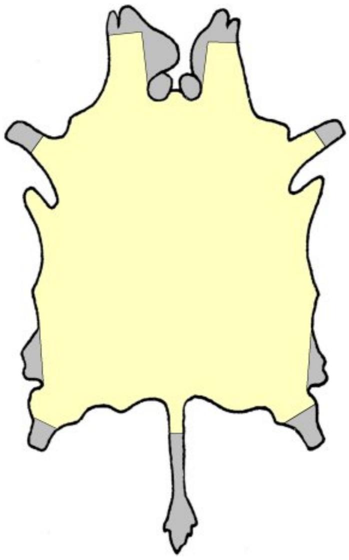

Figure 2.4. Average shape of a mammal hide/skin

This shape can still be divided according to specific production requirements.

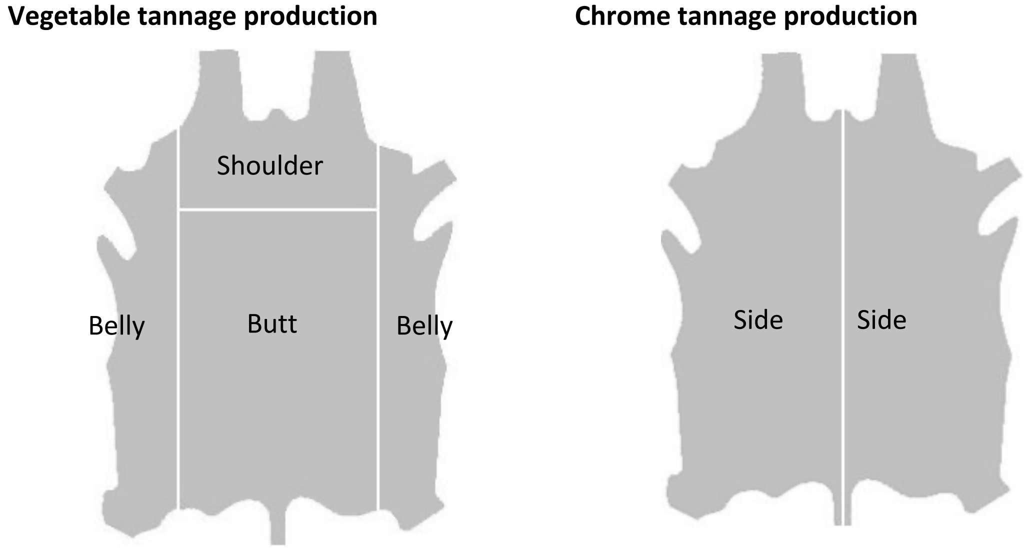

Figure 2.5. Normal cutting areas of a hide according the type of tannage production

Bellies are regarded as the structure with the loosest fibre structure whilst the butt presents a compact fibre structure (therefore ideal for sole leather production).

In chrome tannage (usually for shoe upper production) the differences in fibre structure can be somewhat reduced in production. The main reason for having sides instead of butts, bellies and shoulders is the need to increase the cutting yield for shoe upper cutting. This yield increases with an increased area available for cutting.

In the case of upholstery production area plays an even more important role. Therefore, hides and skins used for this purpose are not divided at all. This, however, requires an entirely new set of production machinery compatible with such a large bovine hide size.

Hides and skin structure

Understanding how the skin can function in these many ways starts with understanding the structure of the 3 layers of skin - the epidermis, dermis, and subcutaneous tissue. The epidermis is removed on soaking and liming, subcutaneous tissue is eliminated through shaving and splitting whilst undesirable constituents of the corium are eliminated in bating and throughout the other operations of the Beamhouse.

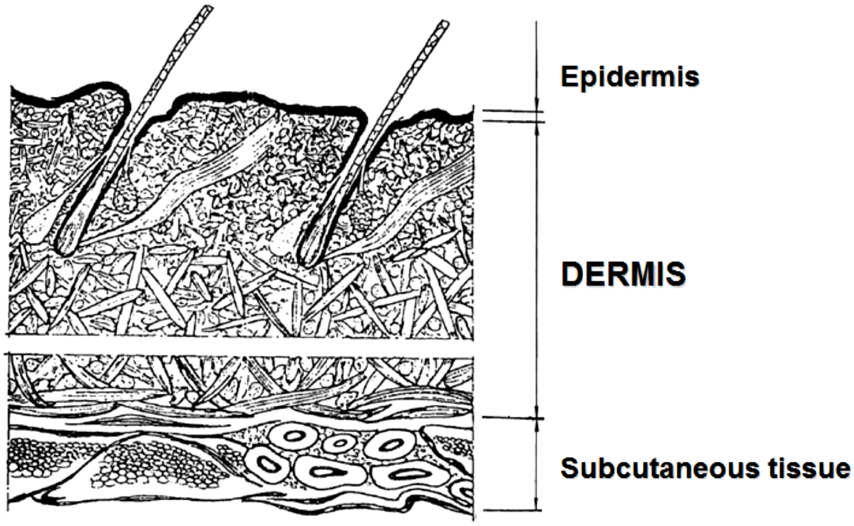

Figure 2.6. Main layers of skin

Epidermis

The epidermis is the outer layer of skin. It contains 5 layers.

From bottom to top the layers are named stratum basale, stratum spinosum, stratum granulosum, stratum licidum, and stratum corneum. As the cells move into the higher layers, they flatten and eventually die. The top layer of the epidermis, the stratum corneum, is made of dead, flat skin cells that shed about every 2 weeks.

Epidermis accounts for approximately 1% of the total hide/skin thickness.

Dermis

The dermis also varies in thickness depending on the location of the skin. The dermis is composed of three types of tissue that are present throughout - not in layers. The types of tissue are collagen, elastic tissue, and reticular fibres. The two layers of the dermis are the papillary and reticular layers. The upper, papillary layer, contains a thin arrangement of collagen fibres. The lower, reticular layer, is thicker and made of thick collagen fibres that are arranged parallel to the surface of the skin.

The dermis contains many specialized cells and structures. The hair follicles are situated here with the erector pili muscle that attaches to each follicle. Sebaceous (oil) glands and scent glands are associated with the follicle. This layer also contains sweat glands, but they are not associated with hair follicles.

Blood vessels and nerves course through this layer. The nerves transmit sensations of pain, itch, and temperature. There are also specialized nerve cells that transmit the sensations of touch and pressure.

The dermis accounts for approximately 85% of the total hide/skin thickness.

Subcutaneous Tissue

The subcutaneous tissue is a layer of fat and connective tissue that houses larger blood vessels and nerves. This layer is important is the regulation of temperature of the skin itself and the body. The size of this layer varies throughout the body and from person to person.

Subcutaneous tissue accounts for approximately 15% of total hide/skin thickness.

The dermis or corium is the most important section of hides and skins for the tanner. In fact a simplified objective of the tanner is to eliminate other constituents (see Section 1.1.5) leaving collagen.

The epidermis is removed on soaking and liming, subcutaneous tissue is eliminated through shaving and splitting whilst undesirable constituents of the corium are eliminated in bating and throughout the other operations of the Beamhouse.

Differences between various types of hides and skins

Leather can be made of a wide range of animal types. Currently the European leather business if mainly focused in producing leather from the following animal origins:

- Bovine
- Sheep
- Goat
- Pig

Other types of animals used for production of leather that can be found in European markets may include Reptiles and fish leathers or others.

2.2.5. Leather by Animal Type

The younger the animal the thinner and smaller the skin, the smoother and finer the grain structure and the less likelihood of damage by diseases, scratches, sores, mites, etc. The more natural the feeding and living conditions, the better the quality. For example, over-feeding gives greasier, weaker skins and starvation thin, weak, misshapen skins, showing skeleton marks. The female skin is usually finer-grained than male and the fibre structure looser, especially in the flanks, giving a somewhat softer, stretchier leather. The less hair or wool there is on the animal the tougher and stronger the resultant skin, especially the grain of the skin.

Bovine

Bovine hides are highly dependent on the size, age and nature of the animal concerned. The terms “bull” and “cow” denote full-grown male and female animals, and “ox” and “steer” the castrated male. “Veals” denote the skins of younger animals, while “calf” refers to youngest bovine animals.

Raw hide weight (and its relationship with size and age of the animal) has an important impact on hide quality and aptitude for specific leather products. A small hide of a calf will show a better grain quality and a compact fibre structure. At the opposed edge a hide of a large animal will most certainly have a loose fibre structure and an overall low grain quality.

Calfskins are a by-product of the dairy industry. These skins are highly valued because of the fine grain structure and usually command three to five times the price of heavy cattle hides. Since calfskins are a by-product of the dairy industry, they are a relatively small source of leather-making raw materials.The main uses of bovine leather are in the footwear industry (uppers, sole, etc.), upholstery, automotive leather, saddlery, leather goods and a small percentage for clothing.

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Ovine – Sheepskin

Sheepskins can be used in a tannery for producing wool-on sheepskins or dewooled leather products. The widely differing characteristics of sheepskins depend on the breed of which there are many, and the amount of wool can weigh more than twice as much as the skin proper. According to their purpose in the tannery sheepskins are selected mainly according to wool quality and size. Sheepskins tend to have a loose fibre structure (this loosens with age of the animal) and a high percentage of fat (especially around the neck region).

Ovine skins are primarily used for clothing (wool on or dehaired) and bookbinding but there are also common applications of sheepskins in footwear, upholstery and leather goods.

Goatskin

Goats are hardy animals that can live on a wide variety of foods, that's why they are adaptable to difficult climates and are popular in Asia, Africa and South America. The original sources of many of the goatskins are villages of widely diversified areas, so the quality varies greatly. Goatskins are closer in properties to bovine rather than ovine. Goatskin fiber density is higher, also is more tightly-fibred than sheepskin and their fat content is usually lower. Due to their compact fibre structure goatskins are usually used for glove and shoe upper leathers.

Pigskin

The main characteristics of pigskins are their high fat content and their hair (called bristle). Another important property of pigskins is that there is no separation between the corium and the subcutaneous tissue (mainly a fat layer). A pigskin is easily differentiated from other types of leather due to their hair follicle distribution. The hair/bristle penetrates through the usable thickness originating holes in a peculiar pattern that is typical of this type of leather. Pigskin leather can be mainly found on shoe uppers and lining, clothing articles as well as upholstery.

There are three general types of pigskin coming from three widely different sources:

1) Wild boar (or Peccary); 2) European pig; 3) United States pig.

Typical grain of different types of skins

Bovine **Ovine** **Goat** **Pig**

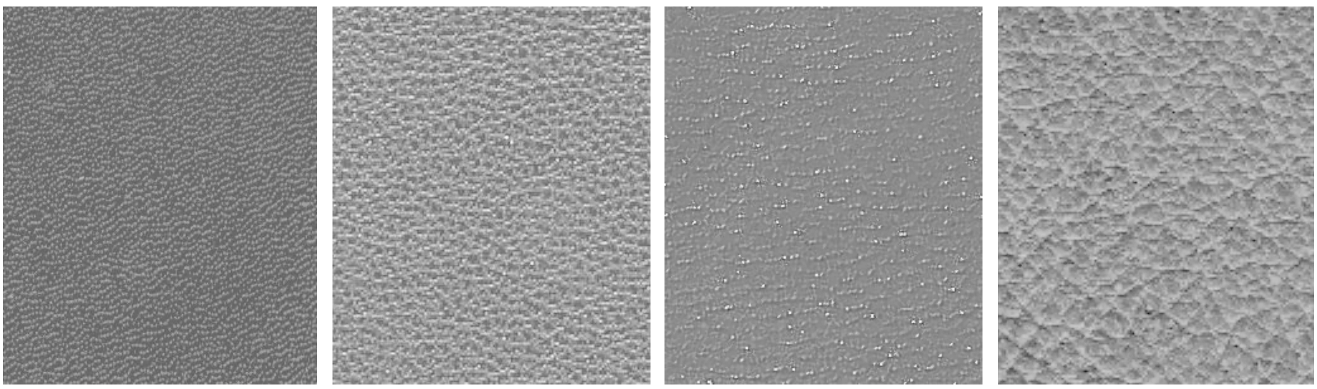

Figure 2.7. Typical grain of main types of skins manufactured

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2.2.6. Chemical composition of hides and skins

Chemically speaking, hides and skins have the following elemental composition:

- 50 % Carbon (C),
- 25 % Oxygen (O),
- 17,8 % Nitrogen (N)
- 7 % Hydrogen (H),
- small quantities of mineral salts and sulphur (S).

As to the biological composition of raw hides and skins, typical values are as follows:

- 65 % Water
- 33 % Proteins,
- 0,5 % Mineral substances,
- 0,5 % Other substances (such as pigments, etc.)
- Fats, with an approximate content of:
  - 2% in bovine,
  - 2 to 10 % in goatskins,
  - 5 to 30 % in ovine
  - 4 to 40 % in pigskins.

Water is therefore one of the main constituents of raw hides and skins. From the 65% water roughly 20% of it is combined with collagen fibres therefore it does not contribute to make the hide/skin feel wet. The remaining water is found loose in-between fibres.

From the protein content of raw hides and skins, the average composition is approximately:

- 94 to 95 % collagen,
- 1 % elastin,
- 1 to 2 % keratin
- The remainder are non-fibrous proteins.

2.2.7. Curing hides and skins (short and long term preservation methods)

Once the hide or skin has been removed from the animal, it is subject to degradation from cellular enzymes from within the skin and from enzymes produced by the bacteria and fungi from the environment. The surface of a live animal is covered in bacterial and fungal spores whilst a recently flayed hide or skin will have its flesh side contaminated by bacteria and fungi from the dung as well as from the air and floor of the abattoir.

Once the animal is slaughtered the metabolic defences are halted and the decomposition of the hide or skin begins. The decomposition process does not affect all areas of a hide or skin to the same extent. It depends on the degree of contamination and moisture of specific areas. Decomposition will remain undetected until a later stage (where significant damage and economic loss has occurred).

An indicator of the degree of decomposition is hair slip and a typical ammonia smell originating from the degradation of proteins. Decomposition is highly affected by environment temperature. In colder climates hides and skins are less subject to putrefaction. In warmer climates the danger of putrefaction is significantly higher because the degradation process will take place at a much faster rate.

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The function of preserving rawstock is to stop all types of degradative enzyme activity. Curing is one type of preservation method where rawstock is treated with salt. Preservation is normally achieved by inhibiting growth and action of bacteria (or fungi) and hence preventing the production of the degradative enzymes.

Bacterial putrefaction can be prevented either by stopping the growth of bacteria or the action of the degradative enzymes. This is normally achieved by one of two ways:

- Killing the bacteria, e.g., biocides.
- Slowing the growth or activity of the bacteria, e.g., cooling.

Most methods of preservation used for rawstock utilise the second method, examples include salt, where the moisture content is reduced preventing bacterial growth, and ice where the cold temperature reduces the rate of growth of bacteria or activity of bacterial enzymes.

There are several curing methods available that can be classified according to the lifetime of the protection envisaged.

Therefore, curing methods are often referred to either short term or long-term curing.

Short term curing

The aim of these methods is to preserve hides or skins for time periods that do not exceed 3 to 4 days. The objective of these methods is to allow sufficient protection time in order to transport hides or skins from slaughterhouse to the tannery.

These systems are usually based on freezing/chilling techniques that are commonly applied for preserving carcasses. They are usually cheaper than long term preservation methods and are often regarded as more environmentally friendly because with this technique the use of salt is avoided.

Short-term preservation methods are:

- Ice
- Chilling/Cooling
- Biocides.

Ice is used either for rapid cooling of the rawstock followed by processing as fresh within four days, or as a method of rapid cooling and prevention of bacterial putrefaction prior to salting.

Another short-term preservation method is chilling/cooling. This process can be carried out in several ways:

- by spreading the hides immediately after stripping on a clean marble floor with the flesh side in contact with the cold floor
- by processing the hides immediately after stripping in a mixer containing chunks or cubes of ice
- by passing the hides immediately after stripping through a tank of glycol-cooled water and adding ice to the storage container
- by using CO_2 snow
- by using refrigerated storage units.

There are, however, several restrictions when using short-term preservation methods such as the use of ice and chilling/cooling:

- ideally the slaughterhouse must be relatively close to the tannery (not overseas)
- the raw material must be processed almost immediately (depending on the icing/cooling method, between one day and twenty days)
- raw stock cannot be bought in great quantity when prices are lower

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- the transport costs can be greater due to either extra weight (ice) or the cost of refrigerated units
- the energy consumption can become prohibitive if the hides are stored for more than one week. The system of collecting/trading hides in any individual country or region may not suit the use of short-term preservation methods; for example, if a substantial proportion of hides are imported or exported, the system may not be practical/economically viable.

All the above points can militate against short-term preservation as it can increase the cost of the raw material. In practice, chilling can be adopted in all countries, but in some countries it is less cost effective than in others.

'Biocide' is the general term which refers to both bactericides (which are effective against bacteria) and fungicides (which are effective against fungi). They act by a number of mechanisms including inhibition of bacterial enzyme systems, as oxidising agents, or by denaturing or crosslinking proteins.

Biocides can be used as an alternative to salt for 'short term preservation' of rawstock for 3-21 days. Longer storage is not possible due to recontamination of the skin or breakdown of the biocide.

Biocides can also be sprayed on as a temporary or emergency measure, when rawstock cannot be processed on schedule. They can replace the use of salt, particularly in warm climates where it is not possible to use ice or chilling. Biocides act by killing bacteria whereas salt acts as a biostatic.

Biocides are no cheaper than salt to use and have a number of other disadvantages; the health and safety implications of using the products, environmental problems and potential resistance problems.

Long-term preservation methods commonly applied

- salting
- brining
- drying
- salt drying.

Salting and drying both work by reducing the moisture content in the rawstock so that bacteria are unable to grow. The process of dehydration is 'reversible' so the leather produced from this rawstock is not significantly different from that obtained from processing fresh rawstock, although some changes do occur to the rawstock during preservation and storage.

There are some "salt loving" (halophilic) bacteria that cause red heat on sheepskins which can cause pitting of the surface of the skin.

Methods of salting are:

- Wet salting where salt is applied by hand or machine to the flesh side of the rawstock. 25% to 30% w/w of salt is used based on the weight of the rawstock (equivalent to approximately 1,5 kg/skin or 10 kg/hide.
- Brining where the rawstock is placed in a raceway containing brine (25% salt solution)
- Drum salting where salt is applied by tumbling the rawstock in a drum
- Dry salting is where the rawstock is treated as for wet salting or brining, followed by air drying.

A well salted hide or skin should have a moisture content of between 40% and 48% of the skin weight (i.e. rawstock weight clipped free of hair or wool) and sufficient salt to give at least 80%-85% saturation in that moisture; this is about 14,5% of salt on rawstock weight when the moisture content is adjusted to 45%.

Air drying is the traditional way of preserving rawstock in warm climates. The rawstock is dried to 10%-14% moisture and are generally dipped or sprayed with pesticide to prevent damage from beetles, moths and rats.

Raw stock warehouse (stocking conditions according to curing methods used)

One of the main concerns when stocking raw hide should be the preservation of good structural conditions for leather processing. The conditions of warehouses differ in accordance to the curing method of the rawstock. In either case a raw material warehouse must ensure adequate protection against rodents and parasites, and against excessive dampness or heat. It should also have sufficient space between stocked hides and skins to allow for air circulation and access to periodic inspections of raw stock.

Wet salted and dried goods require different conditions. Wet salted stock requires low temperature rooms (conveniently insulated from sources of heat such as sunlight) and slopes to allow drainage of excess brine or salt in solution.

Dry salted raw stock requires more protection against rodents (e.g. elevated stocking platforms) and careful control of humidity to prevent excessive dampness (thus increased putrefaction) of the raw stock.

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2.3. Lesson 2: Wet stage leather processing – from the beamhouse to the tannyard

Author: Joaquim GAIÃO - CTIC

- Different kinds of wet leathers
- Beamhouse operations
- Tanning operations

2.3.1. Leather Processing

Vessels

There are different types of vessel that can be used in the leather manufacturing.

Traditionally any immersion treatment of hides or skins was carried out in a pit where penetration of the water and its solutes into the fibre structure depended on the diffusion.

Most modern processes employ vessels where some degree of mechanical stirring, mixing or drumming is available to assist such solution penetration. Drums and paddles actually are the traditional vessels used for most tannery processes.

For the majority of light leather production, drums have become the most important type of vessel; however, pit tanning is still used for the production of heavy leathers. It is a lengthy process that can take up to 60 days.

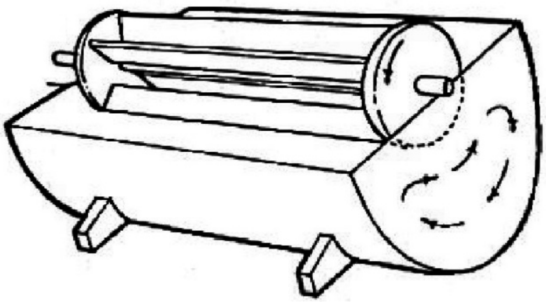

Figure 2.8. Scheme of a wooden paddle

Figure 2.9. Wooden paddle

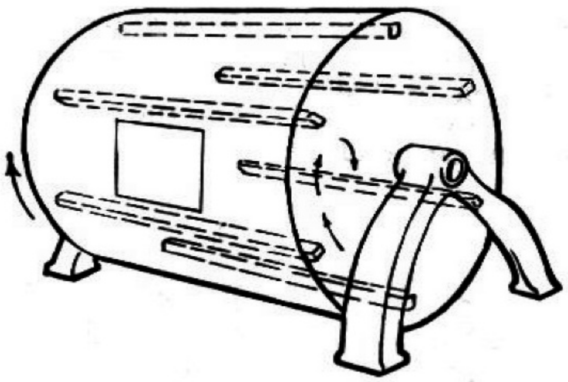

Figure 2.10. Scheme of a wooden drum

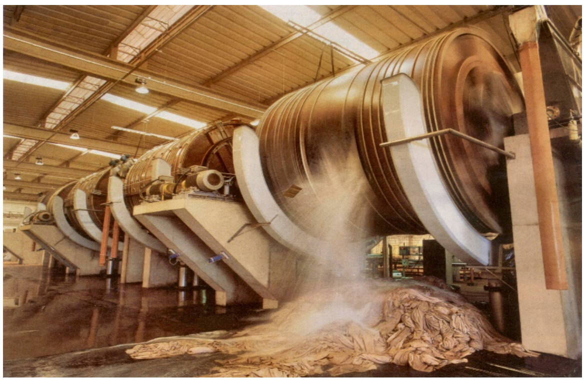

Figure 2.11. Wooden drum

Skivers and wool-on sheepskins are processed in paddles, because the mild mechanical action of these vessels is appropriate to these kinds of skins.

The degree of mechanical action for any particular vessel can be altered by the gearing or speed of the motor and two-speed or variable speed drives are not uncommon.

The drum is by far the most prevalent type of processing vessel in the modern tanning industry. It is a cylindrical structure mounted horizontally on hollow axles with shelves or pegs inside and a sealed door. Liquors can be added and, in some cases, removed via the axles while the drum is rotating.

The liquor may fill the drum to the axles (a "long float") giving a level of mechanical action similar to a paddle, alternatively the drum can be run virtually dry.

During last decades, developments in special stainless steels (resistant to tannery chemicals), corrosion resistant polymer covered steel and rigid “plastics” have allowed drums to be made from materials other than wood, giving the advantage of easy cleaning, no corrosion and flexibility of design. One of the first designs to be used commercially was similar to the concrete mixer, now developed and referred to as a “hide processor” or Mixer.

Processing vessels parameters

Processing vessels must be chosen depending on the type of leather to be produced. The parameters which require to be evaluated are:

- Vessel dimension.
- Peripheral velocity.
- Internal configuration.
- Material from which the drum is made.
- Capacity.

Processing vessels for hides should be wide enough to allow full opening of the hides.

The internal configuration will also determine the degree of mechanical action.

The drums chosen must be capable of coping with the daily production.

Drums and paddles are the traditional vessels used for most tannery processes.

Mechanical action is provided by the rotation of the vessel.

The degree of mechanical action for any particular vessel can be altered by the gearing or speed of the motor.

Pits tend to be used for soaking sheepskins and dried hides. They are often used for liming and tanning heavy vegetable leathers.

Mixers are now being used increasingly for a range of processes for both skins and hides.

2.3.2. Production Stages

The first stage of the leather manufacturing in the tanning industry is the Beamhouse.

The term “beamhouse” refers to the processes in the tannery between the removal of skins or hides from storage and their preparation for tanning.

The term dates back to the time when the hair was removed from the skins by means os a hand beam, i.e., on a sloping, curved table or large log using a two-handled knife.

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This stage includes different steps, which for the main types of skins are soaking, trimming, fleshing, unhairing, and liming. After that, is necessary to prepare the unhaired hides or skins, chemically and physically, for tanning, including three processes usually conducted as sequential steps in a single batch operation, which are deliming, bating, and pickling.

The second stage is the tanning. Tanning may be defined as the treatment of hides and skins for preservation and conversion into useful articles of commerce. But once a skin is tanned and transformed into leather is not already proper to apply into shoes or other final articles. Before that, it has to be transformed into crust condition. For that, the next stage includes steps like shaving, rettaning, dyeing, fatliquoring, and drying.

The first three stages in the process – beamhouse, tanning and post-tanning treatment – are performed in aqueous media. After the leather is dried and is in crust condition, it can be already applied in final articles but it's not the usual, because, both from a utilitarian and an aesthetic point of view, the leather needs to be finished.

Finishing is the third and last stage of leather manufacturing and is not simply a matter of painting the surface to cover up the mistakes of the previous operations or to improve it by concealing scratches. Finishing contributes to the durability and beauty of leather and must be an integral part of the process. However, the compatibility of materials, type of tannage, colouring, and fatliquoring all play an important role in the character of the leather and the kind of finish it will take. The leather manufacturing process can be represented by a schematic representation as the one included below.

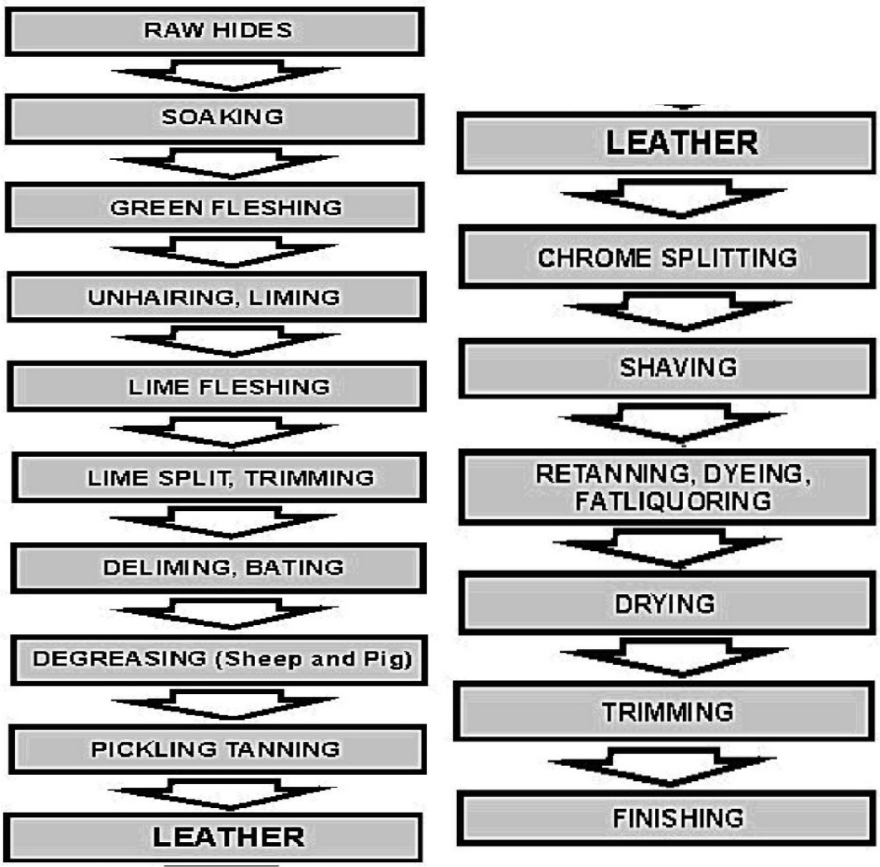

Figure 2.12. Schematic representation of the leather manufacturing process

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2.3.3. Soaking

Objectives

- Restore the moisture content of hide and skin fibers to a similar content as in the living animal (around 65% throughout the cross section of hides or skins).
- Effective separation of fibre and fibrils allowing penetration of chemicals that will be used in subsequent operations
- Eliminate undesirable components of hides and skins such as globular proteins, salt, fat and dung.
- Preparation of the hides or skins for unhairing and/or further processing (creating a media for penetration of chemicals added in subsequent processing).

Chemicals used

The most commonly used chemicals are:

Acids or alkaline agents

The main objective for the use of acids or alkaline agents is trying to reduce the time required for soaking. Collagen in hides and skins has two pH peaks in which water absorption is more effective: pH 2.4 and pH 11.6.

Therefore these are the pH values that are looked for when using either acids or alkaline agents to assist soaking.

Acid soaking is mainly used to prevent hair slip and preserve hair or wool for hair-on or wool-on leathers.

For dewooled or dehaired leathers the most common practice is to produce an alkaline environment for soaking. In this case the chemicals used to produce this effect are usually sodium carbonate, sodium hydroxide or ammonium hydroxide.

Spent lime liquors (high pH) can also be integrated in the soaking process to produce the alkaline environment without the need of adding alkaline chemicals.

Neutral Salts

The use of some neutral salts (especially sodium chloride) can greatly assist in soaking. Apart from helping water absorption, sodium chloride also assists in the solubilisation of globular proteins and prevents bacterial growth.

Liotropic Agents

It is a well-known fact that certain products such as calcium chloride have a liotropic effect on hides and skin structure. This effect is related to the breaking of hydrogen bonds between fibres and can contribute to accelerating water absorption. The use of such products is mainly in soaking of dried hides or skins. These products are not usually employed as gross chemicals but instead they are usually available as commercial compounds and mixtures produced by specialised leather chemicals companies.

Surface Agents (surfactants)

Surface agents can have a wide range of chemical nature. In leather processing the most common types are obtained through condensation of fatty alcohols with ethylene oxides.

Surface agents have different characteristics according to their HLB value. HLB stands for hydrophilic-lipophilic balance. Surfactants with a low HLB tend to make a water-in-oil emulsion while those with a high HLB are more hydrophilic and tend to make an oil-in-water emulsion. The HLB value of each surfactant is determined by specific analysis and is often stated in the chemical's technical literature

Depending of this balance it will be assigned a HLB value in a scale of 1 to 20. Commonly used surfactants range between 3 and 19. As a general rule the following classification can be applied:

Lipophilic surfactants - HLB < 9;

Neutral surfactants > 9 to < 11;

Hydrophilic surfactants > 11.

Another rule used for practical application in leather technology is that Lower HLB surfactants are mainly used for their degreasing properties. Higher HLB surfactants are used for their cleaning and moisturising abilities.

In soaking as both actions are sought the tendency is to use a combination of high and low HLB.

Apart from this classification surface agents may also be classified, according to their ionic nature, in three categories:

- anionic
- cationic
- non-ionic

Anionic surfactants are mainly used in neutral or slightly alkaline pH environments. Their ability to produce desired effects is lost in acidic environments. Cationic surfactants are only used in acidic environments whilst non-ionic surfactants can be used in either acid and alkaline environments.

Enzymes

Some commercial enzymatic preparations are available for accelerating soaking. These preparations are based on proteolytic enzymes and were specifically design to facilitate soaking of dried hides or skins. Currently they are also used to reduce soaking time on hides and skins preserved by other methods. As with all enzyme technologies care must be taken to prevent excessive enzymatic action that could lead to irreversible defects and downgrading of leathers.

Disinfectants (bactericides / fungicides)

During soaking the curing effect is lost (e.g. salt being washed out on salt cured hides/skins) and some favourable conditions for bacterial growth are created. For this reason it is important to implement preventive measures to hinder the resulting degradation processes.

This can be achieved with the use of disinfectants such as sodium hypochlorite, borax or other commercial products based on phenolic compounds.

Relevant Parameters

Temperature

The use of different temperature ranges is a trade-off between reducing process time and increasing bacterial attack. Temperatures must be kept below 40ºC in order to maintain some security level against thermal degradation of raw hides/ skins as the maximum shrinkage temperature (the temperature at which hides will begin an irreversible degradation-shrinking process) at this stage is around 60ºC. For this reason soaking is usually performed at temperatures around 18ºC–20ºC in order to ensure sufficient performance and limited bacterial attack.

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Mechanical action

This is particularly relevant in the case of dried hides/skins soaking. In this case fibres are stuck together and there is reduced flexibility of hides/skins. If mechanical action is applied at this stage there can be a risk of fibres being cracked by forced bending.

As a general rule soaking should start with as little mechanical action as possible (static soaking for dried hides/skins). As hides and skins take up water their fibres become more flexible thus allowing any mechanical action being applied to accelerate soaking.

Float

Float level restrictions are related to mechanical action. A lower float volume will significantly increase mechanical action therefore it is not advised. On the other hand, water will be absorbed by hides and skins therefore the use of large float volumes is also advisable to prevent excessive mechanical action caused by a reduction on the float volume available after absorption.

2.3.4. Unhairing/Liming

Objectives

The function of unhairing is to remove hair or wool, the epidermis, residual interfibrillary components (particularly dermatan sulphate) and to open up the fibre structure.

Other objectives are also achieved during the process such as:

- Swelling. This weakens the reticular structure and favours penetration of chemicals added in subsequent phases.
- Increase the reactivity of collagen favouring fixation of subsequently added chemicals.
- Saponification of natural fats converting them to a more soluble and easier to remove material.
- Prepare hides/skins for a more efficient fleshing and/or splitting. This is achieved by the swelling effect that increases the thickness of hides/skins.

Unhairing methods

Unhairing can be achieved by two main methods:

Painting

Where an alkaline unhairing liquor, called paint, is applied by hand or by a spray machine to the flesh surface of the skin. The paint penetrates through the corium to the follicles and the wool roots are degraded, so the valuable wool can be removed by “pulling” prior to processing and selling. The pelts are then treated by a conventional liming/pulping process described below.

Liming or pulping

Where hides or skins are immersed in an alkaline unhairing liquor, so the keratin of the hair and epidermis can be degraded by alkali from both the flesh and the grain surface. During this process other components of the hide or pelt are degraded and washed out into the liquor. The hide or pelt will swell under the alkaline conditions and the fibre structure is “opened up”.

These processes can be manipulated and modified by altering the choice, concentration and order of chemicals used in the unhairing liquor, and by modifying the process conditions, particularly the duration of the process and the type of mechanical action.

Chemicals used

The following unhairing chemicals (alkaline reducing agents) can be used during liming:

- Sodium sulphide
- Sodium hydrosulphide.

The following alkali can be used in conjunction with the unhairing chemicals to aid the process:

- Lime (calcium hydroxide)
- Caustic soda (sodium hydroxide).

Conventional liming is carried out with sodium sulphide and lime and the duration is approximately 18 hours. To speed up the process the use of enzymes and higher temperatures can be adopted. To achieve flatter leathers the use of sodium hydrosulphide is advised.

Sodium sulphide

This can degrade keratin without the addition of any other alkali; however, the process is too slow and uneconomical, so sodium sulphide is usually used in conjunction with lime. Typically the offers used for liming hides will be 2.5% w/w sodium sulphide flake and 3% w/w lime. It is also common for some of the sodium sulphide to be substituted with sodium hydrosulphide (see below). Liquors containing sodium sulphide must be isolated and oxidised to sulphates, thiosulphates and sulphites, during the treatment of the effluent. This is to ensure that sulphide is not released to the sewage system where hydrogen sulphide may be produced.

Lime (calcium hydroxide)

Use of lime in pulping/liming

Lime is often the preferred alkali as it buffers at pH 12,5. When painted pelts are limed it is questionable as to whether any additional lime is required. The lime present in the paint residue (even though a proportion will have become carbonated) is in excess of the amount required to saturate a float of 200%.

Use of lime in painting

Lime acts in two important ways in the paint. Firstly, it acts as a thickener to give satisfactory retention of paint on the surface of the pelt. Secondly, it acts as a reservoir of alkali to bring the pelt to the required pH of 12,5 (the pH of saturated lime solution).

Sodium hydroxide

Sodium hydroxide can be used to provide the alkali requirement in a lime-free system. However, care must be taken in its use because the pH of the solution can exceed pH 12,8, where collagen can swell excessively.

Sodium hydrosulphide

Sodium hydrosulphide has been used to supplement the action of sulphide without any significant rises in alkalinity. It is claimed that a flatter pelt and grain is achieved when this chemical is used.

Relevant Parameters

Temperature

Temperature control is very important, as it will have a significant influence on operation efficiency. Higher temperatures (around 26ºC) will significantly decrease the time needed for complete hair removal. However, temperatures in this range require extra care because of the risk of collagen degradation (hydrolysis). For this reason, the operation is normally carried out on the range of 15ºC to 20ºC. This ensures a good balance between process efficiency and good risk management.

Mechanical action

Mechanical action can help hair removal. However, it may also produce some abrasion that can lead to a substantial decrease on grain quality. Since this is a time-consuming operation slower rotation speeds (around 4 –5 rpm) are used and the operation of drums is not continuous. Common practice is to run drums for the initial stages of liming (for a complete diffusion of chemicals) and then use a 5 min. rotation /1-hour full stop operating pattern overnight.

This is done to prevent abrasion of grain and to allow for a change in the position of hides and skins relative to the liming float in order to ensure that the goods are subject to a uniform treatment.

Float

Float control is very important because it will influence hair removal efficiency and the swelling effect. In fact, swelling is cause by an uptake in water. If no water is available there can be no swelling at all.

The float is usually calculated as a function of the required degree of swelling.

For heavy vegetable tanned leather, a high degree of swelling is required. This will ensure the appropriate opening up of the fibre structure to allow penetration of the tannin molecules.

A low level of swelling is required to prevent excessive opening up of low-quality hides or skins (e.g. Hides/skins from older animals with a loose fiber structure).

2.3.5. Fleshing

The adhering fat and tissues on the underside of the skin form a significant barrier to the penetration of subsequent chemicals. Thus, removal of this 'flesh' at an early stage is highly desirable. The fleshing operation not only removes flesh, but assists in relaxing the skins and it also aids in the removal of any remaining hair roots out of the skin.

Fleshing is carried out by mechanical means using a fleshing machine. The pelts are carried through rollers and across rotating spiral blades by the fleshing machine. Fleshing can be carried out immediately after the soaking phase - when it is known as green fleshing. If fleshing is performed after the liming and unhairing it is called lime fleshing. Sheepskins may be fleshed in the pickled state.

Figure 2.13. Fleshing roller with cylindrical knives

Figure 2.14. Feeding of fleshing machine

Figure 2.15. Trimming after fleshing operation

Figure 2.16. Fleshing operation

2.3.6. Deliming

Objectives

The main objectives of deliming are:

- To eliminate lime and other alkaline products added in the previous operations;
- Eliminate the swelling effect produced by the high pH range of the liming operation;
- Modification of the hide/skin pH from an initial value of around 12-13 to 7-8 if bating is required or around 5 is the subsequent operation will be direct pickling (for example in the case of vegetable tanned leathers).

In simplistic terms, the aim of deliming is to take the limed pelts or hides to the optimum condition for bating. Therefore, two main changes have to occur:

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Reduction in alkali (pH) and swelling

The principal action of deliming is to neutralise the alkali in the pelts gradually to avoid violent changes in pH which could lead to distortion or disruption of the tissues. As the pH is reduced the hide or pelt is depleted and the swelling reversed, resulting in a flat flaccid hide or pelt. Drum speeds should not be excessive during deliming as the mechanical action will promote looseness until swelling has been removed throughout the thickness of the skin. It is necessary to remove calcium salts before the pelt or hide is pickled, otherwise calcium sulphate may be precipitated within the structure, and its low solubility (0.21% at 30°C) makes subsequent removal difficult.

Sulphide also needs to be removed before the pH of the pelt or hide drops below 7.0 to avoid the release of hydrogen sulphide, the concentration of which should not exceed 10 ppm in the atmosphere. The pH prior to bating should be accurately controlled and consistent in order that each batch is bated to the same extent.

Increasing the temperature

The limed hide, or pelt at pH 12.5 is sensitive to heat damage at temperatures as low as 35°C. Consequently, it is essential that the temperature of deliming is progressively increased only as the pH of the hide, or pelt, falls. The temperature during liming should not exceed 30°C, with changes of float or incremental additions used to bring the temperature up to 35°C prior to bating once the pH has fallen to 11 or less.

Chemicals used

Ammonium salts

Ammonium chloride and ammonium sulphate are the two salts most commonly used in deliming. Ammonia is a weak base and is displaced from its salts by lime or caustic soda. Ammonium chloride is often preferred, as the calcium chloride formed by its reaction with lime is more soluble than calcium sulphate, although calcium sulphate is more soluble in ammoniacal solutions than in water.

These salts have the great advantage that because of the buffering action of the weak base and strong acid addition of excess ammonium salt to the liquor is unlikely to bring the pH much below 6,0. Generally, the ammonia released maintains a pH in the liquor of between 8,5 and 9,0, ideal for enzyme action during the subsequent bating process. For this reason, ammonium salts are safe to use and careless additions to the deliming liquor are unlikely to damage pelts.

Sodium metabisulphite

This is an acid salt with a pH value of about 5,0 when in solution. The sulphur dioxide reacts with sulphide to give free sulphur. At high pH this salt is capable of producing sulphur dioxide gas (SO2). Sodium metabisulphite is used in small quantities to reduce the sulphide content of the limed pelt or hide. It is not generally used as the sole deliming agent and is often used to neutralise hydrogen sulphide gas or as a bleaching agent (e.g. sheepskins). It has a weak buffer action and could bring the pH to 6.0 or below, too low for bating, if the quantities used were not carefully controlled.

Inorganic acids (e.g., hydrochloric and sulphuric acids)

The use of these types of acids presents serious risks and should be avoided. These products are used for superficial deliming of lower quality products where production costs must be kept to a minimum.

The addition of hydrochloric or sulphuric acid requires careful control. It should be added in several small portions to avoid large changes in pH at the grain surface and the rapid release of hydrogen sulphide.

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Hydrochloric and other strong acids

Hydrochloric acid is a strong acid that reacts readily with lime or caustic soda, forming calcium or sodium chloride which are soluble salts and therefore easily removed from the pelt. The use of such a strong acid has an advantage over ammonium salts with regard to cost, but its use has a serious drawback.

A very small excess over that required to neutralise the alkalinity will lead to a low pH in the deliming liquor, too low for any action of conventional bating enzymes.

The use of hydrochloric acid requires careful control over the addition of the acid. The amount used must be related to the weight of the pelts in process at the time. It should be added in several small portions to avoid large changes in pH at the grain surface and the rapid release of hydrogen sulphide.

Use of organic acids

Formic and lactic acids have pH values of about 3,7 and form soluble calcium salts. They have been used commercially for deliming, but still require careful control, because they can make the pelt too acid. They are, however, a safer alternative to any strong acid such as hydrochloric acid.

Use of commercial products

Commercial deliming products often contain one or a mixture of other deliming agents, for example, weak acids. Product data or Health and Safety sheets must be used to determine the type of deliming agent contained in the formulation. Information may also be gleaned from examination of titration curves.

Relevant Parameters

Water

Average quality water has a low concentration of bicarbonate ions (CO3H-) that can react with limed pelts to produce lime blast in the grain surface. Therefore, care should be taken to ensure the water used in the deliming operation is checked for bicarbonate concentration.

Thickness

Total deliming time is heavily dependent on hide/skin thickness. The thicker the hide/skin the more time is required for deliming. The total offer of deliming chemicals is also dependent on the thickness of hides/skins.

Temperature

An increase in temperature (not exceeding 35ºC) increases deliming efficiency and accelerates the process. Temperatures above 35ºC present serious risk of denaturalisation of the collagen structure and should be avoided. A common temperature for the deliming operation is around 30ºC.

Mechanical action

Mechanical action favours deliming operation; however, in the initial stages of deliming when the hides/skins are still swollen, mechanical action can be undesirable and can lead to fibre and grain burst. Typical deliming drums should operate around 6 rpm.

Operation time

As previously mentioned, operation time is heavily dependent on the thickness but also on the initial and final pH and the operation temperature.

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Operation time is also dependent on the type of deliming that is required (either full cross-through - longer operation times, or with a lime streak – shorter operation times).

Depending on the desired effect, thickness and other operating parameters, deliming can take as little as 30 minutes and can extend to operating periods as long as 4 to 5 hours.

Type of deliming

The first step in deliming is to wash out the superficial lime.

The initial washing should be performed carefully due to the reduced flexibility of swollen hides/skins. The decision on the deliming type depends on the requirements of the production.

Two main types of deliming are mostly used. Either a full in depth deliming or a deliberately insufficient deliming that leaves an inner stripe of higher pH on the cross section of the hide/skins. This last practice is mainly used in bovine hides for shoe upper articles where some degree of firmness is required.

For clothing and other soft articles, a full cross-through deliming is required. The reason for the differences caused by these types of deliming is not specifically based on the deliming effect in itself but rather on the effect of the subsequent operation (bating). Differences in pH across the section can be controlled with specific indicators. These differences will become visible in a cross cut with phenolphthalein as follows.

Cross-through deliming **Lime streaked deliming**

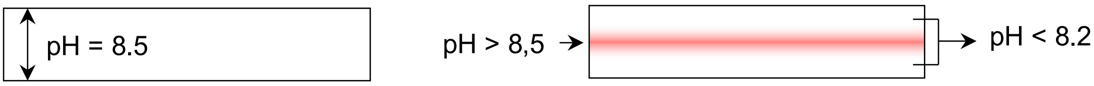

Figure 2.17. Control with phenolphthalein of different types of deliming

In both cases the operation usually takes place in a warm bath (around 30ºC) that is buffered to a pH around 8/8,5. These conditions are well suited for deliming but specifically for the subsequent operation – bating – where the use of enzymes requires such specific conditions. More recently there has been a tendency to substitute ammonium-based chemicals by non-swelling acids. Carbon Dioxide deliming is an option that is used in small skin treatment or calf hides.

Advantages and disadvantages of different types of deliming systems

The main advantages and disadvantages are shown in the table below.

Table 2.1. Main advantages and disadvantages of different types of deliming

Deliming System	Advantages	Disadvantages
Ammonium Salts	Cheap Buffers at pH for typical bating enzymes	Environmental, health & safety profile Consent limits Occupational Exposure Standards limits (OES)
Organic Acids	No ammonia Relatively safe	Control of pH Can be slow
Mineral Acids	No ammonia Cheap	Difficult to control pH Risk of damage

The production of ammonium salts in the effluent and ammonia gas in the workplace have been the motivation for the development of alternative systems. This has also been driven by legislation with consent levels in effluent and Occupational Exposure Standards.

2.3.7. Bating

Objectives

The aim of bating is to degrade unwanted components that are still left in the hides/skins after the previous operations. In particular, bating targets the removal of epidermis, hairs and "scud" on the surface of the hides/skins as well as some fibrous protein that can interfere with the desired qualities of the final products.

Bating promotes softness, stretchiness and flexibility of the final products. The degree of bating will be decided according to balance of these factors in the final product, e.g. for sole leather a small degree of bating is required whilst for clothing leathers an in-depth bating operation is required.

The bating process is achieved because the enzymes in the bate will degrade chemically treated hair and other residual proteins, leaving the hide or pelt clean and ready for pickling. However, the process has to be carefully controlled to avoid undesirable digestion of collagen (hide substance). Bating can be a dangerous operation if not carefully monitored. The enzymes used in the process have the ability, eventually, to degrade the collagen fibres to an extent that will render them inappropriate for leather production.

Chemicals used

A range of enzymes are available for leather processing.

Mild alkaline pH 8.0-9.5

This is the typical pH range of pancreatic enzymes such as trypsin and also the optimum pH range for most enzymes isolated from the bacterial species Bacillus subtilis, although some enzymes isolated from different strains of subtilisins are relatively stable at pHs above pH 12.

Alkali stable

Alkali stable enzymes are generally subtilisin enzymes which are isolated from bacterial strains which can tolerate high pH conditions (10-12.5); they have significant residual activity at this pH so that they can be used in the liming stage of leather processing.

The most important bacterial genus exploited for the production of alkaline proteases is the Bacillus genus, in particular *Bacillus subtilis*. Another commonly used strain is the bacteria *Streptomyces alkalophilus*.

Acid acting enzymes

These also fall into two categories:

- The true acid acting enzymes which are often isolated from fungi and have an optimum activity between pH 1-4.
- Bacterial enzymes with an optimum activity in the range of pH 7-9, but with sufficiently broad activity to have residual activity in the acid range.

Acid acting enzymes are often used for bating fur or wool-on skins in the pickled state. They are also of interest for use in increasing the softness of pickled pelts or partially tanned material (in order to avoid de-pickling or raising the pH prior to re-bating).

Neutral acting enzymes

Many bacterial enzymes can be used at neutral pH values, e.g., for soaking or bating after carbon dioxide deliming.

Whilst these have an optimum activity at pH 8.5-9.5, they have significant residual activity at neutral for them to be useful. There are also some neutral acting enzymes that have a true optimum activity at this pH for example *Bacillus polymixa* has been utilised extensively for the production of neutral proteases.

The characteristics of bacterial and pancreatic enzymes

As pancreatic enzymes become less readily available or more expensive, bacterial enzymes have been used as substitutes. If they are used at low enough concentrations or in the presence of certain deliming salts, then it is possible to minimise their elastase activity and simulate the bating effect of pancreatic enzymes.

Conversely, new bates are now available which deliberately exploit the elastase activity in order to benefit from the added softness, area yield and flatter structure.

Their activity may be affected by deliming salts, and hence, it may be more effective to use such bates in a fresh bath without any ammonia salts.

The other major advantage of bacterial (and fungal) enzymes is that they can be selected for activity at specific pH ranges. This therefore permits their use outside the pH range of 8,5-9,5 employed during bating after deliming with ammonium salts, and has enabled their use in a number of other stages of leather processing.

Relevant Parameters

Temperature

Increasing the temperature increases the rate of a chemical reaction (up to a point) and this is true for enzymes. In the range 10oC-40oC, mammalian enzymes, i.e., pancreatic, are roughly twice as active for every 10 degree rise in temperature, as shown in the following diagram.

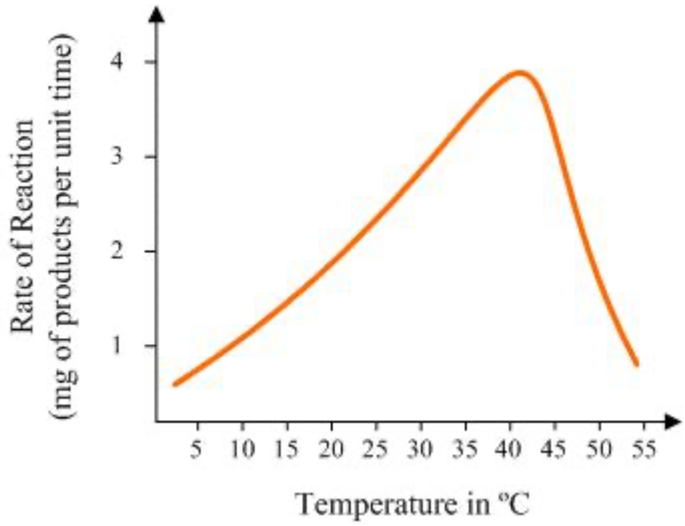

Figure 2.18. Temperature profile of pancreatic trypsin

Deliming and washing are normally carried out with a sequential increase in liquor temperature. Just prior to bating the maximum temperature for water entering the vessel should be 39oC compared to the 30oC maximum for washing limed hide or pelt. This is because of the relative sensitivities of the hide or pelt to heat damage at pH 12,5 and pH 8,5. If temperature control is not possible the float should not be heated above 35oC once the bate is in the liquor.

pH

The active site of an enzyme is also susceptible to changes in pH, and every enzyme has a range of values at which activity is optimal, as shown in the following diagram.

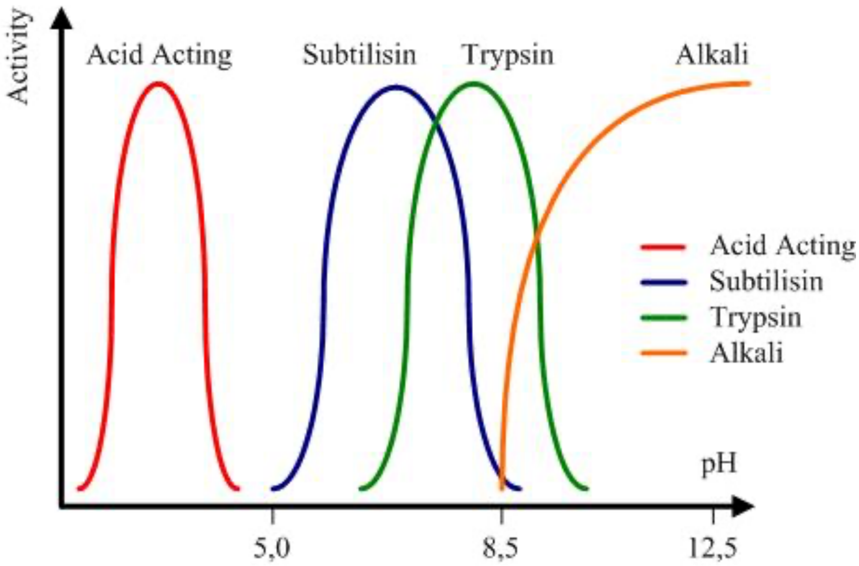

Figure 2.19. pH profile of enzymes

Enzymes can aid the production of cleaner leathers as their selective use can assist in the removal of specific components of the hide or pelt.

By using them in conjunction with processing chemicals they can act synergistically to either speed up the process or reduce the offer of chemicals. This can facilitate cleaner leather processing as a more economic process can be used with less discharge to the effluent.

Enzymes in their own right are used at very low concentrations and constitute an insignificant effluent loading. In fact, they may be used selectively to degrade protein and fat in effluent liquors to aid biological treatment.

Operation Control

The effectiveness and efficiency of bating (and the use of enzymes in general) is dependent on accurate process control. Deliming conditions must be optimised so that the hide and the liquor are at the correct temperature and pH for the enzyme to work efficiently.

The float levels and drainage of the vessel will influence the concentration of the enzyme in use, which can result in variability if inaccurately controlled. Process duration will also be a significant factor particularly when the process is on a 'knife edge' and other parameters are poorly controlled.

Enzyme processes are particularly hazardous to the tanner in that excess heat, duration or enzyme concentrations can result in degradation of the collagen substance.

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Mild overbating will result in:

- Looseness
- Grain loss
- Weakness

Severe overbating, particularly if the goods become overheated will result in:

- Holes
- Gelatinisation
- Solubilisation (i.e., skin soup).

By comparison, underbating the skins will result in:

- Residual scud
- Residual hair
- Under opening-up

Measuring bating efficiency

A properly bated hide or pelt will be clean, relaxed and soft with no residual hair or epidermis (scud).

The fibre structure will be relatively open as all the degraded components will have been removed. This permits air to be forced through a hide or pelt and a thumb print can be left in the surface of the hide or pelt. These tests can, therefore, be used to determine whether the bating process is complete or whether the goods have to be left longer in the bate.

Wash after bating

Cold water should be used to wash out after bating.

This serves two purposes; to reduce enzyme activity and to clean the hides or pelts, removing degraded protein debris from the structure, ready for pickling. This also ensures that the goods are cold prior to pickling as the addition of hot acid, or acid onto hot goods, could result in acid/heat damage.

2.3.8. Pickling

Objectives

The role of pickling during the processing of hides is to ensure that the collagen is at a sufficiently low pH (cationic) so that the chrome salts can penetrate without an immediate reaction on the surface. The effect of the pickling acid on collagen is to suppress the ionisation of the carboxyl groups and thereby render them inactive to the fixation of chrome. Thus, by pickling the skin, the penetration of the chromium salts through the skin is increased and combination with the skin protein is initially reduced. This occurs until the pH is raised sufficiently to allow ionisation of the carboxyl groups to occur.

Most chrome tanning is carried out in the pH range 3.5-4.0, although the process will usually start at pH 2.5-3.0, to which the pelt must be adjusted prior to chrome addition.

One other objective of pickling could be providing an acceptable storage condition. This is considered a preservation technique and is commonly used in the shipment of sheepskins (especially from Australia and New Zealand).

Pelts are pickled in acid and salt so that they can be held over periods of several months or, if necessary, a year or more. Pickling preserves the pelt, partly by the low pH due to the acid present and partly through dehydration.

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Sheepskins and, to a lesser extent, goatskins and bovine hides may be given a storage pickle with an expected shelf-life of at least six months.

By using a combination of acid and salt, it is possible to use less salt than would be necessary for adequate preservation by salting alone. The conditions required for satisfactory pickling (storage pickle) were determined by many investigations in which pelts were pickled with various salt and acid levels and then stored under warm conditions.

From these trials, the key control parameters are that at equilibrium the liquor should contain:

- 12%-14% w/v sodium chloride (measured by specific gravity)
- 0.55% - 0.65% w/v sulphuric acid (measured by titration with 0,1M alkali).

Such an equilibrium pickle should give adequate storage for intercontinental transport, although under the circumstances it is normal to add a fungicide.

Chemicals used

Salts

Sodium chloride

This cheap salt is widely employed as the neutral electrolyte to prevent acid swelling.

For process pickles (i.e., immediately prior to tanning), the amount of salt will depend on the float length and skin type. The objective is to have a concentration of 4%-6% w/v sodium chloride taking into account both float and pelt moisture (moisture would be 50%-60% w/w bovine goods and 70%-80% w/w wooled sheepskins).

For storage of pickled pelts, it is recommended that a freshly made pickle liquor should contain between 16% and 17% w/v sodium chloride so that, by the time water has been drawn out of the pelts, final concentrations at equilibrium will be between 14%-16% w/v of salt. Each time the liquor is reused, additional salt needs to be added to return it to the initial concentration.

Sodium sulphate

This salt is sometimes used in the pickling of calf and veal skins for full chrome tannage. It has little hydrolytic effect on collagen and suppresses the hydrolysis of chromium salts. This means that the pH of the chrome liquors in tannage does not tend to fall so much and better chrome fixation is obtained.

Acids used in pickling

The choice of acid can have an influence on the reactivity of the hide or pelt to the tannage and therefore the characteristics of the final leather.

Various acids and salts can be used for process pickling, the most common are sulphuric and formic acids, frequently used together with common salt.

Sulphuric acid

This acid is cheap and is suitable for use in tannages employing basic chromium sulphates. It tends to produce plump leather with a round handle.

Hydrochloric acid

This is a monobasic acid and therefore has a more pronounced effect than sulphuric acid on collagen swelling at the same acid (hydrogen ion) concentration. It may have some inhibitory effect on chromium fixation.

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Formic acid

This acid is more expensive. It is used to introduce formate ions into the system, giving a less astringent tannage, with a more rapid chrome penetration and more even layerwise distribution of the chrome. A similar effect may be obtained by using sodium or calcium formate plus mineral acid.

Non-swelling acids

There is now a wider availability of weak aromatic acids (for pickling pelts prior to chrome tanning), as they do not cause the pelt to swell. The earliest of these was naphthalene sulphonic acid, but more recently more complex hydroxy-aromatic acids have been introduced for this purpose.

They allow the reduction of the pH of the pelt to a suitable level for chrome tanning in the absence of dehydrating neutral salts. This results in fuller, firmer leather, requiring less retannage than leathers produced by more conventional methods.

Inhibition of microbial growth and use of fungicides

'Biocide' is the general term which refers to both bactericides (which are effective against bacteria) and fungicides (which are effective against fungi). They act by a number of mechanisms including the inhibition of microbial enzyme systems, as oxidising agents, and by denaturing or crosslinking proteins. A product which is a good fungicide may not be a good bactericide and vice versa.

The ideal bactericide should have:

- Good activity in the presence of high levels of organic matter.
- Some substantivity to protect skins for short term preservation and after draining off from the soak (or washing).
- No damage or staining to the hide or skin and no tanning effect to interfere with the leather manufacturing processes, particularly unhairing and dyeing.
- No adverse effect on the wool which will adversely affect dyeing.
- No effect on enzyme activity, used in the soak or later in processing.
- Safe environmental and Health and Safety profile

The ideal fungicide should have:

- Good activity to a range of spoilage fungi.
- Stable under acid conditions without an adverse interaction with processing chemicals.
- A balance of solubility and substantivity so the fungicide can penetrate the wet blue rather than being deposited solely on the surface and is not washed out in subsequent processes and can persist during the storage period (6-12 months).
- No damage or staining to the hide or skin to interfere with the leather manufacturing processes, particularly dyeing.
- Safe environmental and Health and Safety profile.

When using biocides or fungicides in the leather making process it is essential that the product selected is effective but is safe to use and discharge into the watercourse or effluent. Concentrated biocide solutions can kill the micro-flora in the activated sludge at the sewage works, and may be harmful to fish life. There is strict legislation concerning the use of biocides for industrial applications and many substances used within the leather industry have been banned. A range of safe, non-toxic leather biocides is given below.

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Table 2.2. Main non-toxic leather biocides

Chemical name	Products used in leather industry
0-Phenylphenol	Preventol O, Dowicide
Copper 8-quiolinolate	As chemical name
2-Benzyl-4-chlorophenol	N/A
Alkyl dimethyl benzyl ammonium chloride	Preventol, R80, R50
Alkyl dimethyl ethylbenzyl ammonium chloride	Preventol, R80, R50
4-nitrophenol (Military leather only)	As chemical name
2-(Thiocyanomethylthio) benzothiazole	Busan 30, Tolcide C30
Methylenebis (thicyanate)	Tolcide MC, Slimicide MC
Potassium N-hydroxymethyl-N-methyldithiocarbamate	N/A
Diiodomethyl-p-tolylsulfone	Amical 48
1,2-Benzisothiazolin-3-one	Proxel LB, Proxel LD
2-Octyl-3(2H)-isothiazolone	Kathon LP, Glokill 80

The list originates from the United States FIFRA (Federal Insecticide, Fungicide and Rodenticide Act). Due to the huge list of banned substances listing them is not practical, and the Act therefore specifies substances which are permitted.

Relevant Parameters

Pickling is controlled by the amounts and ratio of acid to salt in the pickle. Preservation comes partly from the dehydration and partly from the low pH due to the acid present. This combination is important because the dehydration is only partial and, unless the pH of the pickle is properly adjusted, a slow growth of micro-organisms will take place, particularly of fungi which can develop under more acid conditions than the bacteria of putrefaction. The removal of water from the skin is an osmotic effect due to the presence of salt. The salt is also present to prevent harmful swelling of the collagen at low pH.

Salt is one of the most difficult components in the effluent to treat and is virtually impossible to remove cost effectively. The spent liquors from the pickle are very acidic and contain a high concentration of salts. It is important that pickle liquors do not mix with lime liquors as this will result in the release of toxic hydrogen sulphide gas. More information on this subject can be found on the Environment and Health & Safety modules.

Hide/skin thickness

The thicker the hide/skin the more difficult it will be to achieve a full penetration of the acids. Therefore, the pickling operation can be substantially delayed in order to achieve a correct balance between acid concentration in the bath and the hides/skins. This effect can be reduced by a careful choice of the acid used and by increasing the mechanical action.

Deliming degree

Pickling can, for obvious reasons, be considered as an extension of the deliming operation. Therefore, it is also obvious that the degree of deliming will have a noticeable effect on the pickling operation. As a general rule, a deeper delimed pelt will require less acid for pickling. On the other hand, when deliming has been achieved to a lesser extent (e.g. a lime streak left on the pelt) the amount of acid and time required for achieving a pre-determined final pickling pH is increased.

Type and quantities of salts

There are specific differences depending on the type of salt used. A low concentration of salt (lower than 5º-6ºBé) will not prevent acid swelling and can lead to irreversible damage to hides/skins. On the other hand, excessive concentrations of salt will increase the dehydration and fibre separation leading to a loss of hide substance and compactness.

Type and quantities of acids

Several types of acids can be used for pickling. A common procedure for chromium-based production is to use a Formic-Sulphuric acid combination (added at different times – usually formic acid first then sulphuric acid). This enables a good balance between penetration capability (formic acid) and pH lowering capacity (sulphuric acid).

The quantity of acid used depends on several production requirements. However, it is a common practice to use around 1%-1.5% of acids on the limed weight of hides/skins. Each acid should be added separately. They must be diluted in water before use and this diluted solution should then be added in small parts to the pickling bath. This will prevent a sudden fall in pH and an excessive attack of the acid on the surface of the hides/skins.

Mechanical action

Mechanical action can help reducing the total amount of time needed to achieve a fully uniform pH of the hides/skins. However excessive mechanical action can lead to a rise in temperature that increases the risk of hide substance losses. This is a specific risk on this operation due to the exothermic profile of the reactions taking place (addition of acids to water).

Temperature

As previously stated, pickling is an exothermal reaction that generates heat. In these conditions the acidic environment can cause degradation of the collagen fibres. In order to maintain a suitable degree of control over the operation, pickling should be performed in a temperature range around 20ºC to 25ºC.

Time

The total duration of pickling is dependent on the temperature, mechanical action and quantity/type of acids used. If a standard pickling method were used, the total duration of the operation would range from 4 to 6 hours.

These operation times ensure that the pH is uniform across the thickness of the hides/skins. Shorter times would lead to undertannage of the inner layers of the hide/skins. Longer periods could increase the risk of degrading the fibre structure.

2.3.9. Degreasing

Hides, and more specifically certain types of skins have a layer of fat that poses some problems in leather production. The following table illustrates the differences between several types of raw materials:

Table 2.3. Grease content of main types of raw materials

Raw Material	Grease Content (%)
Deer	4 - 6
Pigskin	30 - 40
Wool sheep (UK, New Zealand)	20 - 30
Wool sheep (Germany)	10 - 15
Hair Sheep (African)	4 - 8

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Goat	3 - 5
Bovine	4 - 8

The presence of fat concentrations in the hides/skins interferes with the ability of chemicals to perform their intended objectives.

One of these effects is the formation of insoluble soaps when fat reacts with mineral tanning agents. On the other hand, the hydrophobic nature of fats cause difficulties in the wetting back of crust leather, risk of fatty spue in finished leather, uneven penetration of tanning agents and dyestuffs.

All of these difficulties will contribute to reduce the uniformity of finished leather and a consequential downgrading of the products.

For this reason, it is necessary to degrease hides/skins.

The operation can be performed at different stages and with different methods. The most commonly used method is to degrease after pickling. This is specially used in sheepskins either treated from raw or purchased in a pickled state.

Bovine and goat hides/skins have low grease contents and are not usually degreased.

Most used methods of degreasing

- degreasing in aqueous medium with organic solvent and non-ionic surfactant
- degreasing in aqueous medium with non-ionic surfactant
- degreasing in organic solvent medium.

Degreasing in aqueous medium with organic solvent and non-ionic surfactants

This is the traditional method to degrease dewooled sheepskins, in which petroleum or white spirit is used as solvent for the natural fat.

This is done by adding the solvent that is already mixed with small amounts of non-ionic surfactant. The surfactant is needed to emulsify the solvent. Once the fat is dissolved, the fat-solvent mixture is emulsified with some more non-ionic surfactant to be removed from the skins into the float.

After this, several washes are carried out with brine (approximately 5 degrees Baumé) and small amounts of non-ionic surfactant.

The non-ionic surfactants, and in particular the nonylphenol ethoxylates, are the most efficient ones.

The need to use salted water for washing (4%-5% sodium chloride) can be avoided if the skins are previously neutralized. The amount of petroleum/white spirit used in this process can be as high as 20% based on the lime weight. The amount of nonylphenol ethoxylates is relatively low (2%-3 % total).

Degreasing in an aqueous medium with non-ionic surfactant

With this technique the natural fat from dewooled sheepskins is directly emulsified in water by means of the non-ionic surfactant.

The most effective non-ionic surfactant is nonylphenol ethoxylate with 8-8.5 moles of ethylene oxide.

The amount to use depends on the fat content of the skins, but it is usually between 4% and 6 % based on lime weight.

Usually, the surfactant is added in a very short float in order to distribute the product uniformly and, after running for a certain period, more water is added to emulsify the fat. The emulsified fat is finally removed by draining.

After this, several washes with water and some surfactants are required. There are several types of non-ionic surfactants able to work properly in this process, but none of them offers the same effect as nonylphenol ethoxylates, either in the efficiency of the degreasing by emulsion or afterwards in the treatment of the effluent by breaking the emulsion and separating the fat phase from the aqueous one.

There are some variations according to the specific characteristics of the skins, the fat content and its nature. Usually, a certain pre-tannage is required to increase the shrinkage temperature. This enables the fat to emulsify and to flow easily when its melting point is too high.

The shrinkage temperature of the skins must be at least 20 ºC higher than the operation degreasing temperature, which can be up to 60 ºC.

Pre-tanning agents that could be used include glutaraldehyde, aluminium sulphate, or syntans.

Another possibility is to neutralise the skins in the first float, before washing, in order to avoid the addition of salt to the water and effluent.

Finally, there are some intermediate versions that incorporate some organic solvent with the surfactant (usually 2 %-3 %). This helps the removal of the natural fat and eases its emulsion in the water.

Sodium carbonate can be used in the degreasing process as a de-pickling agent to facilitate the extraction of the emulsion once the skins have been treated with surfactants, but it cannot be considered as a degreasing agent.

Dry degreasing in organic solvent medium

This process is applied by extraction at an intermediate temperature directly in solvent, usually trichloroethylene or perchloroethylene.

The use of the chlorinated solvents is due to the non-flammability of these products, in contrast to other solvents.

Normally this process is applied to wool-on sheepskins in crust stage to equalize the residual fat and to assure a steady dyeing in further operations.

The degreasing is carried out in closed machines; the used solvent is automatically distilled and re-used.

The distillation is quite effective, although never absolutely total. As the technique uses solvent alone, the pelts have to be in dry state otherwise the solvent cannot come into contact with the fat. And because non-tanned pelts cannot be dried completely, the pelts have to be tanned before drying.

The limited size of the closed machines is the reason why this technique only is used when aqueous degreasing is not possible or not efficient enough and has to be completed by degreasing in the dry state.

Possible cases are wool-on sheepskins, very fatty skins (domestic English, Australian, etc.) and fatty wet-blue imported as such.

2.3.10. Tanning

Tanning converts a putrescible pelt into a non-putrescible material called leather. Different leathers are produced by controlling the amount and the type of tanning material used.

Chemically speaking, there are two families of tanning compounds available: inorganic (mineral origin) and organic (vegetal and animal origin) materials.

Each tanning material imparts to leather different characteristics such as e.g. colour, flexibility, density and heat resistance.

The leathers tanned with chromium when in wet condition after tanning operation, have a typical pale blue colour, that's why commercially the name "wet-blue" was given to leather in that state.

The leathers tanned mainly or totally with other tanning materials, with low content of chromium or chrome free and in wet condition after tanning operation, having a typical white or near white colour, commercially are known as "wet-white".

Chromium now forms the basis of virtually all light leather manufacture. It is relatively cheap, has a well-established technology and most auxiliary chemicals used to enhance leather performance have been developed on the basis of a chrome tanned substrate. The unique characteristic of chrome tanned leather is a shrinkage temperature >100oC, which allows it to 'withstand the boil' for a period of time (one to three minutes).

Tanning types: Tanning with mineral (inorganic) compounds

Mineral tannages involve the use of mineral salts, such as the chromium (III) sulphate in chrome tanning, which can crosslink and stabilise the collagen molecules within the fibrils.

Other mineral tannages can be achieved through the sole use or combination of mineral salts of e.g. aluminium, titanium, zirconium and other minerals.

Chrome tanning

Nowadays, 70 – 80 % of all leather is still tanned with chrome, in spite of all the discussion concerning heavy metals in general and chromium in particular, forming the basis of virtually all light leather manufacture.

There are a number of reasons for this:

- The biggest advantage of chrome tanning is the high degree of thermal resistance that can be achieved in a relatively simple way, through chrome tanning.
- The quality of chrome-tanned leather is unsurpassed in terms of its resistance to high temperatures. The unique characteristic of chrome tanned leather is a shrinkage temperature >100ºC, which allows it to 'withstand the boil' for a period of time (one to three minutes).
- This enables sufficient thermal stability in order to withstand the high vulcanisation or injection temperatures (around 130ºC) used in shoe production.
- Other of the biggest advantages of chrome tanning when compared with other tanning technologies is the degree of flexibility it can provide. Many different types of leather can be prepared from wet blue. A chrome tanned leather can be used as a basis for the production of such dissimilar articles as shoe uppers and clothing leathers.
- Wet blue is traded worldwide.
- Machinery and manufacturing techniques in the leather goods industry are geared to working with chrome-tanned leather.

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- It is relatively cheap, has a well-established technology and most auxiliary chemicals used to enhance leather performance have been developed on the basis of a chrome tanned substrate.
- Chrome tanned leathers are also known to have a high degree of elasticity and an excellent dyeing ability.

Chemicals used

Basic Chromium Sulphate

The main chemical used is obviously a suitable source of chromium. Nowadays chrome leather tanning is a sufficiently mature technology that has stabilised around the use of basic chromium sulphate salts. These are produced by the multinational chemical companies and can be found in slightly different forms. There are chromium sulphate compounds with a chromium oxide content (Cr2O3) ranging from 10% to 30%.

The most commonly variants have around 22% to 30% Cr2O3. Another important characteristic of chromium tanning salts is their basicity. When dissolved in water, chromium sulphates give a green solution and produce sulphuric acid and basic chromium sulphate. These solutions may have a low pH (2-3) and a reduced tanning power. By adding an alkali this acid is neutralised but the chromium sulphate will tend to hydrolyse further producing more sulphuric acid and more basic chromium sulphate. The following table relates the addition of alkali to basicity and tanning power.

Table 2.4. Influence of alkali addition on chromium compounds basicity and tanning power

Compound Description	Alkali added*	Basicity**	Tanning Power
Chromium Sulphate	0	0%	Poor
Usual Chromium Sulphate	25%	33%	Good
High Basicity Cr Sulphate	33%	45%	Very Astringent
Very high Basicity Cr Sulphate	50%	66%	Surface tannage
Completely basic Cr sulphate	75%	100%	None

* Amount of Soda Ash added based on the weight of actual chromium sulphate present.

** Basicity according to Schorlemmer scale, defined as the number of hydroxyl groups combined with one unit of chromium and expressed as a percentage of the maximum allowed combinations per unit.

Some notes are important regarding basicity:

- As basicity increases, so does astringency
- As basicity increases the solubility reduces
- This is true until 66% basicity when the basic salts become insoluble and hence useless for practical tanning
- For normal chrome tannage the commonly used basicity is 33%
- For rapid and increased fixation 45%-50% basicities are used.

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Basification chemicals

Basification is performed during the tanning operation in order to neutralise pickling acids and any acid produced in reaction with the collagen.

At the same time, the reactivity of chrome complexes is enhanced on account of their basicity; it increases steadily from 33 % up to 66 % at the end of the tanning process.

Sodium hydrogen carbonate is often used as a basification agent.

Usually, the dosage is given towards the end of the tanning process in several portions in a total amount of 0.8%-1.2 % on pelt weight in order to achieve a final pH 3.8-4.2 in the float.

Magnesia, usually containing 60% MgO, may also be used as a self-basifying agent. Owing to its low solubility, the latter reacts very slowly with acids. It can be added at the start of tanning in an amount of 0.6%-0.8% on pelt weight, gradually increasing the float pH to 3.8-4.2.

Chrome tannins containing a self-basifying component based on MgO or dolomite are also commercially available. In that case, the basification agent need not be added separately.

In a conventional procedure, the tanning and basification operation should be finished at a float temperature of 35°C-40°C. The drumming time should be at least 6-8 hours. As a rule, the chrome concentration in spent float is in a range of 3.5g-7.0g Cr_2O_3/l. In order to improve the chrome tanning process, it is essential that the chrome uptake be increased so as to reduce the chrome concentration in residual floats to a maximum degree.

Masking Agents

Masking is defined as the incorporation of certain reactive groups, i.e. ligands, into chrome tannin complexes.

The purpose of masking by monobasic salts is to enhance the chrome penetration rate and permit basification to higher pH: i.e. to increase the pH value at which the chrome complex precipitates.

Crosslinking masking salts can enhance chrome reactivity, but reduce penetration rate.

Dicarboxylic acids are well-known masking agents. Short chain dicarboxylic acid salts will produce cyclic, chelate complexes if the ring size is 5-7 membered; this will reduce the reactivity of chromium. Longer-chain dicarboxylic acid salts cross-link in order to make the chrome species bigger, thus increasing the reaction rate but decreasing the penetration rate. By including an organic acid, the complexes are less cationic, thus reducing the astringency or affinity to the collagen. The masked chromium salt penetrates the substance more easily and chrome distribution over the cross-section is more uniform.

Today masked chrome tannins are commercially available. Tanning liquors with a low degree of masking are produced when acid dichromate is reduced with molasses.

Several other tanning auxiliaries are available on the market, usually based on some cross-linking function, e.g. aliphatic dicarboxylates, low molecular weight polyacrylates and syntans. They may be applied at the start of the tanning process or even form a part of the basification system.

Another example refers to the use of a mixture of aliphatic dicarboxylic acids in the pickle and sodium aluminium silicate for basification.

A more recent development is to increase the complexity of poorly bound or unbound chrome by applying low molecular weight polyacrylates during tanning or re-tanning.

Relevant Parameters

Mechanical action

Mechanical action is the prime means of transporting chemicals into the substrate.

In the case of chrome tannins, intensive agitation is indispensable to achieving good chrome penetration and securing the time needed to complete the reaction of the whole system.

The intensity of agitation is primarily governed by the drum dimensions and speed. In practical terms, optimum mechanical action is given when the drum speed is some two thirds of the critical rate

Concentration and chrome offer

The efficiency of chrome tannin uptake depends on the concentration in the solution which, in turn, is a decisive factor in diffusion. The higher the chrome concentration in the float, the faster the chrome penetration into the fibre structure. Similarly, the lower the concentration, the slower the rate of the reaction between collagen and chrome. Good penetration is a precondition for the final through-reaction in all layers of the pelt. All tanning recipes address this fact and prescribe a certain excess offer of tannin agent for reasons of safety and quality. However, this always causes problems with the chrome and other chemicals remaining in spent floats.

The efficiency of chrome tanning, defined as a proportion of the chrome offer fixed to the collagen, is illustrated in the following figure:

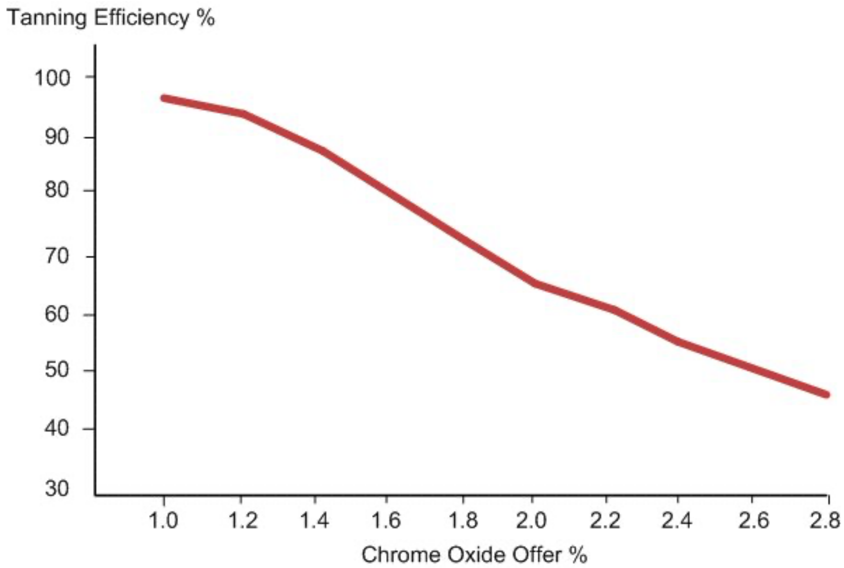

Figure 2.20. Relation between chrome offer and tanning efficiency

Under standard conditions, the efficiency of chrome tanning and the simultaneous exhaustion of chrome from the float increases when the chrome offer decreases.

However, there is a limit to reducing the chrome offer with respect to the shrinkage temperature. The effect of chrome offer on shrinkage temperature is shown in the next figure:

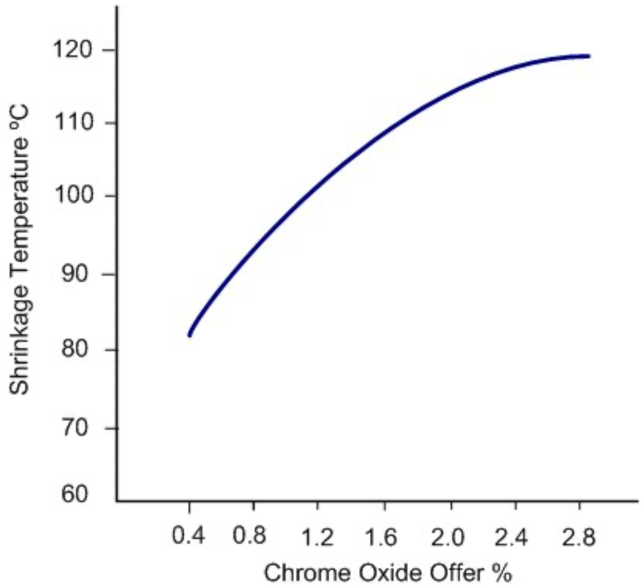

Figure 2.21. Relation between chrome offer and Shrinkage Temperature (TC)

Approximately 2% Cr_2O_3 is sufficient to achieve a shrinkage temperature of 110°C or more; this affects the boil fastness of leather. Increasing the chrome offer further yields no practical benefit.

With an offer of 2% Cr_2O_3, chrome tanning reaches an efficiency of only 65% (see Figure 2.16), whereas in practice efficiencies of 60%-80% can be achieved with less.

A shrinkage temperature of 100°C can actually be reached with an offer of about 1% Cr_2O_3. However, under normal conditions, applying a chrome offer of less than 1.6%-1.7% Cr_2O_3 may make it difficult to achieve boil fastness and obtain a uniform cross-sectional distribution of chrome throughout the leather.

If the chrome offer increases, the chrome content in leather will also increase. Leather tanned with an offer of about 2% Cr_2O_3 contains 4%-5 % Cr_2O_3. In practice, a chrome content of about 3.5% Cr_2O_3 is needed in order to achieve a shrinkage temperature of 100ºC.

For quality reasons, when applying a standard tanning procedure, the tanner has to take care to minimize the chrome offer and reduce the chrome concentration in effluent. When aiming to reduce the chrome concentration in effluent without impairing leather performance and quality, the tanner should make every effort to optimize other process parameters and/or modify the tanning process.

Reaction time, pH and temperature

The tanning reaction is an equilibrium system.

The increase in reaction time means that the reaction will finish closer to the point of equilibrium, i.e. the longer process time results in more chrome being fixed to the collagen. Under constant conditions, chrome content in leather and shrinkage temperature increase with tanning time. More efficient chrome uptake, increased chrome content in leather and higher shrinkage temperature can also be achieved using higher pH values. The effect of pH on the tanning reaction is associated with the pH influence on chrome species.

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It is known that a chrome complex solution of 33% basicity has pH 2.8 and contains mostly binuclear species while a chrome complex solution of 50% basicity has pH 3.5 and contains more astringent trinuclear and larger ions.

It is important to recognize the difference between pH and temperature in terms of their impact on chrome fixation and the corresponding shrinkage temperature. Increasing either the temperature or the pH of chrome tannage will always increase chrome fixation. It is also generally true that increasing the chrome content of a leather will increase the shrinkage temperature. However, it should be remembered that increasing the temperature primarily governs chrome fixation, whereas increasing pH primarily governs the rise in shrinkage temperature. Furthermore, the relationship between chrome uptake and shrinkage temperature depends on the manner in which the tanning reaction is conducted: more specifically, the timetable for temperature and pH rise during tannage.

- The earlier the heating is started, the higher the chrome uptake will be. In other words,
- the later the heating is applied, the lower the chrome uptake will be.
- The heating timetable has little or no effect on the shrinkage temperature ultimately achieved. Conversely, the basification timetable has little or no effect on the chrome uptake.
- Early basification is likely to yield a lower shrinkage temperature, but late basification will have neither a positive nor negative effect on shrinkage temperature.
- Maximum shrinkage temperature is achieved by slow, regular increments in pH during basification.

In an effort to increase the chrome uptake and reduce the chrome concentration in effluent, tanners tend to carry out the tanning process at elevated pH and temperature levels. The problem is that of maintaining the reaction between the chrome complex and collagen and avoiding chrome precipitation.

By slow and careful basification, it is possible to basify to pH 5.0 without causing chrome staining and so achieve the highest chrome uptake. However, for commercial applications, such a procedure should not be recommended unless very strict process monitoring and control systems are in place.

Mineral tanning with other metal salts

Other possible alternatives to chrome-tanning agents are salts of aluminum, titanium and zirconium. Their properties compared to those of chrome are summarized in the table below.

Table 2.5. Properties of some metallic tanning other than chrome

Tanning salt	Colour of leather	Type of leather	Shrinkage temperature	Price
Chromium	Pale blue	All types of leather	Resistant to boiling	
Aluminium	White	Dense, compact	Ca. 80 ºC	Similar to Cr
Titanium	Yellowish white	Dense, compact	Ca. 80 ºC	More expensive
Zirconium	White	Dense, compact	Ca. 75 ºC	Much more expensive

As can be seen from the table above, all the other mineral tanning agents give much denser, more compact leathers than chrome, and only leathers tanned with chrome are resistant to boiling. Aluminium salts are the most cost-effective and they give white leathers, as zirconium salts, which respond very well to dyeing.

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Tanning with organic compounds

Vegetable Tanning

Vegetable tanning is a process which has been used for centuries, and is still used today, especially for tanning firm, heavy leathers. Vegetable tanning employs the use of extracts from the bark or woods of various trees as the tanning agent.

Tannins occur in varying degrees in nearly all forms of plant life. Depending on that degree a plant can be selected for tannin extraction based on the efficiency, cost/benefit relationship or, in some cases, because of local geographic availability.

Since the introduction of chrome tanning, vegetable tanning has decreased in importance. Soles of shoes have been traditionally vegetable tanned. Vegetable tanning is also used to produce leather used in crafts such as bookbinding.

The traditional method of tanning was by the use of pits. The tannage was started in a pit containing weak or nearly spent liquor and continues through progressively stronger liquors to achieve the necessary conditions for good penetration at the start and fixation towards the end.

Improvements to the method have reduced the time considerably. The addition of a paddle wheel to stir the liquor in a pit was a major innovation and gave rise to a large increase in the rate of penetration and at the same time, the concentration of the liquor is kept uniform throughout. For the majority of light leather production, drums have become the most important type of vessel.

Chemicals used: Vegetable extracts

Vegetable extracts are a complex and heterogeneous mixture that have the common ability of producing a tanning effect on hides and skins. These tannins are mixtures of phenolic compounds formed by molecular aggregates of relatively large sizes. The most widely used vegetable tannins are the following:

Mimosa

Mimosa Extract or Wattle Extract is derived from the bark of a tree (*Acacia Mollissima* or *Acacia Mearnsii*) which is cultivated in Africa and Brazil and is very long established, perhaps the most widely used tanning material in the world. Mimosa tannins penetrate rapidly and uniformly even through very thick pelt, effectively tanning the individual fibrils of the hide throughout its full substance, and as such is used as a base for many rapid drum tannages.

Chestnut

The tannins obtained from Chestnut wood are of pyrogallol nature and belong to that group of glucoside tannins which are easily hydrolysable. Chestnut extract contains a convenient quantity of acid groups and of natural organic acids, which determine its considerable astringency and the property to fix in large amount to the hide substance.

These properties make chestnut extract especially suitable for the tannage of heavy hides and of sole leather in particular, as by its use it is possible to obtain a high weight yield, a firm, compact yet flexible, elastic leather of good colour, lightfast and with a low water absorption.

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Quebracho

Quebracho extract is obtained from the heartwood of the Quebracho tree which grows in South America and the tannin extracted belongs to the catechol or condensed group. Ordinary or warm soluble quebracho (also known as insoluble quebracho) is the natural extract obtained directly from the quebracho wood.

Cold Soluble Quebracho extracts are obtained by subjecting the ordinary extract to a sulphiting. The cold soluble Quebracho extracts are the most universally known and used types. The main properties of these extracts are: a very rapid penetration, a high tannin content and a relatively low percentage of non-tannins. These extracts can be blended either among themselves, or with other vegetable extracts, phenolic syntans, naphthalene and phenol-naphthalene syntans and they can be used in all stages of vegetable tannage (pit/drum, rapid and semi-rapid tannage etc.), in retannages of chrome tanned leathers where good fullness, roundness and buffability are required.

Gambier

Gambier is an extract obtained from the leaves and stems of *Uncaria Gambier* a plant which occurs in Asia both cultivated and wild. Used alone, Gambier produces rather soft leathers with a fine touch. These extracts are recommended for the retannage of heifer skins and chrome tanned side leathers.

Myrabolan

Myrabolan extract is obtained from the fruits of *Terminalia Chebula*, a tree which grows in Asia. It is a hydrolyzable (pyrogallic) tannin, astringent, with a good light fastness. Tannage with only Myrabolans gives light-green leathers with a full and soft touch.

Tara

There has been a recent increase in the use of Tara tannins in the leather industry. Tara is practically free from colouring substances and consequently it is possible to obtain very bright and lightfast leathers. Moreover, Tara imparts to leathers fullness and softness, maintaining a fine and tight grain. The grain of leathers tanned with Tara has a higher resistance to breaking load than that obtained with any other vegetable tannin. This is particularly suited for unconventional applications of vegetable extracts.

This extract was traditionally obtained by extraction of dried sumac plant leafs (C*oriaria myrtifolia*). Sumac tannin is of the pyrogallic type and it is easily hydrolysable in a warm solution. It presents good penetration properties and it is often used in leather goods manufacture as it tends to give a light coloured and soft touch to leather.

Valonea

Valonea extract is obtained by extraction of Valonea (*Quercurs aegilops*) nuts. It is a very astringent extract that is mainly used in sole leather production. It tends to give a yellowish leather.

Relevant Parameters

Vegetable tannage can be carried out straight after deliming or after pickling and pretanning; in each case the initial pH of the hides or pelts must be adjusted prior to tanning. Pickled hides or pelts should be de-pickled prior to tanning to pH 4,5-5,5, the optimum pH with which to start vegetable tanning. The hides or pelts must be depickled all the way through the cross section. Bated hides or pelts should be acidified with formic acid to pH 7 through the cross section before tanning can begin.

Vegetable tanned leathers are generally heavier in weight compared to other tanned leathers, they are brown in colour and when dyed it is difficult to get bright shades. They have shrinkage temperatures between 70oC and 80oC, depending on the degree of tannage and on the type of vegetable extract used.

- Tanning in pits

  Pit tanning is still used for the production of heavy leathers. It is a lengthy process that can take up to 60 days. The hides are lightly tanned on the surface for a few days using exhausted tan liquors (low concentration). The leather is then progressively tanned in different pits with increasing tan liquors strength, for example using a counter current process. At full penetration of the tannage, the temperature of the tanning liquors is raised to 35°C-40°C to increase the reactivity and fixation of the tannins.

- Tanning in drums.

  This rapid method of vegetable tanning was developed mainly for light vegetable tanned leathers. The process can vary from 8 hours for sheepskin pickled pelts, to 48 hours for bovine hides or sides. This type of tannage gives softer and mellower leather compared to the pit tannage.

- Tanning in a combination of pits and drums.

  The combination of pit and drum tannage was developed to produce medium or medium-heavy leathers in a much shorter time compared to pit tannage. Initially the hides or pelts are 'coloured' by placing into a weak (exhausted or used) solution of tan liquors for a period of 2 or 3 days. This will 'set' the grain and make it less susceptible to grain damage. Then the hides are moved into a drum and tanned for 48 hours with a strong tanning liquor.

  The degree and speed of uptake of tan is influenced by a number of factors which may be controlled during tannage. Normally, the aim is to achieve a uniform tannage throughout the thickness of the leather which is brought about by an initial tanning stage under conditions which favour penetration and allowing fixation to take place in the later stages. This avoids over-tannage of the surfaces leading to a rough grain that is weak and brittle. Temperature is also very important in vegetable tanning. In the first steps of production lower temperatures should be used because of the shrinkage temperature of the untanned hides.

  One adverse effect of increasing temperature is favouring the risk of tannin oxidation, what can lead to undesirable dark coloured leathers. However, with a temperature increase there will be a shortening of operating time thus reducing this risk. An adequate balance has to be achieved in order to improve results. Mechanical action also has a positive effect on the penetration of tannins. One of the reasons is related to the stirring of the liquors allowing for a homogenisation of the liquors. Another reason is related to the physical effect of fibre torsion and extension that will create additional spaces for penetration.

Vegetable tanning and chrome tanning in comparison

Excluding the Tara tannin, all the other commercially available vegetable extracts have some limitations when compared with chromium compounds; when comparing these tanning methods, we can state de following:

- With vegetable tanning it is very difficult to obtain soft, flexible leathers, especially at medium, high thickness.
- The lightfastness of vegetable-tanned leather is unsatisfactory.
- The heat resistance of vegetable-tanned leather is unsatisfactory.

- Vegetable tanning agents have their own intrinsic colour, in browned shades, so many bright, brilliant shades cannot be obtained on vegetable-tanned leather.
- Iron stains can be formed.
- Large amounts of vegetable tanning agents are required to replace chrome, so this would result in greater proliferation of monocultures of crops such as mimosa etc.

Tanning with other reactive organic compounds

Wet white pretanned leathers can also be obtained with reactive organic compounds. Aldehydes are highly reactive organic compounds and in these dialdehydes give the best results.

Syntans are the most important group of tanning agents from the point of view of retanning. They generally consist of condensation products of hydroxyl-substituted aromatic compounds with special amides or with formaldehyde.

Other possibility is the use of resin tanning agents. These products improve the fullness of the leather, especially the loosely structured areas of the skin. They ensure that the fullness of the leather is as even as possible across the whole surface of the skin. They can also be used to improve the tightness of the grain and the leather's response to buffing. A variety of different tannages can be applied to wet white, depending on the type of leather that is to be produced.

Table 2.6. Properties of some tannages for wet white

Tannages for wet white		
Tannage	**Fastness**	**Type of leather**
Chrome	Depends on retannage	All types of leather
Vegetable + syntan	Unsatisfactory to acceptable	All heavy types of leather, e.g. shoe uppers, upholstery leather
Syntan + polymer	Acceptable to good	Shoe uppers, upholstery leather, garment leather
Polymer	Very good	All types of light leather, e.g. automotive leather, upholstery leather, garment leather

Full polymer retannages give the best results in terms of lightfastness and heat resistance. The relative advantages and disadvantages of wet blue and wet white tanning processes are summarized in the following table.

Table 2.7. Relative advantages and disadvantages of wet blue and wet white tanning processes

Wet blue versus wet white		
Properties	**Chrome-tanned wet blue**	**Wet white**
Colour	Pale blue	Yellowish or white
Shrinkage temperature	> 100 ºC	70 – 80 ºC
Restrictions on dyes (excluding forbidden azo amines)	No restrictions	Dyes are often required to be free of heavy metals
Drying temperature of finished leather	Ca. 70 ºC	40 – 50 ºC
Waste leather and trimmings	May be classified as hazardous waste	Can be dumped and incinerated

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2.4. Lesson 3: Wet stage leather processing – from tanning to finishing

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- Properties and applications of wet leather types
- Tanning operations
- Post-tanning operations
- Leather finishing operations
- Tanning process machinery

2.4.1. Sammying and setting

After tanning, the leathers are drained, rinsed and either horsed up to age, or unloaded in boxes and subsequently sammyed to reduce the moisture content prior to further mechanical action, such as splitting and shaving.

The setting out operation can be carried out to stretch out the leather. Machines exist which combine the sammying and setting action. After sammying and setting, hides and skins can be sorted into different grades after which they are processed further or sold on the market.

2.4.2. Splitting

The function of the splitting operation is to cut through skins or hides at a set thickness. If the hide/skin is thick enough splitting can yield a grain split and a flesh split which can both be processed into finished leather.

There are various types of machines used depending on the state of the materials (e.g. limed, pickled, wet blue and dry) and on the type of work required.

Different levels of sophistication are available on splitting machines. These include automatic compensation, which accounts for the differences in the various parts of the hide (e.g. bridge bending for the bellies, calibrated lifting of the bridge for the neck) and step-by-step programming.

Basic principles of the operation

The material is fed through to the gauge roller, grain up. The section roller will pivot, to allow for unlevelness on the flesh side as the continuous band knife cuts the leather.

Operating requirements

Parameters such as knife tension, knife bevel, etc. must be carefully set, controlled and monitored.

As with all machinery, training of the operators is essential and, in the case of splitting, a supervisor with specialist knowledge is usually required for the various settings. In all cases, routine and preventative maintenance, lubrication, cleaning etc. of machinery should be performed to the manufacturer's specification as set out in the instruction manuals. Additional cleaning regimes for both machine and the surrounding work area should be implemented.

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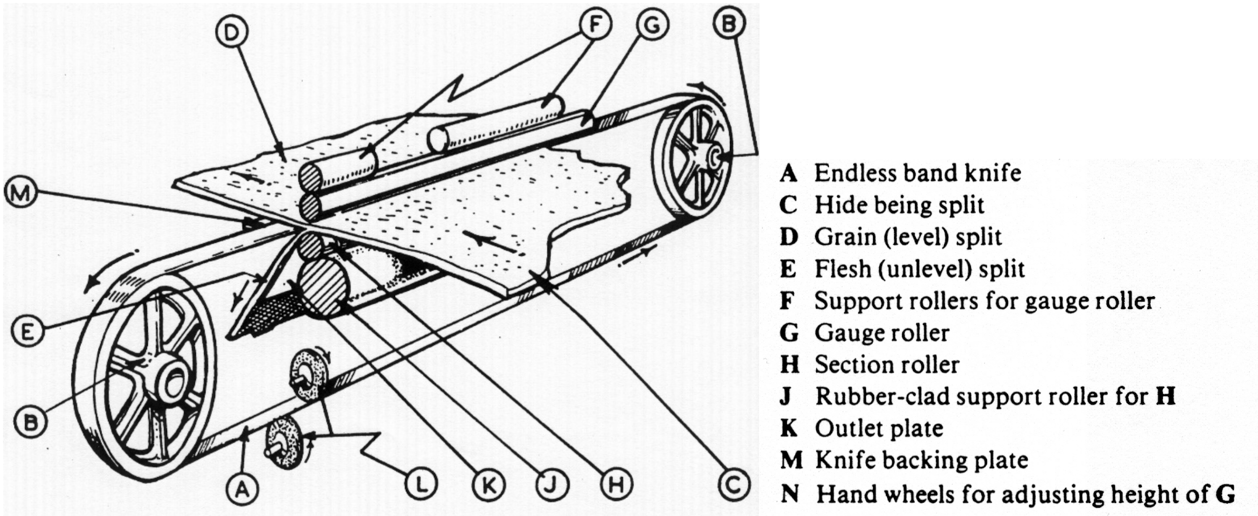

Figure 2.22. Band knife splitting machine – diagrammatic section

Figure 2.23. Splitting operation

After the leather is splitted, the final thickness desired as to be adjusted by shaving.

2.4.3. Shaving

Shaving of skins has two important objectives, firstly to level out the substance (thickness) of the skin, and secondly to bring the substance to a precise figure. Hides and skins all have areas where the substance is naturally heavier - the spine, the butt and the neck, and areas where it is noticeably thinner - the bellies.

The act of shaving the skin reduces the variation that occurs, although in many cases, the substance will still be less in the belly edges. The shaving machines can shave to a surprising degree of accuracy – down to ± 0,05mm.

As mentioned above, one of the tasks that has to be carried out by the sorter is to grade the skins for substance. The reason for this is that it is important that too much of the skin's substance is not removed. If a skin that could make an end substance of say 2,0mm was shaved down to 0,6mm the leather produced would be equivalent to a skiver with very little of the corium being left, and would result in a very weak skin.

Care therefore has to be taken to ensure that only a minimal amount of shaving takes place wherever possible.

Figure 2.24. Shaving operation

2.4.4. Washing

The aim of washing after tanning is to remove shaving residues left on the hides/skins, remove excessive superficial tannins in the case of vegetable tanned leather or excessive tanning salts in the case of mineral tannages.

Washing will also ensure that the moisture content is increased (re-wetted) and reduce the acidity of tanned leathers in order to prepare them for neutralisation. This washing can be performed with no additional chemicals or can use a small percentage of surfactants for increased re-wetting and cleaning of the tanned hides/skins.

2.4.5. Neutralisation

Expected Results

The specific aims of neutralisation are:

- Eliminate residual acidity left by the tanning operation.
- Reducing the hides/skins cationic charge (positive charge).

This is required in order to reduce the affinity of leather to the chemicals (anionic charged) used in post tanning operations. If this is not sufficiently achieved there will an excessive effect of these chemicals (fatliquors, dyes, retanning agents, etc.) on the superficial layers of the hides/skins and insufficient penetration into the inner layers. In some cases, neutralisation can be also considered as a retanning procedure as the neutralising chemicals used may have some retanning abilities.

Neutralization can be achieved in different steps:

- Initial washings before the addition of any neutralising chemicals in order to eliminate excessive chromium and acidity.
- A treatment with specific neutralising agents that must be designed taking in account the thickness of the hides/skins and the final pH of the neutralisation.
- Final washings to eliminate neutral salts that were added or formed through the neutralising operation.

Chemicals used

The most commonly used neutralising agents can be divided into three groups:

- Neutralising agents
- Neutralising and masking agents
- Neutralising and retanning agents

Neutralising agents

Sodium or ammonium carbonates and bicarbonates are examples of purely neutralising agents. Their only objective is to produce an increase in pH and hence the neutralization effect.

This group is often associated with a superficial neutralisation effect.

Neutralising and masking agents

Sodium or calcium formates. Sodium acetate, polyphosphates, organic acid salts and sulphophthalic acids are examples of neutralising and masking agents. These chemicals have good penetration abilities that provide a deep neutralisation action.

Neutralising and retanning agents

The neutralising and retanning agents are usually auxiliary or substitution syntans (synthetic tannins) specifically designed for this operation. Apart from the neutralising action they will also have the ability to change the properties of the collagen fibres.

Relevant Parameters

The most important parameters influencing neutralisation are:

- Type of tannage
- Initial washings
- Hide/skin thickness and intended penetration of neutralisation
- Temperature
- Float
- Neutralising agents

Type of tannage

Higher amounts of chrome left in the hides/skins combined with insufficient basification will result in an increase of the neutralising agents and processing time required to produce the desired effect. Higher resting times after tanning will promote and increase of residual acidity left in hides/skins and therefore will also increase the requirements in terms of neutralising chemicals and operation time.

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Initial washings

These should be always performing in order to eliminate unfixed chromium that could precipitate with the addition of the neutralising chemicals. This, in turn, could produce stains reducing the commercial value of the leathers. The water used in the washing must be checked for excessive hardness otherwise there could be also staining problems.

Hide/skin thickness and intended penetration of neutralisation

Hide/skin thickness combined with the intended penetration of neutralisation are the most important factor in selecting the chemicals used, the amount required and the total operation time. It is obvious that thicker hides are much more difficult to neutralise. Therefore, the neutralising operation must be designed in order to take advantage of shorter floats, increased temperature, neutralising agents with increased penetration abilities and longer operating times.

The penetration and degree of neutralisation will produce differences in the final product. A higher neutralising pH with complete penetration will increase softness and elasticity of the final product. Lower pH and less penetration will favour compactness and firmer handle.

Temperature

Temperature has a positive effect on the neutralising operation. It will favour penetration and reduce the time need for equilibrium between bath and the leathers. Care must be taken if sodium bicarbonate is used because at higher temperatures it will be converted into sodium carbonate. This will produce a sudden increase in pH that can be sufficiently high to precipitate any free chromium that may be present.

Float

As a general rule, shorter or no-float systems tend to increase the penetration of chemicals. This effect is also true in the neutralisation therefore shorter floats should be used when high levels of penetration are required, especially for thicker hides/skins. However, the major drawback of low-level floats is that they increase friction between leathers in the drum. In excessive conditions this can cause irreversible damage to the leathers (buffed grain and broken fibers).

2.4.6. Retanning

Expected Results

The most important objective of retanning is to produce a modification in the properties of leather in order to comply with the requirements of the final product to be produced.

The sequence of post-tanning operations is determined by production requirements.

Depending on those requirements, retanning, dyeing, fatliquoring and even neutralisation can be performed in several distinct sequences.

For the purpose of this manual retanning is considered the use of retanning agents in any phase of chromium tanned leather production.

The phases of production where retanning agents can be used are:

A) As a single product in tanning.

B) As a pre-tannage

- In the pickling operation;

- In the tanning float just before the addition of chrome;
- As an intermediate treatment after pickling and before tanning, but in separate baths.
- Before pickling;

C) As a mixed tannage, together with chrome added for tanning.

D) In retanning:

- Before neutralisation, in a separate bath;
- Instead of neutralisation;
- Before, at the same time or after neutralising agents are used;
- After neutralisation, in a separate bath;

E) Together or after dyeing and fatliquoring, in these cases retanning agents can be added:

- Before dyes are added;
- Dissolved along with dyes;
- After dyeing and before fatliquoring;
- Along with the fatliquoring emulsion (this is not usually done because of the danger of breaking the emulsion);
- After fatliquoring, before fixation with formic acid;
- Together or after fixation with formic acid;
- In a separate bath after dyeing and fatliquoring.

Retanning agents can be used on many different occasions. It will all depend on the intended objective and the agent properties.

Chemicals used and relevant parameters

Vegetable extracts

Vegetable tannins are often used to retan chrome tanned leather owing to their unsurpassed power to fill the fibrous structure, and by doing so impart desirable characteristics to the leather.

The ability of chrome tanned leather to combine with vegetable tannins is well known, and remembering that relatively small quantities of vegetable tannins are offered during retanning processes, efficiency of uptake and fixation is very high. The use of vegetable extract in retanning is always designed to increase firmness and compactness of the leathers, enhance embossing retaining properties or enhance the ability of leathers to be buffed. The most commonly used extracts are those with less astringency levels. This will reduce the smoothness of the grain layer. Such extracts are mimosa, sulphited quebracho, gambier and sweetened chestnut. When using vegetable extract in retanning one should consider the factors that influence its fixation and penetration capabilities. For further details on these conditions please refer to the vegetable tanning chapter.

As a general rule consider that higher neutralisation pH, shorter floats and colder temperatures have a positive effect in reducing the astringency of vegetable tannins. Another positive effect could be achieved with the combination of vegetable extract with syntans. These conditions would enhance the penetration ability of the vegetable extracts. For these reasons it is not common to use vegetable extracts before neutralisation. This would increase the risk of over-fixation at the superficial layer and oxidation of extracts, thus giving a dark leather with reduced grain cracking resistance. The amount of extract used ranges from 2% to 10% depending on the "vegetable" character that is sought in the final products. Higher offers of vegetable extracts will have a strong impact on the intensity of the leather colour. Therefore, the use of vegetable extracts should be carefully planned when intense vivid colours are sought in an article. Light fastness is also negatively affected by the use of vegetable extracts.

Substitution Syntans

Substitution syntans have similar properties to vegetable extracts although they will not affect light fastness and colour intensity in such a negative way as vegetable extracts do. They also present less risk of affecting grain smoothness. Their molecules are slightly smaller than vegetable tannins and therefore they have better penetration abilities. Their combination with vegetable extracts is an effective way of balancing desired and undesired characteristics of vegetable tannins.

Acid auxiliary syntans

These are synthetic tannins that by themselves are not able to tan a leather.

They are usually naphthalene derivatives and their most common application is in vegetable tannage as they are good dispersing agents of vegetable tannins. Their use in chrome-based tanning processes is limited, although they can be applied, especially for masking purposes.

In chrome retannage they can be used for replacing excessive superficial chrome due to their acid nature. This can be useful for enhancing grain smoothness. It will also be useful to prevent chrome precipitation when used before neutralisation. If they are used after neutralisation, they can be helpful as masking agents in order to improve penetration of dyes and other retanning materials. Neutral syntans tend to modify the ionic charge of leather, whilst auxiliary syntans only produce effect in lowering the pH without substantial changes in the ionic charges. This makes them more suitable when penetration and colour intensity are, at the same time, required.

Neutral Syntans

As retanning agents, neutral syntans can be added before vegetable tannins, resins or substitution syntans to improve the dispersion and penetration abilities of these chemicals. It has a strong effect reducing the cationic charge of chrome tanned leathers making them less reactive. They can also be used in the dyeing phase either before the addition of the dye or added into the dyeing solution. In this case their intended use is as dyeing equalizers, increasing the uniformity of the superficial colour.

For this reason, they are especially useful in the dyeing of pale and pastel shade leathers. In darker shades, an excessive use of these chemicals may impart an undesirable effect on colour intensity. They can also be used after dyeing if poor dye penetration has been detected.

Chrome containing syntans

These types of syntans are available with a chromic oxide content ranging from 8% to 12%. Their main application is to increase softness and affinity for anionic retanning chemicals, dyes and fatliquors. They are often used before neutralisation, immediately after washing. This application favours softness and compactness of leathers. This effect can be further increased if these syntans are applied in the neutralisation stage.

However, care must be taken to prevent chrome precipitation. Their use after neutralisation is limited due to the danger of dyeing stains. However, they can be applied after the addition of formic acid in order to increase further fixation of dyes and fatliquors.

Resins

These can be used either in tanning or retanning. The chemical basis of these products can vary but the most commonly found resins in leather production are urea-dimethylol, melamin and dicyandiamide derivatives as well as acrylates.

Resins are almost all cationic in nature. However, in order to introduce them in leather retanning they must undergo a sulphonation treatment in order to render them anionic and suitable for use. Depending on the degree of sulphonation a resin can remain cationic, can acquire up to a completely anionic charge or can be produced in order to ensure a balanced anionic/cationic charge – in this case they are called amphoteric resins. Resins are often used in retanning in combination with vegetable extracts or syntans. They can be also successfully applied on paler shade leather production and as dispersing agents.

One of the most important properties of resins is their selectivity. They will tend to penetrate more into the parts of leather with a loose fibre structure and less where fibres are more compact. This will favour uniformity of the final products in terms of compactness and thickness equalization.

Aldehydes

Formaldehyde and glutaraldehyde are often used in retanning. These materials react to form very strong bonds with the un-ionised basic side-groups and tend to polymerise under alkaline conditions to create large molecules which are able to cross-link protein chains. The resultant leather is rather thin and empty but has an extremely high resistance to washing out of the tanning material.

2.4.7. Fatliquoring

Expected Results

In the production of leather, fatliquoring is usually the last operation in the aqueous phase before drying. This process is generally carried out using either fish oils or synthetic oils that have been emulsified to allow their use in aqueous solutions. Like the retannage, it is of decisive importance for the quality and properties of the leather. The fatliquoring process largely determines the mechanical and physical properties of the leather. If the leather is dried without fatliquoring, it becomes hard and tinny, because the fibres are not lubricated.

The function of the fatliquoring is to separate the fibres in the wet state so that they do not stick together too much during drying. Adequate lubrication and elasticity of the fibres after fatliquoring is essential to give a soft supple handle. Too little fatliquor will reduce the tensile strength, whilst too much can lead to poor adhesion of the finish coats.

To ensure the required degree of penetration of fatliquors, hides and skins must be neutralised appropriately. The neutralisation can be either through or partial (sandwich type) according to the final requirements of the leather. Fatliquoring normally takes place after neutralisation, retannage and dyeing. This is a very broad generalisation and there are many permutations of the order of the three operations retan, dye and fatliquor.

Cationic fatliquors can be used after dye, retan, main fatliquor and fixation (pH 3-3,8) to give a waxy surface or to impart a silky nap on suede. The amount of dyes and retannage material already present in the leather, and occupying sites on the leather fibre, will influence the penetration and fixation of the fatliquor.

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Chemicals used

A fatliquor is essentially a combination of oil(s) and emulsifier(s). Without the presence of an emulsifier, oil placed in water will form droplets when agitated. When the mixing stops the two components rapidly separate to form two distinct layers. An emulsifier decreases the interfacial tension between the oil and water, enabling the oil droplets to remain separate. The hydrophobic ('water-hating') end of the emulsifying group attaches to the oil, while the hydrophilic ('water-loving') end attaches to the water, forming an emulsion.

Fatliquors are generally based on three main sources of raw material:

Natural oils, fats and waxes

These can be sub-divided into animal and vegetable and the main types are shown in the table 'Types of Natural Oils, Fats, Waxes'. The animal and vegetable oils and fats are all chemically similar and consist essentially of glycerol (glycerine) combined with various fatty acids, the compounds being known as glycerides.

The fatty acid associated with the oil, combined with the technique for rendering it emulsifiable (e.g. sulphation or sulphition), are the principal determinants of the performance of the fatliquor. As a generalisation the natural oils and fats have good 'feeding' properties, that is, they import a natural, mellow and 'round' feel. The waxes differ from the oils and fats in that they are esters formed by the union of fatty acids, similar to those in oils and fats, with alcohols other than glycerol, such as cetyl alcohol and oleyl alcohol.

Mineral oils and waxes

Mineral oils and waxes are obtained from hydrocarbons and are volatile (can be distilled without decomposition). Fatliquors derived from mineral oils (such as petroleum) and mineral waxes (such as paraffin wax) are used in leather manufacture. The oils themselves have no polar groups and therefore no ability to bond to the leather fibre. They therefore have good penetration properties, but are also prone to migration, especially when the leather is subjected to heating. Vacuum drying can cause mineral oil fatliquors to migrate to the surface of the leather.

Other characteristics are that they can give a greasy surface, which can be desirable (e.g., industrial gloving on hide splits), or undesirable, depending on the end product. They have poor 'feeding' action, which can result in a soft, but thin, empty, rag-like leather.

Mineral oils are often used as part of a mixture with sulphated oils: (e.g., sulphated marine oil) to give variations in leather handle and properties. A small addition of mineral oil will reduce the risk of free fatty acid spue as free fatty acids are soluble in hydrocarbons.

It is better to avoid using mineral oil if the leather is to have a nitrocellulose top finish as mineral oil is very soluble in nitrocellulose and may cause finish adhesion problems.

Synthetic oils

These can be thought of as 'artificial' or 'pure' synthetic oils.

Artificial synthetic oils seek to imitate the chemical structure of natural oils. For example, glycerine trioleate produced by synthesis imitates neatsfoot oil, the principal component of which is glycerine trioleate. Similarly, a synthetic version of sperm oil is produced by the esterification of oleic acid with oleic alcohol to obtain oleyl oleate. The 'pure' synthetic oils are mainly of petrochemical origin, with physical properties (viscosity, melting point, etc.) appropriate to their use on leather, but whose chemical structure is not found in nature.

As a generalisation, synthetic fatliquors are considered to give a drier, less nourished leather than natural oils but with more stability to light, heat and oxidation. The presence of polar groups on the oil is a major difference

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between the synthetics and mineral oils, which are non-polar, and so do not ionically bond to the leather. Mineral oils are therefore more prone to migration.

Another method for classification of fatliquors is via the charge on the fatliquor: either negative (anionic), positive (cationic) or neutral (non-anionic). In addition to these types are the multi-charge fatliquors, which are a combination of two or more of these types. The principle behind these multi-charge products is that, as one type of fatliquor within the blend drops out of the emulsion and is deposited among the leather fibers, the others continue penetrating the leather structure. A multi-charge fatliquor can therefore be designed to combine the lubricating and penetrating properties of the anionic, cationic and non-ionic types.

Anionic Fatliquors

Anionic fatliquors are those with a negative charge and include sulphated, sulphited and soap fatliquors. Oil emulsified with anionic surfactant and sulphochlorinated synthetic oils are also classed as anionic fatliquors.

This is the category of fatliquors used most predominantly, often after neutralisation, retanning and dyeing.

Cationic Fatliquors

Cationic fatliquors which have a positive charge are produced by blending the raw oil with a cationic emulsifier, such as quaternary ammonium compounds.

They can be used during chrome tannage or as 'topping' fatliquors after fixation to modify the surface feel or appearance. They are often used in this way to modify the nap on suede leathers or to give a grain surface which will release readily from paste drying plates, for sides intended for corrected grain leather.

Non-ionic Fatliquors

These are made from raw oil combined with a non-ionic emulsifying agent. Their lack of charge allows good penetration of the pelt and they can aid penetration of other fatliquors and dispersion of natural fats.

However, they are not substantive to the leather. Care should be taken using non-ionic fatliquors with vegetable tanning.

Relevant Parameters

Application order

There are no set rules governing at which stage during the post-tanning process fatliquoring should take place. The traditional method is to add anionic fatliquor after neutralising, retanning and dyeing as the last operation before acidification/fixing. However, variations may occur to suit the end requirements of the leather and local processing conditions. A proportion of the total fatliquor offer may also be made during neutralisation or retannage, to ensure good penetration of the fatliquor and to assist other chemical actions. Should the fatliquor have an adverse effect on the final colour of the leather, then fatliquoring before dyeing may be performed and the dye bath colour adjusted. Waterproofing fatliquors are often added in two stages to ensure maximum penetration, with a final capping with a mineral salt after fixation.

pH

Fatliquors are most often used in the pH range 5 – 6.5. Fixation takes place as pH is lowered to 3 – 3.5, causing the oil to drop out of the emulsion. Addition of the oil at too low a pH, or too rapid acidification, may cause the emulsion to split prematurely, resulting in a greasy leather surface.

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Sulphited anionic fatliquors containing a small quantity of non-ionic emulsifier and cationic fatliquors have been designed which are stable to acid conditions and high electrolyte concentrations and they can be used in pickle and tanning baths.

Temperature

Normal fatliquoring temperature is 45°C-60°C, though more stable fatliquors (e.g. highly sulphited oils) can be used at lower temperatures. Temperatures of 55°C-65°C are used to maintain the emulsion long enough for it to penetrate the leather. Too low a float temperature may cause the emulsion to break prematurely.

Water hardness

The emulsifying properties of some fatliquors can be reduced by hard water, where calcium or magnesium ions bond with the fatty acid component to form insoluble soaps. The emulsion breaks and the oil is deposited unevenly on the surface of the leather. Above a figure of 80 ppm $CaCO_3$ of hardness, care must be taken to either soften the water or choose fatliquors which are not sensitive to hardness.

Fatliquor nature and type

Some oils affect the plumpness of the leather and this is generally a function of their penetration and deposition characteristics, and the thickness of the film covering the leather fibres. Mineral oils give little or no fill; fish oils are good to medium.

Neatsfoot and neatsfoot/sperm oil substitutes are very good. Fill can sometimes be measured using a substance gauge, but is often a subjective assessment. Combined with softness and surface touch, fill gives rise to other subjective (but vitally important) judgements such as handle, roundness, nourished feel, etc.

Grain tightness can be influenced adversely by inappropriate fatliquoring, rather than enhanced by a good choice of fatliquor (e.g., non-ionic fatliquors may lead to increased looseness). It is not clear exactly how poor fatliquor choice or application causes looseness or pipiness, but it is probably related to an irregular distribution of the fatliquors through the leather cross-section, e.g., oversoftening of the middle layer of the hide or skin, leading to a slight delaminating effect between grain and corium.

The same mechanism by which fatliquoring increases softness, that is, by allowing the fibres to slip over one another, also increases leather strength, as measured by tear and tensile strength. The increase is due to the alignment of the lubricated fibres when placed under tension. Conversely, treatments which embrittle fibres (such as inappropriate retannages) or substantially reduce lubrication among the leather fibres, can reduce leather strength. Weakness may develop over time due to secondary chemical reactions.

Emulsion

Manufacturers vary in their recommendations as to how a fatliquor emulsion should be prepared. Generally, an oil-in-water emulsion is required, prepared by adding the fatliquor to the water whilst stirring vigorously. The volume of the water should be four to six times the volume of the fatliquor and should be at a temperature of 50°C-65°C. Adding the water to the oil can produce a water-in-oil emulsion, which may separate rapidly when it is diluted on addition to the float in the drum. Oil would then be deposited on the surface, giving problems of greasy feel, uneven dyeing and poor finish adhesion. Certain emulsified oils require the water to be added to the oil - see manufacturer's recommendations. Too low an emulsifying temperature and/or insufficient agitation can result in poor emulsification and thereby poor penetration of the fatliquor. Whenever possible, a mechanical stirrer should be used when emulsifying fatliquors to help provide a finer, more stable emulsion.

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Water repellence requirements

Water repellent synthetic fatliquors are available which contain free carboxyl groups and complexing emulsifiers. After fixation of the fatliquor, the leather is treated with a further after-treatment with metal ions which react with the emulsifier component of the fatliquor, eliminating its hydrophilic nature. Zirconium, aluminium and, most commonly, chrome salts are used in this after-treatment, which is variously referred to as 'chroming on' or 'capping'.

2.4.8. Dyeing

Expected Results

The history of the dyeing of leather goes right back to ancient times, when natural dyes such as dyewood extracts lacked with metal salts were used.

The processes for using these products were complicated, and the range of colours was limited. With the advent of the "aniline" (synthetic) dyes at the end of the last century, dyeing became simpler and it became possible to dye virtually any shade. Currently we use anionic dyes that are descendants of the original aniline dyes, having improved physical properties (especially lightfastness) but at the same time being safer to produce.

Dyeing methods

There are a number of different dyeing methods that can be chosen according to the objectives of production.

Normal dyeing

This method is used when sufficient affinity of leather-dye is ensured. The usual procedure is done in a 100%-200% float at around 60ºC. The dyestuff is pre-dissolved and then added to this float.

Common rotation times of around 40-45 minutes are sufficient to ensure penetration of dye. Once that has been achieves dyes are fixed with formic acid in the usual way (final pH around 3.5 / 4).

Sandwich Dyeing

Sandwich dyeing is a process for achieving a coloured cross-section of the leather with a strong surface shade.

The leather is drum dyed in the usual way with an addition of dyestuff to achieve good penetration and then exhausted with acid. A second addition of the anionic dye is then made to the acidified leather.

This second addition of dye will fix rapidly to the surface of the acidified leather and hence build up the surface shade. The build-up of surface shade by the second dye addition can be improved further by the use of a cationic intermediate treatment between the two dyestuff additions. This intermediate treatment could be of a cationic dye (a basic sandwich dyeing), in which case the disadvantage of the cationic dye's poor light-fastness is introduced, or it could be a cationic dye fixing agent.

Basic topping

In this process the leather is dyed with anionic dyes in the usual way to achieve penetration and then fixed with formic acid. An addition of basic dye is then made which strongly colours the surface of the leather.

The addition of the basic dye should always be made in a fresh clean bath, otherwise co-precipitation of the basic dye with any anionic dye remaining in the float could occur, resulting in unlevel dyeing with marked grain-to-flesh contrast having very poor rub-fastness. Unlike the sandwich type there is no addition of anionic dyestuffs after fixation.

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No float dyeing

No float dyeing is a technique for achieving rapid penetration of the dyestuff into bovine suede leather (particularly suede splits) by vigorous mechanical action. It is not generally used for grain leathers since uptake on the grain surface can be uneven due to varying wettability over the area of the material and the mechanical action can cause looseness.

Pigment dyeing

Pigments are sometimes used as an alternative or a complement to traditional dyes. In most cases the purpose is to increase the colour intensity to assist hiding minor faults on the leather surface, with possible economic advantage. Generally, pigments give rise to surface colouration only, with the advantage of improved light-fastness but possible reduction in rub-fastness.

Chemicals used

Dyestuffs

Basic Dyes

Basic dyes are characterized by their brilliance and intense hues. Unfortunately, they have poor light-fastness on leather. Basic dyes are often used in conjunction with acid dyes when deep shades are required. The acid dye is used to give the penetrated dyeing and an intense surface shade is achieved by 'topping' with the basic dye, which fixes to the anionic acid dye. The free base of cationic dyes obtained under alkaline conditions is of poor water solubility. For this reason, basic dyes are often pasted with a little acetic acid before dissolving in water, to increase solubility.

Acid Dyes

Acid dyes are salts of coloured organic acids, usually sulphonic acid. Acid dyes require an acidification process to achieve fixation to the leather. There is a very wide range of colours available. However, the individual dyes may have vastly different dyeing characteristics and fastness properties. The depth of shade is affected by the tannage, neutralisation and the retannage.

If the leather is positively charged, the attraction of the anionic dye will lead to rapid dye fixation on the leather surface. Various techniques can be used to achieve the required balance between surface build-up and penetration of the colour. For instance, more acid stable penetrating dyes can be used in combination with higher affinity acid dyes. Within the range of acid dyes is the premetallised category.

Premetallised Dyes

These are metal complex dyes which have the advantages of mordant dyes (i.e. good wash and light-fastness) without the disadvantage of requiring a metal after-treatment. However, these dyes are more expensive than the unmetallised acid dyes and are therefore used extensively on aniline leathers where high light-fastness is required and where the higher cost can be justified.

There are two types of premetallised dyes:

- [1:1] Premetallised Dyes

These dyes have one dye molecule for every metal atom and have good wash-fastness and generally five pale, level, penetrated dyes.

- [2:1] Premetallised dyes are more surface dyeing and are able to achieve a stronger surface shade with a low degree of penetration.

Direct Dyes
Direct dyes are so called because they can directly dye cotton without any mordant pre-treatment.

They are of similar structure to acid dyestuffs with sulphonic acid solubilising groups; however, they are generally of much larger molecular size. Direct dyes are used in exactly the same way as acid dyestuffs. As a group they penetrate less than acid dyes and give solid, full colours when used on chrome tanned leather. They are therefore useful where strong surface shades are required, e.g. black.

Mordant Dyes
Mordant dyes are a type of anionic dyestuff which have the ability to complex metal ions (the mordant), e.g. chromium, to form a metal complex. They are applied as acid dyes and then after-treated with the mordant.

This after-treatment results in improved wash and light-fastness. However, it may also change the shade of the dye, making matching more difficult. The range available is limited and mordant dyes are now used to a lesser extent and have largely been replaced by the premetallised dyes.

Reactive Dyes
Reactive dyes are so called because they react chemically with the fibre to form a covalent bond. Although they are anionic dyes, their fixation mechanism does not depend on anionic fixation. In contrast to other anionic dyes, reactive dyes are fixed by the addition of alkali to raise the pH of the leather to 8,0-9,0. Reactive dyes can be expensive, but give extremely good wash-fastness because the dyestuff is covalently linked to the leather. However, although there is a reasonable range of reactive dyes available, it is difficult to achieve strong shades.

Solubilised Sulphur Dyes
Sulphur dyes are made by fusion of aromatic amines or phenols with sulphur or alkaline polysulphide. They can be prepared as water soluble versions by converting to the thiosulphonic acid derivatives and it is these solubilised sulphur dyes which find usage on leather. In general, they are applied in the same way as other anionic dyes. As such they give good fastness properties with good penetration into the leather. Their colour range is limited to the dull colours, and strong shades are difficult to achieve. However, they are one of the cheapest types of dyestuff and this, together with their performance properties, is responsible for their popularity as leather dyes.

Natural Dyes
Natural dyes based on animal or vegetable origins (such as wood extracts, other than vegetable tanning agents) are infrequently used in the leather industry. However, some have been used as the basis for technical development of synthetic dyestuffs.

Oxidation Bases
Generally used within the fur trade. Health and safety regulations have tended to reduce the usage of such types of dyeing methods.

Pigments
Some pigments, selected for their particle size, can be used for the dyeing process.

Solvent Dyes
This type of dyestuff is applied in a solution of organic solvent. They are generally used to adjust shade by means of a spray application. Another use is for the colouration of exposed cut edges during the manufacture of shoes and bridle/harness leathers.

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Dyeing Auxiliaries

Cationic agents

These are available mainly to intensify anionic dyeings. These fix not only anionic dyes but retanning agents and anionic fatliquors and often lead to an improvement in fastness to wet treatments, e.g. water, washing and perspiration. Naturally, if applied before dyeing, they may reduce dye penetration or influence the compatibility of dyes.

The range of cationic colour intensification treatments includes:

- **Pre-dyeing Treatments**
    - Mineral retanning agents based on chrome, aluminum and zirconium.
    - Cationic resins.
    - Speciality cationic auxiliaries (these include dye fixing agents).
- **Post-dyeing Treatments**
    - Cationic fatliquors.
    - Cationic dye fixing agents.
    - Mineral dye fixatives, e.g. aluminum salts.

Anionic agents

Anionic agents are used to facilitate the penetration of dyestuff into the leather. Such agents can be ammonia, syntans, neutralising agents, etc. The use of these chemicals can favour plumpness and opening up of leather so a careful balance between dyeing objectives and these drawbacks must be considered.

Relevant Parameters

Temperature

The rate of fixation of a dyestuff on leather is dependent on the temperature.

In order that dyeing times are not too long, dyeing is normally carried out in hot floats (45°C-60°C). The temperature of the float, however, is limited by the shrinkage temperature of the leather. Chrome tanned leather is normally dyed at about 60°C. Occasionally, however, when full penetration is required it may be necessary to carry out dyeing cold, or begin dyeing at a low temperature where the dye is able to penetrate and increase to 60°C during the course of the process.

Operation Time

Whilst normal dyeing times are 30 to 90 minutes for the penetration phase, the duration will vary depending on the types of chemicals used and the other process variables. For a given process, penetration is dependent on duration.

pH value

Float pH has an effect on the ionisation of the leather and the materials added. Ideally the pH selected should allow the material to be in solution and the leather in the correct condition for penetration or fixation. The pH is the main parameter controlling the various steps of the dyeing process.

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Before dyeing commences it is essential that the leather has reached the correct pH so that level dyeings can be obtained. If fully penetrated dyeings are required it is important that the neutralisation has penetrated through the entire leather cross-section, otherwise anionic dyestuffs penetrating into the leather will meet the acid layer just below the surface and will rapidly fix, making dye penetration more difficult.

Neutralisation through the cross-section of the leather can be easily checked by cutting the leather and using a suitable indicator on the cut, e.g. bromocresol green pH 3.8-5.4 and bromocresol purple pH 5.4 – 6.8. At the end of the dyeing process the pH is adjusted again to achieve fixation. If the pH adjustment is incorrect, this may lead to poor dye exhaustion with probable poor colour fastness properties.

Chemicals used in other operations

All anionic retanning agents influence, to a greater or lesser extent, the dyeing properties of leather. When retanned chrome leathers are compared with unretanned ones, all show increased dye penetration for a given dye offer and hence a reduced surface colouration intensity.

Although retanning agents are primarily chosen for their effect on the handle and the mechanical and physical properties of leather, their influence on the dyeing process must be considered. In general, heavily retanned leathers require dyes with good build-up, a high colour yield and good exhaustion. Lightly retanned leather require dyes with a low to medium rate of dyeing in order to preserve levelness. The main effects of some retanning agents are considered below.

Vegetable Tannins

They have a marked dulling effect on dyestuffs and make it difficult to obtain bright shades. They frequently adversely affect the light-fastness of dyes, although, with certain browns, the reddening and darkening of the tan on exposure to light may compensate for the fading of the dye.

Vegetable retanned leathers are often very difficult to dye to deep shades with anionic dyes and some form of cationic treatment, e.g., cationic resins or basic dyes etc., are used to enhance colour yield.

Anionic syntans

These often improve grain appearance, break and grain elasticity. They improve levelness and penetration of dyes but reduce surface colour intensity. Bleaching syntans should be avoided where depth of shade is required.

Resin tans

These give marked improvements in grain tightness, filling of looser areas, buffing and embossing properties. Dyeings remain relatively bright, but depth of shade can be much reduced.

Auxiliary tans

Some types of auxiliary syntans can have a very strong effect on the dyeing process by improving the penetration of the dyestuff and levelness (but at the expense of the depth of shade).

Selection and mixing of dyes

When used together dyes should be compatible with regard to solubility, penetration rates, rate of dyeing at any given pH and rates of exhaustion. If they are not, then fluctuations in dyeing conditions will result in pack-to-pack colour variation. Where possible, formulations should not contain more than three different dyestuffs and avoid formulations that use very small quantities of one component (e.g., one component should not be less than 10% of the total mixture).

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Recipes should not be formulated from dyes which are widely different in hue, i.e. greens should not be formulated from mixtures of blue and yellow as slight differences in penetration characteristics, coupled with day to day variation in dyeing conditions, can lead to severe pack to pack colour variation.

2.4.9. Drying

Objectives

Drying consists of the removal of the free and most of the capillary water from the material. There are a number of ways of achieving this and some can be used in combination. The objective is not only to dry the leather, but to do this with economy in terms of cost and time and also to achieve the best quality and maximum area. In describing the various possibilities, their influence on these characteristics will be mentioned. In the search for optimum quality, some possible economies may have to be sacrificed.

The choice of the drying method is determined by the initial moisture content of the leather, e.g., very wet leather should be sammed and/or set-out to squeeze out free water. This is the cheapest and most convenient way of removing free water. Drying will always be a compromise in the achievement of maximum area, cost of drying and quality.

The removal of moisture (water) from leather is carried out by two methods:

- Moisture removal by physical means (samming/setting).
- Moisture removal by drying.

The leather drying process removes moisture by evaporation from the leather surface. Initially moisture is removed by simple evaporation. Once the free water has been removed the water has to be drawn from inside the leather and from inside the fibres (from about 60% moisture content to about 14% moisture content 'dry-leather'). This is what happens in the normal drying operation. If the leather is over-dried there is a danger of removing the bound water.

The bound water helps to keep the leather fibres apart; if it is removed the fibres can come close together and the charges on the fibres react - this can cause fibres to stick together and make firm or hard leather. Sometimes this is not reversible and is the reason why leather should not be over-dried and reconditioned.

Drying theory

The action of drying generally consists of turning liquid water into gaseous water. The vapour pressure is a measure of the ease with which this happens. The vapour pressure increases with temperature, and at the boiling point of water the vapour pressure equals the external air pressure and the water turns into vapour very readily. Because temperature raises the moisture carrying capacity of the air and also increases the vapour pressure of liquid water, an elevation of the temperature increases the rate of drying.

Under static conditions a saturated layer of air forms at the surface of the leather. Unless this layer is disturbed an equilibrium is reached and no further evaporation can occur. Air flow can displace this saturated layer and drying can then continue. The greater the air flow rate (if properly directed), the greater the rate of drying. There are patented systems for directing air jets over the surface for more effective drying rates.

Under constant conditions it might be expected that increased time gives increased moisture removal. This is generally true; however, the evaporation rate does vary with time. When 'free' water is available evaporation is approximately constant, depending on air flow and temperature. When the free water has been removed, moisture removal depends much more on the rate of migration of water within the leather, and despite constant external conditions, the rate of drying reduces with time.

In general, the longer the time, the greater the removal of water, but this assumes that the external conditions do not change. Different methods of drying can differ considerably in the time required to achieve 'drying', e.g., in a vacuum dryer a leather may take 5 minutes to air dry, but hanging the same piece in the normal atmosphere may take 2 - 3 days.

Target moisture levels of drying

Target moisture levels for various stages are as follows:

Drying	12%-16%
Conditioning	16%-20%
Staking	16%-20%
Milling	12%-16%
Finishing	12%-14%
Dispatching	12%-14%

Drying also affects the chemical reactivity of the leather. If leather is dried to 4%-6 % moisture content, then some of the water in the chrome complex will also be removed; it is not possible to replace the water in the chrome complex and one effect will be to make the leather more waterproof. A compromise between improved water resistance and reduction in leather quality must, however, be considered in this case.

It is important to ensure that leather is not over-dried as the removal of some of the 'bound' water may lead to irreversible hardening of the leather as fibers stick together.

It is therefore essential to monitor the speed and temperature of drying to avoid over-drying. Traditional methods of hanging leather in a shed with louvered sides and relying on natural weather conditions was very slow and lacked control.

- Drying too quickly is difficult to control and can lead to damage.
- Drying too slowly causes build-up of goods in process and takes up a great deal of space.

Before finishing leather must be dried; before the drying itself, to remove the water in excess and to flatten the leathers, they are sammyed and setted-out.

Figure 2.25. Sammying and setting-out operation

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Drying Technologies

Vacuum drying

There are different possibilities for drying but in the majority of cases the drying process starts passing the leathers through a vacuum dryer. Vacuum drying involves drying the leather under tension, with reduced air pressure leading to evaporation at lower temperatures.

Whilst this can give a uniform drying, generally it is unusual to dry the leather completely by this method. (Fully vacuum dried leather, particularly skins, can be difficult to recondition due to the high temperature attained on the surface of the leather which is in contact with the plate). It is more common to dry only until the grain is set and the skins/sides are removed and drying is completed by hang drying.

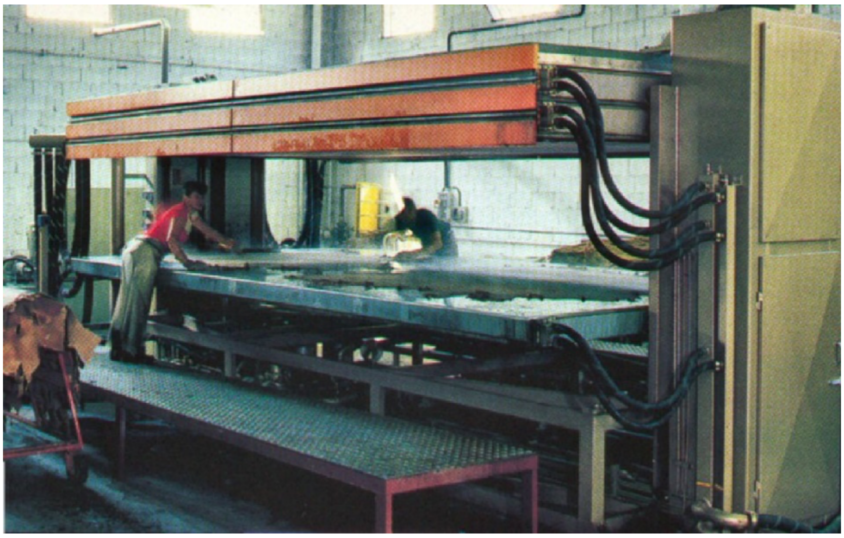

Figure 2.26. Vacuum drying

Vacuum dryers consist of a heated metal plate on which the skins/sides are 'slicked' out. A hood with an air seal diaphragm is lowered onto the plate and air pressure is reduced by a vacuum pump withdrawing air between the hood and the plate.

The vacuum created lowers the temperature of evaporation of the water and latent heat of evaporation is supplied by the heated plate. Complete drying is possible, depending on the temperature and time, e.g. skins dried in approximately 5 minutes at 70°C. The hood is fitted with a mesh to assist extraction but sometimes this mesh is replaced with felt to avoid marking of skins.

Generally, grain leather is placed on the machine with the grain next to the plate. Wet wheeled suedes may also be dried with the grain next to the plate to avoid the nap being too compacted by the plate. In this case, a felt may be used instead of mesh to avoid mesh marks on the suede side. Vacuum dryers may be single or multi-plate machines. They can be flat or the plate angled and also circular (three tables around a drum).

Overhead Drying / Ambient temperature drying

This drying system involves hanging the leather on a conveyor, usually overhead, within the factory space.

Instead of being actively dried by a heated air flow, the leather is passively dried in the ambient temperature of the factory. This is a very energy efficient method but can involve long drying times and consequently long conveyors with higher levels of goods in process.

Figure 2.27. Overhead drying

Tunnel drying

Tunnel drying normally consists of an open-ended wooden or insulated metal tunnel. The leather is hung on a conveyor system, travelling from one end to the other. The drying time will be controlled by the conveyor speed. Air flow can be in the direction of the conveyor or counter-current. The latter is the more efficient as the driest air meets the driest leather, and drying is both more efficient and even. In tunnel drying there is the additional possibility of humidity control in the various sections of the tunnel. This can prevent over-drying and also control the drying rate to achieve optimum quality.

A very efficient drying system based on tunnel drying involves the use of a heat pump. This extracts water from the moisture laden air and recycles the dried air and also warms incoming fresh air. The process is very energy efficient and yields leathers of the desired handle, but care must be taken to keep the air/heat interchangers free of dust.

Figure 2.28. Tunnel drying

Paste drying (Pasting)

Paste drying involves drying the leather under tension, generally through a tunnel drying system. This gives a uniform drying and reduces the area loss associated with hang drying methods.

In general, this method of drying is only used for splits and leathers where the grain surface is subsequently 'corrected' by buffing, which also removes any residual paste. It is rare to achieve the ideal situation where the leather sticks to the plate throughout the drying process and all the paste remains on the plate when the dried leather is removed. Leathers are usually dried to a minimum moisture content (approximately 14% moisture) and then reconditioned to the required moisture content for further processing.

The paste dryer consists of large frames with glass, metal, or enameled plates. The plate is first covered with a thin layer of 'paste'; this is usually a starch solution, but it may contain some other auxiliaries to correct the viscosity and tack levels. Application is normally by airless spray. The leather is then 'slicked' out onto the plate (grain next to the plate); slicking is performed by hand or machine. The leather is then dried and the paste holds the leather under tension, preventing any area loss. The formulation of the paste should allow:

- The leather to stick to the plate throughout the drying process.
- A paste-free grain on removal of the leather.

Adhesion of the paste can be reduced by adding carboxymethyl cellulose or increased by adding starch.

Adhesion of the paste to the grain can be reduced by surface fatliquoring of the leather.

Figure 2.29. Paste drying

Toggle drying

Toggle drying involves drying the leather under tension, generally through a tunnel drying system (continuous process). This gives a uniform drying and reduces the area loss associated with hang drying methods.

Leathers are dried to a minimum moisture content (approximately 14% moisture) and then reconditioned to the moisture content required for further processing. Extra tension can be applied to the leathers by mechanical means (toggle frames that expand) but there is a compromise between maximising area yield and required quality. Over-stretching can give a thin, tinny leather of poor lastometer distension with subsequent grain crack and firm/hard handle.

The fundamental part of a toggle drying system is a toggle frame. This usually consists of a perforated metal sheet onto which the wet leather can be attached by means of spring clips called toggles. The wet leather is 'toggled' out under tension and dried in very similar systems to that of hang drying, e.g. cabinet or tunnel drying can be used. Other variations of the system include toggle frames that expand through one or two dimensions and where the toggling process has been automated.

Figure 2.30. Toggle drying

Influence of drying in area yield

In general, the higher the temperature, the lower the relative humidity and lower the area yield. However, higher temperatures coupled with higher relative humidity air can modify drying rate and give a better than expected area yield. It is the high drying rates that generally give lower area yields.

There is, however, an important point to be made about the drying rate. The drying rate in the initial stage (with capillary water present between the fibres) can safely be much greater than at the point where the capillary water is virtually removed and fibre to fibre contact is made. At later stages the drying rate should be low.

Note: A slow drying rate tends to give a higher area yield, but this does not mean that higher rates cannot be used at the early stages as long as the rate is dropped at the critical later stages. Area yield, whilst a factor in profitability, is not to be divorced from quality. It is not advisable to maximise area yield at the expense of a 'quality' leather. A suitable compromise must be achieved.

Wet leather from retannage, dyeing and fatliquoring has a fibrous structure which is well spaced; the spaces being occupied by water. Drying results in shrinkage, as the water is made to evaporate, so the fibre structure collapses, the fibres approach each other and (depending on drying conditions and fatliquor) may well adhere to each other. On rehumidification some increase in area will result but this may be limited by sticking of the fibres, giving not only hard leather, but lower area yield. The effect on area yield is strongly dependant on the drying technology used.

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Here are the major impacts of drying technology selection on area yield:

Vacuum drying

Vacuum drying gives an area yield which is higher than that of hand toggling. Although the leather is held by the pressure of the cover, some shrinkage can occur during the drying period. The actual conditions of temperature and time can make a significant contribution. New low temperature dryers claim excellent area yield. Vacuum drying is practised for its flat grain setting characteristic more than for area yield.

Hang drying (Overhead drying)

As there are no restraining forces, this form of drying gives the lowest area yields. There are, however, considerable variations in area yield depending on the actual drying conditions (i.e. the various conditions under which hides and skins can be hang-dried); the best area yield is obtained when the drying is carried out at ambient temperature.

Oven drying gives a lower area yield and, the higher the temperature, the worse the yield. If the air flow is increased the area yield is further diminished. On the other hand, the higher the relative humidity, the lower the rate of evaporation and the greater the yield. Yield is also affected by the residual moisture content, e.g. the higher the residual moisture content, the higher the area. Incorporation of a heat pump can lead to lower drying temperature and increased area yield.

Paste drying

Paste drying gives probably the best area yield apart from split frame toggling. However, residual paste on the leather limits the finishing possibilities (mostly corrected grain leather).

Toggle drying

Toggle drying prevents the leather from shrinkage to a certain extent and the area yield is a considerable improvement on hang drying. With split frame toggling (e.g. where mechanical or hydraulic forces separate the frames, thus stretching the leather), the area yield can be one of the highest available by any method. However, there is a loss of quality and the resulting grain distension capability can be very low. A more recent development is toggling onto a sectional circular framework. Hydraulic pressure is applied to the centre of the sectional framework, causing it to expand in a manner similar to an umbrella.

Parameters affecting conventional drying

Moisture

If skins/sides have been allowed to become too dry after samming/setting-out, it will be difficult to slick them onto the vacuum dryer or the plate of the paste dryer.

Length of conveyor/tunnel

The longer the tunnel, the longer the time available at a given speed to dry the leather, enabling milder and more gradual drying. A longer tunnel also allows for changes in drying conditions as the leather passes along.

Tension

The tension of the leather being dried will affect the handle and yield of the leather.

Air Speed

Movement of air is essential to remove moist air, but direction is as important as total volume. In general, the higher the air speed, the more rapid the removal of moisture.

Relative Humidity

Principally controlled by temperature but also affected by ambient conditions. In general, the higher the relative humidity, the slower the rate of drying.

Time

This is a function of length of tunnel and speed, whereas, in general, longer time equates with greater moisture removal, the drying rate is very much influenced by other factors. For vacuum and paste drying, the time the leather is in the machine is directly linked to the amount of water removed.

Temperature

The heat capacity of the air is available for the latent heat of evaporation required by the water to convert to vapour. Temperature influences relative humidity, e.g. the capacity of the air to absorb moisture. Excessively high temperatures should be avoided. The temperature for drying may range from ambient up to 70ºC.

Rate of Drying

Controlled by relative humidity, air speed and direction, rather than absolute temperature. To achieve softness the rate of drying has to be slow as the water evaporated changes from 'free' to 'capillary', in order to minimise fibre sticking. If the leather fibres are stuck together they move less freely, which makes firm leather; it may also lead to looseness of the grain.

2.4.10. Finishing

Pre-finishing operations

Conditioning

After drying, the leather can vary in moisture content depending on the type of drying it has received. On the other hand, there are differences in moisture content across the leathers, e.g. the edges are drier when compared to the centre of the hide/skin.

For this reason, it is vital to equalise moisture content of hides/skins in order to ensure proper conditions for staking and remaining finishing operations.

The conditioning operation can be carried out in different ways:

- By applying water to the dried crusted leathers using a spraying conditioning machine or using a conditioning drum.
- By applying water to sawdust and piling the leathers with a layer of wet sawdust in between each hide/side/skin.

In some cases, it is possible to dry the leather to a suitable moisture content, removing the need for the conditioning operation. This is possible using low temperature vacuum drying and drying tunnels. In order to avoid problems with the leather break, changes to the retanning process may be necessary.

In certain countries it may be possible to dry the leathers without the use of drying machines by hanging the wet leathers in open sided or louvered sheds. The leathers will be dried and conditioned within these sheds by reaching a natural equilibrium with the surrounding atmosphere. Quality problems can be encountered in later processing if the leather is either underconditioned or over conditioned. In both cases, the result could

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be loose leather and poor grain break. Underconditioning would tend to give a firm handle. Overconditioning would tend to give flaccid handle and possible looseness.

Staking

Staking is a softening operation which is normally carried out prior to finishing. Control of moisture within the leather is critical: too low a moisture content (below 14%) and uneven or reduced softening is achieved, and weakening of the leather may result; too high (in general above 25%) and unsatisfactory results can be obtained (e.g. looseness).

Staking machines fall into two categories: those which achieve a softening effect by pulling the leather under tension against blunt blades (e.g. Slocombe or rotary machines); and those which involve the leather being acted upon by banks of blunt pins or hammers to soften it (e.g. Molissa).

The choice of machine will depend largely on the suitability to a particular type of leather, together with the effective staking they can have an effect on area yield.

Staking machines are usually of the following three types:

Slocombe staker

The lower arm of a Slocombe staker contains a series of up to 4 blades. These blades can be either plastic/perspex or, for more intense staking action, they may be metal and may even be slightly sharpened.

The top arm generally contains three rollers and often one blade at the front of the arm. With each stroke of the arms the leather passes over the blades and is forced in-between the rollers, giving the mechanical action that imparts the softening (the front blade on the upper arm can be exchanged for a pad or block of narrow wood, covered with carborundum paper or even a carborundum stone to give a nap raising effect to suedes - this is often referred to as 'stoning'). The operators grip the leather against the machine with their waists and manoeuvre the leather around the machine with their hands. These machines are gradually being replaced by rotary and, more particularly, through-feed machines.

Figure 2.31. Slocombe staking

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Through-feed staking machines

Through-feed staking machines generally consist of banks of blunt pins or hammers that pummel the leather as it passes through the machine. The leather is held in place in between two belts made from rubber (neoprene) or, more usually, synthetic fabric such as Lycra. The oscillating pins on the lower bed of the machine slot into receiving holes in the upper head of the machine.

The leather is thus flexed by many pins as it passes through the machine. The degree of softening is regulated by adjusting the receiving head so that the pins either penetrate deeply into the holes (heavy staking) or conversely the pins only penetrate a short way (light staking).

Figure 2.32. Through-feed staking

Rotary stakers

There are many versions of rotary staker but they all work on the same principle.

The leather is fed into the machine on a roller and is stretched/softened by the action of a 'V' bladed cylinder.

The design of the blades can vary from the usual straightforward configuration to blades which are wavy in form. The degree of softening achieved can be varied by adjustment to the machine. This machine is more suitable for small animal skins.

Trimming

After the skins have been staked and are soft again, before proceeding to the finish they are trimmed to make it more rounded by removing unnecessary tips and parts that could somehow create problems in the course of the finish as they are passed through the machines.

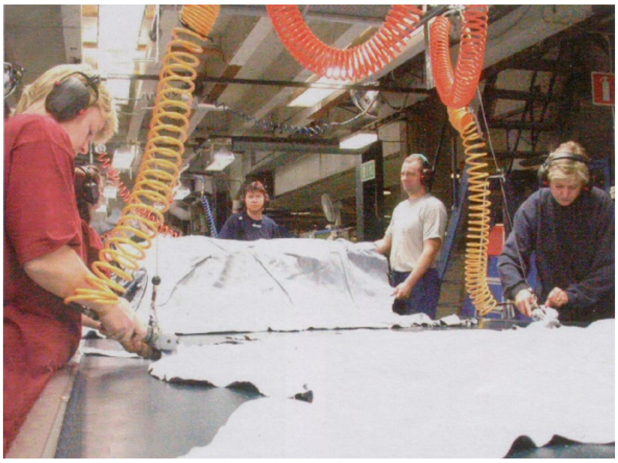

Figure 2.33. Trimming before finishing

Chemicals used in finishing

Film forming resin binders

These are the most common binders used in finishing. They are all aqueous based and consist of resin particles in emulsion form which yield a film by evaporation of water and the coalescence of the resin particles. The properties of the finish are determined mainly by the resin composition but are also influenced by other components such as the type and concentration of pigment and auxiliaries. These can modify the film formation and the tactile qualities of the dried film. The resin emulsion is also responsible for imparting the degree of tackiness of the finish film when it is being sprayed or roller coated.

Although the finished dried film may have little or no tack, the leather surface, at intermediate stages of spraying, may be distinctly sticky. This is usually due to insufficient cooling of the leather after spraying and drying or insufficient drying of the finish film itself where some solvent (or water) is still present.

Amongst the various types of resin emulsions, the most commonly used in leather finishing are:

Acrylic resin emulsions

These are the most commonly used synthetic resins in leather finishing. They are obtained from the polymerisation of esters of both acrylic and methacrylic acid.

There are a wide range of properties, reflecting the diversity of the monomers, among which are the following:

- methyl acrylate: hard, with good abrasion resistance
- ethyl acrylate: soft and extensible, with good adhesion
- butyl acrylate: very soft, tacky
- methyl methacrylate: very hard

Butadiene resin emulsions

In practice butadiene resin emulsions consist of styrene-butadiene copolymers, which are available in a variable range of hardness, or copolymers of styrene-butadiene acrylates.

Butadiene resin emulsions are often used in corrected grain or split finishes

Polyurethane resin emulsions

Polyurethanes can also be formed by the addition of isocyanate with amines or carboxyl groups.

This offers an almost infinite variety of resins by the changes possible in the selection of both base components. It can be justifiably claimed that polyurethanes can be tailor-made to meet all applications and they are used in almost all forms of surface coating and other applications of plastics.

Because of the wide choice available of base components for the polyurethanes, a far wider range of properties can be achieved with these than with acrylics or butadienes. Polyurethanes can meet the needs of the finishes from impregnation, through main pigment binder, to topcoat.

The drawback is that the resins are expensive.

Protein binders

These include finishes based on casein (derived from milk) and albumen (derived from egg and blood), and may contain additives such as plasticisers, waxes and shellac (derived from a species of beetle). Their main characteristic is that they are applied as very thin films and in general can be glazed (polished with frictional heat) to give a high gloss. Because they are thin and smooth they give a pleasant, natural handle.

Glazing highlights (enhances) the natural grain appearance. As the casein used is solubilised some fixation is required; traditionally formaldehyde was used as fixative, but nowadays casein fixation can be achieved with other cross-linkers such as phosphonium sulphate, aziridines and isocyanates. Although casein can be used on its own, it can also be modified by additions of albumen to give enhanced gloss, or shellac, which tends to harden the finish. Most casein finishes are glazed to enhance their gloss and to give an impression of depth.

Pigments

Pigments form the most significant colouring agents used in leather finishing. They are the water insoluble, coloured components of a finish, which:

- give colour
- give hiding power covering uneven dyeing or minor skin/hide defects
- improve uniformity of colour
- improve light-fastness compared to dyes.

Pigment dispersions for leather finishing are prepared by specialist manufacturers, and are supplied normally as casein bound or casein free. The former has casein, a protein derived from milk, as the dispersing agent (e.g. the medium which surrounds the individual pigment particles and prevents aggregation or settlement), while casein free dispersions utilise products such as acrylics, sulphated oils and surface-active agents as dispersing agents. Personal preference tends to dictate which type is used.

If different pigment ranges are involved, the finisher should check compatibility when initially selecting a pigment, by making up a mix with the new pigment, and a range of established pigments and resins, and check this for viscosity, settling and precipitation over time.

Dyes

Dyes are generally transparent colours which are unable to cover the leather grain and defects.

Dyes find several applications in leather finishing;

- to modify the colour of crust leather prior to finishing (dye staining)
- to give colour to unpigmented finish coats (aniline finishing);

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- in combination with small amounts of pigment to give 'assisted' aniline effects (semi-aniline);
- to colour topcoats applied after fully pigmented base-coats (two-tone effect, also known in certain cases as semi-aniline effect).

Dyes used in finishing are supplied in liquid form, being dissolved in water with solvent added to aid solubility and stability. They require good general fastness properties, and particularly light-fastness.

Lacquers

Nitrocellulose lacquers

Nitrocellulose lacquers and lacquer emulsions are the commonest topcoats for resin finishes, the former being solvent based (~85% solvent), the latter being water based (~55% solvent). Lacquers are made by dissolving nitrocellulose in solvent (e.g. ethyl acetate, methoxypropanol, methyl isobutyl ketone). These solutions can be emulsified with water and surfactant to give lacquer emulsion.

In general, the solvent lacquers give tougher, brighter films than the lacquer emulsions. As a general statement, solvent based finishes have good film formation, superior wet and dry rub-fastness, good feel and excellent flow out, giving uniform gloss and appearance. However, solvents are expensive, equipment can be difficult to clean and there are hazards of toxicity and flammability.

Limitations have been set for volatile organic compound (VOC) emissions in many countries. Chlorinated solvents are deleterious to the ozone layer. Water based finishes can be applied at greater solids and are generally cheaper; they also have good hold-up.

Nitrocellulose gives good feel, good print retention and moderate to good fastness. It can yellow on exposure to light and/or heat and is, therefore, not suitable for whites or very pale shades.

Nitrocellulose emulsions give films of little or no extensibility (compared to polyurethane lacquers, which are better film formers). Hence, they are not very good at carrying or 'binding' solids, e.g., pigments (they are generally applied as relatively thin films compared to resin emulsions).

Dyes can be incorporated into nitrocellulose lacquers.

Due to the poor extensibility of the nitrocellulose films the flex resistance of leathers finished with such films is lowered compared to a water-based finish.

Polyurethane lacquers

Where very high fastness properties are required, for instance flex and abrasion resistance for upholstery leather, polyurethane lacquers are often employed.

As previously mentioned, when discussing polyurethane resin emulsions, these are very versatile, and gain their fastness properties from the strong bonds between the molecules.

Polyurethanes are sometimes described as being either aliphatic or aromatic. As a broad generalisation aliphatics can be thought of as being softer, elastic and lighter-faster, and the aromatics harder, stronger and with the possibility of yellowing to light and/or heat in some cases. Aliphatics tend to be more expensive.

Polyurethane lacquers can be used in two component systems, where one component reacts with another in situ to give a fully reacted, 'cured' film or they have crosslinkers added to enhance the performance of an otherwise one component system. However, it is more common today to use a fully reacted, one component system. Polyurethane lacquers are more expensive than nitrocellulose lacquers and have a less attractive surface touch.

Auxiliaries

Waxes

Wax emulsions are commonly used as auxiliaries. These are dispersions of wax in water, readily miscible with resins and pigment. The waxes used can be quite varied, from natural waxes such as carnauba (used in burnishing top coats), candelilla and montana to a wide range of synthetic paraffin and polythene waxes. Waxes are commonly used to facilitate plate release, reduce sticking in the pile or modify surface feel. Excess use can result in poor inter-coat adhesion of the finishes.

Penetrators

Where good finish adhesion is crucial, or when low viscosity is required (such as for impregnating systems), penetrators are used. These are water-miscible solvents (e.g., isopropyl alcohol), often mixed with wetting agents.

Fillers and matting agents

Fillers work by disrupting the finish film, increasing the degree of light scattering, thereby increasing cover power and/or reducing gloss. They are generally based on silica or china clay. If excessive additions of fillers and matting agents occurs, the final dried finish film may show white creases when flexed. On the other hand, the aesthetic qualities of the leathers could be compromised.

Handle Modifiers

Some resins have a somewhat plastic feel. The ideal surface 'touch' to many people is probably that of a well fatliquored, unfinished leather.

To achieve this natural feel, handle modifiers can be added to the top coat. Feel is subjective and ultimately it is the customers’ opinions which count and, of course, the requirements of surface feel will vary with the end use of the leather. Additions of wax and oils are used to impart feels which are often described in subjective terms: 'waxy' and 'oily' are fairly easily understood, but 'warm', 'draggy', 'loggy', 'buttery' are open to interpretation. Silicone is also used, in emulsion or oil form, to give added slip and reduce tack; an excess of silicone gives an artificial slippery feel.

Finishing operations, or part of the finishing process

Impregnation

This is an optional operation which can be carried out on full grain or corrected grain leathers. Its principal aim is to improve break and reduce looseness. Although it can be the first finishing coat, it can also be considered as the last stage of retannage, in that it modifies the characteristics of the surface, without being a surface coating. Impregnation is nowadays performed with acrylate solutions of fine particle size. The relevant properties of the impregnant are hardness, molecular weight, weight of solid polymer applied and the penetration of the applied material. Typically, impregnation will involve the use of a small (< 100 nanometres) particle size resin, applied at about 2 grams to 4 grams of resin solids per square foot.

Initial theories as to the mechanism of grain tightening suggested that impregnation improved bonding at the grain/corium junction within the leather. However, later investigations showed that the impregnating resin very often only penetrated to a depth of 1/2 to 1/3 of the grain layer. It is believed that in sufficient concentration the resin will act as a filler in this grain layer to modify the behaviour of the fibre structure as the grain is bent inwards. Impregnation therefore improves break, resulting in finer wrinkles on the leather

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surface. Impregnation is typically applied by roller coater, curtain coater or pad, and application rates can be high generally (circa 30g per square foot for 'correct grain' in one or two applications).

Buffing

Buffing consists of grinding the leather surface with an abrasive material. It is primarily used for removing or correcting superficial defects thus giving a more uniform surface.

The degree of buffing is controlled by:

- the grit size of the buffing paper
- the way in which it is coated on the paper
- the number of passes
- the pressure applied by the buffing machine.

Snuffing is a term used for mild abrasion of the surface in which finer papers (400, 600 or 1000 grit) are used. Buffing can be intended for superficial film application (e.g. in the case of corrected grain) or as a final finishing operation (e.g. in the case of nubuck). The quality of the nap obtain can be achieved by selecting the correct buffing papers and using them in the correct sequence.

For the production of corrected grain:

- First use 180 paper.
- Then use 240 or 320 paper.
- Finally use 400 paper.

For the production of nubuck:

- First use 320 paper.
- Then use 400 paper.
- Finally use 600 paper.

If the leathers are buffed too deeply, the nap will be woolly, containing long corium fibres; if the leathers are not buffed deeply enough, patches of grain will be left on the leather. If leathers used for corrected grain are roller coated with the nap going in the opposite direction to the feeding roller, the leathers produced can have a rough grain. If they are too wet, chatter marks will appear during the operation. Chatter marks can also be produced by paper badly fitted.

The type and quantity of fatliquors used during the post-tanning process, and the quantity and type of resin used, can have an adverse effect on the buffing operation by clogging the buffing paper, which would then be unable to abrade the leather. The leathers ready to go through the buffing machine must be flat and adequately trimmed to prevent any damage during the operation (i.e., cuts, scratches, tears etc.). If the leather to be buffed is of variable substance, the result will be an unlevel buffing. For small thickness discrepancies it is possible to compensate by using a softer feed roller.

Base coats

These are the major finish coats which tend to control the performance of the finish, and may be applied by pad, roller coater, spray, or combinations of these. These coats contain pigment which gives colour and cover to the desired extent. Ideally the pigments should match the dyed colour of the leather so that if the finish is scuffed or pulled off, the contrast with the leather is only slight. More often, a pigmented finish is seen as a means of economising in dyestuff and the pigment coat is matched to achieve the final desired colour but applied to a rather lighter dyed substrate. On finish removal, a contrast in colour is immediately seen and it becomes important that the fastness of the finish is such that it stands up to reasonable wear without failure.

One of the unrecognised problems of flex test method results is that they tend to give no indication of the visibility of the damage once the finish has failed. A leather finish with a flex failure of 50,000 and a grey scale contrast of 3 will be much more acceptable than a leather with a similar flex resistance of 50,000 but a grey scale contrast of 1.

The cover of the coat can be varied by a mixture of inorganic and organic pigments but, for bright shades requiring mainly organic pigments, a 5% to 10% addition of titanium white will improve cover with minimal change in the brightness of the shade. Similarly, a dull inorganic matching can be 'brightened' by use of 5% to 15% of an organic pigment without losing the good cover of the inorganic pigment.

For good flexibility and adhesion, the pigment must be sufficiently bound by the resin in the formulation. The resin must also bind any waxes or fillers in the mix. As a rule of thumb, the pigment to binder ratio will normally be in the range of 1 part pigment to 1.25 to 1.75 parts of binder, assuming a resin emulsion solids content of 40%. To avoid flex problems, use somewhat softer resins, reduce pigment to the minimum and minimise contrast in colour between coatings.

Top coats

The final component of the finish is the lacquer or lacquer emulsion which forms the top or fix coat. The objectives of the topcoat are primarily to improve water, rub and scuff resistance, to make the finish harder wearing, with secondary objectives being to give the required surface feel, level of gloss, and sometimes ability to withstand printing. Lacquer or lacquer emulsion coats can be dyed to achieve two-tone effects and, occasionally, pigmented to give extra cover (especially in the case of white leather).

Solvent based lacquers, lacquer emulsions and, more recently, tough aqueous resin emulsions are used as top coats. These control the final gloss, feel and, to some degree, the fastness of the finish, and normally will be applied by spray application, and in some cases by roller coater.

The concentration of these products will influence the fastness and gloss achieved. In general, the more dilute the top coat, the lower will be the fastness (e.g. rub-fastness) and gloss. Silica based auxiliaries may be used as matting agents in both water and solvent based top coats, and a wide variety of oils, waxes and slip agents are available for use in top coats to modify surface feel. They may also be applied as separate spray coats after top coating.

It should be noted that in many applications lacquers and lacquer emulsions are being replaced by solvent free, water-based systems, because of environmental concerns about solvent emissions. To achieve the toughness and water-resistance of the solvent systems, water-based topcoats often require the use of crosslinking agents. The choice of top coat may depend on subsequent mechanical operations like embossing and not just on the final physical appearance.

Plating and embossing

These operations are done by pressing the leather surface against a heated hard metal surface under a specified pressure for a specified time. If the hard surface is raised and patterned, it is called embossing and if the hard surface is smooth and polished, it is called smooth plating or ironing (through-feed machines).

Embossing can:

- give a pattern to the leather surface as a decorative effect
- hide some natural grain faults such as scar tissue, tick etc. This will upgrade leather quality.

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Smooth plating (or ironing) can:

- increase gloss
- improve rub-fastness and smoothness of feel
- seal basecoats to allow better build-up of subsequent coats.

Embossing and plating may harden the leather so care should be exercised to balance the temperature, pressure and dwell time to obtain the required handle. Normal printing/plating conditions would be temperature 80ºC to 120ºC, pressure 50 kg/cm_2 to 200 kg/cm_2, and pressing times ranging from 0 to 10 seconds.

Milling

Milling or dry drumming involves tumbling the load of dry leather in a wooden or metal drum. The mechanical stresses created separate the fibres within the leather structure, increasing leather softness and often imparting a more pronounced or pebbled grain appearance.

Control of leather moisture content is critical: too low a moisture content and the softening effect will be uneven, and weakening of the leather may occur; too high a moisture content and the leather may become loose.

Dry drumming may be carried out before finishing commences, in between finish coats, or after finishing. An effect similar to shrunken grain may be obtained by printing leathers prior to dry milling and subsequently drumming them at high moisture contents (40% to 50%). Dry drumming can also be used to enhance the shade of splits or suede leathers. The operation is carried out by manipulating the moisture content of the leathers. During dry drumming waxes or other chemicals can be added to modify the final handle of the leathers.

Finishing equipment

Buffing machine

Machines can be single roll (approximately 0.3 m) or continuous through-feed buffers with a working width of up to 3 meters to deal with whole hides. For the buffing and snuffing of skins, buffing wheels can be used instead of buffing machines. These machines do not use buffing papers but they are regularly gritted with the required abrasives, which are glued directly onto the wheel. The wheeling operation can be carried out on wet blue or dyed crust, and is most commonly used to produce skin suede. During the buffing operation, it is important to observe the buffed surface and monitor the appearance of this surface to ensure that scratches do not appear due to too coarse a paper, and that the abrasive action is not reduced due to clogging of the paper. The paper must be regularly checked and changed

Types of abrasive papers

There are several types of buffing and snuffing papers available. The abrasives can be emery, carborundum, aluminium oxide, with the adhesive directly applied to the paper, or the abrasive can be applied to the paper and coated with the adhesive. It is claimed that where the adhesive coats the particles that the paper is 'self cleaning', whereas when the adhesive is applied to the paper this can lead to quicker clogging of the paper.

The papers that are usually used in a tannery vary in coarseness from 100 to 1000. The lower the number the coarser is the buffing paper. Buffing papers sometimes use special support and adhesive in order to work in wet conditions (wet blue buffing for example). They are normally presented with a different colour support in order to be easily recognised.

Curtain coating

In curtain coating the finish is applied as a liquid curtain. The leather is placed on a conveyor which is in two parts. The first part takes the leather up to the curtain, then shoots it through the curtain (supported by stationary blades) on to a take-off conveyor.

There are two types of curtain coater. The 'gap' type controls the thickness of the curtain by the gap between two plates in the trough containing the finish. There is an overflow pipe, where any excess finish pumped into the trough is recycled into the reservoir of finish.

The second type of curtain coater is the 'weir' type. The finish in this case is controlled by the flow of finish over a weir. The finish that is not caught by the leather is collected in a trough and recirculated. The quantity of the finish applied is determined by the pump and the level between the top of the weir and an internal overflow to a reservoir. This type of curtain coater gives rather more stable curtains and allows the application of smaller quantities of finish.

The main application of curtain coating is for impregnation coats where large quantities of finish are applied as a single coat. As the reservoir has to have an appreciable volume of finish, this application process tends to be limited to large production runs. Curtain coating can also be used for the application of base coats on corrected grain leathers, although roller coating is, in this case, generally preferred (finishing performance is improved by the mechanical action of the rollers).

The curtain coater applies a fairly large quantity of finish in one coat. Problems can occur with the drying of such large quantities of finish, necessitating long take-up conveyors. However, as stated above, curtain coaters are mainly used for impregnating corrected grain leathers, and these are usually piled overnight before drying.

Gun spraying

In gun spraying, compressed air and liquid finish are combined in a spray gun to atomise the finish and then to transport the droplets to the leather. A very even application is possible. The droplets combine to give a film on the leather surface. Spraying is still the most popular method of finish application.

Advantages of gun spraying

- Even application.
- Amounts applied can be widely varied.
- Effects easily achieved, e.g. angle spraying.

Disadvantages of gun spraying

- 40% to 60% material waste.
- Environmental concerns over emissions of finish materials to atmosphere.
- Adhesion and intercoat adhesion problems possible.
- High energy requirements.

Spray guns are fitted in a spraying cabinet. The spraying cabinet houses the spray gun arrangement, protecting the tannery personnel from contact with the rapidly moving arms, and confines the excess vapour produced during spraying. An exhaust system then extracts these excess vapours. The upper cabinet carries fixed and sliding windows and the lower section beneath the moving conveyor is built up from removable panels.

A conveyor is fitted to allow the leather through the spraying cabinet and dryers. This conveyor consists of parallel strings spaced approximately 2 cm to 5 cm apart and made from either 2 mm diameter nylon or woven Terylene (polyester).

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Figure 2.34. Loading leathers onto spray finishing line

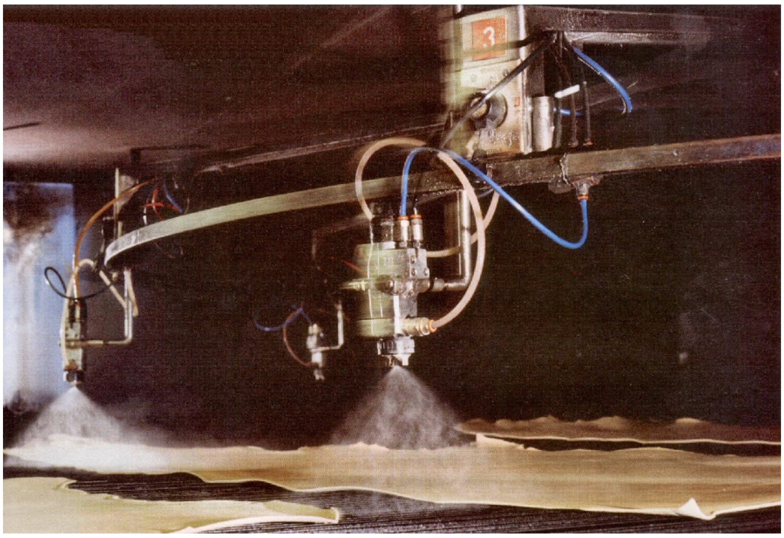

Figure 2.35. Detail of spraying operation

There are different types of spraying guns that can be fitted, amongst these types are:

Conventional air atomising gun

The air atomising spray gun is the heart of an automatic spraying machine and must be set up correctly to achieve satisfactory results. While air atomising spray guns predominate, other types of gun can be used for special work, e.g., airless and airmix spray guns. The greatest care must be taken when stripping, cleaning, reassembling and adjusting spray guns as they are delicate pieces of equipment.

The basic function of the air atomising spray gun is to use compressed air to break up the finish material into small droplets and direct them towards the leather surface. The mixing of the air and material usually takes place outside the spray gun between the horns of the air cap and is described as 'external mix' atomisation.

Where the mixing takes places inside the air cap it is called 'internal mixing'. The spray gun is automatically triggered on spraying machines and differs in several aspects from the hand triggered spray gun.

For example, its triggered control system utilises compressed air to operate a piston, which allows compressed air to flow just prior to retracting the needle from the fluid nozzle orifice. The finishing fluid then emerging is immediately atomised by the air issuing through the air cap.

High-Volume Low-Pressure Gun (HVLP)

Instead of using the high pressure of a normal air atomised gun, it is possible to spray with larger volumes of air but at lower pressure. The atomisation is still good but, because of the lower pressure, the 'bounce-back' is considerably reduced and efficiency of finish transfer improved (less waste). It is claimed that the spray efficiency is increased to 75%, from around 40% to 60% for conventional guns. The air supply to the guns is critical for HVLP guns just as it is for conventional air atomised guns. However, in the case of HVLP guns, it is the volume of air that is important (generally 1400 l/min) and not so much the air pressure at the guns (which can be as low as 0.2 to 0.3 bar).

Normally, HVLP guns will operate in the region of 8 psi to 10 psi at the gun compared to 30 psi to 35 psi on a conventional gun. It is important, therefore, to ensure that not only is there sufficient air pressure at the guns but also that the pipe diameter is large enough to carry the volume of air required.

In general, the distance between the gun and the leather to be sprayed will be less for HVLP guns than for conventional air atomising guns. Because the atomised particles of finish have a lower velocity for HVLP guns, they are more likely to have the stability and shape of the fans distorted if the carousel speed of the guns is too high or the extraction system is too powerful.

Roller coating

This is a way of applying finishes which has become more popular in the last ten years because of its economy and flexibility. The top roller has an engraved surface, which picks up finish from a reservoir. The finer the pattern of the engraving, the smaller the amount of finish applied. The transfer of finish is also dependent on the direction of rotation. Smaller quantities are applied if the roller moves in the same direction as the leather (forward roller coating) and larger quantities are applied by reverse roller coating. Most finishes that are used for spray application can be adapted for roller coat application simply by cutting down on the amount of water in the mix and adjusting the viscosity with a proprietary thickening agent.

Flow agents and anti-foam may also have to be incorporated. (Most solvent finishes for base coats would not lend themselves to such modification as they would evaporate from the gravure application roller during coating and cause the finish to dry in the engraved parts of the cylinder. However, applications of solvent top coats with a fine roller can be achieved without modifications.)

Mixes need to be made shortly before they are to be used as they do continue to thicken with time. Viscosity checks need to be carried out during production runs, particularly if the mix has stood overnight. Typical values for the viscosity required are in the region of 20 to 60 seconds using a No. 4 Ford cup.

Forward roller coaters are also used to produce pull-up effect leathers, particularly on bovine grains. The roller coater is equipped with a hollow roller and connections to allow oil to be pumped through it via the axles. The oil itself is heated in a reservoir before being pumped round through the roller. In this way, the coating roller is temperature controlled. Usually, the engraved pattern on the roller is fairly large as large amounts of oil and wax are to be deposited on the leather. The material to be used for coating is usually a mixture of oil and wax. The quantities and types of each used determine the required look and feel expected in the finished leather.

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This material is also mixed and heated in a reservoir and is pumped to the doctor blade and the heated roller in the usual way. The excess is returned to the heated reservoir. After application, the wax/oil mix cools in the leather and solidifies to give the pull-up effect. It is not unusual for the leather to be passed through the roller coater twice in order to get the correct amount of oil/wax on the leather.

Figure 2.36. Operating a roller coating machine

Roller coating advantages and disadvantages

In this application there is minimal wastage of finish. It is not as flexible as spraying, in that the amounts transferred depend mainly on the screen of the roller. With soft leather problems can arise of adhesion to the roller and pleating of flank areas which are then not coated. Reverse coating cannot be used for soft leathers.

Advantages

- Low waste (none into atmosphere apart from solvent in finish).
- Application rate can be varied quite widely:
    - forward roller application for top and contrast coats (typically 1g/sq ft to 5g/sq ft)
    - reverse roller application for heavier coats (typically 3g/sq ft to 30g/sq ft).
- Better adhesion imparted than spraying.

Disadvantages

- Shear stability of finish needs to be good to avoid 'balling-up' on the roller.
- Finishes need to have viscosity adjusted for roller coating (typically 20 to 60 secs to Ford Cup 4).
- Tracking (sometimes called 'turkey tracking') occurs if roller speed, conveyor speed and finish viscosity are not in balance.
- Drying of finish on the roller or leather fibres can cause lines in the finish.
- Areas of low substance can be missed, especially with forward machines.
- Limited capability on thin, soft leathers (pleating).

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Note that, with forward roller coating, patterns can be applied to the leather and printed leathers can be tipped with a contrasting colour.

Foam finishing

Foam finishes can be applied by roller coating or HVLP spraying, low pressure spraying being required to stop the foam from collapsing.

The foam is produced from normal finish formulations of resins, pigments, fillers etc, but with added thickener and a foam stabiliser developed to give a smooth consistent and stable foam. The size of a foam's bubbles is very important. If they are too big, they will collapse and if they are too small the effect is lost.

A foam can be produced for demonstration by using a simple food mixer, but to obtain a consistent product a system is required that can carefully control the pumped liquid and air flow rates into a mixing chamber. The quality of the foam produced can be checked by measuring its density which is typically 200 g/l to 500 g/l.

Foams once made cannot be stored and any leftover must be allowed to destabilise and then be refoamed.

Padding

The formulated finish can be applied most simply by hand padding. The finish is held in a tray and the pad dipped in; excess finish is lightly scraped off on the side of the dish and the finish-laden pad is rubbed over the leather surface. The pad itself consists of a wooden block covered in plush velvet. Brushes are sometimes used in place of pads to give a more vigorous 'working-in' of the finish to increase adhesion.

If the viscosity and formulation are correct, it should be possible to cover the surface with a few strokes, giving an even application without streaks. If the finish is absorbed too quickly, then (a) some thickener should be added to reduce absorption or (b) the finish should be diluted to prevent too rapid 'setting' of the finish and to prevent streaks or (c) the leather should be pre-sealed or impregnated to reduce absorption of subsequent coats.

The advantages of padding are that it gives very good adhesion of the finish, it compensates for areas which may be more absorbent, and it can provide a good impregnant or base coat. The method normally requires subsequent spray coats to achieve uniformity; it is not suitable for topcoats, and is labour intensive. Padding machines are available but do not generally give such a good result and, in some tanneries, eveness is achieved by an initial machine padding followed by hand padding on the conveyor.

Embossing and plating equipment

Two main types of machines are available: hydraulically operated presses and through-feed rotary machines.

Presses are considered as generally enabling better print definition, but have the drawbacks of longer throughput times than the rotary machines, and the need for great care to avoid overlap marks. In terms of the various prints used, presses offer greater flexibility, as large numbers of print plates can be stored conveniently in racks; printed rollers are not only more expensive than plates but also much more problematical to store and transport within the tannery. Rotary machines often come with 3 or 4 rollers housed within the machine itself, with one being smooth and the others representing the prints most commonly used at the particular tannery.

Care must be taken when using through-feed rotary machines to print leather that is potentially loose as the action of the nip in the rollers can exacerbate the looseness.

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Figure 2.37. Hydraulic press

Milling drum

Drums used for the dry drumming operation can be made either of wood or steel. The internal configuration of the drum is hollow, with pegs or shelves depending on the degree of mechanical action required.

The degree of mechanical action determines the softening effect and is controlled by:

- load size - too small means little pummelling action; too large means insufficient movement; optimum size is normally arrived at by experimentation
- drum speed (typically 15 to 20 rpm) - too slow means little movement so little softening; too fast means the leather may be held by centrifugal force against the drum wall, also resulting in reduced mechanical action and therefore little softening
- drum size and internal configuration (typical sizes are 2 to 3 meters diameter and length; pegs give a stronger mechanical action than shelves).

Dry drums are now available with humidity and temperature control, as well as extraction to remove leather dust generated within the drum. The fully computerised dry drums are capable of conditioning, drying and dedusting the leathers as well as softening them.

Finishing types

A finish is a surface coating which is applied to leather to provide:

- protection from contaminants (water, oil, soiling)
- colour, either to modify or reinforce the colour provided by the dyes, to make the colour more even
- modification to the feel, gloss and physical performance of the leather
- attractive fashion and fancy effects
- quality improvements by disguising surface defects.

A relatively extensible film which may be coloured by dyes or pigments is applied to the leather; this is followed by a tougher film which imparts greater resistance to wear and tear and which may also be coloured. The basic components of the finish are binders, colouring agents (pigments and dyes), auxiliaries and lacquers/lacquer emulsions.

The effects created by finishing are essentially visual. They are determined by:

a) The intensity, wavelength and direction of light striking the leather surface.

b) The manner in which the coating absorbs and reflects light. Colour is perceived by the partial absorption and reflectance of the light striking a surface.

c) Surface texture, embossing or grain pattern.

The leather industry takes advantage of these possibilities to produce a wide range of articles that can serve different purposes and requirements. These articles can be recognised by the following types of finish.

Aniline

The academic definition of aniline leather would be a finishing procedure exclusively based on aniline dyestuffs. The only mechanical operation would be glazing or polishing. Nowadays this definition has been extended to include some other treatments but the basic objective of aniline production still remains the same: produce a leather with a natural transparent grain.

Semi-aniline

Semi-anilines are the group of leathers that which have been aniline dyed or stained, but incorporating a small quantity of pigment, not so much as to conceal the natural characteristics of the hide. The main objective is to level out the colour of leather with the minimum opacity necessary.

Corrected grain leather

This group of leather refers to those that had the outer surface of the grain removed by an emery wheel to delete or “correct” blemishes. They are usually heavily pigmented in order to seal the grain.

Glazed leather

The main characteristic of glazed leather is the application of a protein-based film forming material (casein) that allows glazing (polished with frictional heat) to give a high gloss. Because they are thin and smooth, they give a pleasant, natural handle. Glazing highlights (enhances) the natural grain appearance.

Nubuck

Nubucks are leathers which are lightly buffed (snuffed) on the grain side to produce a fine nap with commercially accepted aesthetical characteristics. Fine emery papers are used to snuff the grain (400 to 1000). The leather to be snuffed is normally fed through the machine in different directions (e.g. neck to butt, belly to belly) to ensure the entire surface is snuffed in a regular manner.

Production of nubuck is a delicate process due to the fine degree of control required to buff to the correct depth in the grain. Not enough snuffing will leave grain on, too much and the buffing will easily cut into coarser fibre layers in the grain, giving a rough nap. Depth of shade is difficult to obtain if the snuffing process is carried out on the dyed crust; for this reason, most nubuck leathers are snuffed at wet blue stage (particularly hides and sides) or at undyed crust stage.

A great variety of special effects can be produced by first printing the crust leathers and then buffing or snuffing the top of the grain layer. The leathers to be buffed must not be too soft or too hard to ensure even buffing and to avoid damaging buffing paper. Buffing requires a high degree of skill as most of the checks are based on personal experience. It is vital that operators using the buffing machine are appropriately trained to carry out the job and the necessary process checks.

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Pull-up

These are usually leathers with a greasy feel that show the pull up effect, which means that on stretching the former dark surface becomes lighter and shows more details of the grain structure. This is usually achieved by the application of a combination of oils/waxes or grease.

Others

There are an enormous variety of speciality finishes that in general are associated with a specific commercial product developed by a tannery. However, these speciality finishes can be grouped into the following:

- Distressed effects, normally produced by applying a hard-top coat darker in shade than the base coat. The dark top coat is then partly removed by milling or spot buffing.
- Metallic or pearlised effects created by the use of specialised pigments in either water based coats or solvent top coats.
- Rub off or 'brush off', two tone or antique effects produced by partially applied or partially removed effect coats to give a non-uniform cover.
- Embossed patterns can be emphasised by tipping with a contrast colour, by angle spraying or by buffing.

2.4.11. Sorting and grading of leathers

This is a very significant operation in the manufacturing of the leather as it will finally decide the value of the finished product. It is vitally important to the profitability of the tannery that this operation is carefully monitored and controlled.

Although there will be many items of detail that will differ with regard to sorting different types of leather in different tanneries, the main areas to be addressed will be the same. These are:

Standards

There should be a library of standards kept for the different types of product produced. These should illustrate the quality standards for each grade and be representative of the quality distribution of the grades. These standards should be agreed by the commercial, technical and production functions of the tannery. On certain occasions, a special grade or type of leather may need to be agreed with an individual customer with regard to the grading parameters.

Standards will need to be reviewed from time to time due to changes in outside market conditions, e.g. raw material availability and price, customer expectations, etc. The standards should also define parameters such as softness, degree of colour variation, gloss, substance, surface touch etc.

Monitoring

It is essential that the required standards are uniformly applied to every pack of leather to be sorted in the warehouse. To do this, it is important that each sorter is fully trained in all aspects of the quality standards they are required to sort. Trimming of finished leather also needs to be carefully monitored.

It is possible, in some cases, to upgrade a skin by trimming out a fault or a hole. However, the increased value of upgrading the leather from (say) a 2nd to a 1st must be balanced against the loss of area involved in the trimming.

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Quality issues

Increasing use of information technology allows detailed investigation of the sorting figures for different packs and types of leather. This data can pinpoint quality issues that need to be addressed, e.g. correlation between wet blue and finished sorting, area yield for certain raw materials or products, colour consistency, softness, etc.

Sorting conditions

Usually, sorting stations have their own individual lighting. This lighting used at the sorting stations is usually more effective at illuminating the surface when it is angled to the surface and not directly above the leather.

To achieve the best result, the finish and crust leathers should ideally be colour matched so that the finisher does not require to spend time and effort rectifying faults from previous processes. Crust selection is interlinked to the previous wet blue sorting selection and will be linked to the warehouse selection. Any errors at wet blue sorting may be corrected at the more accurate stage of crust sorting. This may lead to saving of finishing chemicals and materials and will give a more positive result at finish sorting.

General sorting criteria

Grain selection

A good grain deserves to be finished as a full grain, requiring the minimum of finish to achieve protection, colour and fastness. The tendency is to finish as many leathers as possible as full grains (in the past more leathers were 'corrected' to give maximum uniformity). Where there is slight damage, such as scar tissue, it is regarded better to finish full grain and give the surface an embossing to break up the scar lines, than to remove them by buffing and put on a corrected grain finish.

Every tannery has a unique grading procedure which must satisfy their customers' quality specification. Due to the limited availability of top-quality crusted leathers, it is important for the tanner to negotiate with its customers a composite order formed by top grade leathers and lower grade leathers. This would help the tanner to avoid the accumulation of the low-end material.

All operators must be trained to correctly sort the crusted leathers to achieve the minimum degree of finish sorting downgrades in the finish leather due to wrong crust selection. Once finish is applied little can be done to recover the material and the production cost encountered (e.g., looseness). In order to achieve good reproducibility of grades between crust sorting and finish sorting, a daily report sheet of the grading should be discussed with every sorter. In cases where a serious sorting error is apparent the sorter who made the mistake must see the leathers to ensure that such an error is not repeated.

Aesthetic quality selection

During sorting the following characteristics of the leathers are checked:

- levelness of dyeing (within skin, skin to skin, pack to pack)
- degree of looseness
- degree of draw
- degree of veininess
- faults (natural and man made).

Usually, the leathers are graded from 1 to 5 (good to poor), and they are compared to an ideal production standard. The rejects will be used for more suitable articles or will be redyed with other unsuitable leathers.

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Handle selection

The handle of the leathers is checked during sorting to ensure that the pack produced has similar characteristics to the original sample given to the customer. The leathers rejected may need reprocessing to achieve the correct handle.

Colour and substance selection

The shade and thickness of the leathers produced are checked against the standard sample approved by the customer.

Lighting and surrounding area

The area where the crust sorting takes place should be lit to a good standard, usually with lights or fluorescent tubes immediately above the sorting table. Artificial daylight or colour matching tubes are often used. It is important that the background lighting is to the same standard.

The area immediately surrounding the sorting area should be a neutral grey colour so as not to affect the assessment of colour of a pack of leather that will be spread across the sorting area to assess the skin to skin colour variation. The leather to be sorted must be placed flat on a table to ensure that all parts are exposed to equal degrees of lighting.

Patterns

An 'A4' size pattern must be available at crust sorting to show the shade, handle and aesthetic qualities of the leather approved by the customer. The crust sorter must have access to the pattern to check the packs. Generally, there should be at least two crust patterns with the tannery: one for use in the factory, the other to be used as the master. The master pattern must be handled as little as possible, and it must only be used as a comparison for the factory pattern to decide when the factory pattern requires replacing.

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2.5. Lesson 4: Best Available Tanning Technologies (BATs) in the tanning of hides and skins

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- Best Available Tanning Technologies for hides and skins

2.5.1. BAT – Best Available Techniques

BAT is the acronym for Best Available Technique. In this following chapter are presented several techniques / technologies that allow a better environmental performance, also generating economic gains, direct or indirect, through reduction of energy consumption, greater ease of recovery of waste, reduction of water consumption and products increase in the quality of the final article, among others.

There are several reference documents describing the BATs applicable to the tanning industry. One of them was created within the framework of the implementation of the European Pollution Prevention and Control Plan, governed by the European Directive 2010/75 / EU. The document itself is called BREF, which in the case of the tanning industry is entitled "Best Available Techniques (BAT) Reference Document for the Tanning of Hides and Skins".

The BAT reference document for the Tanning of Hides and Skins forms part of a series presenting the results of an exchange of information between EU Member States, the industries concerned, non-governmental organisations promoting environmental protection and the Commission, to draw up, review, and where necessary, update BAT reference documents as required by Article 13(1) of the Directive. This document is published by the European Commission pursuant to Article 13(6) of the Directive.

As set out in Article 13(5) of the Directive, the Commission Implementing Decision 2013/84/EU on the BAT conclusions contained in Chapter 5 was adopted on 11 February 2013 and published on 16 February 2013. It is possible to consult the document in its entirety through the electronic address:

http://eippcb.jrc.ec.europa.eu/reference/BREF/TAN_Adopted552013.pdf

BATs described in the above-mentioned document and others resulting from the field experience of the CTIC technical team, but applicable to the tanning process, were selected for inclusion in this training manual. All BAT's included here have proven industrial application, being in practice in several manufacturing units, in Portugal or on the rest of the World.

Soaking

Salt removal

The hides are received at the tannery factory in a fresh or preserved state. The vast majority of companies receive hides and skins preserved by salting. One of the problems of beamhouse effluents is their high salinity, a high content of chlorides. The possibility of recovering the salt used in the preservation of hides, partly avoiding their dissolution in the waters of the soaking is a technique that, despite some constraints, has an interest in reducing the environmental impact of a tanning unit. This technique basically consists of tumbling the leathers dry, in a specific equipment, releasing them from part of the salt they contain, which is separated.

PRACTICAL APPLICATION

Some of the salt used in salting the hides is absorbed by the fibrous structure of the skin. Another part is released from the fibre, and this is recovered by the present technique, which corresponds to 6-8% of the total amount of salt that the salted leather contains.

The reuse of this salt in the preservation of hides, as such, without any kind of treatment, is inadvisable due to its high degree of microbiological and chemical contamination - bacteria, proteins and fats.

Even for application in pickling this salt is not suitable, if not treated, due to its high protein content.

Carrying this protein into the pickling / tanning bath produces a masking effect of the chromium, reducing its tanning power. The presence of natural fats can also generate the formation of chromium soaps, which cause difficulties in the subsequent dyeing.

There are, however, membrane filtration systems which allow to clean and perform a partial sterilization of a brine prepared from this salt, which can then be used in the pickling operation. This solution allows solving the greatest constraint in the application of the present technique, which is the destination to be given to the salt used.

Despite being a solid waste, most of the landfills do not receive it due to their high solubility. Even receiving it, its cost makes the application of this technique uninteresting.

ECONOMIC VIABILITY

The implementation of this technology involves investment in equipment to tumble the salted hides and a filtration and sterilization system of a brine prepared from the salt used.

Figure 2.38. Equipment for removing salt

Figure 2.39. Equipment for filtration of recovered salt

- Investment Cost: 100.000 €

Table 2.8. Summary production vs. return on investment

Anual Production (ton salted hides)	Recovered Salt (ton)	Operation Costs (€/ton sal recuperado)	New salt quotation (€/ton)	Anual earnings (€)
500	25			6.875
2.000	100	25	300	27.500
5.000	250			68.750

- Investment return time: For a production of 2,000 tons of salted leather per year, the implementation of this technique generates the return on investment in less than 4 years.

Reuse of washing effluents in the soaking

It is considered as good practice, which is already implemented in some Portuguese tanneries, the use of effluents from washes in the soaking phase. This procedure brings significant water savings, without any damage to the quality of the skins, if these effluents present the necessary requirements.

PRACTICAL APPLICATION

It is advisable to reuse the effluent from the first wash after the fleshing and the wash after the bating.

The effluent from these two washes can be mixed and stored in a holding tank from which is then fed to the drum where the soaking takes place. The following scheme illustrates what is described herein, in the case of processing of bovine hides.

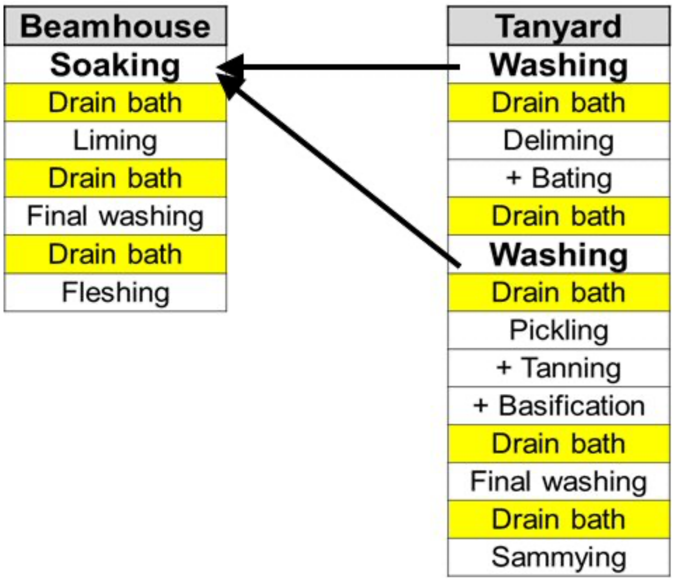

Figure 2.40. Schematization of the reuse of wash water

A typical characterization of the mixture of these washing effluents for beamhouses that work bovine hides is presented, and for the parameters that allow to evaluate their potential of use in the soaking.

Table 2.9. Effluent characterisation

Parameter	Test Method	Result
Total Hardness (CaCO3)	NP 424:1966	9,5 × 10^2 mg/L
Oils and Fats	SMEWW 5520 B D:2005	2,3 × 10^2 mg/L
Quantity of microorganisms at 22ºC	ISO 6222:1999	1,5 × 10^5 N.º/mL
Quantity of microorganisms at 22ºC after 24 hours	ISO 6222:1999	1,4 × 10^6 N.º/mL

As a French degree (ºHf) equivalent to 10 mg/L of CaCO3, the total hardness of the analysed waters corresponds to 95 ºHf. It is considered that a water is very hard above 30 ° Hf and it is known that the harder the water, the more difficult the soaking process becomes, thus making it convenient to correct this excessive hardness, for example by the dosage of a polyphosphate sodium to about 0.2% (on the mass of salted hide to work). This will be sufficient to reduce the hardness of the water to values lower than 8 ºHf, below which water is considered as being soft.

With regard to the parameter "Oils and fats", we will explain the approach to be taken. The hide in its natural constitution (having a moisture content of about 65%) is about 2% fat.

The skins are usually preserved by dehydration processes, as in the case of salting or drying, and are stored with about 15% moisture. With this moisture content, the fat content in the skin will be around 9%.

Estimating the dosage of 100% to 200% water on the raw skin weight in the soaking, and having the effluent from the washes about 0.023% fat, we would be introducing on the raw skin weight, in the maximum, about 0.046% of fat, which, compared to the natural fat content of the skin (± 9%), has no meaning.

Therefore, the content of oils and fats present in the washing waters is not prevent an impediment for their use in the pre-soaking operation.

In relation to the quantity of microorganisms present in these effluents, their elimination will be the most advisable procedure, which can be done by the addition of a bactericide.

By testing the dosage of 0.5 g/L of a cationic bactericide – benzalkonium chloride –, the treatment is fully effective, as shown by the following data resulting from the analysis of washing effluents after addition of said bactericide, according to the test method ISO 6222: 1999:

- Quantity of microorganisms at 22ºC on effluent: 4 Nr/mL;
- Quantity of microorganisms at 22ºC on effluent, after 24h: 4 Nr/mL.

Washing waters can be reused in the soaking operation by adding to the usual formulation the following assets (percentages calculated on the basis of the raw leather weight):

- 0.2% de sodium poliphosfate;
- 0.1% of benzalkonium chloride.

ECONOMIC VIABILITY

The economic viability of this technology will naturally have to be analyzed on a case-by-case basis and will be a function of the company's production and of what already exists in its facilities in terms of equipment that enables the implementation.

Considering the market prices of chemical products that need to be added to the soaking and a minimum cost of discharge in the WWTP of beamhouse effluent of 4 €/m3, there is a hypothetical case, as an example:

- Need for investment in retention tank, pipes and pumps: 20,000 €;
- Annual savings of the company, considering a production of 400 Ton/month: 6,600 €.
- Return on investment time: about 3 years.

It is important to keep in mind that the savings per tonne of leather worked are around € 1.5.

Fleshing

Green fleshing

Traditionally, bovine leather fleshing is performed after the liming operation – lime fleshing - since at this stage the fiber is already numb, presenting a certain swelling of the skin, which increases the exposure of the subcutaneous tissue and is then more easily removed in the fleshing operation.

However, the lime fleshing generates a waste, called lime fleshings, which, because of its high content of lime and sulphides, creates serious constraints on its material recovery, leaving as the only viable option the deposition of the waste in the landfill.

The alternative to perform green fleshing then arises, wherein the fleshing operation is performed before the liming, the skin having been subjected to only a slight soaking.

In this way, the waste generated - green fleshing - can be targeted for material recovery, for example in the production of gelatins and detergents.

Figure 2.41. Green fleshing operation

PRACTICAL APPLICATION

The implementation of green fleshing does not require investment in industrial equipment, since it can be done in the same machine that is used to lime fleshing.

In order to be subjected to green fleshing, the skins must be soaked incompletely, since if the skin is completely soaked, and for the fleshing to be effective enough, it will be necessary to close the machine too much, running a serious risk of reaching the dermal substance, which usually results in more open bellies and slight loss of mechanical resistance.

Therefore, it is advisable to prepare a pre-soaking before green fleshing, which should follow a formulation similar to the one shown:

150%	Water at 28ºC
0.1%	Wetting surfactant
0.3%	Bactericide

Operation Time: 10 minutes on low rotation; 1 hour resting; 2 hours at slow rotation.

The fact of making the green fleshing process does not invalidate the need to carry out new fleshing after liming. Incidentally, this is usually necessary since the skin does not get completely clean of the subcutaneous tissue after only the green fleshing.

Depending on the way the industrial unit is assembled, this may or may not lead to productive constraints. Usually, the productive flow is as follows:

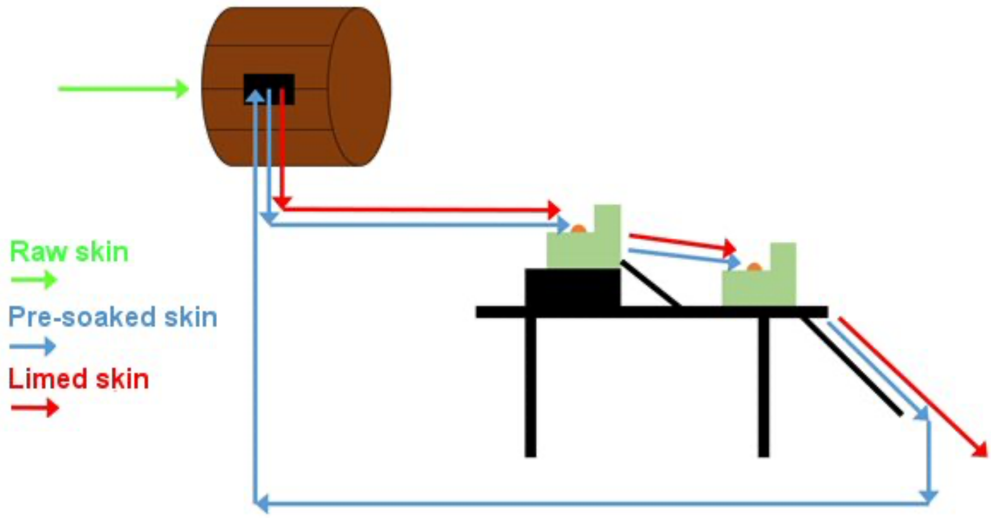

Figure 2.42. Production Flow Scheme of the green fleshing / lime fleshing operations

During the morning, the fleshing line is fleshing the limed skins that stayed over the night before in the liming. In the afternoon, are submitted to fleshing the skins coming from the pre-soaking, carried out during the same morning.

ECONOMIC VIABILITY

The economic viability of this technology has to be analysed on a case-by-case basis. By following a productive scheme similar to that described above, it may not be necessary to purchase a new fleshing machine.

However, more labour will surely be needed. There will also be cases where there is a need to acquire new fleshing machine(s), which can cost between € 100,000 and € 150,000.

➢ Benefits or gains:

- Material valorisation of the "green fleshings" residue, which is rarely the case with the residue "lime fleshings".
- Global savings in chemicals in the beamhouse that will be between 10% and 20% when compared to the normal process.

Liming

Depilation without hair destruction

This technique allows to carry-out the depilation of the skin in aqueous medium, without destruction of the hair, which is removed from the bath by filtration. In this way it is possible to reduce substantially the organic load of the liming bath and to potentiate a possible valorisation of the new solid residue that is generated here: hair.

PRACTICAL APPLICATION

Hair removal without hair destruction has been developed specifically for the treatment of bovine hides.

The hair is made up of keratin, a high strength protein, when compared to collagen, for example. Along the length of the hair the level of "maturity" of the keratin is different, being low at the level of the root, which generates in this zone a lower resistance of the fibre.

The destruction of keratin is effected through the action of strong reducers (sulphide and sodium sulphydrate), which destroy the sulphur bridges that are in its composition. Strong bases, such as sodium hydroxide (caustic soda) and calcium hydroxide (lime slaked), allow to "immunize" the hair, that is, to give it a greater resistance to the chemical attack of reducing agents. Nevertheless, the root remains fragile, being easily destroyed by products like sulphide and sodium sulphydrate. Therefore, the hair removal process without hair destruction involves a liming formulation which begins with the immunization of the hair through the dosage of caustic soda and / or slaked lime.

This first phase should last about two hours, after which depilation is promoted in the root zone through the use of enzymes, sodium sulphide and sodium sulphydrate. Throughout the process, the bath is filtered, retaining there the hair that is released from the skin.

Usually, this technique allows to reduce the amount of sulphide used, which generates a lower pollutant load in the effluent. Also, the fact that the hair is not solubilized generates environmental gains, considerably reducing the COD and the nitrogen in the same effluent.

In the following images, the mass balance is shown, for example, in a traditional liming process, and the equivalent, after application of this technology.

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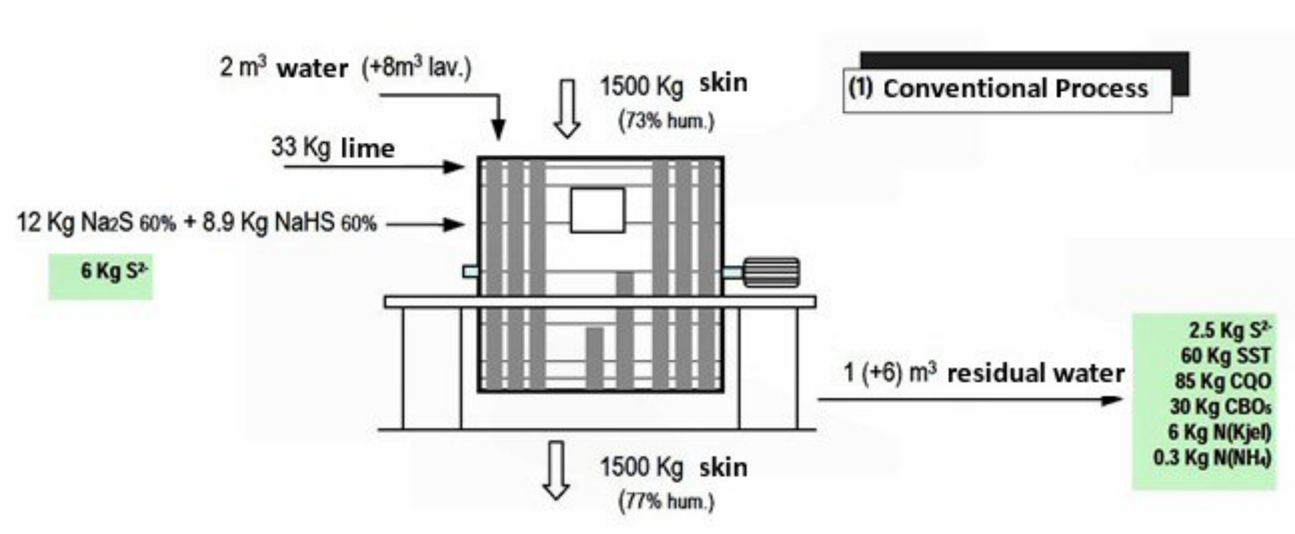

Figure 2.43. Schematization of the conventional hair removal/liming process

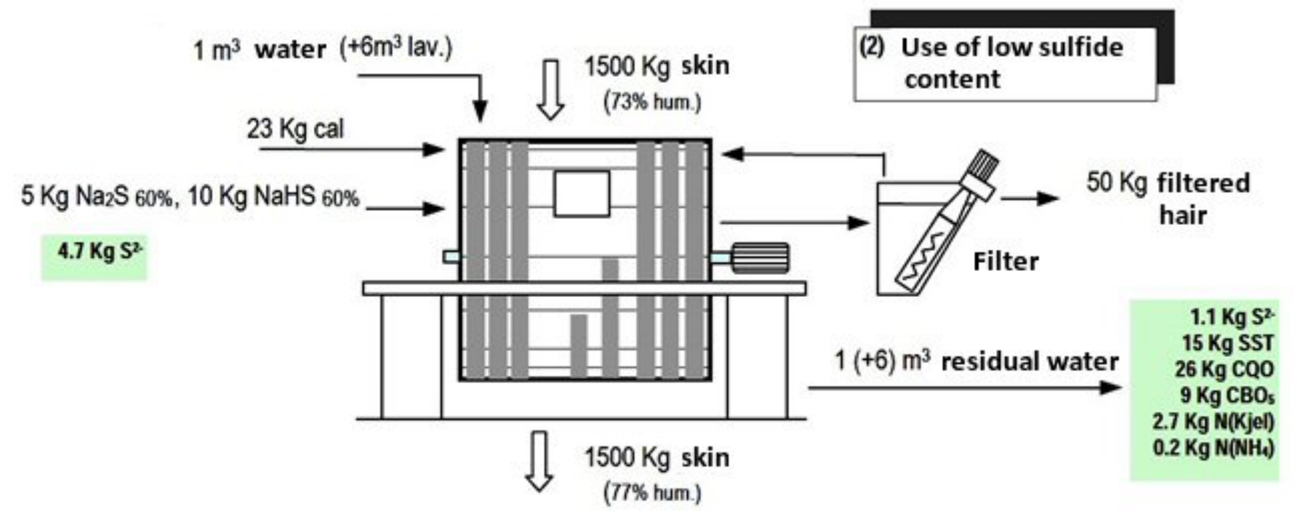

Figure 2.44. Schematization of the process of depilation/liming without hair destruction

ECONOMIC VIABILITY

The savings related to the implementation of the hair recovery processes can be evaluated in a generic way by weighing the additional costs and benefits resulting from the application of the technology.

The costs and benefits to be considered will be:

➢ Benefits or gains:

- Saving on chemicals. The savings in chemicals resulting from the application of this technology could vary between 2€/Ton and 10€/Ton, depending on the process that each company currently uses.

- Cost savings in treatment of effluents and deposition of solids/sludge due to the decrease in the treated/deposited volume or the pollutant load (COD, CBO5, SST, N-Kjel)
- Possible improvement in the quality or quantity of skin produced (possible increase of skin area). It will not be considered in the economic evaluation because it is very variable, depending on the reality of each company.
- Sale of the hair. It will not be considered in the economic evaluation, due to the fact that there is currently no known market in Portugal for this potential by-product.

➢ Investment:

- Purchase and installation of filters and pumps for bath recirculation and hair removal. The installation of hair filtration systems, by drum, can vary between € 6,000 and € 10,000.

As example is presented the possible return to a company that can save 4 €/Ton, which has three liming drums and produces 400 Ton/month:

- Investment cost: 22,500 €;
- Savings on chemical products: € 17,600 / year.
- Return on investment time: < 2 years.

It should be noted that in this rough analysis of economic viability, environmental gains were not considered, i.e. the potential reduction in the cost of effluent treatment.

Figure 2.45. Hair Separation Equipment

Enzymatic Depilation

The two main goals of the liming are the numbness of the fibres and the depilation of the skin.

Reducing agents, such as sulphide and sodium sulphydrate, as well as calcium hydroxide (slaked lime), surfactants and other chemical auxiliaries, such as anti-wrinkling agents, are used.

The effluent resulting from this operation contains high levels of pollution, one of the main problems being the high sulphide content.

It was studied and implemented in several beamhouse industrial units the depilation by means of enzymes, allowing to considerably reduce the amount of sulphide used in these processes.

It has been proven that in enzymatic depilation it is essential to use not only keratinases, which attack the hair protein, but also amylases and lipases.

Together, these three types of enzyme generate a very interesting synergistic action, allowing to reduce the amount of sulphide to be used, and also contributing to a drastic reduction of the hair root, resulting in higher quality skins, especially when the final objective is the production of light colours in very natural articles.

PRACTICAL APPLICATION

The application of this technology will have to be studied case by case, according to the specificities of the beamhouse in which it is applied.

As an example, the experience of the application of enzymatic depilation in a Portuguese beamhouse is presented.

The usual process of the company concerned, working on bovine hides weighing always more than 20 kg, involved the dosage of 2.5% to 4% of sodium sulphide and the dosage of about 3% of slaked lime.

After application of this technology the amount of sulphide was reduced to 1 to 1.5% and the amount of lime dosed was maintained.

Following are photographs that make the action of the enzymes clear. This photographic record was in all cases, in production batches after 12h of liming, and the samples were always removed from the area of the shoulder.

1.5% of slaked lime

1.5% of sodium sulphide

1.5% of slaked lime

1.5% of sodium sulphide

0.3% of keratinase

1.5% of slaked lime

1.5% of sodium sulphide

0.2% of keratinase

0.3% de amylase

0.3% de lipase

Figure 2.46. Specimens of skins tested

The conjugation of these three enzymes leads to a better depilation of the limed skin due to the fact that there are proteins in the hair follicle between skin and hair as well as polysaccharides and fats.

These enzymes should be applied together about 30 minutes before the first dosage of sulphide.

Subsequently, the first dosage of sulphide should be applied, followed by various dosages of sulphide and lime.

The use of an anti-wrinkle product together with the first dosage of sulphide is also positive.

While it has been found that 1.5% of lime is generally sufficient to obtain good hair removal, it is considered that for the fibre to "open" conveniently a dosage of lime close to the conventional values, i.e., about 3% is necessary.

<u>ECONOMIC VIABILITY</u>

The implementation of this technology does not involve any investment in equipment.

By introducing this technology, it is possible to reduce the dosage of the following chemicals compared to a traditional process.

Table 2.10. Comparison of dosages of a traditional process vs enzymatic process and savings

Product	Dosing in the traditional process (%)	Dosing in the new enzymatic process (%)	Product Quotation (€/kg)	Savings for the annual production of about 100 tons of raw skin (€)
Sodium sulphide	2.5	1.5	0.83	830.00
Sodium sulphyidrate	1.0	0.0	0.98	980.00
Anti-wrinkle	1	0.5	1.90	950.00

The introduction of the enzymes in the liming process involves a cost increase that is summarized as follows:

Table 2.11. Comparison of dosages traditional process vs enzymatic process and cost

Product	Dosing in the traditional process (%)	Dosing in the new enzymatic process (%)	Product Quotation (€/kg)	Cost increase for the annual production of about 100 tons of raw skin (€)
Amilase	0.0	0.3	2.60	780.00
Lipase	0.0	0.3	2.95	876.00
Keratinase	0.0	0.2	1.97	394.00

Thus, by the introduction of the enzymatic process in the stage of liming, a direct saving of 710.00 € is achieved.

However, more important than this direct benefit is the benefit arising from the increase in quality that is obtained by eliminating the problems associated with the hair root.

Deliming

Deliming with CO2

Carbon dioxide, when used as a deliming, acts as a weak acid by neutralizing the calcium hydroxide and generating calcium carbonate, which then passes into the soluble form, such as bicarbonate. The use of carbon dioxide to replace ammonium salts (conventional process) drastically reduces the contamination of the effluents in terms of ammoniacal nitrogen and sulphates.

PRACTICAL APPLICATION

Carbon dioxide deliming may be applied to limed skins of a thickness of less than 3 mm. In the case of bovine hides weighing more than 10 kg (hair weight) it is necessary to proceed to lime splitting so that the application of this technology is viable. It is in any case advisable to add a small amount of ammonium salts, about 0.5%, to make the process sufficiently rapid. In any case, the operating time is always longer than the conventional process.

The amount of carbon dioxide needed to perform the de-scaling depends on the thickness of the skin, and can vary between 10 kg and 20 kg per ton of salty skin (1-2%).

In this process it is convenient to add hydrogen peroxide after the injection of the carbon dioxide, to promote the oxidation of the sulphides to sulphates and thereby to prevent the formation of hydrogen sulphide.

Oxygenated water (0.1 to 1.5%) should be used in excess, since in addition to sulphides it is also consumed in the partial oxidation of soluble proteins.

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Injection of CO2 can take place in two ways: directly on the drum using a nozzle/distributor or by means of a venturi coupled to a recirculating system of the bath. In the case of direct injection, the drum must be adapted by means of the introduction of an oval bell inside it, to protect the injector of other gases that is formed during the process.

The following two figures show the expected reduction in the ammoniacal nitrogen content (N (NH4)) of the effluent by application of this technology.

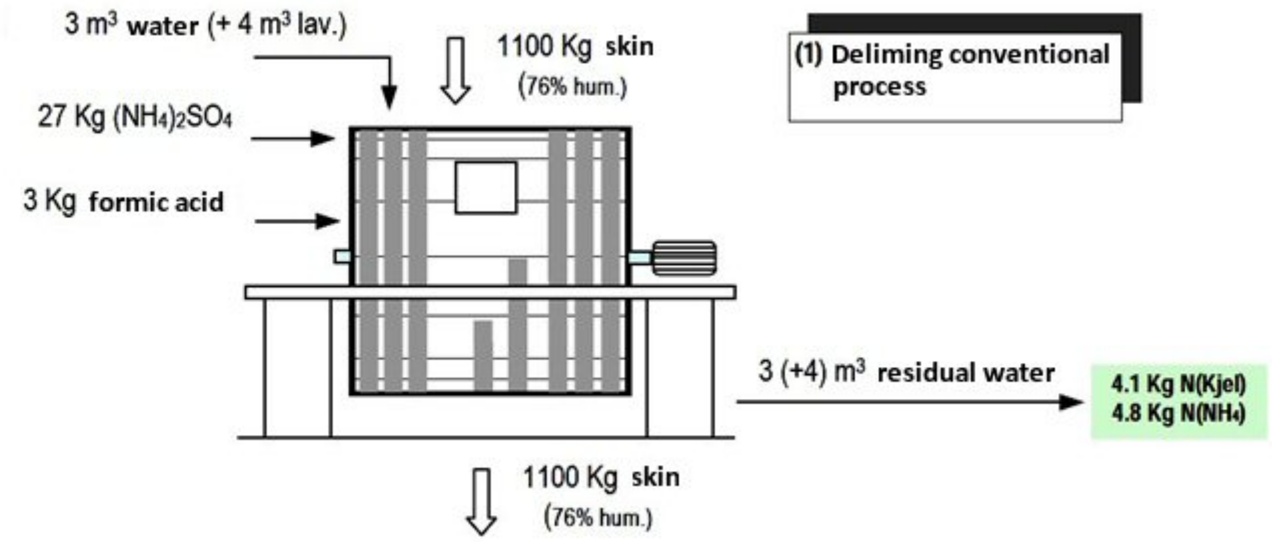

Figure 2.47. Schematization of conventional deliming process

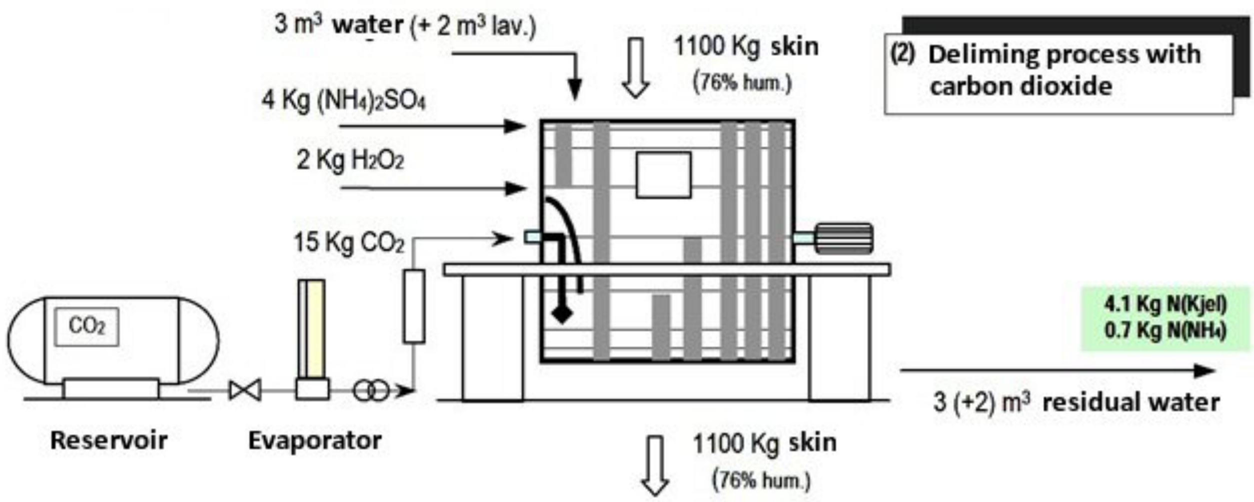

Figure 2.48. Schematization of deliming process with carbon dioxide

The application of this technology allows the ammoniacal nitrogen content in the effluent to be reduced by about 85%.

ECONOMIC VIABILITY

The application of this technology implies a change of the chemical products used, also requiring modifications at the equipment level.

The costs and benefits to be considered in applying this technology will be:

➢ Additional production costs:

- Costs of new chemicals.

➢ Benefits or gains:

- Savings in the consumption of conventional chemicals.
- Savings in effluent treatment costs.

➢ Investment:

- Gas installation and adaptation of the drums. The investment is relatively small, consisting only of the inlet piping, the rotameter and the injector, in addition to the adaptation of the drum.

An example is the possible return to a company that can save € 4 / Ton, which has three liming drums and produces 400 Ton / month:

- Investment cost: 3,750 €;
- Savings on chemical products: € 17,600 / year.
- Return on investment time: 4 months.

It should be noted that in this rough analysis of economic viability, environmental gains were not considered, i.e., the potential reduction in the cost of effluent treatment.

Pickling

Pickling with salt reduction

The presence of chlorides in industrial effluents from tanneries comes from two sources: the soaking phase, where the salt that is absorbed by the skin is dissolved in the process bath; and the so-called pickling operation, which is an acidification of the skin to the appropriate tanning pH.

This acidification is intense, leading the skin to pH values close to 3.0.

Before the fibre is chemically stabilized, i.e. before the tanning operation, the skin is very sensitive to acid swelling, which generates dramatic losses of resistance in the fibres. It is therefore necessary to use an electrolyte which generates a reverse osmosis effect, thereby controlling the absorption of water by the skin, thereby preventing said loss of resistance.

The salt normally used for this purpose is sodium chloride, in a dosage which allows a density of about 7 ° Bé in the process bath.

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This means a high concentration of salt in this bath.

A concentration that is around 10% in mass. A considerable reduction in the dosage of salt in the pickling bath is possible through the use of non-swelling polymeric sulphonic acids which are commercially available.

PRACTICAL APPLICATION

In fact, as mentioned above, the salt reducing pickling processes have as their main assets non-swelling polymeric sulfonic acids.

Other products may be used as additives in order to increase the stability of the fiber upon reduction of the pH, functioning as pre-tanning agents.

Among these products are the sodium polyphosphates.

It is also common in these processes to use low basicity chromium salts, thereby facilitating the penetration of chromium into the skin, even at higher pHs than usual.

An example of a tanning process for which the pickling is carried out with salt reduction is as follows:

Raw-material: national hides (30-35 kg) lime splited to 3.5 mm. The process is already done until the pickling, that is, after deliming and bating, with a final pH of 7.5.

70% Water at 25ºC

2% Sodium chloride

Run 15 min.

Control: density = 2 ºBé

4% Non-swelling polymeric sulfonic acid

Run 60 min.

0.2% Sulfuric acid (1:10)

Run 150 min.

Control: cut = green (indicator: bromocresol green) / pH = 3.1

2% Chromium salt of low basicity

Run 30 min.

4% Chromium salt with 33% basicity

Run 90 min.

1% Basifying agent based on magnesium oxide

Run 90 min.

Control: pH = 3,9

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The use of this type of process allows to reduce the pollutant load of the tanning effluent, in the following measure:

- Chloride content is reduced about 70%;
- Chromium oxide content is reduced about 40%.

ECONOMIC VIABILITY

In fact, as mentioned above, the salt reduction pickling processes have as a main consequence a considerable reduction in the environmental impact of the tannery effluents, which generates a gain, although it is difficult to quantify. The implementation of this technology **does not involve the need for investment in equipment**.

As for the operating costs, there is **no increase in temperature or dosing of water**, compared to the normal process.

There is, however, a **slight increase in costs with chemicals, which generates an increase in the cost of the final product of 0.02 - 0.04 € / ft2**.

Tanning

Processes of chromium high exhaustion

Chromium exhaustion processes are based on the control of the operating conditions and/or the addition of appropriate organic compounds to improve diffusion of the chromium, prevent its early precipitation or stabilize the complexes formed in the skin. It is therefore possible to operate with lower levels of chromium, while reducing its consumption and discharge.

PRACTICAL APPLICATION

Chromium exhaustion processes do not require any additional piece of equipment, as they are based solely on the reactivity of the chromium in the skin. Next, data are presented that allow to compare three alternative processes of tanning to chromium.

A) Conventional chrome tanning.
   a. Consumption of basic sulphate of chromium (25% de Cr_2O_3): 7%
   b. Equivalent dosage of Cr: 1.2%
   c. Fraction of chromium effectively fixed on the skin: about 75%
   d. Chromium content in effluent: 4.0 – 4.5 g/L

B) Tanning with high exhaustion by use of sequestering agents, namely di or polycarboxylic acids or polycarboxylates
   a. Equivalent dosage of Cr: 0.9%
   b. Fraction of chromium effectively fixed on the skin: about 98%
   c. Chromium content in effluent: 0.2 – 0.3 g/L

C) Tanning with high exhaustion by use in pickling a collagen activator - glyoxylic acid.

a. Consumption of basic sulphate of chromium (25% de Cr_2O_3): 6%
b. Equivalent dosage of Cr: 1.0%
c. Fraction of chromium effectively fixed on the skin: about 93%
d. Chromium content in effluent: 1.0 – 1.5 g/L

ECONOMIC VIABILITY

The factors to be considered in the case of the exhaustion processes are closely related to the variation in the costs of the chemical products, although there are other factors to take into account, as described below.

➢ Additional production costs:

- Costs of new chemicals.
- Additional energy costs, due to the mechanical effect of short baths.

➢ Benefits or gains:

- Savings in the consumption of conventional chemicals, mainly in chromium sulfate, but also in the basifying agents.
- Savings in effluent treatment costs.
- Cost savings in effluent treatment and waste disposal, mainly due to the reduction of discharged chromium, which is reflected in the consumption of chemical products in the WWTP and the amount of sludge formed.

➢ Investment:

- In the processes of exhaustion there are no significant investments to consider.

The variation of energy costs and environmental costs will not be considered in this analysis. It should be noted that in none of the exhaustion processes evaluated was an economic benefit obtained by the application of prevention technology. Chromium savings are not enough to offset the cost of additional reagents, which are significantly more expensive than conventional basic chromium sulphate.

The alternative of performing exhaustion without auxiliary tanning additives, i.e. by simple control of the operating conditions of the bath, is an obviously cheaper option. Also, in cases where the companies intend to install or modify the WWTPs, the investment costs should be lower in the case of the use of exhaustion processes, since the equipment design will take into account the decrease of the amount of sludge produced.

In any situation, however, the advantages of an environmental nature cannot be subordinated, because this type of concern must be an integral part of the management policy of the companies that want to be modern, advanced and competitive.

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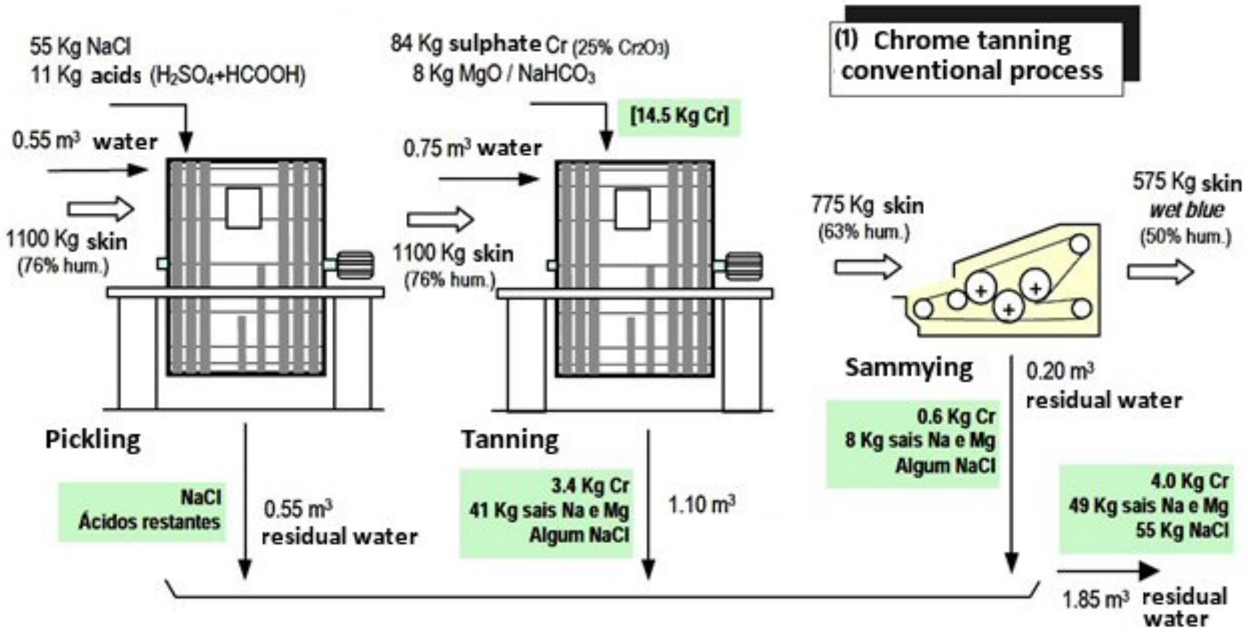


Figure 2.49. Schematization of chrome tanning conventional process

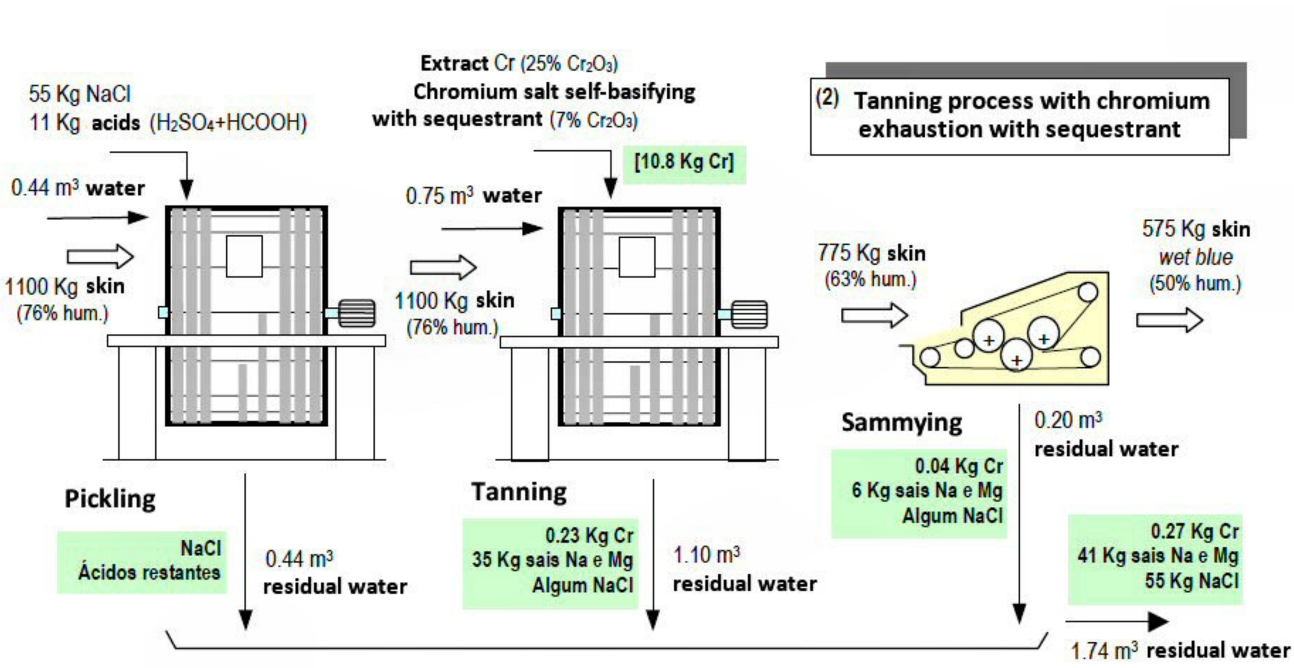


Figure 2.50. Schematization of tanning process with chrome exhaustion with sequestrant

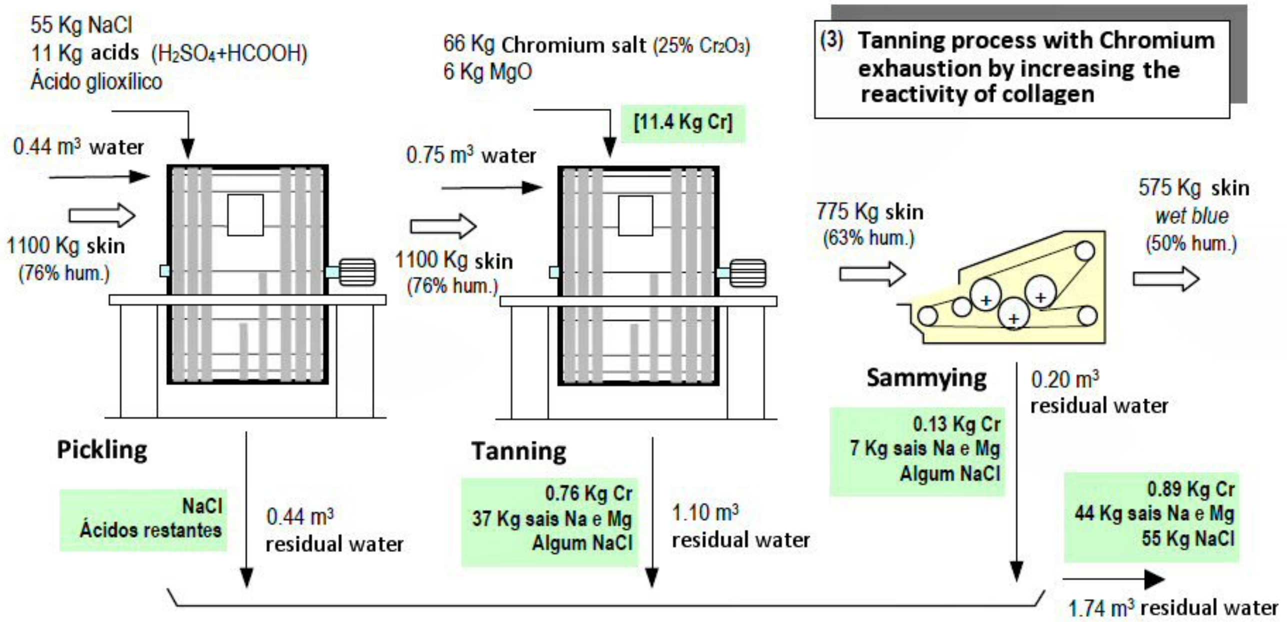


Figure 2.51. Schematization of tanning process with chrome exhaustion by increasing the collagen reactivity

Tanning baths recycling

Chromium recirculation technology consists of reusing the residual chromium contained in the exhausted tanning baths by treating and reusing them.

This technology is an alternative and does not complement the exhaust processes, as it is not expected that a chrome recirculation process will be applied in a bath where the concentration of the chromium is already quite small.

PRACTICAL APPLICATION

Chromium recirculation technologies require, unlike exhaustion processes, the association of equipment with the traditional process. Specifically, filtration of depleted liquors prior to recirculation to remove impurities should be considered.

The use of decanters, floats or hydrocyclones is also desirable to prevent accumulation of fats that may cause discoloration of the skin.

Content above 45 mg/L fat is not recommended. The recirculation processes can be carried out in very different ways using parts or the total of the depleted liquors, which can be reused in the following tanning and / or pickling baths. A possible arrangement of such processes is exemplified in Figure 52.

In this case, 80% of the spent tanner bath is passed through a filter (or other apparatus such as a hydrocyclone or a float) for removal of the suspended solids and fats, then 60 % of this volume recirculated to the next tanning bath and the remaining 40% recirculated for the pickling together with the runoff water.

The pickling bath is always totally discharged in each cycle, while only 20% of the tanning bath is purged. This purge is for the control of the accumulation of the neutral salts in the recirculation process, thus being able to maintain the concentration of these salts to feasible levels.

With the presented arrangement only, a make-up of 0.22 m3 of water (83% of the water required in the conventional process) is necessary, which is achieved not only by the action of recirculating the bath but also by the use of the existing water in the resulting skin of the strong moisture variation between the skin in the wet-blue state and in the pre-tanning state. In this recirculation process the chromium fed is reduced by 16% and the chrome discharged by about 60%. In spite of this, the concentration of the tannery effluent (picket included) does not change from the conventional process (2.2 g/L) although the amount discharged is much lower, as already mentioned, by the effect of the decrease in volume. Chromium utilization efficiency is 86% (14% higher than the conventional process).

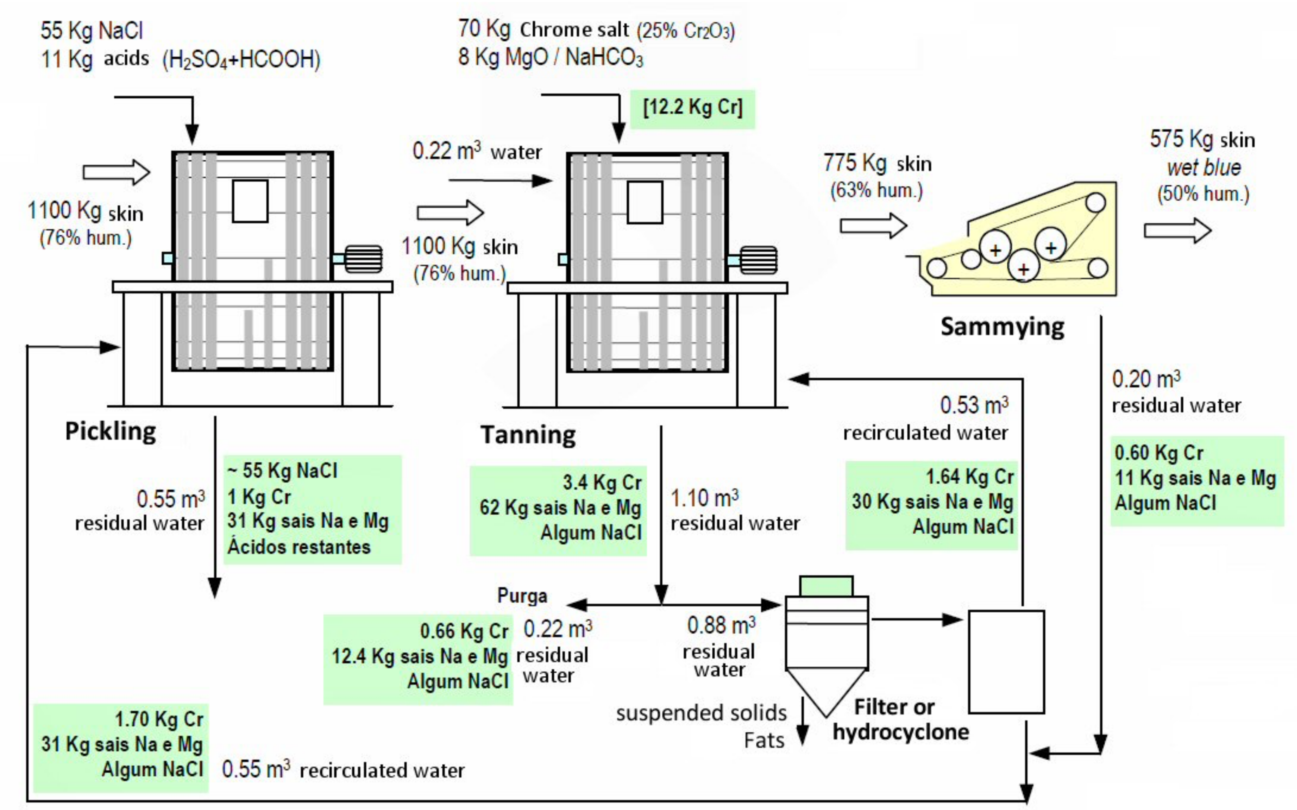


Figure 2.52. Schematization of recirculation of pickling and tanning baths

ECONOMIC VIABILITY

In the recirculation process of spent chrome liquors there is no need to consider the use of new chemical reagents, as opposed to the exhaust processes.

Variations in labour and energy costs will also not be significant. So, there will be no additional production costs. The economic viability will therefore be evaluated by comparing expected benefits with the necessary investments:

➢ Benefits or gains:

- Savings in the consumption of conventional chemicals, mainly in chromium sulphate.
- Cost savings in effluent treatment and waste disposal, mainly due to the reduction of discharged chromium, which is reflected in the consumption of chemical products in the WWTP and the amount of sludge formed.
- Earnings using Chromium depleted liquor recirculation system: 57,200 €/year.

➢ Investment:

- Installation of filters and eventually hydrocyclones to remove suspended solids and grease, and also from recirculation pumps.

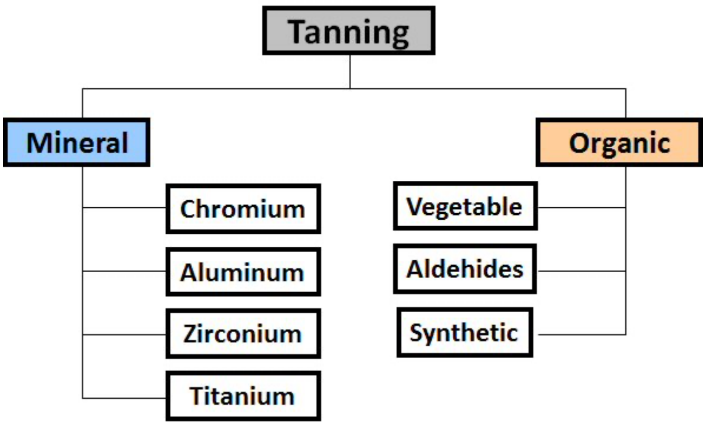
An example is the possible return to a company that has three liming drums and that produces 400 Ton/month:

- Cost of investment for the installation of filters: € 35,500;
- Cost of investment with hydrocyclone included: € 80,000;
- Return on investment time: approximately 2 years.

It should be noted that in this rough analysis of economic viability, environmental gains were not considered, i.e., the potential reduction in the cost of effluent treatment.

Chromium alternative tannings

As already mentioned herein, the tannery corresponds to a treatment, usually carried out in the same pickling bath, with the suitable tanning agent, in order to give the skin thermal stability, strength and other specific properties in each case. There are different types of tanneries, which are divided into two large groups, according to the following scheme.



Wet-white

In view of the latest developments in this area, it has been found that the tanning processes which allow obtaining properties closer to the chromium tanner are those in which a mixed tanner is used with synthetic aldehydes and tannins.

The way to do this type of tanning is shown below.

PRACTICAL APPLICATION

There are several tanning processes with aldehydes and synthetic tannins already developed and available in the market.

Nowadays, following this type of processes, it is already possible to obtain stabilized skins, ready to be shaved, with the following characteristics:

- Skin white or yellow, depending on the type of aldehyde and synthetic tannins used;
- Temperature of contraction of approximately 80ºC.

In the case of tanning of bovine hides, this type of process is safer when working skin lime splitted, at least 3 mm. At this thickness it is possible to obtain a through tanning by a process with a duration similar to that of the chromium tanning. Depending on the type of aldehyde and synthetic tannin used, the penetration of the tanning into integral skins is more difficult, ie, more time consuming, which may require a processing of 24 hours more than is normal in the tanning with chromium salts, for the same type of article.

Nowadays, aldehydes used in such processes are commonly referred to as modified glutaraldehydes, resulting in whiter skins and with greater thermal stability than when glutaraldehyde is used. Another substance has turned out to be interesting as a possible substitute for glutaraldehyde - the oxazolidine.

In general terms, these processes have the following sequence:

1. Lowering of skin pH to about 3.0 (pickling).
2. Modified glutaraldehyde addition.
3. Rising of skin pH to about 4.0.
4. Addition of synthetic tannin and dispersant.
5. Addition of sulphited fat and emulsifier.
6. Lowering of skin pH to about 3.5.

When it is desired to increase the mechanical strength of the skins in the tanned state, it is common to introduce a small dosage of aluminium sulphate together with the synthetic tannin.

The synthetic tannins to be used are function of the priority: greater filling and mechanical and thermal resistances, or whiter. If practically white tanning is desired, it is best to use synthetic white tannins, such as dihydroxydiphenyl sulfones. If fuller skin is desired, replacement synthetic materials should be used.

One conditioning of the wet-white tanning is the decrease in the skin's reactivity to all anionic products, in particular acid dyes. This impacts into a decrease in colour resistance, namely in reducing the solidity of the dyeing to the migration in aqueous medium.

This condition can be minimized by the introduction, in tanning or retanning of other metals, other than chromium, such as aluminium or zirconium.

ECONOMIC VIABILITY

Wet-white tanning processes are generally more expensive than conventional chromium tanning. In addition, the retanning and fatliquoring of skins with this type of tanning are also more expensive, forcing the dosage of a larger amount of extracts / tannins, resins and fats. Overall, an increase in the cost of the final article is easily reached at about € 0.30 / ft2.

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There are, however, the gains associated with green marketing and the possibility of valorising the tanned solid waste resulting from shaving and trimming operations. This type of waste can be valued in the production of fertilizers, technical gelatins, etc.

Figure 2.53. Hides in wet-white state

Vegetable

The vegetable tanning represented for centuries the most used form of tanning, along with the alum tanning and the oil tanning.

Although later on, chromium tanning has appeared, vegetable tanning continues to be suitable for the manufacture of certain articles intended for footwear, leather goods and accessories, such as lining, insoles, and soles, riding articles, belts, bags, wallets and fashion accessories.

The preference for vegetable tanning is associated with differentiation characteristics that value it, such as breathability, antibacterial power, plasticity and beauty in aging.

Vegetable tanning agents are the natural tannins extracted from the bark, leaves, fruits and wood of plants.

Tannins, chemically divided into two major classes - pyrogallics and catechins - are designated according to their plant origin and geographical origin:

Table 2.12. Vegetable origin and geographical origin of some tannins

Extract	Origin	Plant part	Tannin content (%)
Quebracho	Argentina	Wood core	14 - 26
Wattle	South Africa, Australia	Bark	22 - 48

Chestnut	Yoguslavia, Italy, France	Wood	6 - 15
Valonia oak	Turkey	Fruit	16 - 38
Myrobalan	India	Fruit	25 - 48
Oak bark	Central Europe	Wood	3 - 10
Sumac	Tropical coastal sea	Bark	16 - 50

PRACTICAL APPLICATION

The vegetable tanning processes can be carried out in different ways, according to the type of equipment in which they are made: vats, drums or mix. All the methods comprise a phase of penetration and fixation of the tannins, the great difference between them being the speed of processing. The process in pits is carried out in a countercurrent, starting in a pit of lower concentration of tannin and lower acidity, and passing progressively to tanks of higher acidity and higher concentration of tannin. The final pits are heated in order to maximize the fixation of the tannin.

The process in drum is faster, due to the greater mechanical action. It starts by deliming and conditioning the skin to a pH of 4.5 - 5.5. A pre-tannage is then made with synthetic tannin, followed by the tannage itself, with successive dosages of the tannins, dispersants and oils, when used.

In the mixed process the penetration phase is carried out in pits, and the fixation phase, which requires elevation of temperature and occurs at lower pH values, is performed in drum. The application of the article to be produced limits its characteristics, namely its thickness, softness and fastness, leading to the selection of the most appropriate mechanical process (type of equipment) and chemical (vegetable and synthetic tannins).

For greater thicknesses, the time of penetration of the extracts is naturally higher, and may be slightly reduced by the addition of auxiliaries, such as dispersants and synthetic tannins which are richer in sulfonic groups. The thinner articles, such as lining and leather for leather goods, require more softness and care regarding tear resistance. In procedural terms, these characteristics are obtained by using more sulphited tannins and also by a higher dosage of electrolyte stable fats and in acid environments.

Vegetable tanning is very sensitive to light, and this characteristic can be improved by the use of more resistant vegetable tannins, such as those found in tara and cashew extracts, as well as the partial replacement of vegetable tannins by synthetic tannins high fastness to light.

ECONOMIC VIABILITY

The cost of a vegetable tanning process is higher than chrome tanning and wet-white production.

Subsequent costs - dyeing and finishing - vary greatly depending on the application of the article. It should also be noted that the ambient light conditions and the characteristics of some equipment are decisive for the proper execution of this type of tanning. The production of vegetable articles requires low light, specific care in shaving and drying operations, and especially in thicker articles, the use of specific machines, such as cylinders. Thus, the option of vegetable tanning can generate the need for investment in the adequacy of facilities and in appropriate machinery. From what has been said, vegetable tanning does not compete directly with chrome or wet-white base articles. This option presupposes the valorisation of its characteristics of differentiation as technical, aesthetic and health advantages.

Dyeing

Good practices for preventing the formation of hexavalent chromium

The formation of hexavalent chromium (Cr VI) in leather is a factor that has been increasingly considered in its commercialization. Hexavalent chromium has a negative effect on health, which is why control of its occurrence is critical. Cr VI is bioaccumulative, very toxic, mutagenic and carcinogenic, due to its high membrane penetration capacity and strong oxidative potential. It is thus fundamental to act in order to prevent the oxidation of Cr III to Cr VI, during and after processing of the skin within the tanning factory.

PRACTICAL APPLICATION

After tanning with basic salts of chromium the skin is stabilized through the establishment of chemical bridges between the protein chains, generated by the complexation reaction between the carboxylic radicals and the chromium in the oxidation state III.

The skin is then subjected to a series of operations in aqueous medium, where small amounts of chromium VI may occur.

The normal sequence of these operations in aqueous medium is as follows, excluding the washes: cationic / metal retanning; neutralization; anionic retanning; penetration dyeing; fatliquoring; redyeing.

Some practices that lead to a higher probability of formation of hexavalent chromium are identified in the literature:

- Use of chromium salts in cationic retanning;
- Very intense neutralization, especially with ammonium salts;
- Use of ammonia in dyeing as a penetrator;
- Use of fatliquors of animal origin with high iodine index
- Storage of crust hides in an oxidative environment

Notwithstanding the above, the experimental evidence shows that the presence of chromium VI in the skins after the end of their processing rarely occurs, which is sometimes caused by the aging of the leather due to exposure to UV radiation in hot and / or humid environments.

Several good procedural practices are known to prevent the formation of chromium VI in the skins, among which it is naturally possible to avoid what has already been referred to as being in its origin.

However, it is often unavoidable to use some of the practices identified above with a view to obtaining certain aesthetic characteristics and technical properties in the final article. In any case, substances which prevent the formation of hexavalent chromium may be added during the processing in aqueous medium, in particular in the retanning, even when the final article is subjected to strongly oxidative environmental conditions.

These substances are as follows:

- Vegetable extracts, even if dosed in small quantities;
- Other retanning agents with antioxidant properties, such as synthetic phenolic tannins and some sulpho-compounds (naphthalenesulfonic acids);
- Vegetable-based fats, in particular lecithins.

After intense experimental work, measures were defined that, when applied in the retanning / dyeing processes, prevent the formation of hexavalent chromium.

These are as follows:

- Non-use of ammonium salts and ammonia;
- To use at least 4% (calculated percentage on lowered weight) of tare extract in the retanning;
- Whenever possible, to incorporate on the fatliquoring emulsion, some lecithin (at least 2% - percentage calculated on lowered weight).

ECONOMIC VIABILITY

There is no type of investment in equipment for these techniques to be put into practice.

The use of the chemicals mentioned does not involve a significant cost increase, since they even allow the replacement of others with similar prices.

Finishing

Aplication of finishes with advanced technologies

The use of advanced finishing technologies, such as applications with low pressure spraying guns (HVLP) or roller machines, allows a minimization of chemical losses.

PRACTICAL APPLICATION

Finishing products (waxes, oils, paints, varnishes, lacquers, etc.) used in the final stage of the process are essential to the quality of the final product, as they give the final appearance to the product according to the customers' specifications.

In addition, these products are usually expensive and are sometimes made up of potentially dangerous volatile compounds. Their correct application and the minimization of losses are therefore essential both in economic terms and in terms of environmental quality. In this context, there are two aspects that contribute to the optimization of procedures at the industrial level: the use of more advanced equipment and the correct choice of the product to be applied, taking into account its potential danger.

The following table presents comparative data on alternative technologies for the application of finishing products. The values given are based on a finishing incorporation base of 150 g/m 2 of skin. The advantages of using HVLP spraying guns and roller machines are obvious.

Table 2.13. Comparison of losses between different spraying guns methods

Technology	Losses (%)	Unit consumption including losses (g/m^2)
Conventional Spraying gun	40	250
HVLP Spraying gun	35	230
Roller machine	15	176

ECONOMIC VIABILITY

In the economic evaluation it will only make sense to compare the conventional spraying gun system with the HVLP system, because the application of finishes with roller machines is not always an alternative to other processes and is commonly used in order to obtain a finish with different characteristics.

In assessing the costs of different finishing processes, the following items should be considered:

➢ Benefits or gains:

- Savings in the consumption of finishing products, by losses reduction
- Saving of effluent treatment costs and sludge deposition, due to the lower contamination of the waste water with the lost products.

➢ Investment:

- Purchase of HVLP spraying guns

An example is the possible return to a company that uses HVLP spraying guns in the finish of 140 m2/h of leathers.

- Investment cost of (12 HVLP spraying guns): 9,600 €

In order to calculate the annual savings in reducing the consumption of finishing chemicals, the following premises were considered:

- 1,940 Hours of annual work;
- Reduction of the average unit consumption of finishing compositions, according to the previous table: 20 g/m2; average cost of finishing composition: € 2.8 / kg.

Thus, the annual savings achieved would be approximately € 15,200, which would mean a return on investment of about 8 months.

Figure 2.54. Spraying system with HVLP spraying guns

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