Italian high technology of TANNING

2nd Edition

TECHNOLOGICAL COMPENDIUM

Italian high technology of tanning gave the tanneries spread all over the world the possibility to achieve highest level targets in terms of quality and productive efficiency; this paper makes a synthesis of the most modern and flexible technologies set up so far from Italian mechanical-tanning companies.

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Summary

Technological Compendium

ITALIAN HIGH TECHNOLOGY OF TANNING

INTRODUCTION

The objective of this paper is to give a general overview on the level achieved from tanning technology in its most critical and important areas.

Italian chemical and mechanical technology has always supported and spurred the tanneries on their growth in terms of volumes, efficiency and, last but not least, in terms of quality. For this reason the Italian tanneries got machineries and systems create and set up on the basis of collective and individual needs, allowing to be asserted on international field.

The companies supplying mechanical and chemical technology had the possibility to adapt their machineries and chemicals products to the real productive needs of their customers and to support the complete and deep set up through a constant comparison with the final user in order to create solutions able to better satisfy the production requirements.

During the years, this synergic development allowed the Italian tanning sector to become a reference point in the fashion, being the first in the world for:

- Innovation in style of suggested products
- Efficiency and constant production
- Reliability and product quality

In order to make "nice" leather in an efficient way, it is necessary to use advanced technologies able to guarantee high standard controls of the process, replicable and consistent quality as well as productive efficiency.

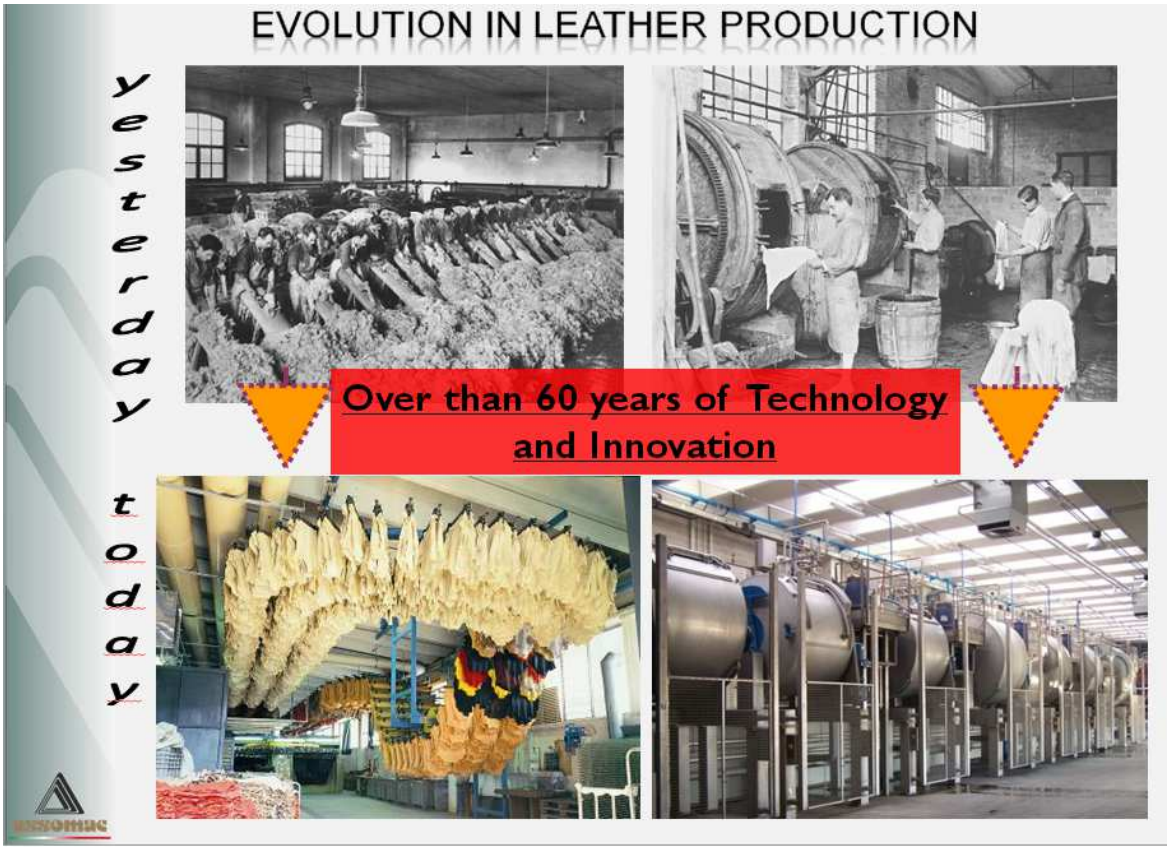
Both the mechanical tanning sector and the production of chemicals have always faced a very delicate productive system, deeply affected by price rise. These "binding mechanisms" of the sector brought the producers of mechanical technology, and in particular the ones producing tanning chemicals, to develop some skills in the use of secondary raw materials, giving more attention to "environmental" problems. The rising demands of "sustainable development" took into the sector the logic of process with a low environmental impact, waste water control and rational exploitation of used resources.

The international industry, as the Italian one, meets always the market requirements and achieves the targets of the modern tanning process with:

- "FASHION" articles technologically avant-garde
- products created following environmental and energetic sustainability standards
- observance of eco-toxicity limits provided by international regulations
- Rationalization of production costs and rational exploitation of resources.

In more than 50 years of industrial history, in Italy the development of the production chain and ennoblement of leather put the basis of development of Italian leather products and appreciation in the markets all over the world.

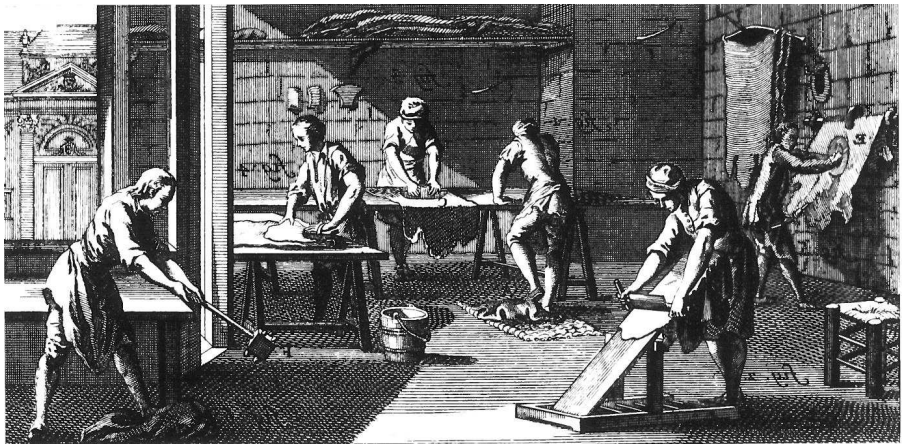
The following pictures mean to underline the developments achieved during this period



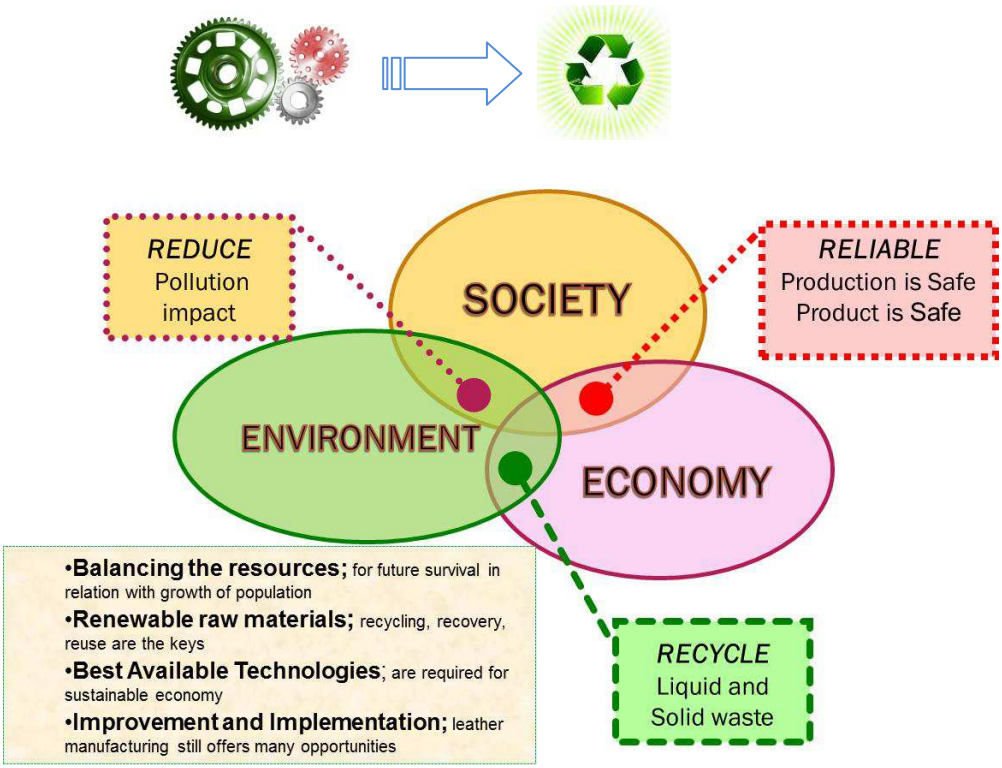
We cannot avoid highlighting that this process of modernization has been supported by the entrepreneurial capacity of Italian companies which are constantly careful to solve problems related to the process and the environmental sustainability.

Innovation does not stop. The Italian industry knows the importance to strengthen its heritage of "industrial culture" suggesting new technologies.

Leather is the oldest recycling process based on a 100% renewable raw material. The ability is to reconvert into a high finishing material, a by-product of slaughter that would be otherwise lost.



The competence of Italian companies, in the present advanced process, takes care of sustainability issues as **commitment in control processing. Particularly in consideration of resource reducing and environmental impact.**



1. TANNING CONTEXT

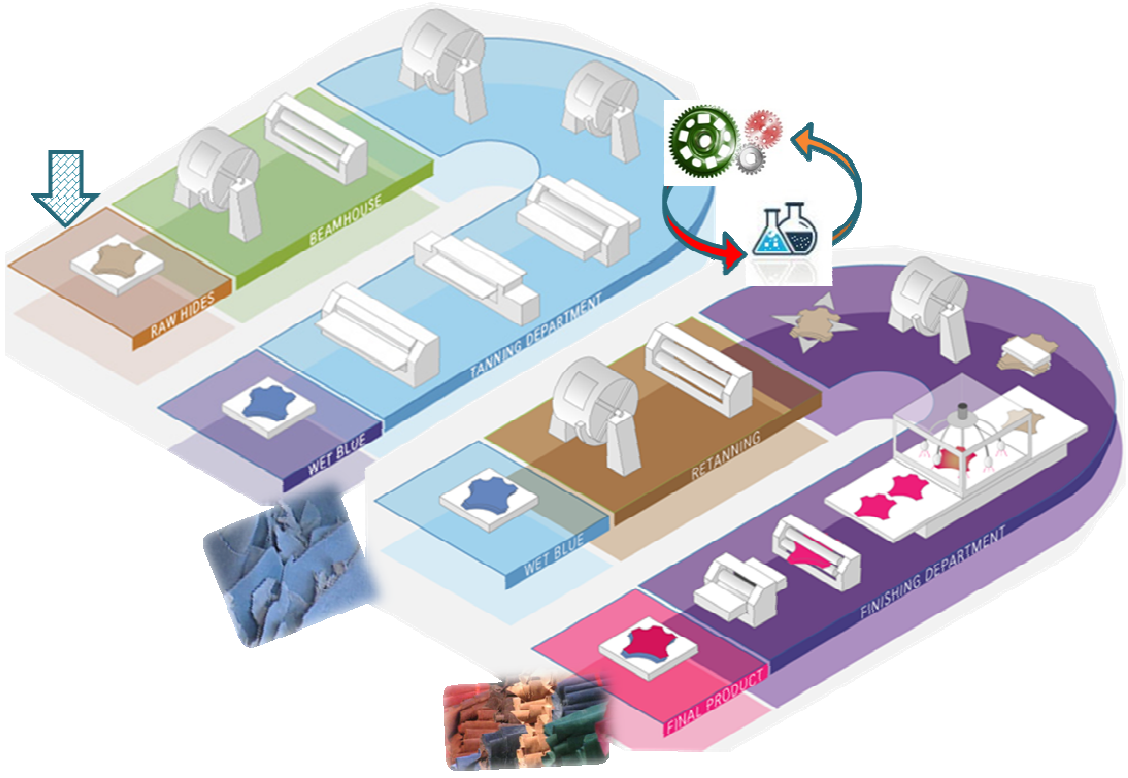
The word "leather" means the hide that, after several physical, chemical and mechanical treatments, becomes a material not subject to putrescence and that can be easily used in manufacturing industry in order to produce shoes, leather goods, clothes, interior decoration, automotive accessories, technical articles, etc…

The leather is obtained from common hides of animals for slaughter (bovine, swine, ovine, caprine, etc…) which represents a food industry sub-product that has a considerable commercial value, if ennobled in the proper way. For this reason the tanning cycle is one of the most ancient examples of regeneration and exploitation of a sub-product.

Being the skin a natural product, it maintains some chemical and physical features over time, furthermore in several processing phases the effect of the workforce is strong. These aspects have not been easily adapted to the industrial production standards.

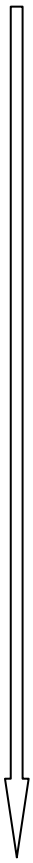
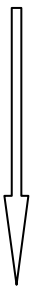
Thanks to an exchange of technological skills between chemical and mechanical component allowed the industrial adaptation of the tanning process. This has been the role, recognized worldwide, that the Italian mechanical and chemical companies played in over 50 years of history of tanning sector.

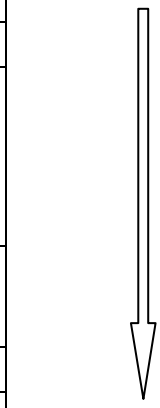
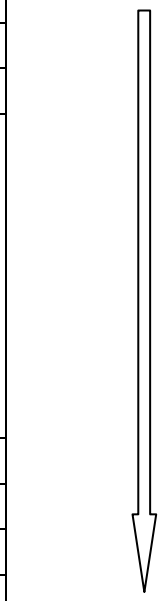
The below diagram shows the phases of tanning cycle and highlights the importance of the support given by mechanical and chemical companies into the productive cycle. This integration is a structural part of the production chain up to the creation of the articles requested by processing industry.



The tanning process is made up of several physical and chemical operations that bring the raw material (not much strong and with an irregular shape) to get a quite constant thickness and some other features as preservability, good flexibility, high resistance to tensile stress and abrasion, possibility to make a good aesthetic refining.

In the following chart it is possible to see the processing phases in comparison with the mechanical systems and the chemicals that take part in the process.

Mechanical system	Product phases	Processing phases	Tanning chemicals
Raw material			
		Selection by families	
Desalter		Desalting process	
		Trimming	
Reel drums		Soaking	Non ionic and anionic imbibers, Bacteriostatic agents, Chloride of sodium Enzymic products Surfactants
Reel drums		Liming	Sulphide of sodium Sulphydrate of sodium CaCO
Filter		Hide regeneration	
Fleshing machine		Fleshing	
Drums		Deliming Bating	Sulphide ammonium Chloride ammonium Lactic acid Enzymic products proteolitic bisulphite sodium
Drums		Scouring	Anionic and not ionic emulsifying Surface-active agents Chlorinated solvents
Drums		Pickling	Chloride of sodium Sulphuric acid Formic acid
Pickled			
Drums		Tanning	<u>Chrome tanning</u> basic chrome sulphate sodium chloride Sodium bicarbonate <u>Vegetable tanning</u> Natural and synthetic
Pressing in blue		Pressing	
Splitting machine		Splitting	
Shearing machine		Shearing	
Wet-blue			

Mechanical system	Product phases	Processing phases	Tanning chemicals
Wet-blue			
Drums		Neutralising	Sodium bicarbonate
Drums		Retanning	Retanning agents
Drums		Dyeing	Acid and metallorganic dyes Ammonia Formic acid Natural vegetable dyes
Drums		Greasing	Natural oils, Sulphonators and emulsifier, Synthetic oils
Hang drying		Hang drying	
Dryers		Drying	
Crust			
Staking machine		Staking	
Buffing machine		Buffing	
Coating machine		Coating	*see booth
Booth		Spraying	Organic and inorganic pigments Casein Albumin Acrylic resins Formaldehyde Sodium Sulphuricinate Natural and synthetic waxes Nitrocellulose Organic solvent
Milling drum		Dry drumming	
Press		Ironing	
Polishing machine		Polishing	
Measuring machine		Measuring	
Finished product			

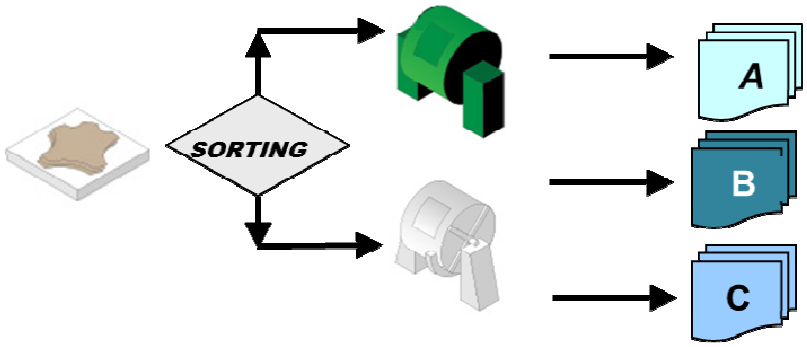
Before entering into technology details, we would like to underline that "industrial process" means a production cycle that creates a finished product with very STANDARDIZED final features. In order to obtain that, it is not possible to leave out of consideration two factors:

- The processing cycle has to be standardized, repetitive and automatized
- The raw material has to have uniform physical and chemical characteristics in order to guarantee the constant quality of produced "articles".

Even if the tanning industry is quite organized, it is still an industry out of the ordinary: it starts from the raw material, made of different "bodies", in order to get a series of homogeneous "finished products".

This consideration should force the industrial tanning organization to reach, first of all, a structured productive organization through a classification by "families".

So, a specific action of "SELECTION" could give the possibility to start the processing from a raw material having characteristics as uniform as possible, in order to get a final optimized production.



There are no standard rules for this operation; each organization follows its own systems, on the basis of local conditions related to supplying as well as the created product required. A proper and deep QUALITATIVE classification, made by an expert who well knows the leathers and the animal species, their weight and origin and the highlighting of the defects due to parasites, decomposition or traumatic events, makes easier the organization of the production process, starting from raw and semi-finished material.

1.1 MECHANICAL EQUIPMENTS

Starting from the after-war period up to today, the entrepreneurial history of mechanics applied to manufacturing sectors is doubtless among the main productive activities that characterized the industrial development of the country. The several activities focused on producing machineries for processing works and have met different productive chains, moving the know-how. For example, so much has been innovated in the clothing, plastic and shoes sector in terms of automation and safety measures.

In line with these dynamics, the mechanical and tanning sector producers updated their own products by applying solutions and innovations aimed at meeting tanners' requirements, it means a technology simple to manage, regulate and plan.

The applied research allowed the production of machineries, lines and plants more safe, competitive and able to guarantee performance and productive profitability. For example through line adjustments, control of energetic consumption and maintenance.

The quality of machineries offered on the market is guaranteed by numerous analyses of structures, constructions, varieties, control and regulation systems, as well as a careful and deep selection of used components, followed by proper tests and inspections.

Furthermore, the present demands of a sustainable tanning process, in terms of energy and environment, drove the technological development of producer companies towards solutions that guarantee:

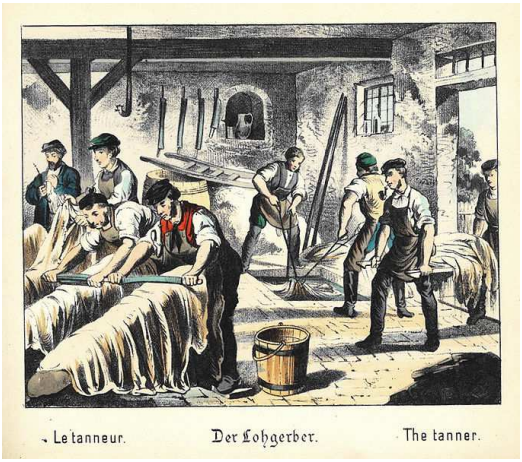
- chemicals efficient consumption
- water resources and wastewaters management
- atmospheric emissions control
- energetic consumption decrease
- workers health protection

This represents a step towards an increasing integration of tanning process and towards the automation able to combine and trace the processing phases.

1.2 TANNING CHEMICALS

Processing a natural product into leather has ancient origins; it is enough to recall the countless series of prehistoric graffito or archaeological finds that have been discovered (Pompei's tannery, 79 a.d.).

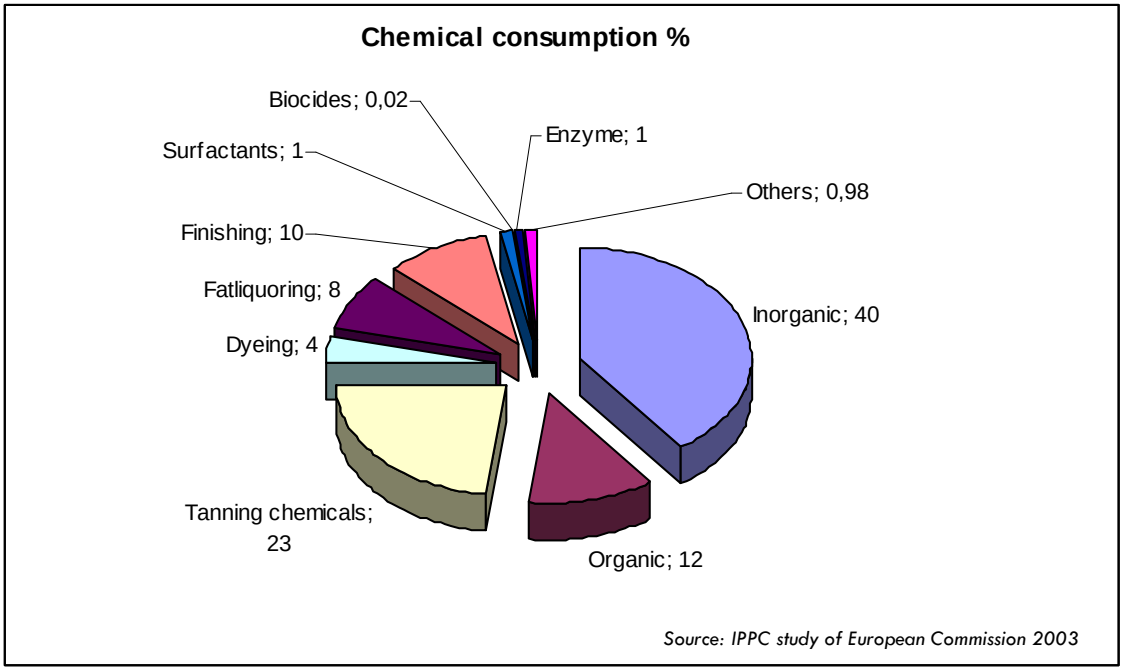
A lot of biochemical processes were applied on killed animals' hide, like treatments in tanks, usage of animal dung (enzymatic treatment), raw lime (stabilization) and vegetable bark essences (tanning and dyeing). Here below a brief summary of the most important evolution phases:



Paleolith	Drying by air Fumigation Greasing with brains, fish oil and animal fats
First civilizations	The hide is used to produce different objects: cloche, shoes, diadems, gloves, leather bags, floats, pipes, etc…
VIII century	Cordovan leather
Middle Age	Origin of first tanners foundations
About 1850	First drum
1856	Chrome tanning
1875	First rotary machine
1888	Slide type staking machine
1897	Polishing machine
1898	Ironing and embossing machine
1904	Semi-automatic fleshing machine
1935	Hydraulic drive in a cylinder machine

Nowadays, in some developing countries, the tanning is still manually made.

Obviously the modern industrial tanning needs to follow a constant, repetitive and reliable process, both in mechanical and chemical sector of raw material processing. In the following chart it is possible to see an example of chemicals categories used and involved in the processing of bovine hides from a fresh salty condition to a finished product.



The production of spending function chemicals for ennoblement, it means chemicals widely used in processing cycles (leather, hide, paper, etc…), of natural or synthetic raw materials properly modified in order to meet the requirements of modern manufacturing industry, taking into consideration the sustainable development.

It is necessary to highlight how the history of Italian chemical industry, more precisely concerning the plant design, has internationally affected the production of chemicals addressed to manufacturing industry. The production skills of Italian chemical industries allowed realizing plant design solutions spread worldwide. It is enough to remember how much has been developed in the production of polymers and/or etossilats, just to mention some of them. These skills, supporting the manufacturing process (clothing, paper, leather, plastic, …) together with the necessary control of industrial costs, have brought the chemical industries to ***Reconversion and Development*** of sub-products, considered as "waste" from other production chains, to products totally integrated in the tanning industry; for example some recycled food oils, non-food caseins, sub-products of distillation and/or extraction … .

These targets have been achieved with important adjustments and investments in the plant design development through a constant process implementation on the basis of the know-how acquired on the field. This constant application allowed achieving the present high levels both in the optimization of production and environmental impact control.

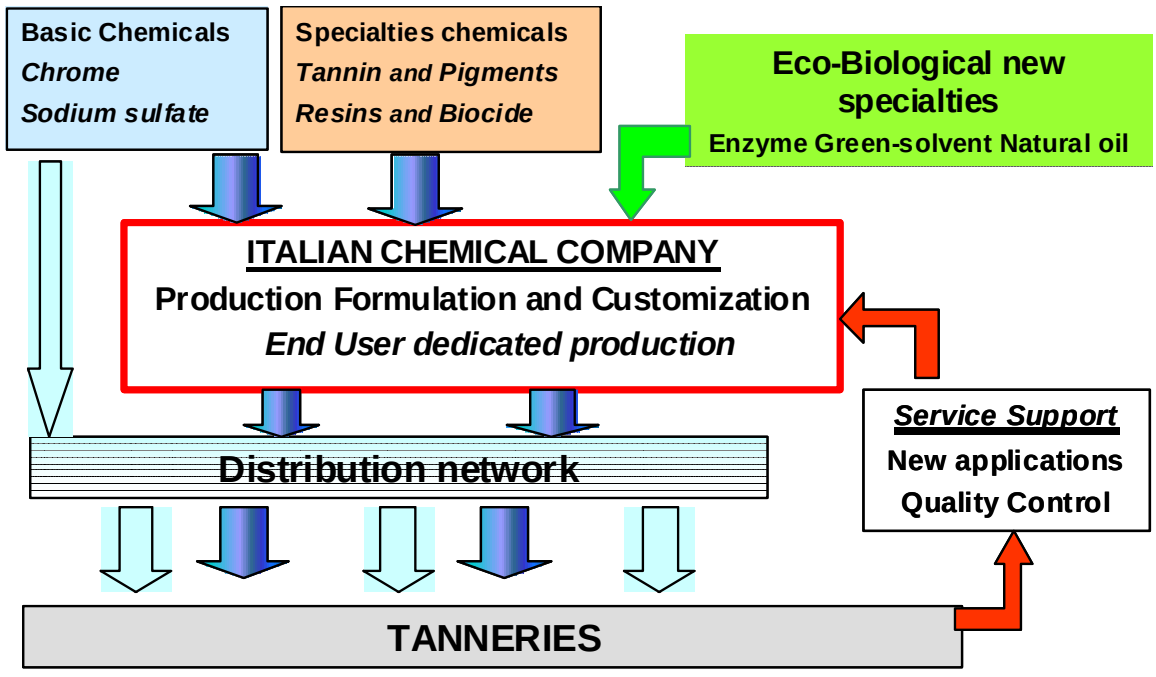
RESEARCH

PRODUCTION

MIXING

The Italian companies, besides a pronounced production activity of raw materials, are specialized in the applicative and formulation phase. This feature has been developed because of low availability of local raw materials, both as rawhide to be processed and as chemical product to be used. In all cases, it is necessary to apply research and development actions in order to satisfy the demands of manufacturing industry.

The activity of companies producing chemicals, as shown in the attached flow-map, focuses on chemical processing through synthesis and on mixing of raw materials or on specific formulation of dedicated active principles. The chart about the distribution of "spending function product" highlights that the passage from raw material to product dedicated to process has a main phase of applicative development, formulation as well as control and analytical support.



Every day the companies, through their laboratories, have to satisfy the pushing demand of innovation and development coming from manufacturing industry for the production of new articles having more and more functions: water-repellent leather, non-toxic, bio-compatible with human skin, not allergic, fireproof and other characteristics functional to consumer's need and taste.

Over the last years, Italian tanneries structures developed a lot in order to make the process sustainable from an environmental point of view (water treatment, control of atmospheric emissions, etc…) and for sure it is possible to get an even bigger improvement.

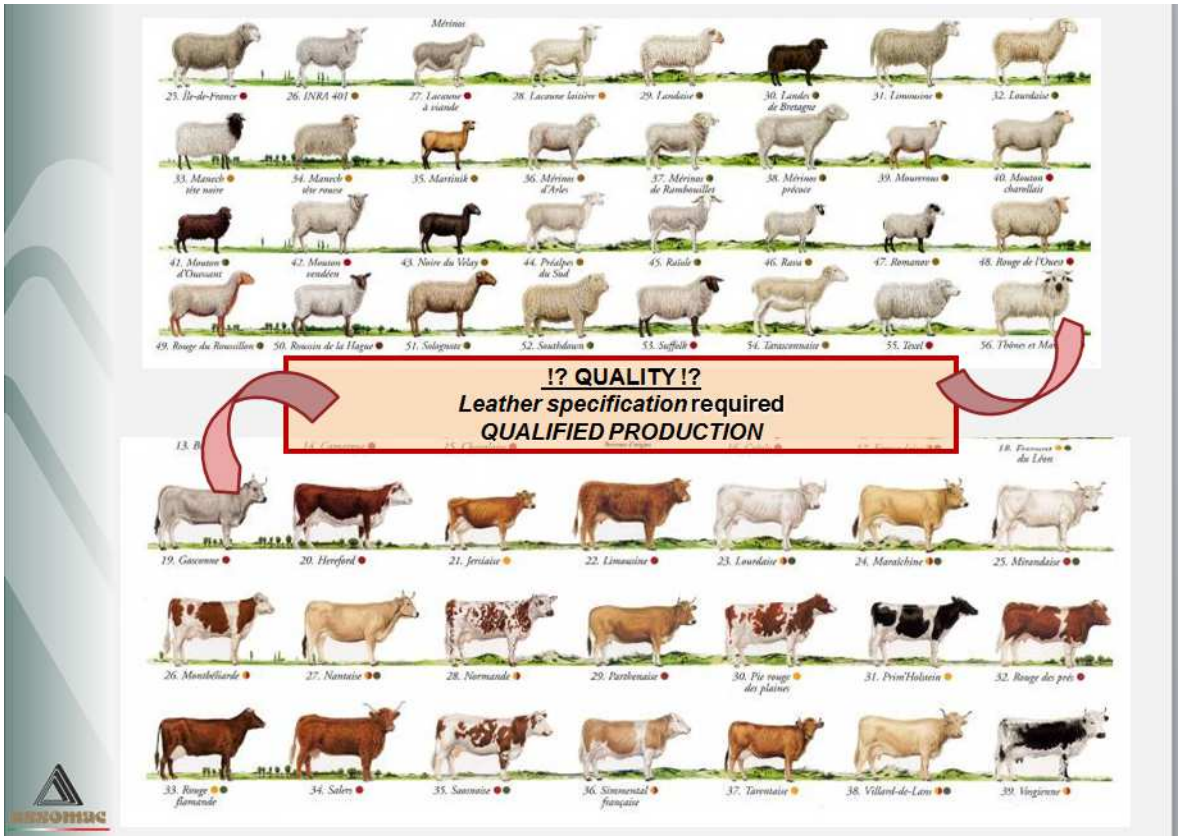
Looking to a bigger sustainable development of tanneries, we cannot conceal that the present technology is still tied to non renewable resources. A lot has still to be done in order to "replace" some phases with systems linked to renewable resources, coming back to origins without losing the necessary industrial reliability.

The recent introduction of strict regulations (REACH 2008) is highly affecting the economic and human resources of companies, especially the SMEs. This situation allows companies to move their "energies" towards a law adaptation instead of towards the development and substitution of non renewable raw materials.

2. SURVEY OF THE MOST IMPORTANT TECHNOLOGIES

The constant market demand of innovative articles requires the necessary flexibility of tanneries, constantly busy in improving product quality. So, it is necessary to give chemical and mechanical support for the modification/optimization of production cycles. These characteristics are the result of several years of technological development and are present in Italy, where the companies producing tanning chemicals and mechanical plant designs make available **applicative laboratories** able to satisfy the demand of new solutions required by the tanning sector: water-repellent leather, non-toxic, bio-compatible, not allergic, fireproof and other characteristics functional to user's need and taste

The mechanical and chemical solutions that have been developed over years were addressed to different productive needs. In any case they are the result of a tight relationship between supplier, producer and consumer, allowing the development and optimization of the product with waste and management costs control.



We can confirm that the Italian tanning industry has got complete and multidisciplinary skills available in the international context.

The main objective of this paper is to summarize, for each production phase, the general innovative aspects that the mechanical, chemical tanning industry helped in improving, even in the light of modern technologies for managing the process and moving of semi-finished products. The final part of the document is on process sustainability:

2.1) Technologies from raw material to pickled

2.2) Technologies from pickled to wet-blue

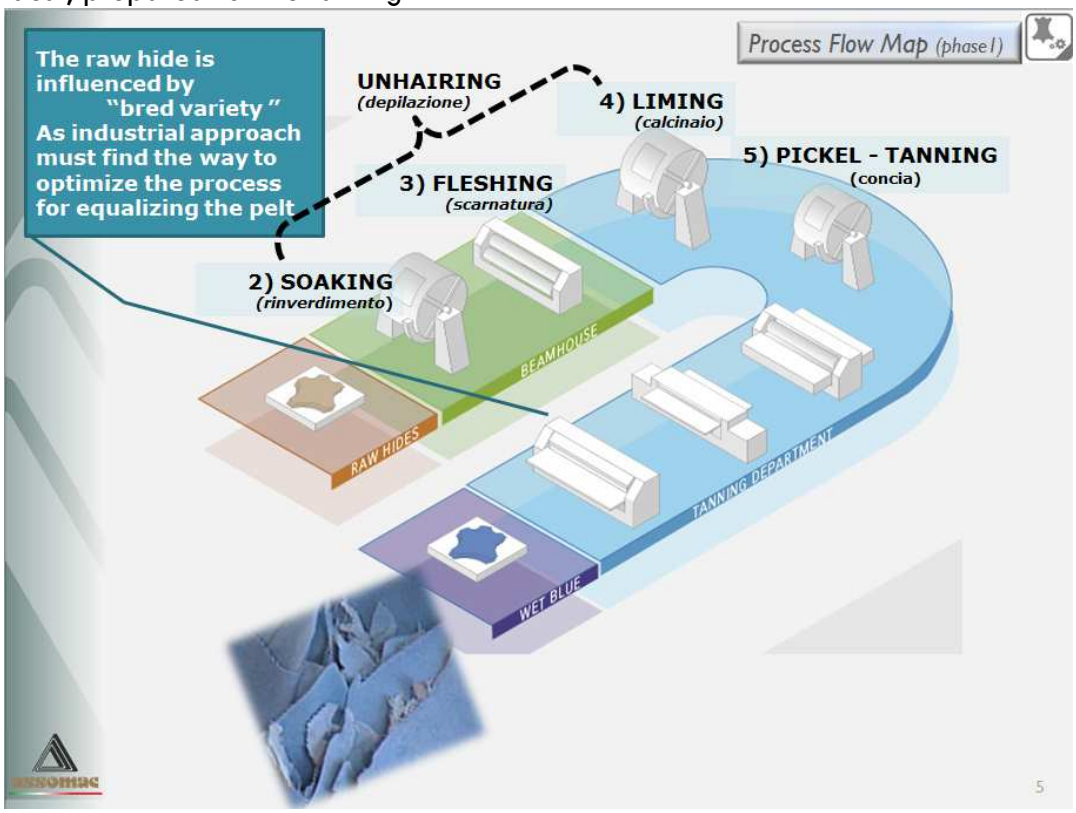
2.3) Technologies from wet-blue to crust

2.4) Technologies from crust to finished hide

2.5) Automation and process management

2.1. TECHNOLOGIES FROM RAW MATERIAL TO PICKLED

The beamhouse process includes all the treatments coming before the real tanning and that prepare the hide or the tanning phase. There are several beamhouse operations including mechanical, chemical and physical treatments. After the beamhouse process, the hides are called "pelt hides", prepared for the tanning.



WAREHOUSING

The quality of the raw material is extremely important on the quality of final results. The incidence of slaughtering operations and the conservation procedure are the first step to preserve the raw hides. Even the warehouse organization still has big incidence, statistically the data collected from waste products show that:

60% is from Bacterial Aggressions due to poor cleaning/bad aeration/preserving agent

35% Traumas due to Flaying; Branding, Thorns, Transportation

5% Aggression by parasites (insects, moulded, verrucas…)

SOAKING

It is applied on rawhides in order to remove the dirt from the surface, the albumins and the soluble globulins as well as the sodium chloride with which the hides are preserved and in order to bring again the hides to the original humidity and reinflation degree.
The soaking is made by washing the hides with a lot of water at 25°C in drum or reel, changing regularly the water in order to remove the microorganisms and the salt released from the hide. The drums are big cylindrical containers, usually in wood but also in steel or plastic.

The tanning chemicals, mixed with a lot of water, are used to make easier the soaking and are made of surface-active agents, alkali (like sodium carbonate, sodium hydroxide), sodium chloride (used just for not salty hides, as anti-swelling) bactericides and proteolytic enzymes. Small percentages of antibacterial substances are usually added (example, pentachlorophenol 0,1-1%) in order to limit the origin of putrefactive phenomena on the hides.

Environmental aspects:
Large quantities of water are used
The waste water is plenty of dissolved substances that affect its quality: the soaking mainly affects the waste water criteria as COD, suspended solids, chlorides and organic nitrogen.

Mechanical equipments:
With high resistance to stress and corrosion. Static systems as tubs or tanks, rotary systems as reels and drums.

LIMING AND DEHAIRING

With the liming, the opening and distress of the hide is made easier in order to increase the soaking of tanned products. Furthermore, the endogenous fats present in the adipose tissue are saponified, while the dehairing removes skin and hair. It is done in the same drums or reels where the hides are soaked, using 300-400% of water, depending on the weight of the hides.

Calcium hydroxide, sodium sulphide and sulphydrate, proteolytic enzymes, dimethylamine sulphide, tensioactive auxiliaries (favoring the penetration of liming vat products and the fats emulsifying) are used. It is important not to decrease the pH less than 10, in order to avoid the release of hydrogen sulfide in this phase.

Environmental aspects:
Water resources are used.
The waste waters, besides the fact that they have an alkaline pH, contribute for the 60% of COD in the tanning waters, mainly due to used sulfides and to organic substances.

Mechanical equipments:
In the liming vat phase, drums or reel are used as well as tanks or concrete mixers, adding slaked lime or other substances.

FLESHING

It is a mechanical operation, through which flesh residual and adipose tissues (present under the hide and called "flesh") are removed.

With the *trimming* the hide border is trimmed by cutting the unnecessary parts (manual operation done with proper knives). Then it is possible to do the *lime splitting* by selecting parts of the thickness, the grain from one side (the most precious part) and the split from the other side, not always usable. The fleshing is carried out with the "fleshing machine".

Environmental aspects:
The fleshing produces the flesh that, like the waste coming from the trimming, has to be treated like a solid residual.
The flesh and trimming sediment for long time could lead to putrefaction with unpleasant smell and ammonia.

Mechanical equipments:
There are "alternative roller" where it is possible to insert the first half of the hide in the machine with crossbar opened. Then the crossbar closes and it is possible to make the fleshing by extracting the hide from the machine.
In the same way, it is possible to insert the second half of the hide into the machine, covering the entire surface with both operations.

DELIMING

In this phase most part of lime used in the dehairing process is removed from the hide. The pH decreases up to levels close to the ones of collagen isoelectric point: in this way the derma deflates and the pH level is perfect for the proteolytic activity of the retting enzymes.

Tanning chemicals: as deliming agents for the pH decrease, it is possible to use strong acids (sulphuric, hydrochloric), weak acids (formic, acetic, boric, etc…) or some salts with acid dissociation as ammonium sulphate or chloride. In this phase it is important to remove completely the sulphides and the sulphydrate used as dehairing agents in the liming vat and that are absorbed by the treated hides. If the deliming is not well done, the risk is to increase the production of hydrogen sulfide (H2S) in the further phases.

Environmental aspects:
The waste water coming from deliming affects the level of COD (due to organic acid and dissolved sulphides) and ammoniac nitrogen.
Because of pH decrease, some chemical reactions lead to the production of gaseous hydrogen sulphide that has to be caught with inhalation systems.
The enzymatic and chemical products used during the maceration phase affect the waste water and change the COD and ammoniac nitrogen levels.

Mechanical equipments:
The operation is made in rolling drums equipped with inhalation systems.

MACERATION

It improves the opening of fibres still not complete during the liming vat phase. It leads to a more hide distressing. In order to do that, it is necessary to remove the elastic proteins that tie the fibres.

Tanning chemicals: the maceration products contain proteolytic enzymes that act on the elastic fibres.

Mechanical equipment:
The operation is usually made in drums.

DEGREASING

It is an optional operation, done only on hides plenty of fats (like swine hides) in order to remove the natural fat substances present on the surface. It is possible to degrease the hide by adding some emulsifiers in the water phase (often mixed with an organic solvent) or using some chlorinated organic solvents. Nowadays, it is possible to use solvents with a bio-synthetic origin that have a low environmental impact.

Environmental aspects:
The washing of hides consumes a lot of water.
The waste water coming resulting from the degreasing, being plenty of fats and chemicals, affect the COD and surface-active agents levels.

Mechanical equipments:
The process is made in drums.

PIKEL

It completes the deliming and definitely stops the maceration process, bringing the hide to a pH level suitable to the further phase of mineral tanning (chrome, etc…).

Tanning chemicals: in the pickling some acid is used (sulphide, chloride, formic) and sodium chloride as anti-inflating agent.

Mechanical equipments:
The process is made in drums.

TECHNOLOGICAL ASPECTS

The problems of this phase are mainly related to the production of a good quality raw material; the following phases are influenced from a good preparation of the initial product.

BEAMHOUSE

PROCESS UNIT	BAT (best available techniques)
Curing and soaking	• To process fresh hides as far as they are available Exceptions: - When long transport time is necessary (max 8 - 12 hours for fresh, unchilled hides; 5 - 8 days if a cooling chain of 2 °C is maintained) - For certain types of end-products - Sheepskins, calf skins • To reduce the amount of salt used as far as possible.
Unhairing & liming	• To use hair-save technology, but economics can be an issue for existing plants when re-use of the saved hair is not possible • To reduce sulphide consumption by the use of enzyme preparations; not for sheepskins • To recycle spent liquors only when processing sheepskins, which are dewoolled by painting
Splitting	• To use lime splitting Exceptions: - When the starting material is wet blue - When a firmer leather has to be produced (e.g. shoe-leather) - When a more uniform and accurate thickness is needed in the final product • To maximise the use of split

Source: IPPC study of European Commission 2003

ENVIRONMENTAL IMPACT

It is one of the aspect internationally recognized and it consists on the control of primary polluting substances. It is possible to shift the polluting agents by moving the rawhides or semi-finished hides. A big contribution is obtained through the raw material desalting; the machineries make easier the treatment and/or the re-use of the salt in a solid shape.

Of course logistic problems and supplying dynamics are decisive. For example, the analysis and evaluation of some data in Arzignano district highlighted the balance between different solutions that deeply modified the charges on the common treatment plant.

Here below some considerations from the "GUIDELINES for reducing chlorides, sulphides and chrome in the tanning waste waters"

CHLORIDE COMING FROM CONSERVATION

The quantity of salt, necessary to guarantee safety long term conservation, amounts to 30% of the rawhide weight. It is estimated that 70% of chlorides present in the waste waters of the entire production cycle comes from the salt used for conserving the hides.

Considered that the depuration ways are very expensive, either for the high investments or the high necessary level of energy and considered that nowadays replacing the salt with other substances and/or alternative non polluting methods is not possible yet, the reducing of sodium chloride used in salting can be done by applying the following measures:

Hides beating:

The quantity of salt that can be removed with this operation varies, depending on the origin of the rawhide, between 6 and 12%, calculated on the weight of the hide.

Use of fresh hides

Processing the fresh rawhides reduces the chlorides in the waste waters of 40% at least. In a mixed production (50% fresh and 50% salty) it is possible to get a reduction of more than 20%. Many European countries use a lot of fresh rawhides.

Reduction of chlorides used in pickled

The water density, compared to the average of the used one (8-9 Bé) can be largely reduced without risking the acid swelling. A density of 6.0-6.5° Bé guarantees a proper operation.

IN ORDER TO REDUCE THE SULPHIDES IN THE WASTE WATER

Most of the sulphides in the waste water come from deliming, pickling, tanning phases as well as from the sulphide in the waste water at the end of the liming vat that becomes sulphate during the depuration phases. Coloring retanning agents bring lower quantities of sulphate.

Reduction of sulphate due to sulphide oxidation

It is known that the sulphide coming from the liming vat waste water can be oxidized to sulphate during the depuration process. If this oxidation is complete, the reduction of 1% of sulphide in the liming vat can lead to a decrease of 300 mg/l[1] of sulphate in the total waste water.

Reduction of sulphates in the deliming phase

In this phase all the sulphates come from ammonium sulphate that is the most used deliming agent thank to its convenient price and buffer effect. By using it, the pH never goes under the safety limit. Unfortunately, it increases the effluent TKN and the deliming of heavy hides with a lot of thickness and with products free from ammonium salts can be hardly applied, because the operation will take long time.

Sulphates reduction in tanning phase

Improving the consumption of chrome, during the tanning, allows the offer reduction. That leads to a big economic advantage. By reducing the chrome quantity offer, respectively of 1% in dust or 2% of

liquid chrome (at 13%), the quantity of sulphates in the waste water decreases of about 200 mg/l, that represents a decrease of more than 6% of the total quantity of the sulphate in the waste water.

Reduction of sulphates due to coloring and retanning agents

Concerning the coloring and retanning agents used in the after-tanning phase, it is not possible to quantify the sulphates, since the numbers vary a lot depending on the tannery.

IN ORDER TO REDUCE THE TANNING CHROME IN THE WASTE WATER

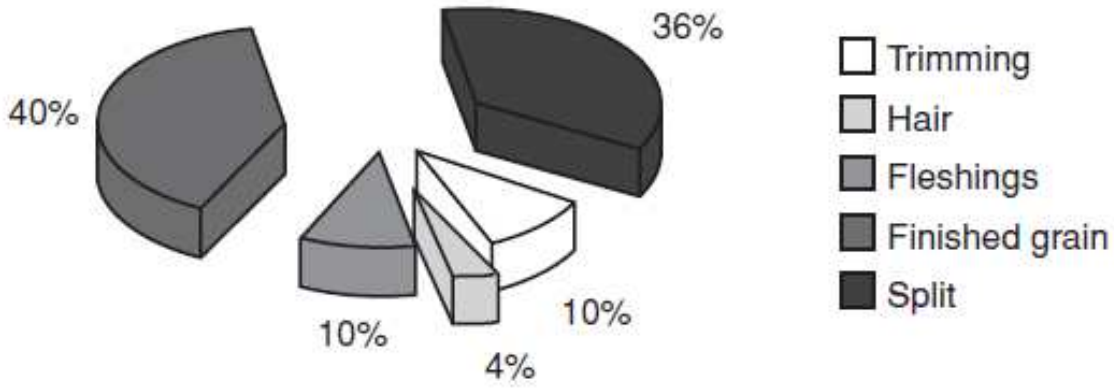
The reduction of chrome in waste water can be mainly done in 2 ways:

- Chrome recovery by precipitation with alkali and redissolution in sulphuric acid. The chrome, properly reintegrated with fresh tanning agent, is used in the subsequent chrome tannings;
- Optimization of chrome fixation on the hide and water removal.

BAT in Beamhouse for reducing chlorides, sulphides and chrome in the tanning waste waters"; INNOTECH 2011 under reprint authorization A.T.O. Valle del Chiampo and A.A.T.O. Bacchiglione

Plain economic factors, as well as ecological factors, make clear that chemical products should not be wasted on the **30-35%** of raw material that will never become finished hide (trimming, hair, fleshings and unused split).

These concepts must be borne in mind and applied in each section of the tannery, especially in the "wet" section where the main problematics are solved regarding good management and the correct set up of the conversion process.



MECHANICAL TECHNOLOGY

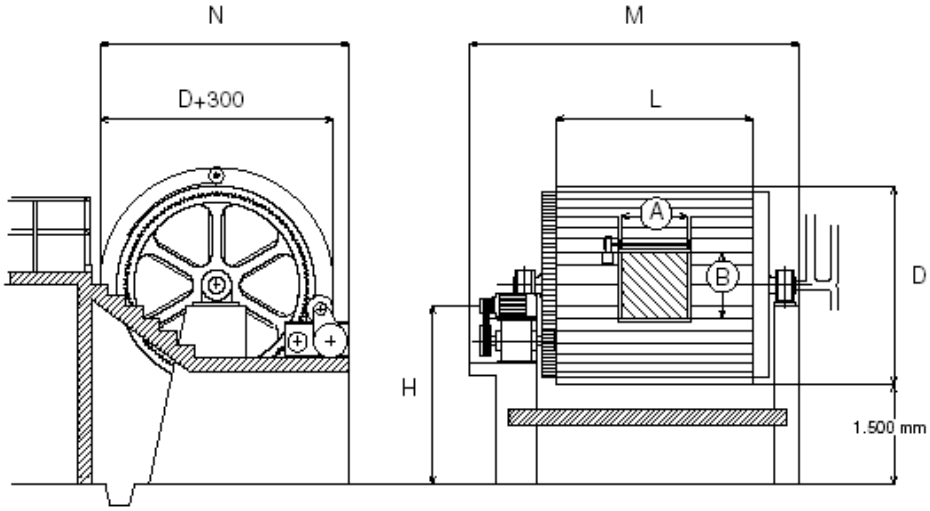
SALT REMOVING MACHINE

The chlorides resulting from rawhide conservation salt can be hardly separated from processing water. Nowadays, an efficient removal of exceeding salt from the hide surface (usually between 3 and 5% in weight) is a fundamental practice for having an environmental-friendly process.

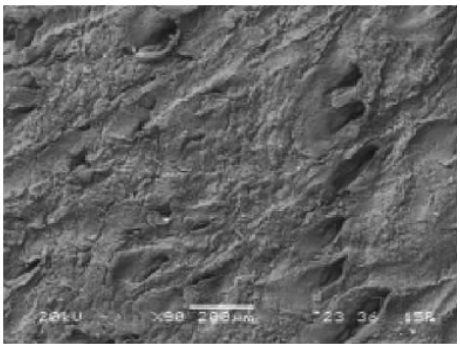
DRUM

It is the tannery symbol-machine, where all the main chemical processes are carried out. Nowadays, it would be more precise to define it CHEMICAL REACTOR. Over the last years the traditional wood drum has been supported by new kinds of drums, produced using different material as Inox, Plypropylene, polyethylene, etc…

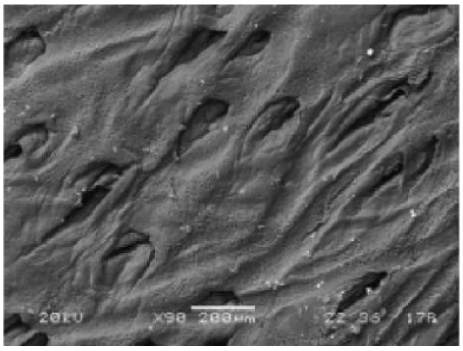
The producers pay particularly attention to obtain very smooth internal working surface (very precise treatment and trimming of the used material) in order to avoid grain abrasions and more and more resistance to chemical corrosion, so that it is possible to guarantee a lower quantity of mechanical maintenance.



Here below some examples of pictures taken by microscope and related to the effects of internal drum surface on the hides:



Treated hide with drum having an internal rough surface or ruined by time

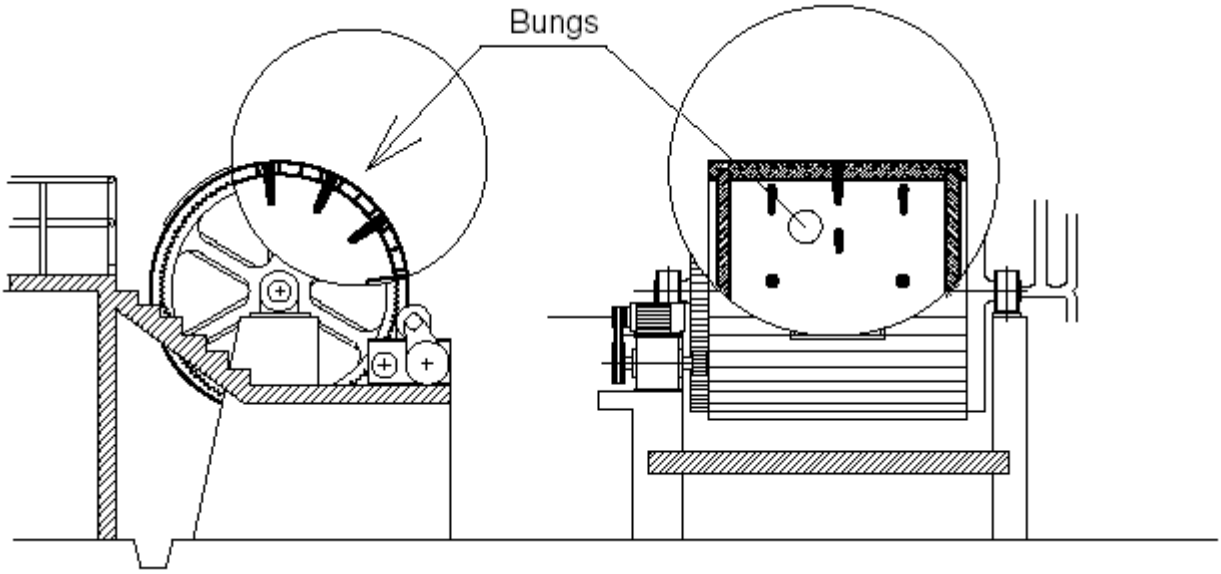


Hide treated with drum having a smooth surface

A further development direction concerned either the geometry of pins and blades or the internal geometry of the reactor that allowed the study and realization of specific configurations that maximize the internal rotation on the basis of the chemical process and the characteristics of treated hides. This leads to low speed rotation and high level of loading.

There are also some drums with internal layouts divided into several sectors or with particular blades that allow complementary productions.

So, big advantages have been achieved in terms of light action on the hide grain.

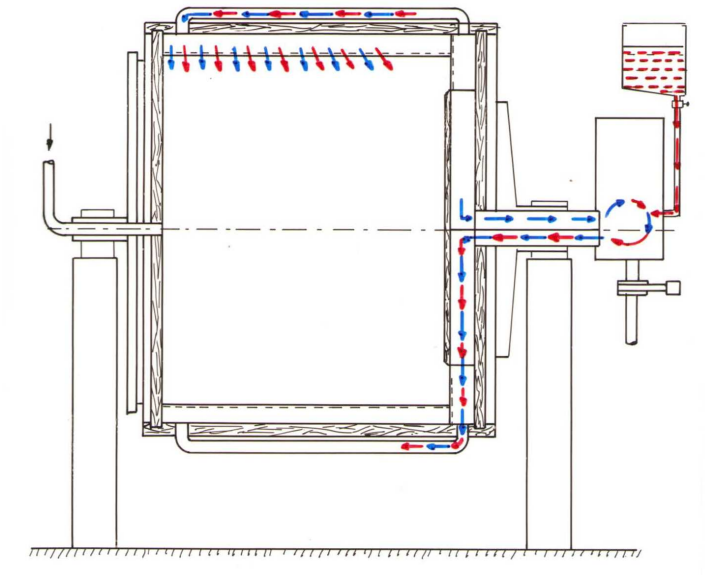


Phase where the drums are used:

Soaking
Liming
Deliming
Maceration
Degreasing
Pickel
Tanning
Retanning
Dyeing
Greasing

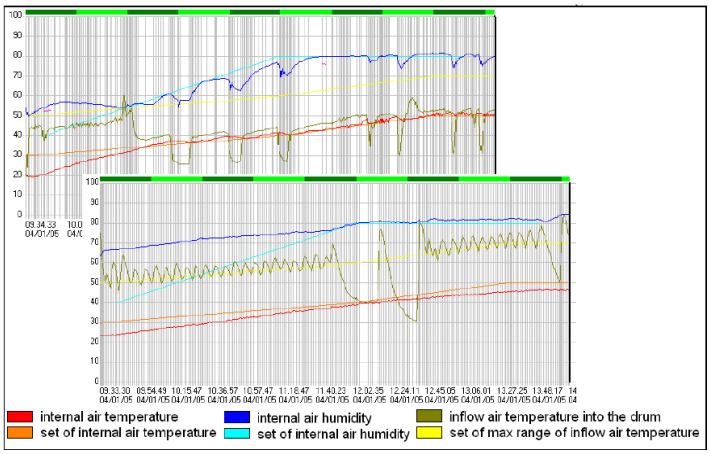
A particular development has been carried out in the bath recirculation plants, in the filtration systems and process parameter controls, including their interface with other auxiliary systems and tannery total automation.

The recirculation system has a high recycle capacity and a homogeneous flow inside the drum.



Example of continuous internal recycle with a homogeneous distribution of chemicals and better process control.

Nowadays, there are systems for constant temperature survey and its increase is controlled from inside the drums, in order to better fix the chemicals.



As for some chemical processes, the modern plants allow:

- Water saving up to 50%
- Reduction of 30% of processing time
- Reduction of 50% of bath drain time
- More homogeneity in the dyeing phase
- Chemicals efficient penetration
- Bigger loading capacity

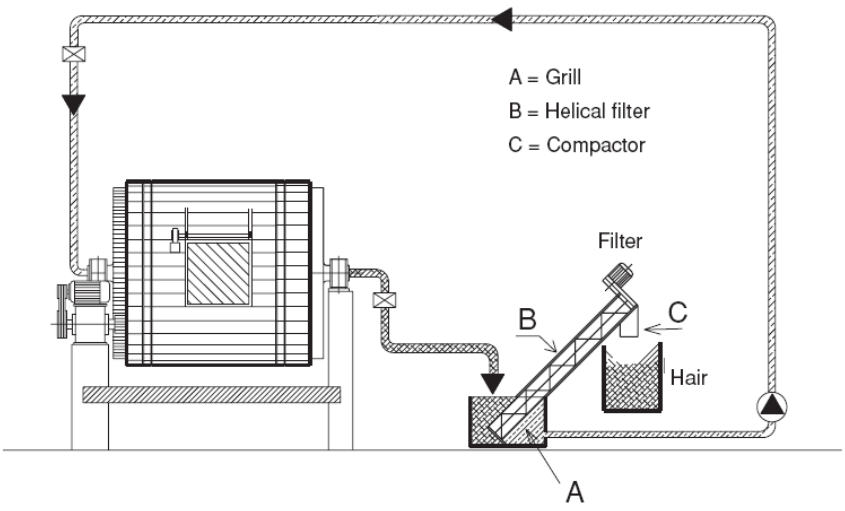
Among the solutions suggested by several producers, there are also some mechanical plant design models with modified structures and washing machines, mixers, reactors with fixed external container and internal rotary basket.

DEHAIRING

Recirculation with hide regeneration.

Over the last years one of the most discussed issues is the hide regeneration system from the deliming bath. Many chemical auxiliary producers worked in order to finalize the products used in the wet phase to remove the hair and avoid its waste, supporting its regeneration. The advantages achieved in the waste water treatment at the end of the tanning process highlight a decrease of more than 15-20% of total tanning waste water.

It means a significant reduction of COD levels in the waste water.



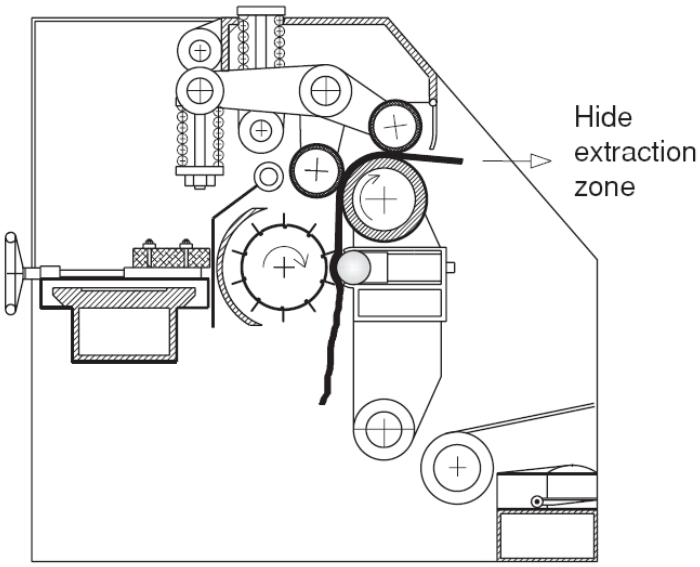
FLESHING MACHINE:

In the fleshing machine some modifications have been carried out and they concern:

- The automatic system for excrements removal from the hair;
- Device able to split bovine hides with hump;
- Sharpening device more functional;
- Continuous machine for high productivity and high level automation.

Environmental aspects:

The fleshing, splitting and shaving operations produce solid residual (crust, shaving dust, dehairing) that have to be disposed as waste or recover as by-products.



RECOVERY of solid fraction

The solid waste comes mainly from the fleshing, splitting, shaving and trimming operations, but a further potential origin is represented by sludge of effluent treatment plants (either the plants of single tanneries or cooperative tannery). Most of these wastes can be considered sub-products and sold as raw materials to other industries.
An example it is constituted from the recovery by extraction. The flesh is submitted to a treatment of alkaline hydrolysis, after that the material is split in 2 phases, one superior thick phase and one inferior protein phase.

The treatment continues with 2 different phases, one related to the fat phase, from which technical fats are obtained and the other related to the protein phase, from which protein hydrolysers are obtained (after sterilization and filtration treatments).

In the filtration phase some panels are obtained from the flesh and they are used as fertilizers in agriculture.

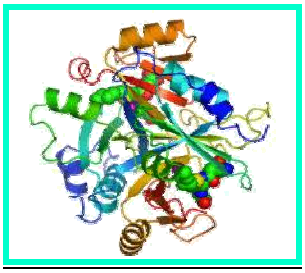
CHEMICAL TECHNOLOGY

The innovations in the wet phase of tanning process are mainly focused on process rationalization.

The rising demands of a productive and sustainable tanning cycle, together with the issue of raw materials exploitation, force to find alternative processes able to replace, totally or partially, some production processes.

For sure, the main expectations concern the contribution and opportunity that the biotechnological process can offer. In some processing phases the products of these modern technologies are already commonly used, in particular:

ENZYMATIC SYSTEMS



The usage of "natural" products like enzymes is spread in the maceration phase in order to improve the fibres opening not completed during the liming phase. So, the protein part, that ties the fibres, is removed by using the selective capacities of enzymes.

The macerating agents include proteolytic enzymes that have a specific action on elastic fibres; these products have a pancreatic origin: both pepsin and trypsin hydrolyzed the elastic fibres allowing their solubility.

The several scientific research activities in the biotechnology field offer some innovations linked to enzymatic families coming from bacteria or fungus. The experience of using these active principles is linked to Italian know-how of tanning process. The systematic integration and increase of the use of these biotechnological systems in the production process would guarantee a radical transformation of processing in terms of environmental sustainability and resource conservation.

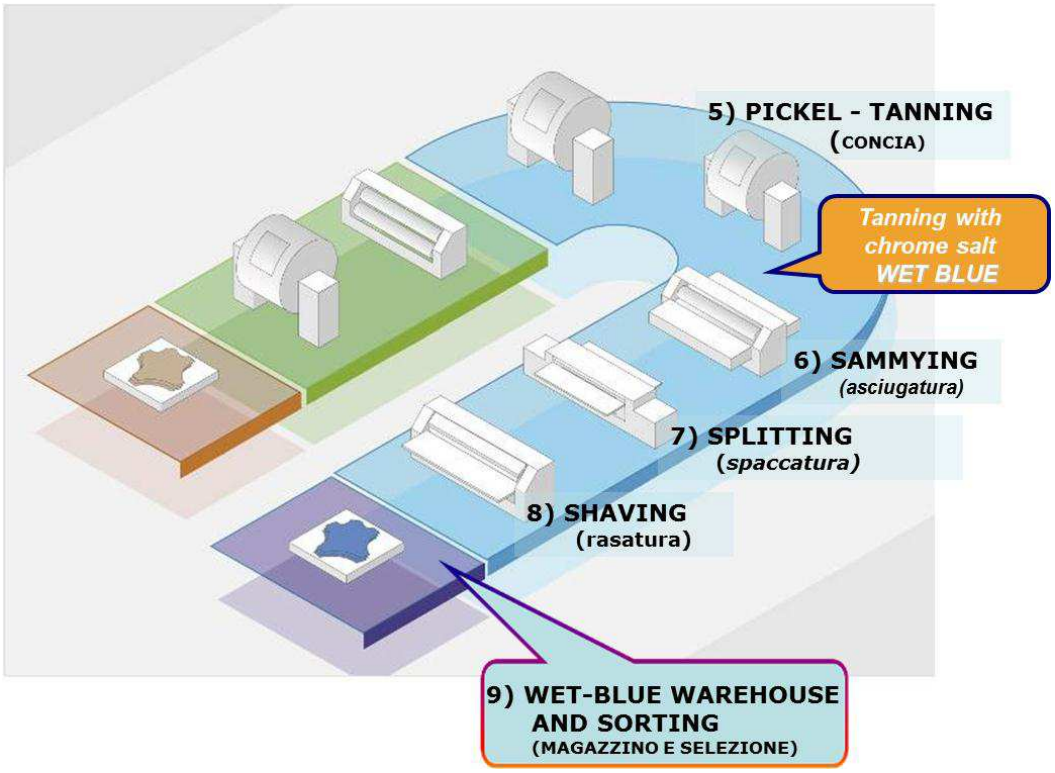
2.2. TECHNOLOGIES FROM PICKLED TO WET-BLUE

TANNING

The tanning phase aims at stabilizing the hide in a not reversible way. Stable and transversal ties are created between the collagen chains, favouring the strengthening of derma from degradation and allowing the hide resisting to humidity, temperature and chemical agents. Several substances can be used as tanning agents: chrome, aluminium, zirconium, tannins, aldehydes and fats, etc…these help the stabilization of fibres and increase their chemical and physical resistance stopping the weight reduction, usually called degradation for putrefaction. The tanning typologies are classified on the basis of the tanning agent used:

- Inorganics: Cr, Al, Fe, Zr, Ti
- Organics: tannins (synthetic or vegetables), oil, aldehydes, chlorosulfonated paraffins. Depending on the nature of chemical ties, the treated hides have different stability to temperature. This feature is known as GT (gelatinisation time or narrowing). The tanning type that has the higher GT is the chrome tanning having a GT bigger than 100°C. Then we have the iron tanning with a GT of about 90°C and the organic tanning between 70 and 80°C GT

Tanning chemicals: the typologies of products used in this crucial phase of hide ennoblement depend on the applied process phases and are strictly linked to the finished product.



Chrome tanning (wet blue) – The tanning with chrome salts can be considered as the most used tanning process. The main characteristics of the finished product are the thin grain, fibrous and closed tissue as well as a characteristic touch. Furthermore, the tanning is faster, more structured and controlled. The tanning is carried out through basic salts of chrome as trivalent salt; the first patents include the use of chrome chloride then replaced by the chrome sulphate.

All the chrome salts are prepared by the chromite, a mineral with formula Cr2O3•FeO largely spread on the earth's crust.

It is a tanning with a sole bath. The first patent of this kind of tanning was obtained in 1910 and it uses a trivalent Cr salt. The processing starts with a pickle bath prepared at pH 2,5-3,0; the trivalent Cr salt is added so that the quantity, expressed in function of Cr203 and calculated on the pelt weight, is between 1,5 and 2%.

Environmental aspects:
Usage of water.
The waste water of chrome tanning contains chrome III, chlorides and sulphates.

Aluminium tanning (wet white) - the aluminium tanning is the most ancient mineral tanning. The first tanning agent used has been the rock alum (mineral with a formula KAl(SO4)2•12H2O) that added to egg yellow as greasing agent and to diatomaceous earth as filling agent it created the so called "glassè" tanning. This treatment produces a white, soft and elastic leather mainly used in producing ram leather gloves.

Zirconium tanning (wet white) - In this tanning a widely spread mineral is used; it is disguised as Zr dioxide (ZrO2) or Zr silicate (ZrSiO2). The patent of this tanning is dated 1931, but its small diffusion is essentially due to the high costs of used salts that, even if the element is quite spread, have a very high processing cost.

Tanning with natural extracts (vegetable) – it is especially applied for producing leather soles, saddles and industrial articles. This kind of tanning is one of the most ancient and spread worldwide, since the reagents' availability, in particular the one of vegetable tanning agents as extracts of chestnut, mimosa and quebracho. The main products used in this process are lime, water and tannin. Different substances were used as tannins, depending on their availability or synthetic tannins were used having a chemical composition similar to the natural ones. They were very long processes, during which the hides were plunged in pits for long time and covered by a bath containing tannin. During this period the hide was processed into leather, and at the end just a greasing was sufficient.

Environmental aspects:
The waste water of vegetable tanning affects the COD, the phenols and the suspended solids.

Oil tanning – it is for sure the most ancient organic tanning agent. It was used to produce chamois leather since the French link with the leather chemists. In order to have some tanning characteristics, oil has to be highly unsaturated. This feature is common in oils of sea animals.

Environmental aspects:
The waste water of vegetable tanning affects the COD, the phenols and the suspended solids.

CHEMICAL TECHNOLOGY

Total bath consumption (Chrome tanning)

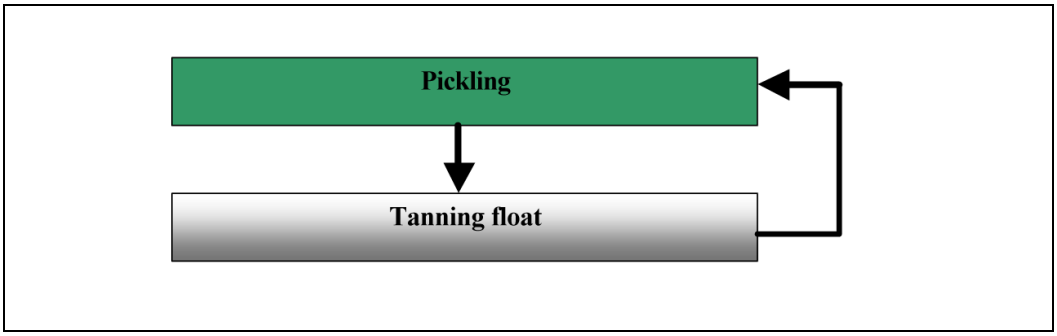
This is one aspect of tanning process strictly linked to tanning layout and processing. The process rationalization, either in batch or in continuous, allows to reutilize the tanning baths up to their total consumption.

The efforts done in the last years, either at a experimental level (pilot scale) or in the process, have brought to results that demonstrate the validity of suggested proposals, both in terms of reduction of chemicals and reduction of costs in the further depuration phase.

The main obstacle is the organization of production flow that requires big investments.

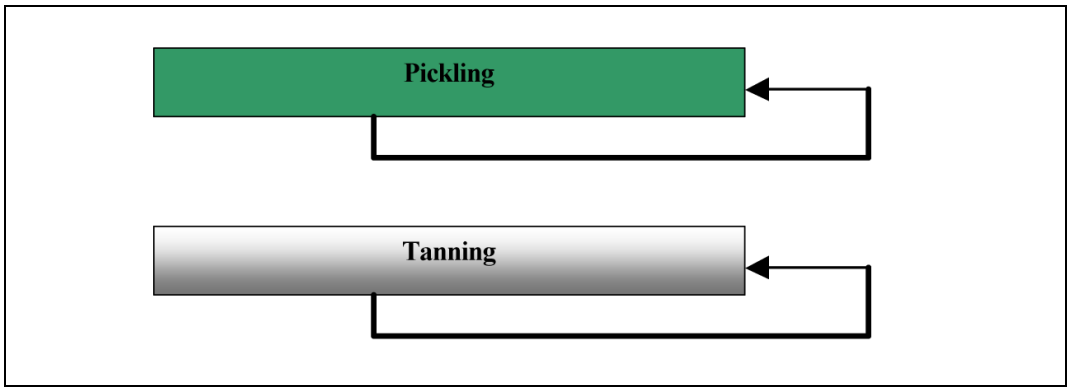
There are different techniques of bath recycling applied at industrial level.

A) Recycle of consumed tanning bath during the pickling phase



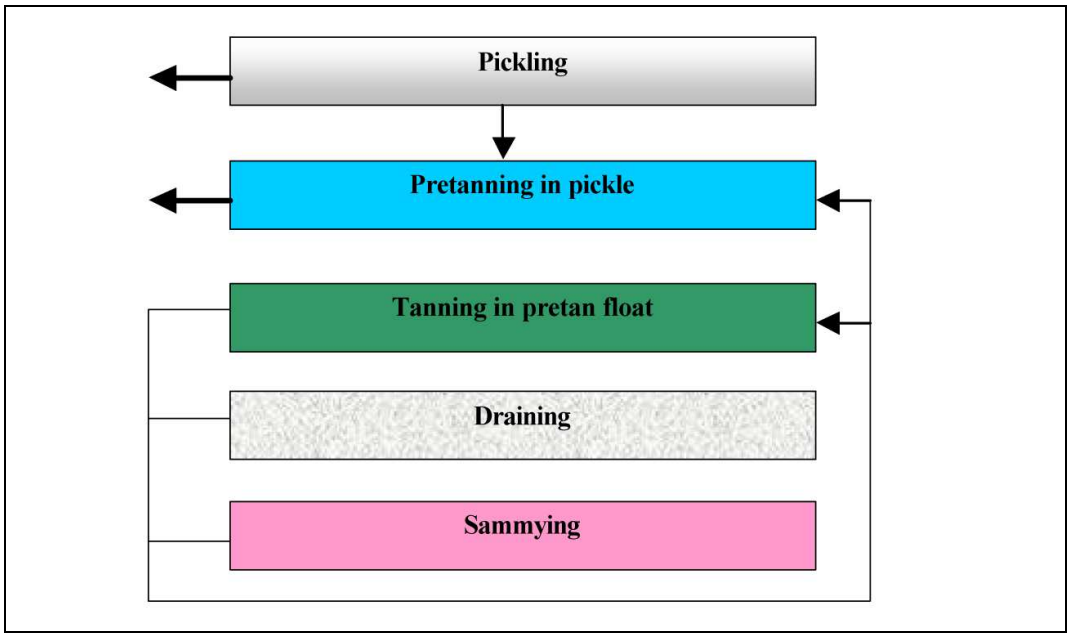
Source: "CHROME MANAGEMENT IN THE TANYARD" report of UNIDO 2000

B) Separated recycle of pickling and tanning baths



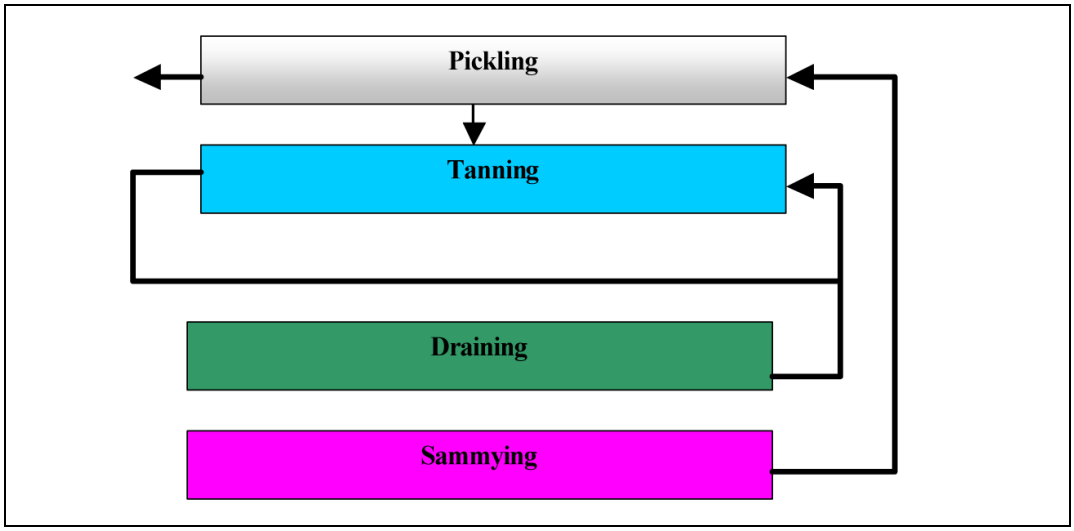
Source: "CHROME MANAGEMENT IN THE TANYARD" report of UNIDO 2000

C) Recycle of tanning baths and recovery waters coming from the first drying operations of wet-blue in the pre-tanning and tanning phase.



Source: "CHROME MANAGEMENT IN THE TANYARD" report of UNIDO 2000

D) Separated recycle of tanning baths and recovery waters coming from the first drying operations of wet-blue in the pickling and tanning phases.



Source: "CHROME MANAGEMENT IN THE TANYARD" report of UNIDO 2000

Total bath consumption (Vegetable tanning)

As for the vegetable tanning technologies with total bath consumption (about 95%) they are commonly available in the "counter-corrent" version (pit-system) and in drum with recycle system.

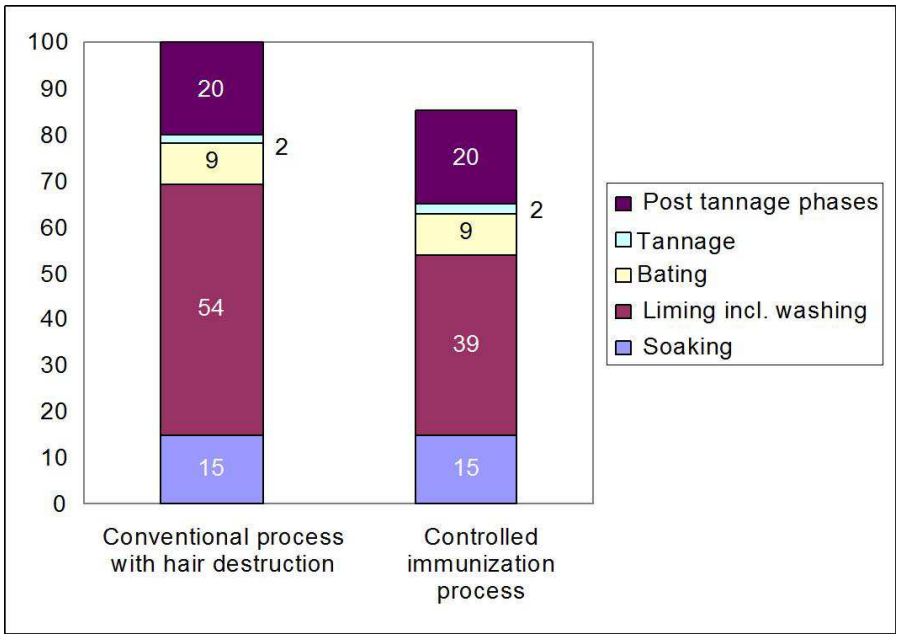
PRESSING, SPLITTING AND SHAVING PROCESSES

During the pressing the hides are compressed through rotary cylinders: in this way the exceeding liquid kept from the hide after the tanning phase is removed. The pressed hides, if they are heavy and thick, are split (they could have been already pelt split) after having left them inside a hermetical container for 24 hours in order to make the humidity uniform on the entire surface. Then it is time for the shaving that makes uniform the hide thickness on the entire surface. That it is possible by removing from the flesh par of the derma and at the end, if necessary, a further trimming is carried out.

The splitting phase can be anticipated in the pelt hide phase. Specific tanning chemicals usually are not used in mechanical processes.

Mechanical equipments:
Fleshing and trimming machines;
Splitting machine to divide the hide in "grain" and "crust", shaving and trimming machines

Environmental aspects:
With the pressing it is possible to obtain low waste water volumes, compared to the ones of tanning washing, with low quantities of Chrome III, chlorides and sulphates.



TECHNOLOGICAL ASPECTS

In this phase it is necessary to define the destination of finished hide. The further phases are strongly influenced by a good preparation of the initial product.

TANYARD OPERATIONS

Deliming and bating	• To make a partial substitution of ammonium salts with CO_2 and/or weak organic acids
Sheepskin degreasing	• To optimise wet degreasing using surfactants, with or without organic solvents • Closed machines with abatement for air and waste water releases when organic solvents are used to degrease skins in dry state
Pickling	• To use partial recycling or re-use of pickle liquors • To use a volume of floats in the range of 50 – 60 % (based on fleshed weight) for ovine skins and bovine hides in order to reduce salt consumption
Tanning (*)	• To increase the efficiency of the chrome tanning process through careful control of pH, float, temperature, time and drum speed, all in combination with chrome recovery through precipitation for waste water streams containing Cr_{total} > 1 g/l • To use high-exhaustion tanning methods where chrome recovery is not possible • To maximise exhaustion of the vegetable tanning liquor with counter-current (pit system) or recycling (drum tanning)

Source: IPPC study of European Commission 2003

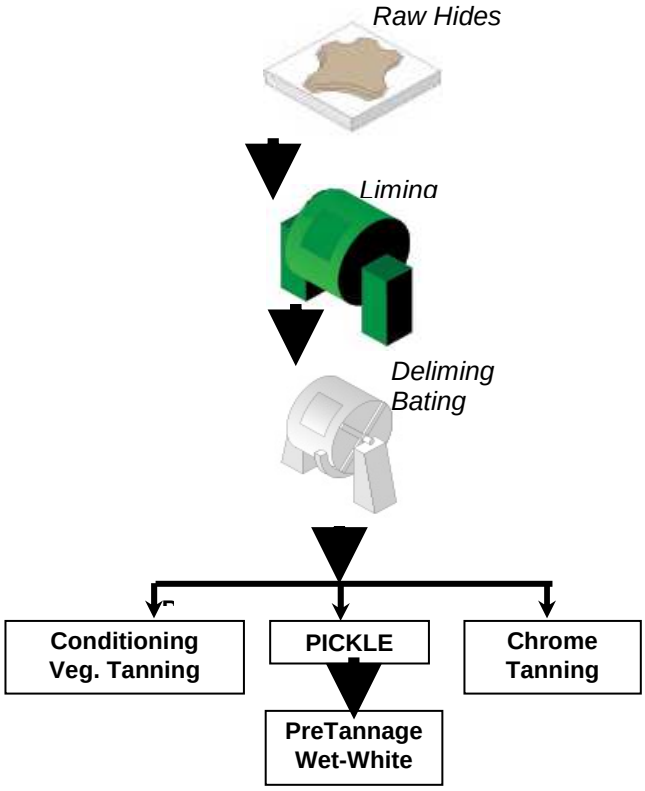
(*) In the phase of chrome tanning some researches showed that the controlled increasing of bath temperature leads to other reductions of residual chrome.

CHEMICAL TECHNOLOGY

Metal-free TANNING

This word identifies the tanning processes that use organic substances alternative to processes based on inorganic products. The word **wet white** means the pre-tanned leather through organic substances free of heavy metals.

In one of the process typologies, after the shaving phase, tanning is carried out with vegetables and synthetic tannins; other chemicals are used, for example synthesis polymers and chemicals of different nature. The final result is a kind of leather called "metal-free" (shrinkage temperature 80°C).



Over the last years the production of metal-free leather raised a big interest mainly due to touch compatibility and low environmental impact.

Even if the chrome tanning is still the main process, either for cost competitiveness or the features of finished products (shrinkage temperature) and its adaptability, the usage of chrome-free and other heavy metals is quickly spreading in some specific sectors, in particular in the automotive one. Within the end of 2015, the European Union means to establish some regulations providing the recycling of 95% of automotives in use.

That leads to some considerations:

- Metal-free leathers are more easy to be treated than the ones containing chrome;
- The possible oxidations from chrome to chrome (VI) are well known;
- Process innovations;

Forward systems of chrome recovery

- Tanning cycle without heavy metals
- Tannins production with limited formaldehyde level

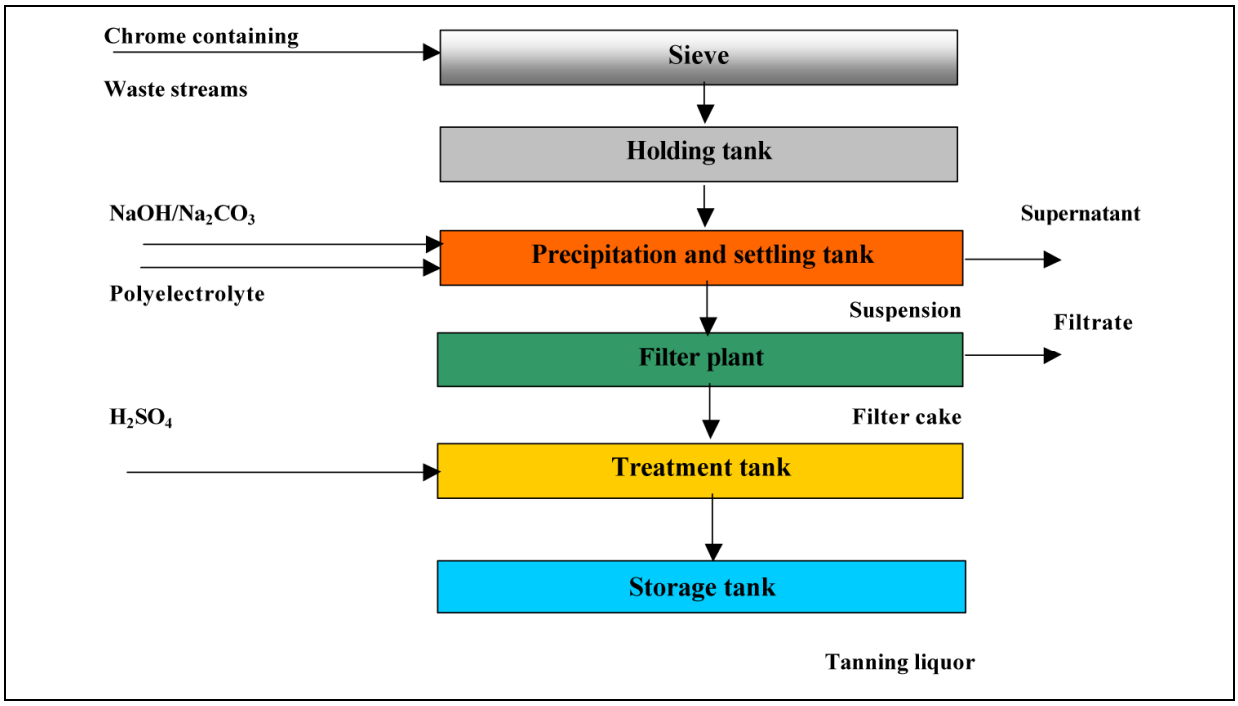
ENVIRONMENTAL IMPACT

CHROME RECOVERY

The chrome recovery from the after-tanning bath through precipitation is an indirect way of chrome recycling and recovery. Through this system the tanner can avoid to increase the baths volume. If the recovered chrome is plenty of impurities, it is not used anymore and it is disposed as waste.

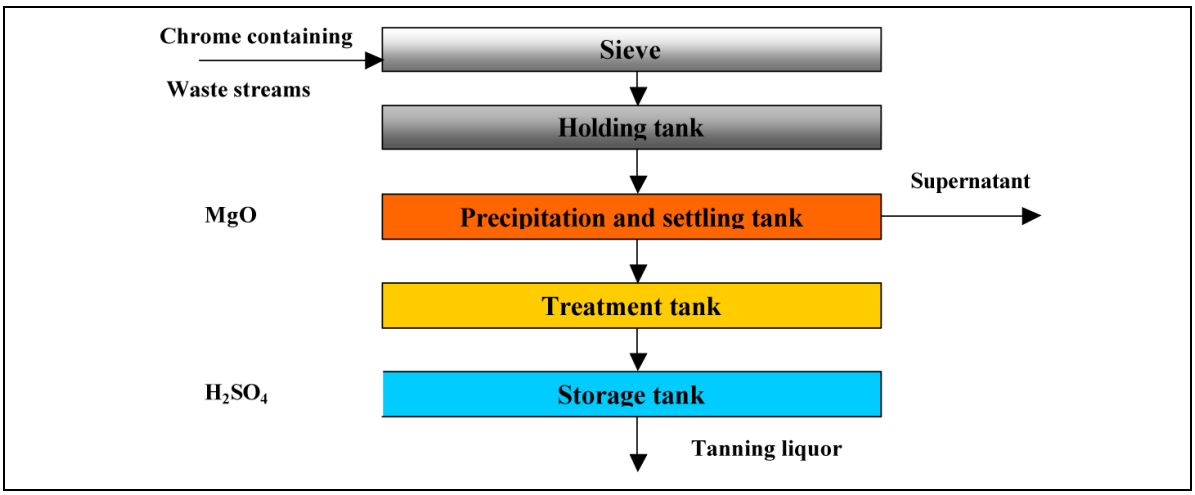
There are mainly two options for the chrome recovery:

1) Quick precipitation with sodium hydroxide or sodium carbonate, better coagulation with polyelectrolyte and then thickening and sludges dehydration by filtration.



Source: "CHROME MANAGEMENT IN THE TANYARD" report of UNIDO 2000

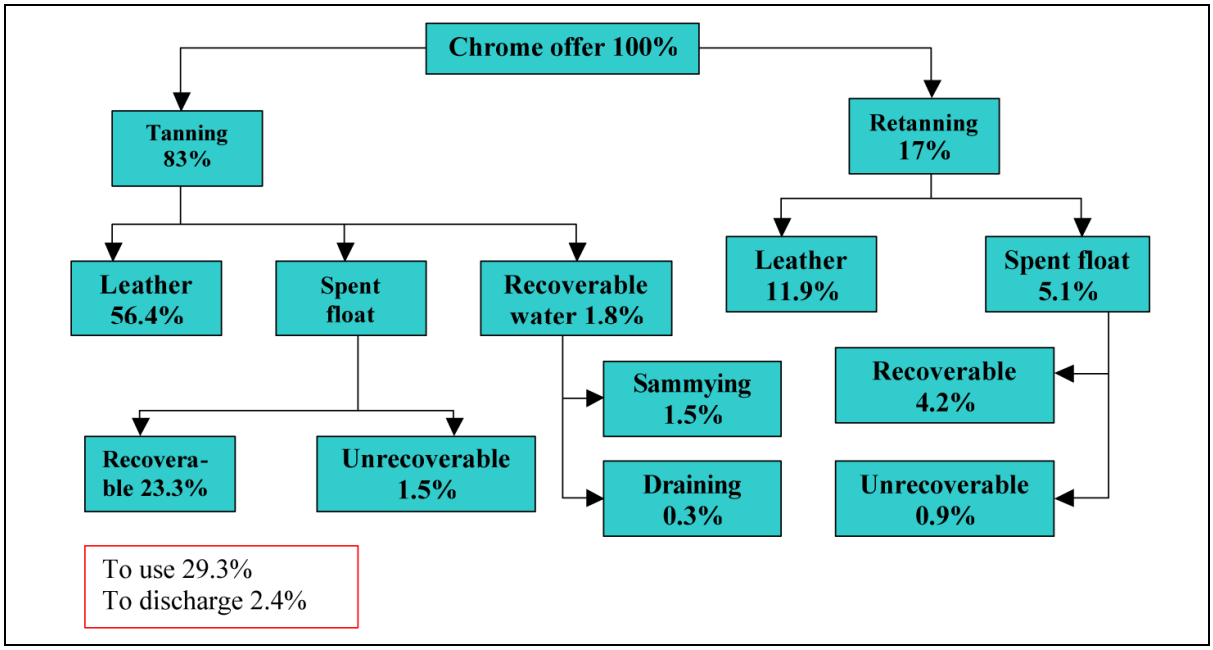
2) Slow precipitation with magnesium oxide, suspension decantation, supernatant separation (without using the press filter) and following the precipitate acidification.



Source: "CHROME MANAGEMENT IN THE TANYARD" report of UNIDO 2000

Chrome Distribution chart in tanning process in case of recovering.

Efficiency of chrome used on the leather: 68% (56,4% in tanning and 11,9% in retanning)

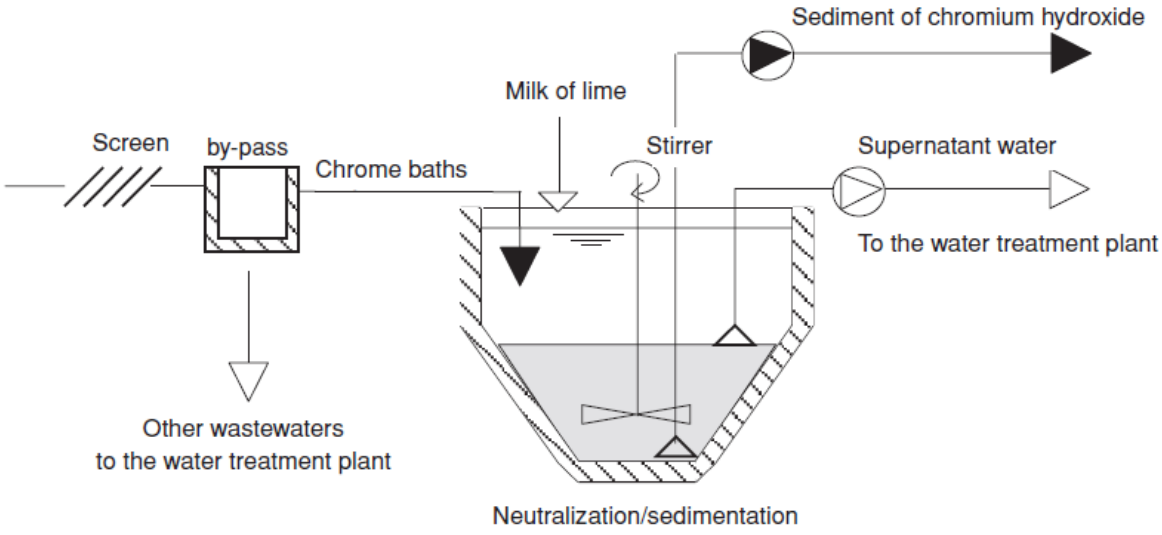


Source: "CHROME MANAGEMENT IN THE TANYARD" report of UNIDO 2000

Without entering into plant design details, we can confirm that the skills obtained so far guarantee the realization of solutions able to reach more than 95% of chrome recovery. The recovered chrome is efficiently used in tanning with noteworthy advantages both in terms of environment, disposal costs and economics; the high costs of cooperative plants for chrome recovery are amortized in a short time (within 2 years).

Here below an example of continuous recovery plant.

PRECIPITATION OF CHROMIUM WITH DISCONTINUOUS PROCESS



Example of data process

Total volume of Cr-effluents (m3/day)	80
Mean Cr III content (1) (g/L as Cr2O3)	3.25
Max. recoverable chrome (kg Cr2O3/year)	65,000
Plant working hours (2)	16 (one shift per day)
Efficiency of recovery %	99 ca.
Residual Cr III in the filtration waters (mg/L as Cr)	5-10

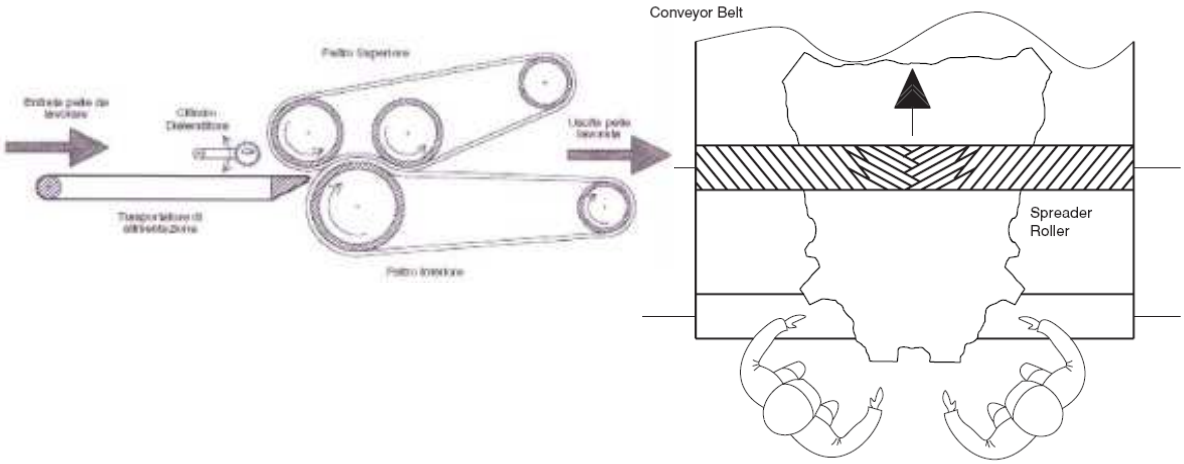
MECHANICAL TECHNOLOGY

WET BLUE PRESS

The drying press of wet blue have been affected by technological developments aiming at improving its pressing power in order to get a more efficient and controlled hide drying.

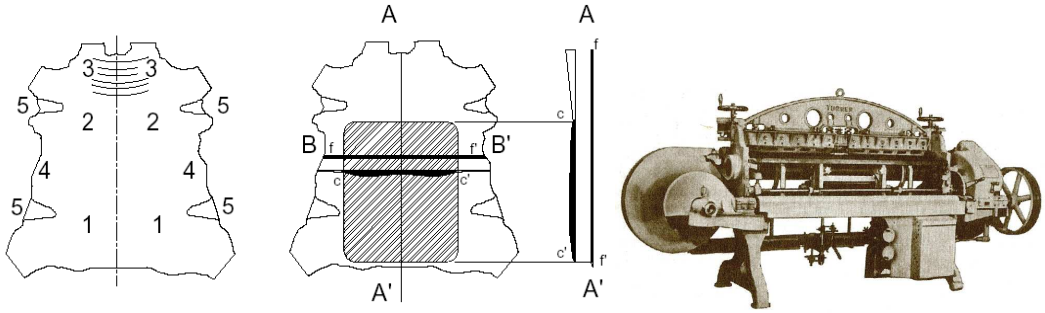
During these years, some solutions have been presented characterized from completely hydraulic systems that use 5-6 cylinders placed in a way that they can guarantee several contact points between the hide and cylinder as well as differentiated pressure.

A further objective achieved by the producers of these machineries concerned the implementation of the execution speed.



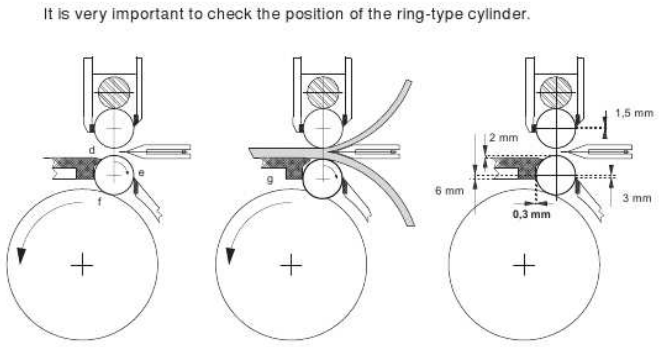
SPLITTING MACHINE

The effort of splitting machines producers concerned the technological evolution in the following directions:

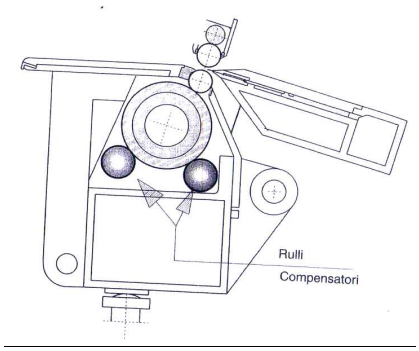


- For the pelt splitting machines, the usage of an electronic device able to catch a variation of the work effort due to different hide thickness and that operates on the inferior crossbar giving it an active movement for a better control of the work thickness;

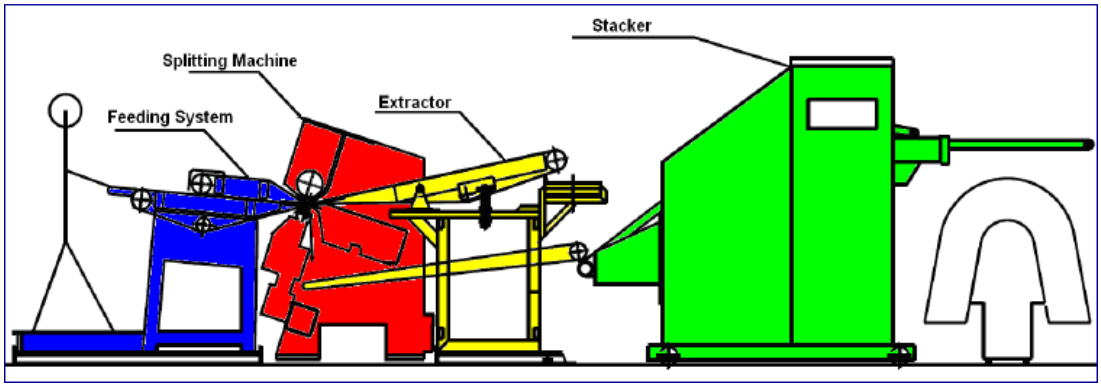
- Extractors for processing leathers lime, blue and dry, provided with pressing rollers with independent motors;



- Solutions to improve the worker safety against the possible risk of cutting. For example devices pulling back quickly the blade or a new concept of splitting machine that works with the grain upside down.



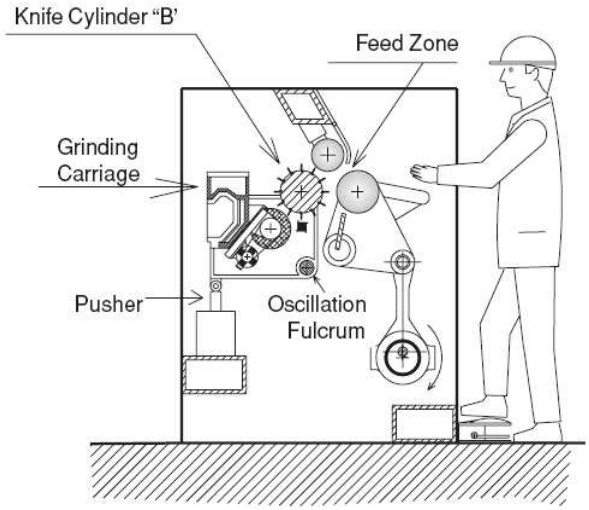
- Automatic introducers for splitting machine that can be used for leathers having specific characteristics.



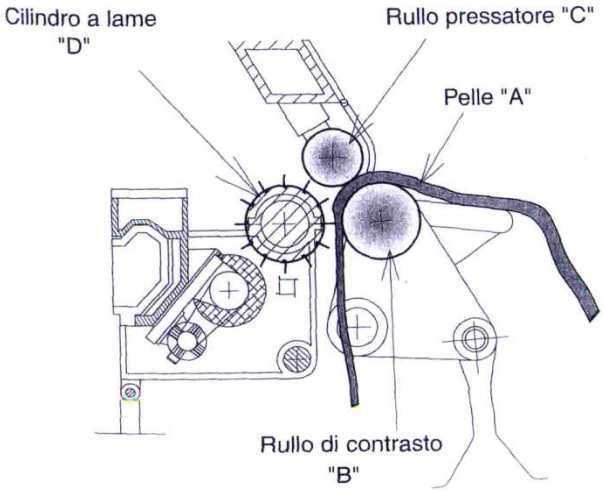
SHAVING MACHINE

The main objective of the recent evolution introduced on shaving machines is to be more precise in making uniform the final thickness of finished hide. In order to do that, the producers made:

- Programmable machines, with the possibility to manage different levels for the leather thickness;
- Automatic device controls of blade consumption able to restore the operating cylinder each 0.03-0.04 millimeter of consumption, using ultrasound feelers able to catch 0.0x millimeter scanning;
- Sharpening devices moving through a geared motor controlled by an inverter and by a significant attrite reduction between the sliding parts of the sharpening truck;
- Control devices of the position between the gummed cylinder and the chromed cylinder in order to guarantee a constant pressure of leather during the entire duration of intervention, achieving a very good result in thickness homogeneity.

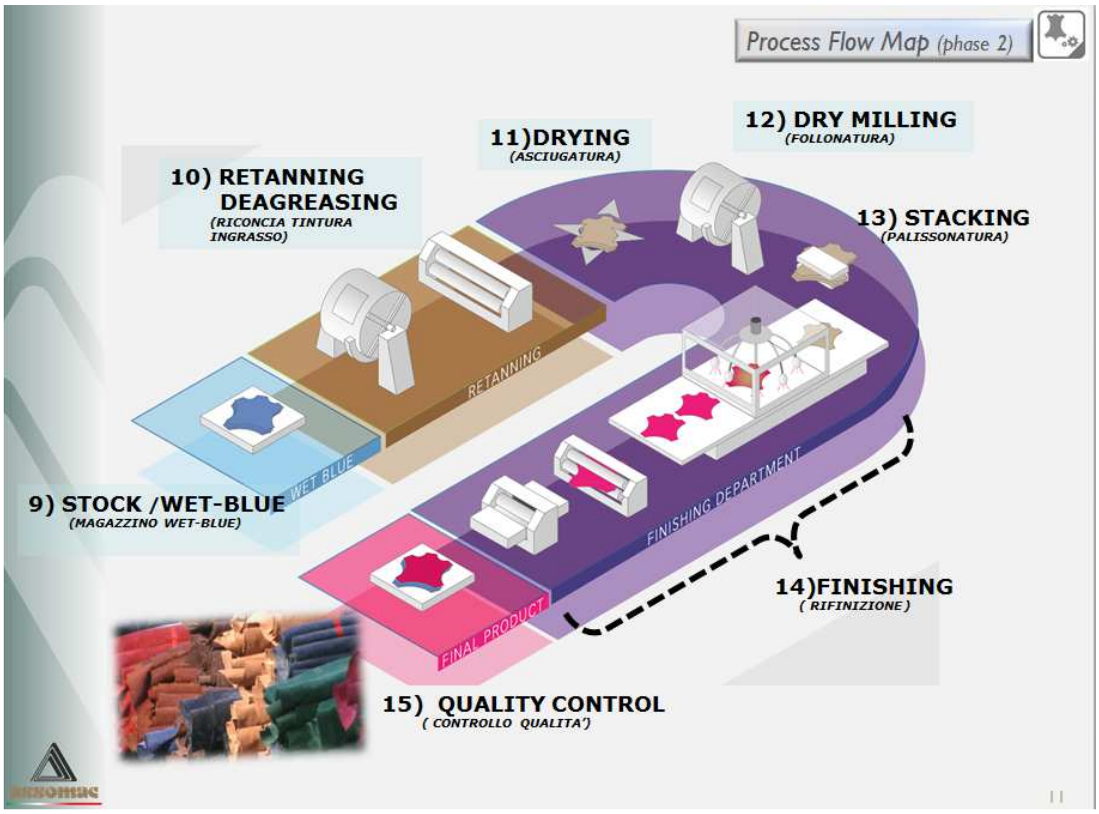


Machine Open



2.3. TECHNOLOGIES FROM WET-BLUE TO CRUST

After the tanning the leather cannot be marketed yet and even if it cannot go bad and it has a good hydrothermal stability, the appearance (color, brightness, grain thinness, etc…) and some mechanical and physical characteristics (flexibility, firmness, softness, etc…) have to be modified. The after-tanning phase includes the neutralization, the dyeing and the greasing, mainly carried out in the same drum by adding water and chemicals.
At this point it is possible to do some specific operations in order to give the leather some properties like waterproofing, gas permeability, resistance to heat and abrasions, etc… so that the leather can have the qualities of the required article. In this phase it is particularly important the worker professionalism integrated and supported by innovative mechanical systems.



RETANNING

The hide soaks other tanning or greasing substances so that the finished product is full, soft, doughy, resistant to heat, etc…

Tanning chemicals: Cr salts, tannins, Al salts, ureic resins, glutaraldehyde.

Mechanical equipments: the retanning is carried out in rotary drums.

Environmental aspects:
Water is used.
The tanning waste water is variable depending on the article; usually they can contain Chrome III, natural and synthetic tannins or synthetic resins.

DYEING

It is the process applying coloring substances on the hide in order to make it nicer and more prestigious. It is possible to have superficial dyeing or section dyeing. The available colorant range is quite wide and includes different chemical compositions: the most used ones are azoic colorant and aniline derivatives. The colorant is weighed and dissolved in hot water (60-70°C) and then added to the bath.

Mechanical equipments: the tanning is carried out in automatic machineries (drums) operating in a closed cycle reducing the contact between the colorant substances, the related losses and the workers.

Environmental aspects:
Water is used.
The dyeing waste water is variable depending on the article; different colorants are used like the ones with a variable vegetable and chemical composition and the ones having different pH. The COD and Nitrogen can be affected by the colorants' nature.

FATLIQUORING

The fatliquoring gives the leather softness and hydrophobicity, improves the mechanical properties and makes the finished hide softer;

- giving pliability to gloves leather;
- preserving sole leathers from oxidation that will lead to a dark color;
- regulating the leather water exchange (decisive characteristic for chrome tanned leathers, whose wettability has to be improved)
- improving the stamping effect on velours and nubuk;
- giving the pool-up effect;
- improving the leather characteristics like tear resistance;

In order to do that, some oils, synthetic oils, mineral oils or fats with animal or vegetable origin are used (sea animal oils).

Tanning chemicals' blends of natural oils sulphited and sulphonator; synthetic oils.

Environmental aspects:
The fatliquoring waste water affects the COD, fat substances and surface-active agents.

DRYING AND NAILING PROCESS

The drying is carried out through several procedures and aims to reduce the humidity contained in the hide up to 15%. Depending on specific needs, after the "hang drying" it is possible to proceed with the following systems:

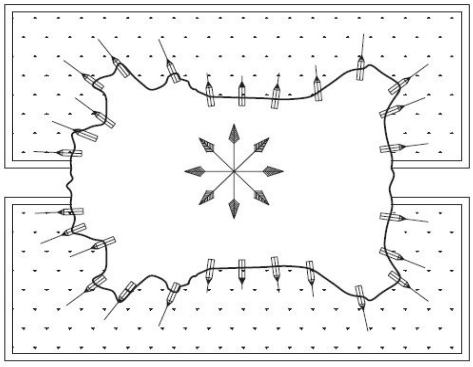
- "pasting"
- "vacuum"
- "high frequency"
- "overhead chain"

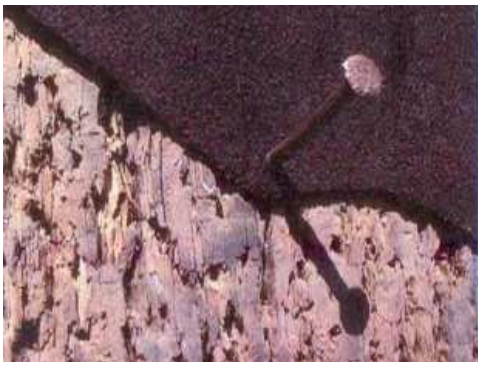
The nailing aims at highly drying the hide and, at the same time, ironing it and stabilizing its size. The leather is stretched on the loom through specific pliers, so that the surface is widened and the fibres are more stretched.

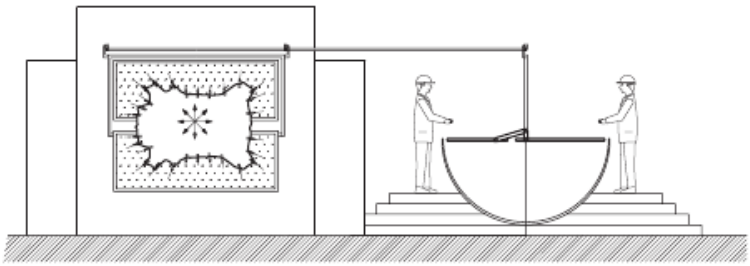
Unlike the drying carried in natural environmental conditions, the usage of specific plants and machineries assures constant, controllable and repeatable productive parameters guaranteeing a product with excellent quality features necessary for the further refining phase. The big management costs are repaid and industrially recognized from all tanneries that care to satisfy markets demands.

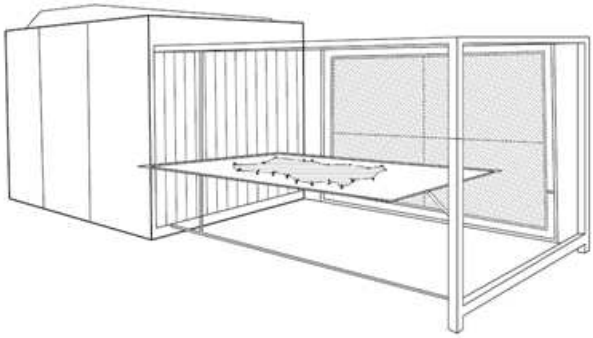
In those mechanical processes, usually, tanning chemicals are not used.

Mechanical equipments: drying systems provided with several engineering techniques (air spring, spring in rooms with forced hot air circulation, thermoplate bonding, vacuum intake, etc…)









TECHNOLOGICAL ASPECTS

Process innovation:

Drying systems efficiency

POST-TANNING OPERATIONS

Retanning, chrome fixation and neutralisation	• To enhance exhaustion of post-tanning treatment agents and fixation of tanning agents in the leather • To reduce the salt content of spent liquors
Dyeing	• To enhance exhaustion of dyestuffs
Fatliquoring	• To enhance exhaustion of fatliquor
Drying	• To optimise mechanical dewatering prior to drying where possible

Source: IPPC study of European Commission 2003

MECHANICAL TECHNOLOGY

SAMMYING AND SETTING OUT

The main machinery and equipment producers improved the continuous process replacing, where possible, the use of alternative machineries working in two loading phases for each hide.

In order to guarantee the drying and widening efficacy, some felt rollers with high pressure have been used, as well as spreading cylinders and electronic adjustment of the main functions.

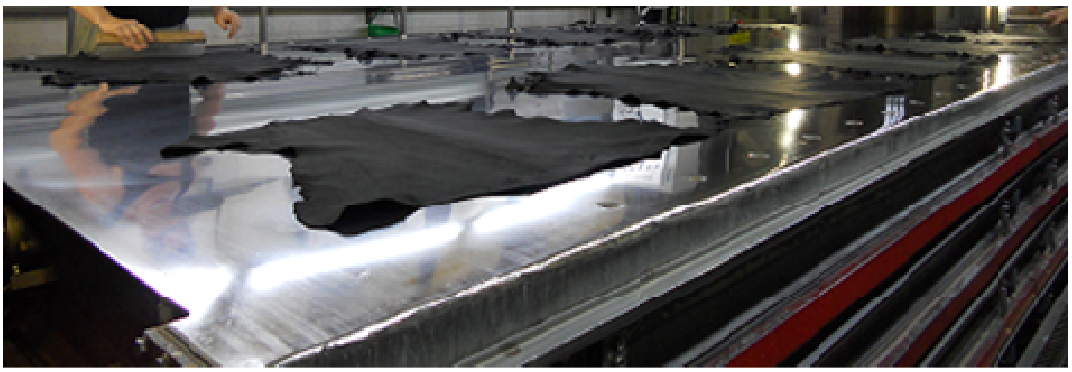
Then there is also some machinery where the hide can be sideways inserted, instead of frontward or backward.

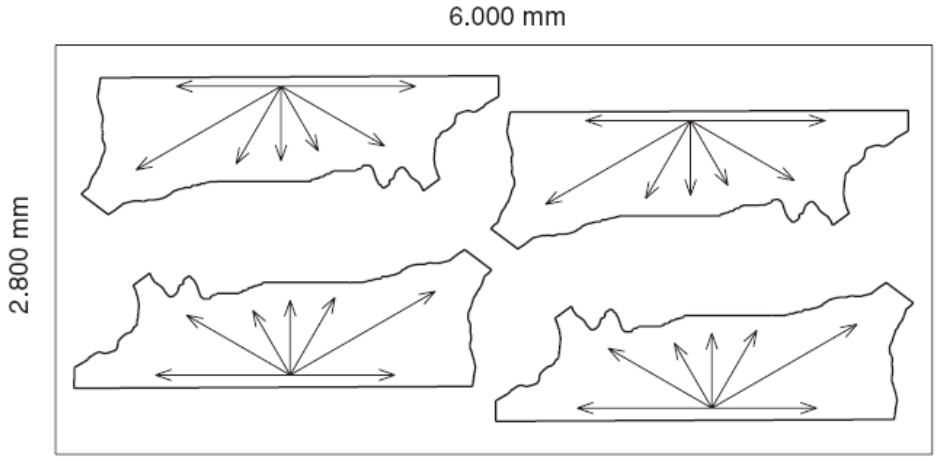
VACUUM DRIER

The development of drying technology through vertical vacuum drove several companies to suggest more and more efficient solutions. Over the last years a lot of innovations and technologies led to excellent results concerning:

- Temperature uniformity on the entire plate surface
- Easy control and modulation of temperature during the processing
- Productivity increase coming from high efficiency of thermic exchange
- Reduction of running times with subsequent energy conservation
- High reduction of energy consumption
- Flexibility of operative temperatures (from 35°C to 90°C)
- Easy cooling system

Some specific automatic production lines have been created from the after-tanning to refining phase; these systems are quiet cheap and fast and have been integrated with vacuum, conditioning and staking plants.





Environmental aspects:
The vacuum dryers need a lot of electricity or combustible, if they use steam of hot water. Generally speaking, the drying systems have to take into consideration the effects coming from atmospheric emissions control through pulling down systems.

CHEMICAL TECHNOLOGY

FATLIQUORS

The fatliquors are mainly based on oil (vegetable or animal origin). The adaptation of this oil needs the modification of some chemical and physical characteristics without deleting its features, so its specific triglyceride structure is kept. The objective to use some secondary raw material, by giving value to oils available on the market, is achieved just using what is not more suitable to the food sector.

The oil processing has been studied in many Italian surveys and a series of plant design innovation has been produced in terms of reduction of effects on the environmental safety.

Oil oxidation: the oxidized oils in the traditional way were made by insufflating air through the oil with high temperature and with a system guaranteeing a contact surface as big as possible. Up to 30 years ago, the air coming from the contact with the oil was released into the atmosphere, mainly through scrubber or combustion. These solutions are characterized from high management costs as well as authorizations difficult to be obtained since their environmental impact. In a market where the oils have a more and more low added value, it has been necessary to find other solutions. Over the last 10 years, for this reason, new technologies have been optimized in order to guarantee high quality oxidative processes, for example through catalyzers or with semi-closed system of air recirculation or adding oxygen to air. These last technologies allowed reducing the quantity of necessary air to make an oxidized oil batch. In this way it is possible to respect the limits provided by the new environmental regulations that control the content of volatile organic compounds (VOCs) contained in the gas effluents.

New fatliquor typologies:

Other innovations developed the usage of synthesis products, like:

A) maleic esters in order to get a soft leather

B) silicone oils in order to increase the impermeability of finished product

C) Fatliquors synthesized starting from petrochemical sub-products (heavy oxo alcohols, heavy esters alcohols).

SYNTHETIC TANNINS

Over the last 10 years, tanning sector requirements meant to have a lower formaldehyde and phenol level both in leathers and tanning products. It has been necessary to modify the recipes in order to better measure the molar relationships. Therefore, some control and measure equipments have been applied in order to comply with the recipes having a low weight error or volume sizing. In particular, several synthetic tannins producers implemented their plant with information control systems provided with DCS. From one side it allowed the automation of the entire chemical synthesis process, obtaining a simple production management, form the other side it required big recipes standardization. This led to a mind changing among the workers that nowadays are not forced anymore to know the product chemistry.

NATURAL POLYMERS

As well the Casein, natural milk protein, is a very important example of usage of secondary raw materials coming from a renewable origin not addressed to human consumption. The Casein is chemically treated in order to create uniform films and it is used in refining or as dispersing agent for pigments.

Casein is used both in pre-coating and thermoplastic coating together with acrylic resins and polyurethanes in order to improve the adherence and reduce the hide adhesion to ironing systems.

2.4. TECHNOLOGIES FROM CRUST TO FINISHED HIDE

Mechanical operations: they aim at improving the leather appearance giving it the required characteristics in terms of colour, brightness, flexibility, firmness, etc…. These operations are carried out during the entire processing activity. The main mechanical operations are:

STAKING, MILLING AND BUFFING PROCESSES

The hide to be treated is enervated by pressing it between two supports with projecting parts and opposing daps, while during the milling some drums are used provided with internal projections. In some cases it is possible to carry out the "buffing" and, after that, it is necessary to proceed with a deep "brushing".

Staking: it is necessary in order to make soft the entire hide's surface. The hides are stretched and stressed with violence, so that the hardened fibres can be stretched again and give the hide a softness characteristic.
The most modern systems are the vibrating ones that operate continuously: the hide is placed on a rolling belt, it is quickly pressed by pistons with an alternate movement and the fibres are stretched.

Milling: the hides rotates inside the drums with or without water or with some sawdust. The staking and the milling work through mechanical stress that increases the hide softness.

Buffing: it makes uniform the leather surface by letting the hide passing on 2 cylinders, one of them provided with an abrasive surface. It is necessary a further dusting phase in order to remove the dust coming from the buffing. The dust is raised using an air blade created by brushing and then it is taken by an inhalation system.

They are mainly mechanical processes where specific tanning auxiliaries are not used.

Mechanical equipments:
Stakers, buffing machines and milling drums.

Environmental aspects:
The buffing produces solid residuals (buffing dust) that have to be removed.

FINISHING PROCESSES

It can be considered the most delicate phase of ennoblement process, since the definitive appearance and manual part is set.

In the finishing phase, several chemical substances are applied on the hide surface. These substances, after drying, produce a firm, elastic and transparent film. The finishing (also called "spraying") is generally made of overlapping layers.

Generally speaking, this phase has an initial degreasing-impregnation process followed by 3 specific phases:

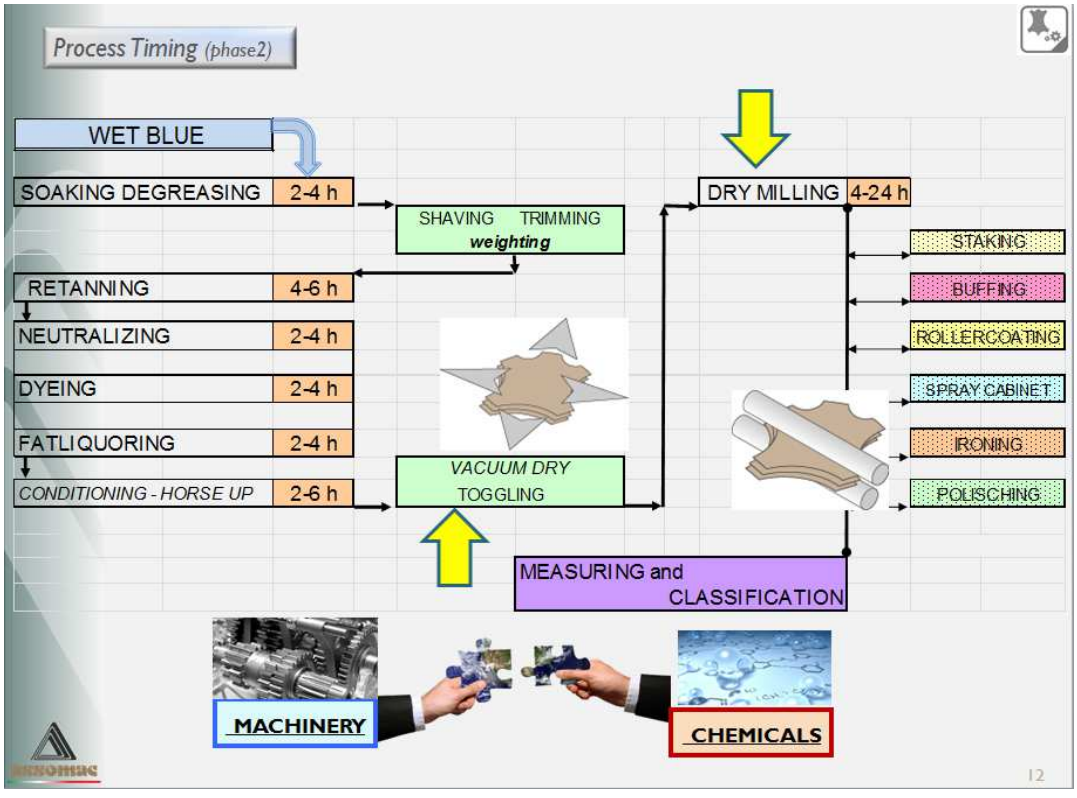
- Binding and Base coat, in order to create an anchorage surface
- Covering, in order to level the surface
- Polishing (size), in order to give brightness and touch

There are also other refining operations like the "polishing" or "glazing jack", the "pressing" and the "stamping". The applied substances are made of organic or inorganic pigments (aniline colorants, titanium, iron, zinc oxides, etc…) binding agents that suspend the pigment (casein, nitrocellulose, synthetic resins) and auxiliary substances (lucids, plastifiers, colorants, thickeners, crosslinkers, solvents and diluents).

In the specific case of nitrocellulose refining, it is necessary the presence of covering plasticizing mixtures (butyl phthalate and castor oil), paints with polyurethane base, solvents and diluents, among them acetates, glycol ethers, alcohols and ketones.

The techniques used for applying the covering mixtures are the spray, buffer and curtain refining. The spray refining is the most spread one and uses an automatic system provided with compressed air guns (pneumatic guns) that "shoot" the paint on the hides placed on roller belts inside specific spray booths.

Tanning chemicals: in this phase several products are applied, whose formulation is made of natural or synthetic origin. Generally speaking, polymeric resins, caseins, waxes, pigments and colorants are applied on the grain in order to give the required colour, cover the defects and give brightness, touch and other characteristics.



CHEMICAL TECHNOLOGY

Specific chemical characteristics are linked to the necessity to obtain "effects" in line with the production of finished hide. Here below an example of formulation division:

LEATHER FINISHING

BASE COAT	
ISOLATION	
SECOND HAND	
TOP COAT	
Wax and/or oil emulsions	carnauba, polyethylene wax emulsion, natural and/or mineral oil/wax emulsion
Matting agents	silica and/or caoline dispersion
Synthetic polymers	acrylic, butadienic, polyurethanic, vinilic
Natural binder	casein
Nitrocellulose water emulsion	
Feeling agent	silicon polymers or waxes (esters, amides…)
Pigment paste dispersions	organic or inorganic pigments, wetting and dispersing agents, thickners, extenders
Refinishing dyes	aniline without inorganic salts residue
Solvents	butylglicol, DPM, PM, MPA
Crosslinkers	Polyisocyanate, polyaziridine, polyurea, imides
Other	

TECHNOLOGICAL ASPECTS

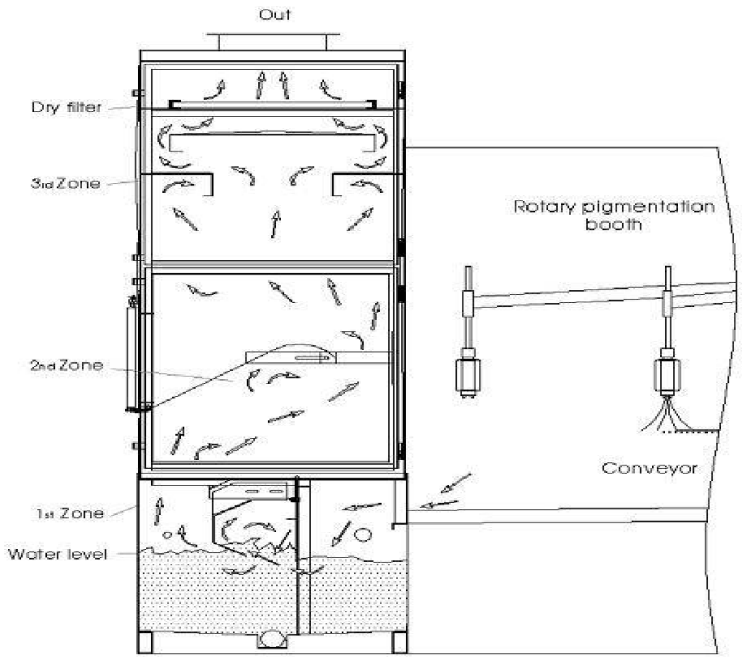
POST-TANNING OPERATIONS

Applying a surface coat	• To use roller coating • To use curtain coating • To use HVLP spray guns • To use airless spray guns Exception for all four above-mentioned techniques: - When very thin finishes are applied, e.g. on aniline and aniline-type leather

ENVIRONMENTAL IMPACT

The environmental impact issue during the refining phase is mainly related to chemical characteristics of used products (pigments, dispersing and binding agents). The main environmental issue concerns the control of volatile organic compounds (VOC). The main innovations concern the replacing of products with organic solvents-basis with products water-basis.

From the plant design point of view, the technological solutions focus on catching the VOC of used products, developing efficient aeration and absorption systems.



Emissions into atmosphere

In tanneries the most spread polluting substances are: hydrogen sulphide (H2S), volatile organic compounds (VOCs), ammonia (NH3) and dust.
H2S is generated by acidification of sulphurs that are largely used in the liming bath. It is spread in tanneries, waste water and depuration plants. The hydrogen sulphide has a very low perceptive threshold (0,0081 ppm), so even low quantities in the atmosphere cause a strong and typical smell that lead to negative effects on human health (more or less if it exceeds 400 ppm). Its presence in tanneries is usually more than 5-10% of the limit provided by law. The pollution is higher during the summer season because of a bigger depuration activity in the waste water. H2S emission is one of the main problems in tanning in terms of "social acceptance".

By the way, the greater impact into the atmosphere is due to VOC. The volatile organic compounds come mainly from refining phase, especially from the spray refining and from the further drying, because of a large use of organic solvents that evaporates quickly (ketones, alcohols, glycols, acetates, toluene, etc…). Even if the perception of pollution due to VOC is lower than the one due to H2S, in the last years more attention has been focused on this issue, especially considering that many of these substances are cancerogenous.

Another typical emission in tanneries is ammonia, a gas with a strong smell and highly irritant. It can be originated in deliming and dyeing.

A particular feature of atmospheric emissions in tanneries is the way they are released: besides the total emissions it is necessary to consider also the diffuse emissions. These are the emissions present in the workplace and in the external environment that cannot be directed and removed. They come mainly from tanks, drums, spray booths, drying tunnels, washing of spraying equipment, stocking

warehouses. Even if there is some pulling down and inhalation plants, it is calculated that diffuse emissions are 40% of total air emissions.

MECHANICAL TECHNOLOGY

Mechanical systems: in the refining process several machineries are used, all of them technologically advanced (for example: spraying machines, stamping machines, polishing machines, etc…)

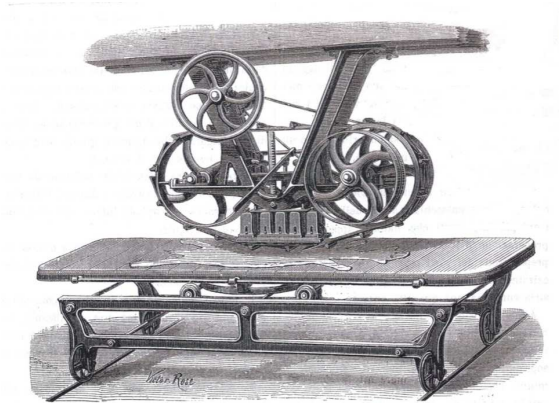
STAKING MACHINE

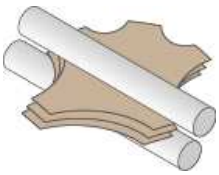
As for the staking machine, producers focused on operative flexibility, adjustment simplicity and production increase thanks to the extension of the operative area.

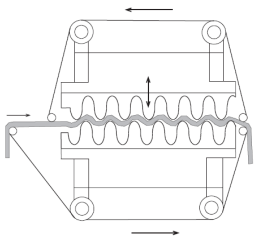
In particular, we highlight the following aspects:

- Programmable adjustment of work thickness by PLC
- Hydraulic shock absorber of staking bench and top head
- Operative area extension
- Supplying of 3 working heads singularly and automatically adjustable.

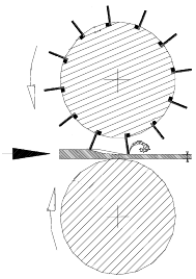
The machines are more and more flexible to specific hide characteristics, both for crust and finished hide and they can obtain very soft hides.







BUFFING MACHINE



Machineries producers focused their efforts mainly on machineries adjustment, process control and buffing efficiency.

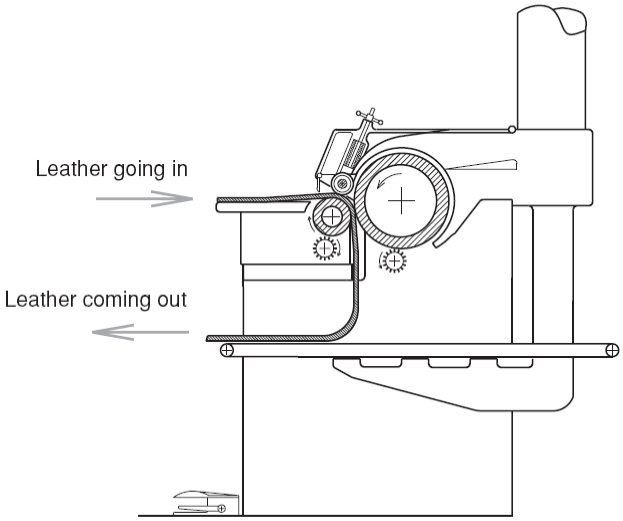
In order to do that, machineries with the following characteristics have been produced:

- Particular inclination, specific for buffing hides with high thickness and/or treated with vegetable tanning
- Automatic devices for controlling the wear and tear of gummed roller, both right and left. The machine is provided with a screen showing the wear level and having other supplementary functions.
- Buffing roller with variable speed
- Water cooling system with closed system for buffing roller
- Special widening carpet provided with inhalation disks and hide stretching device

There is also a version of machine provided with buffing belts instead of buffing cylinder. It operates on non uniform or very thick hides. The investment cost is higher than the one of the traditional machines.

As for the dusting devices, the following characteristics have been developed:

- System with combined action of units with hydrocyclones and dust washing
- Presence of forth buffing and inhalation head in order to improve the grain cleanness
- Depressor system for soft hides
- Permeable carpets allowing the passage of air in order to completely level the going-in hide and a homogeneous removal of dust from the entire surface
- Automatic centring of carpets
- Antistatic and anti-spark crossbars for safety reasons
- Not much noisy air intake system in order to control loud emissions when the hide passes under the head

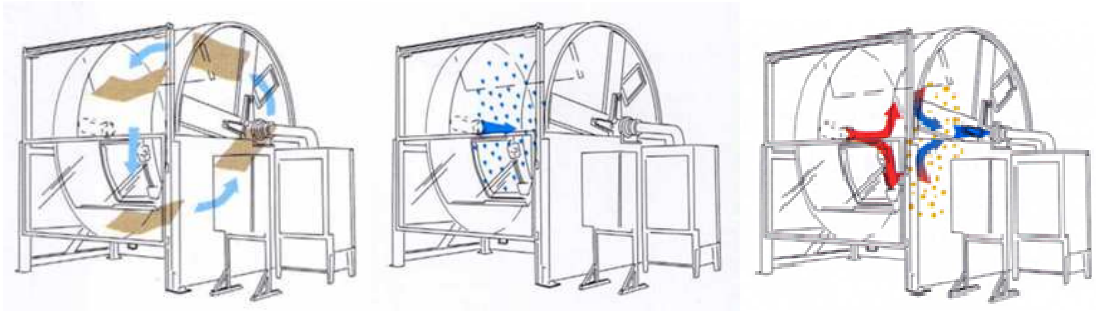


MILLING DRUMS

In the past these machines were characterized by old drums not anymore suitable for operating with water. Nowadays, they are considered "conditioning machines" more and more technologically advanced.

Several equipments have been applied to these machines in order to make them suitable for the following actions:

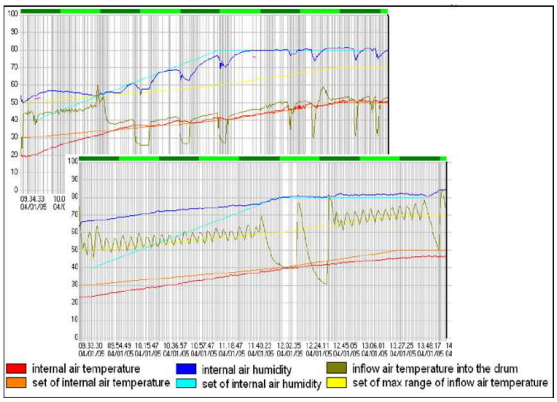
- Dusting
- Milling
- Conditioning (adjustment of humidity level)
- Application of chemicals like: degreasing, softeners, waterproofers, enliveners, fixatives, etc… (Usually applied by spraying).



Among the characteristics developed during the last years, we highlight:

- Management and control of humidity, temperature, clockwise and anticlockwise rotation times, breaks
- Software and registered data storage

- Dust extraction system
- Hide loading and unloading system integrated in the drum control system
- System of chemical injection allowing an uniform hide absorption



Besides the wood version, there are also the stainless steel and polypropylene versions, widely spread thanks to the advantages brought to process control.

ROLLER COATING MACHINE

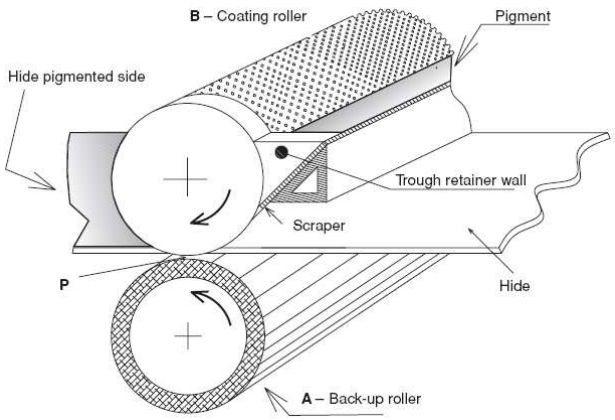
Over the last years, the technological innovations brought by mechanical and tanning producers to roller coating machines aimed at solving the main problems of this refining technology concerning all hide typologies, even the most soft and thin ones.

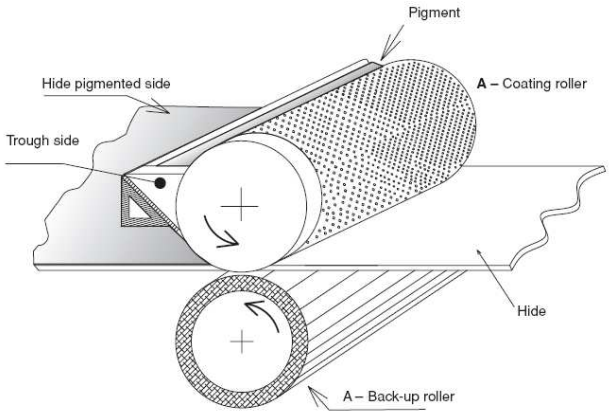
Nowadays, it is possible to refine in reverse even entire hides, thin and soft, for furnishing and automotive sector.

The main technological innovations distinguish for the following aspects:

- in reverse introducer for soft hides, allowing the continuous processing with more in line machines without the worker
- new design of hide transportation that can be automatically changed on the basis of hide typology
- automatic predisposition from synchro to reverse and vice versa without modifying the position of the coming out carpet
- mechanism of moving squeegees towards the cylinder assuring an uniform and continuous movement
- incised cylinders able to rotate quickly and guaranteeing a uniform spreading of chemicals on the hides

Particular attention has been given also to modern devices for safety of mechanicals, rubber feeder, incised cylinder and in-going blade during sudden blocks due to a wrong hide supply.





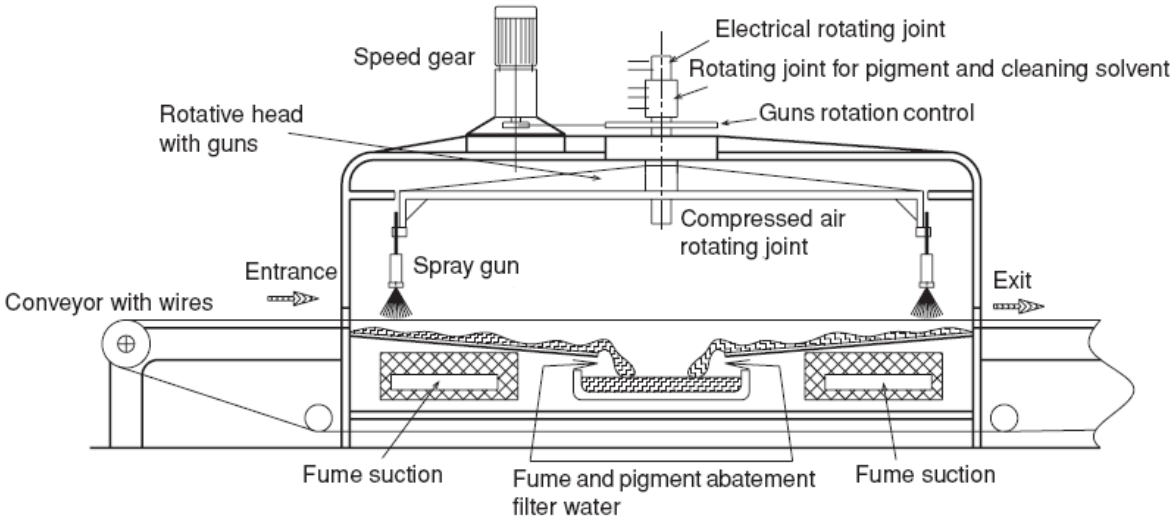
SPRAYING BOOTH

The main innovations characterizing spraying booths concern the control of chemicals losses.

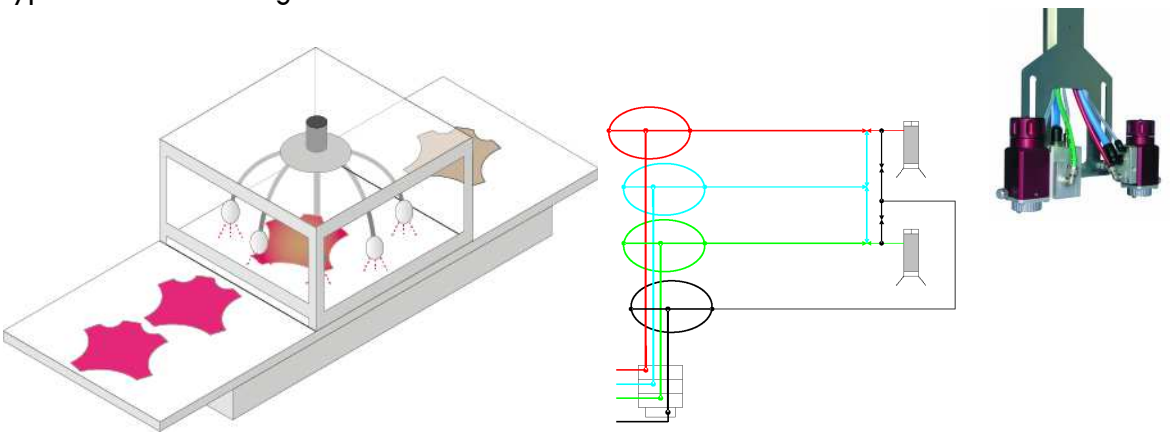
Developed and/or improved technologies:

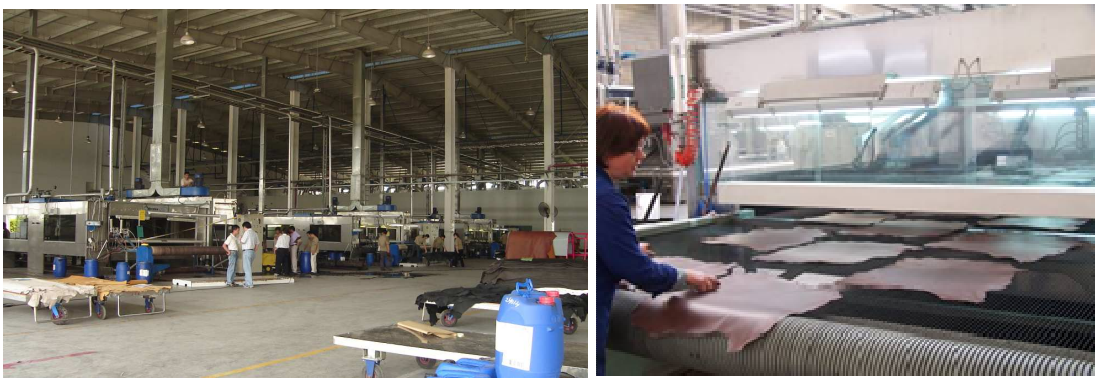
- painting booth provided with different guns having different characteristics in order to satisfy any kind of painting with low consumption and environmental respect
- guns working at low pressure in order to reduce the over-spray saving some chemicals
- paint economizer controlling management costs of painting operation

Also from an environmental point of view, some efficient systems for catching and pulling down the atmospheric polluting agents have been developed.



In the last years there are more air-less guns that use a high pressure spray as well as volumetric guns HVLP (*High Volume - Low Pressure*). They partially solve the overspray and losses problem, typical of traditional guns.





TUNNEL

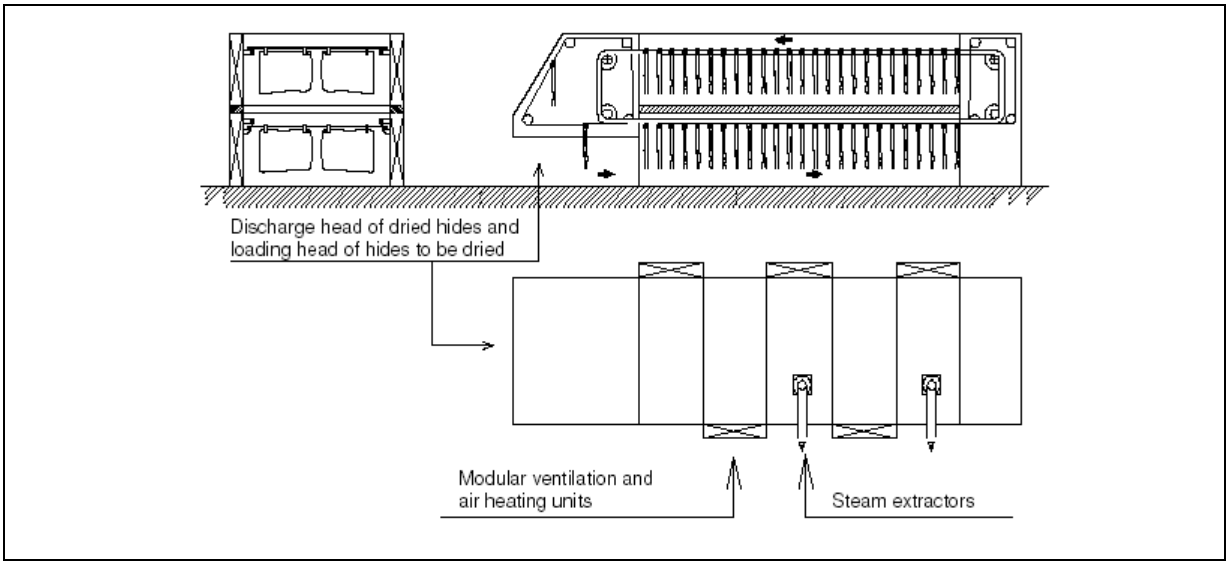
Drying tunnel producers have continuously looked for solutions and technologies able to control the processing plant costs, the overall dimensions and treatment timing.

There are electrical irradiation heating systems and systems using methane gas burner as well as steam systems.

Concerning the electrical irradiation solution, we can underline the following aspects:

- lack of air input with further removal of dust and light hides stability on the conveyor
- constant and uniform temperature with reduction of equipment overall dimensions
- electrical device placed on machine border provided free from steam sources or other thermic fluid
- heat recovering system provided with exchanger of hot smokes coming from drying tunnel by previously heating the air that will be put into the tunnel

An example of drying vertical tunnel:



Other significant technological innovations concerned the plant designs, assuring the control and adjustment of operative parameters sector by sector.

There are also drying tunnels provided with chain conveyors in order to make different interventions on more hides in order to get the required humidity and temperature levels.

Then, using updated sensors applied in the tunnel allowed to optimize the process by quantity and quality through an efficient system for monitoring humidity and temperature parameters.

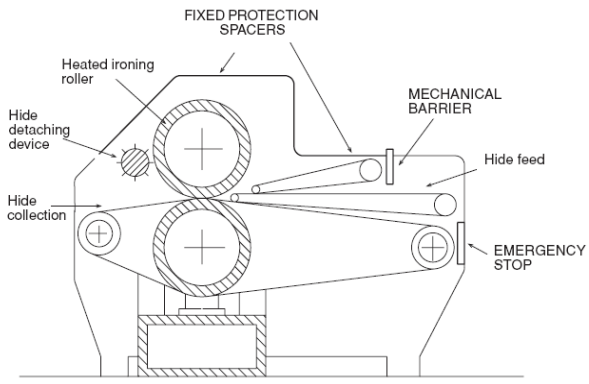
PRESS

The ironing rotary presses used into the refining department are more and more utilized from tanneries that want to offer to their customers' products differentiated by:

- usage of several cylinders having an easy and fast selection
- electronic management able to use rollers with different diameters and to adjust the working speed
- possibility to increase or decrease the hide contact surface with the roller through particular positions of ironing roller, for example forward inclined compared to the counterpressure roller
- hide pre-heating through the contact of roller with further softening of refining products, improving and reducing the contact time of hide
- stretching carpet in order to make easier the hide input

Concerning the platen presses, the producers focused on improving the respect of safety measures in order to protect workers' health. Other characteristics are:

- higher closing and processing power
- electronic management and auto-analysis program
- steam/smoke inhalation device during the processing of wet hides
- easy and fast work together with worker's comfort



SELECTION, MEASURING AND PACKING

These are the final phases of leather production cycle that guarantee product quality.

The "selection" is a delicate phase still assigned to human experience.

The "measuring" is carried out through precise automatic systems.

At this point the hide is ready to be sent and become, in its turn, a starting point for countless "natural" products.

MEASURING MACHINE

The technological solution provided by measuring machines producers allowed using them not only for finished hide but also in controlling and identifying semi-finished products in the different phases of production process.

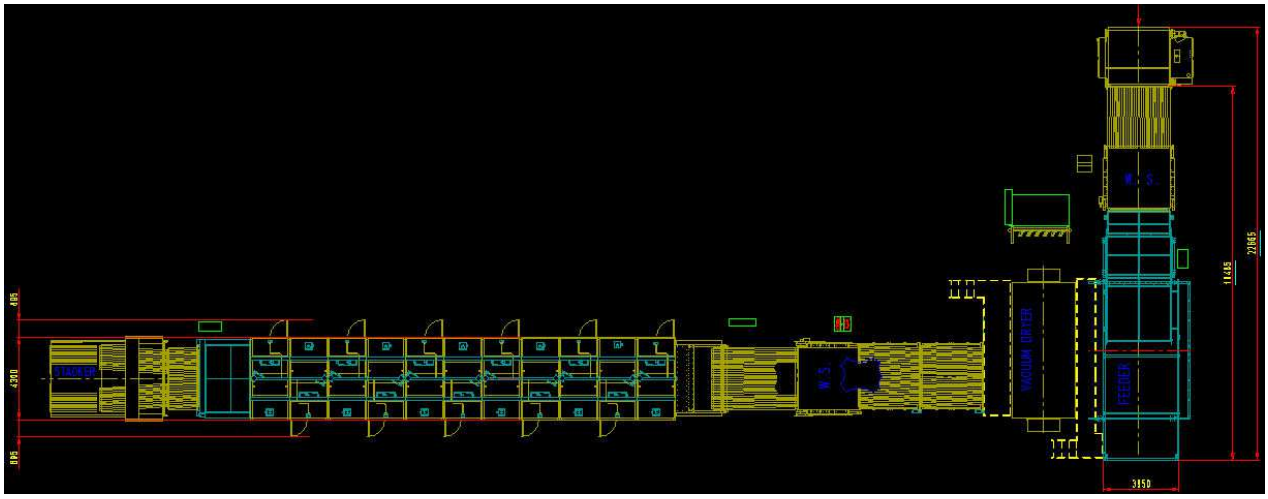
In particular the following devices have been developed:

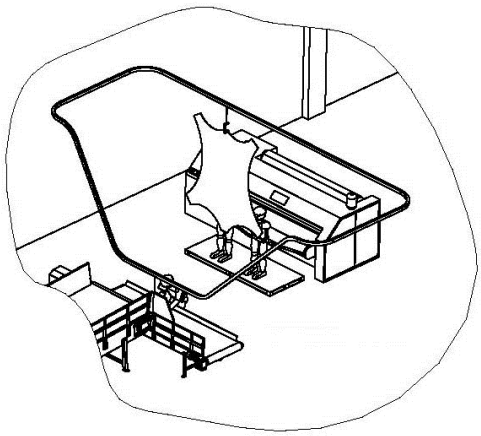
- Electronic measuring roller machines provided with a system able to survey the hide thickness. Thanks to the instant thickness survey, this machine can be used to control the quality of finished hides or for the crust pre-selection
- Measuring wheel systems placed directly on the input carpet or inside the machine, allowing an excellent measuring of soft hides during the pressing phase
- Measuring roller machines provided with motorized carpet that introduces the hides under the measuring rollers so that every kind of hide, including the soft ones, can be properly stretched on the input carpet
- High precision table measuring machines for reptile hide (snakes, crocodiles, …)
- Automatic systems stamping on the flesh the producer logo or a specific code, with the possibility to be installed on electronic measuring machines or stackers and cluster preparers.

2.5. AUTOMATION AND PROCESS MANAGEMENT

Over the last years the development of automation, control and process management systems are been improved because of greater demand and attention from tanneries.

Italian machineries producers focused on understanding customers' requirements and finding the most efficient solution among the ones suggested by hardware/software automation, motion control and process management sectors.





The quality of finished hide is strongly affected by natural characteristics of raw material as well as processing environment, temperature, humidity, times, etc… That has always been the main obstacle for spreading management processes that can be easily used from all tanneries. Every time that positive results have been achieved in automation and process management sector, it happened thanks to a tight cooperation between leather producers, technology suppliers and automation and control expert.

Here below we present the most significant technologies, divided into 3 areas:

1. Wet phase, drums and their automation
2. Semi-finished hide handling
3. Process control systems

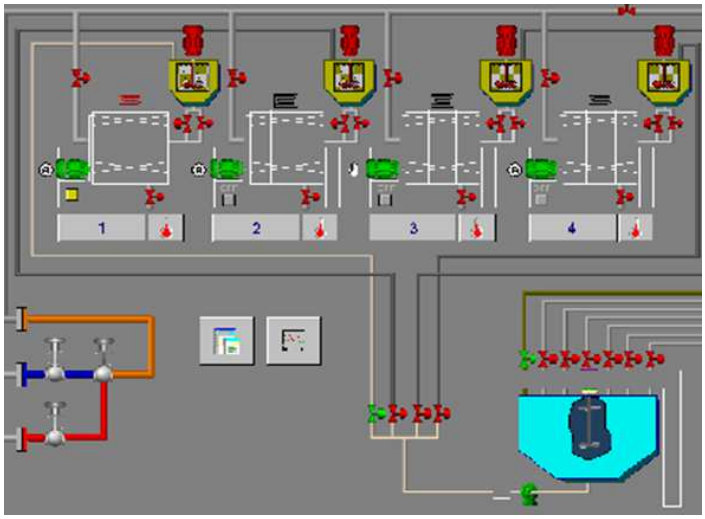
WET PHASE, DRUMS AND THEIR AUTOMATION

Drum automation plant where it is possible to see in real time the status of each drum and its systems.

New system for mixing and dosing water and products inside the drums.

It is totally characterized by:

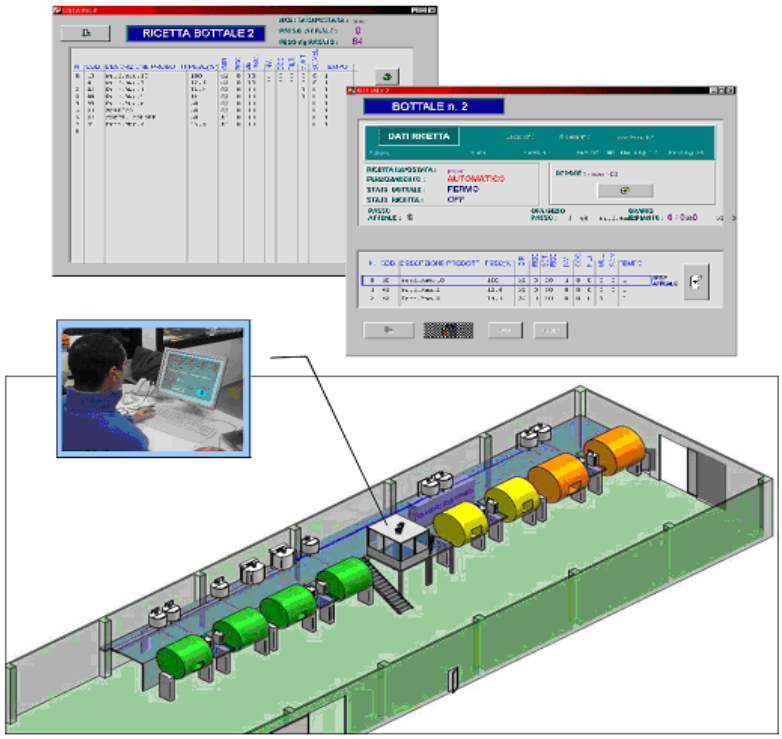
1. Drums automation system of "Plc drums" iterations, of all alarms during processing phase and of water and chemicals dosing plant.
2. Detailed supervision of entire plant
3. Processing recipes editor with archive function
4. Product warehouse with automatic unloading
5. Costs allocation by orders or data archive
6. Historical archive of all drums operations and working reports
7. Liquid chemicals dosage and weighing of solid chemicals
8. Temperature control and adjustment



Computer-based plant for stocking, dosing and mixing colorants and auxiliaries in order to produce refining baths.

Main characteristics:

1. precise computer-based dosage of each component (0,1g)
2. possibility to carry out the automatic homogenization of components previously dosed through a specific mixer placed inside the dosage distributor
3. possibility to prepare from 1 to maximum 150kg batches
4. automatic labels sticking showing the dosed weight on each batch
5. automatic moving of containers
6. management and control of entire process through PC



SEMI-FINISHED HIDE HANDLING

Universal stacker having the following characteristics:

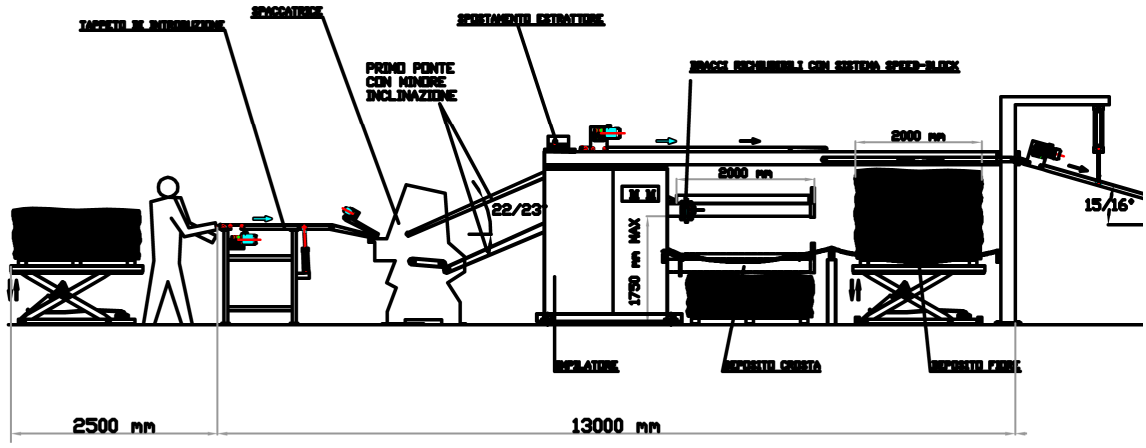
- Longitudinal stacking
- Transversal stocking of hides on tower, table and pallet, both for jugs and entire hides
- Precision and working speed
- Compactness
- Electronic control system with simple user interface
- Absence of noise
- Intrinsic safety system
- Low maintenance

Double bundle preparer for whole hides and sides. The system, after stacking the required number of hides, is able to double bend them.

This equipment is used after the measuring machine or the ironing press. The further operation is the cluster closing and it can be carried out by a sole worker more quickly than a machine does.

The universal compact stacking machine is provided with:

- New "TOUCH SCREEN" panel
- Possibility to close the track of sliding trolley saving some space when it is not used
- Transmission system with low noise emission



Automatic de-stacking for hide handling and transporting:

- Intake of hides from pallets moving them towards the refining lines
- Backward integration of hide moving on air chain supplied with automatic loading and unloading

Patented and continuous re-bending machines:

- New module for bending big size hides to be stacked in pallets;
- Uniform and constant bending of side layers on central part of hide;

- Non-stop working cycle allowing to save time and human resources as well as guaranteeing a good quality;
- Total automation and operative flexibility;
- Synchronized loading and rotation devices for bending either a sole hide or a batch at a time;
- Universal usage of each stacker and machine or interfacing with a carpet provided with a conveyor roller, since the possibility to be placed at any height of the working station.

Small size loading machine for moving the hides from a bench to staking machine, spraying booth, press, etc…

Stacker on longitudinal tower for better placing the hide with upper side and upright bone.

PROCESS CONTROL SYSTEMS

Thickness gauge for wet-blue hides, with the possibility to see the hide map on a screen provided with 7 wheel sensors.

Automatic weighting device, very precise and that can be integrated with any production process.

3. ENVIRONMENTAL SUSTAINABILITY

Considerations on environmental aspects

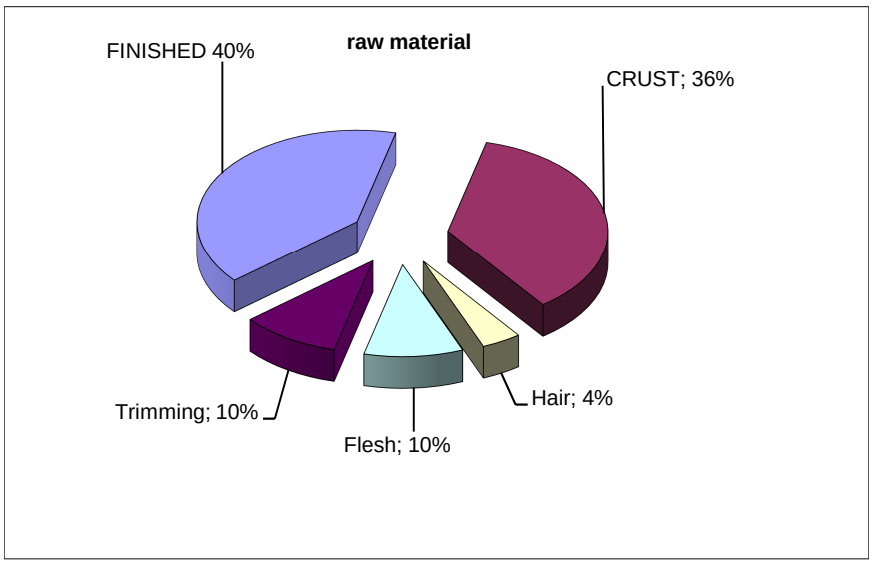
Tanning sector is known for being among the industrial sectors having greater environmental impact. As already said in the previous chapters, leather processing uses a lot of water and chemicals that are afterwards released into the environment. The issue is even more emphasized due to fact that tanneries are located in specialized industrial districts. This high concentration in the same place causes a strong environmental pressure that affects mainly local inhabitants. Tanning is characterized from discontinuous processes, so the emissions coming out from different phases are usually short. In some cases the emissions release could not happen for long time, since different production cycles are carried out depending on market demands.

RAW MATERIAL SELECTION

Simple economic and ecologic factors have to drive towards a rational process organization, avoiding treating the raw material that cannot be processed to finished hide (hide trimming, hair, flesh, not usable crust).

Let's take into consideration the weight of different rawhide parts, for example bovines (see chart below). At the end of process it is possible to notice that:

- Not more than 40% of the raw weight will be processed into a finished hide;
- Not more than 18% of raw weight will be processed into finished crust



It is necessary to remember these conceptions and apply them in each tannery department, in particular in "wet" department where a good management has to be carried out in order to obtain an economically sustainable semi-finished hide and technically in line with market demands.

Each phase that makes up product processing from raw to finished stage, through pickled, wet-blue and crust uses specific technologies that have been developed on the basis of production needs.

The below chart summarizes the input/output flows giving a general balance of bovine hides tanned with chrome.

INPUT		OUTPUT			
Chemicals	~ 500 kg	**Leather**	200 -250 kg		
Water	15 – 50 m³	**Water**	15 – 50 m³	COD	230 – 250 kg
				BOD	~ 100 kg
				SS	~ 150 kg
				Chrome	5 – 6 kg
				Sulphide	~ 10 kg
Rawhide	1 t	**Solid waste**	~ 450 – 730 kg	Untanned	Trimmings ~ 120 kg
					Fleshings ~ 70 – 350 kg
				Tanned	Splits, Shavings, Trimmings ~ 225 kg
				Dyed / Finished	Dust: ~ 2 kg
					Trimmings ~ 30 kg
Energy	9.3 – 42 GJ			Sludge from treatment	(~ 40 % dry matter content) ~ 500 kg
		Air	~ 40 kg	Organic solvents	

Source: IPPC study of European Commission 2003

Inputs	Product phases	Processing phases	Outputs
	Raw material		
		Selection by families	
Energy		Desalting	Salt, Odours
		Trimming	Trimmings
Water Alkali Wetting Agents Surfactants Enzymes Biocides		Soaking	COD, BOD, SS, DS Dung, blood Salts N-org AOX Emulsifiers, Surfactants Biocides
Water Lime, Alkali, Sulphides Thioalcohols Surfactants		Liming	Sulphides COD, BOD, SS, DS Proteins, hair Lime High pH N-org, N-NH_4 Biocides Hydrogen Sulphides NH_3 Odour
		Hair regenaration	Hair
		Fleshing	Fat, connective tissue, lime
Water Ammonium salts Organic and Inorganic Acids CO2 Enzymes		Deliming	COD, BOD, SS, DS Excess bating agents N-NH4 Sulphides Calcium Salts
Water Surfactants Organic Solvents		Degreasing	COD, BOD, SS Fat Surfactants NH3 H2S
Water Organic and Inorganic Acid Salts Fungicides		Pickling	COD, BOD, SS, DS Salt Low pH H2S Acid fumes
	Pickled		
Water Basifing salts Complexing agents		Tanning	COD, BOD, SS, DS Chrome Tannins
		Pressing	
		Splitting	Splits
		Shearing	Shavings
	Wet-blue		

Inputs	Product phases	Processing phases	Outputs
Wet-blue			
Water Organic and Inorganic Acid Salts Fungicides Basifing salts Complexing agents Synthetics agents Synthetics-mineral based oils Sulphonated animal vegetable oil and fish oil Chlorinated organic compound		Retanning	COD, BOD, SS, DS Salt Low pH Chrome Tannins
		Dyeing	
		Fatliquoring	
		Hang drying	
		Drying	
Crust			
		Staking	
		Buffing	Trimmings Dust
Lacquers Auxiliaries		Coating	COD, BOD, SS Organic solvents Heavy metals Auxiliaries
Lacquers Auxiliaries		Spraying	COD, BOD, SS Organic solvents Heavy metals Auxiliaries Aerosol
		Dry drumming	
		Ironing	
		Polishing	
		Measuring	
Finished product			

The necessity to replace some chemicals used in tanning is due to 2 environmental sustainability aspects:

1) Ecologic: besides some intervention already mentioned in the previous paragraphs, like usage limitation and replacing of detergents (nonylphenol) with alternative products (ethoxylate alcohols), it has been necessary to intervene in the process without changing it radically

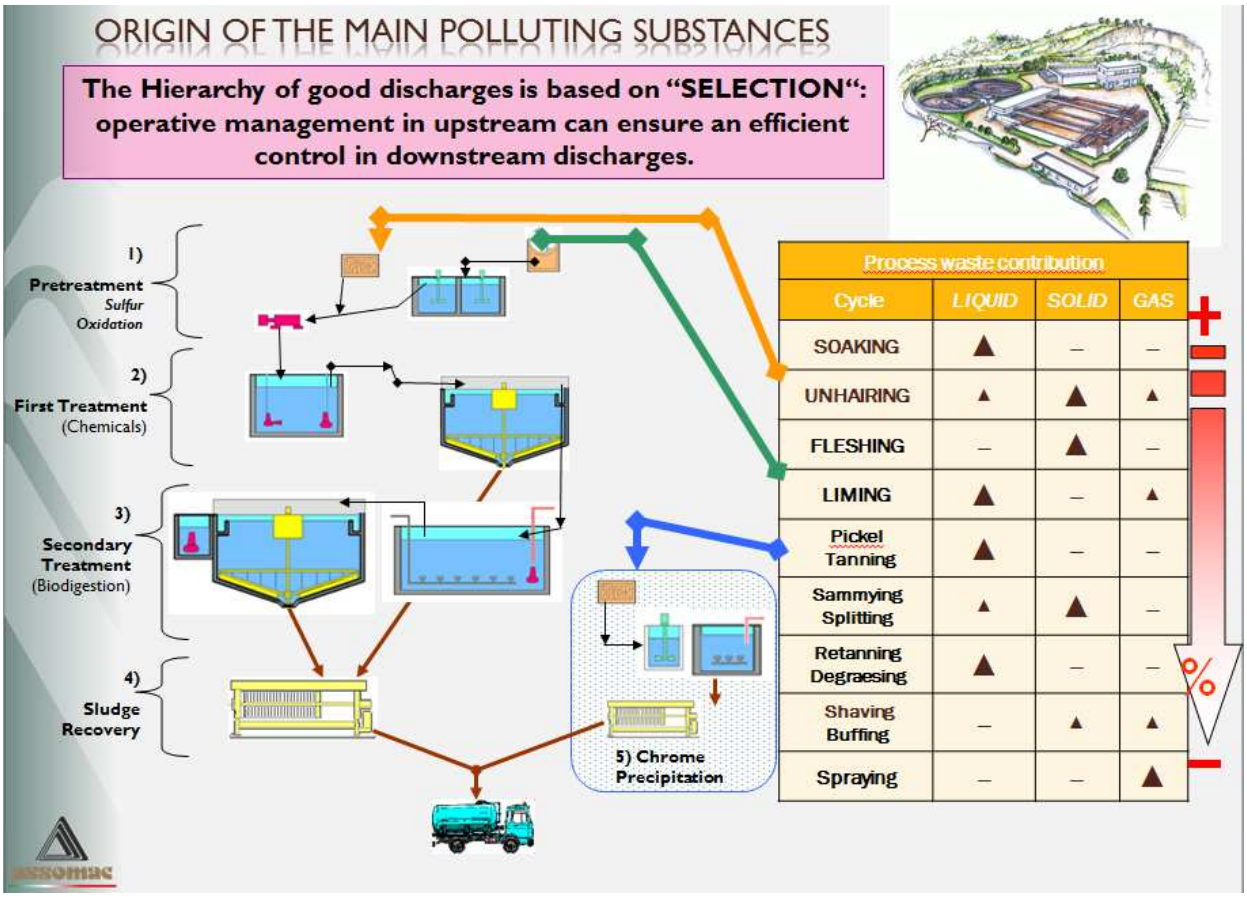
2) Resources: the issue related to rational use of energetic and raw material resources involves different production chains. Tanning is based on primary resources' utilization (water-energy) and raw material (chrome) that have to be reused in a sustainable way.

The chart below shows the main intervention lines used in chemicals replacing and suggested by a very articulated European study

SUBSTANCE	BAT SUBSTITUTE
Biocides	• Products with the lowest environmental and toxicological impact, used at the lowest level possible e.g. sodium- or potassium-di-methyl-thiocarbamate
Halogenated organic compounds	• They can be substituted completely in almost every case. This includes substitution for soaking, degreasing, fatliquoring, dyeing agents and special post-tanning agents - Exception: the cleaning of Merino sheepskins
Organic solvents (non-halogenated) The finishing process and the degreasing of sheepskins are the major areas of relevance.	Finishing: • Aqueous-based finishing systems - Exception: if very high standards of topcoat resistance to wet-rubbing, wet-flexing and perspiration are required • Low-organic solvent-based finishing systems • Low aromatic contents Sheepskin degreasing: • The use of one organic solvent and not mixtures, to facilitate possible re-use after distillation
Surfactants APEs such as NPEs	• e.g. alcohol ethoxylates, where possible
Complexing agents EDTA and NTA	• EDDS and MGDA, where possible
Ammonium deliming agents	• Partially with carbon dioxide and/or weak organic acids
Tanning agents - Chromium - Syntans and resins	• 20 – 35 % of the fresh chrome input can be substituted by recovered chrome • products with low formaldehyde, low phenol and low acrylic acid monomer content
Dyestuffs	• De-dusted or liquid dyestuffs • High-exhausting dyes containing low amounts of salt • Substitution of ammonia by auxiliaries such as dye penetrators • Substitution of halogenic dyes by vinyl sulphone reactive dyes
Fatliquoring agents	• Free of agents building up AOX - Exception: waterproof leathers • Applied in organic solvent-free mixtures or, when not possible, low organic solvent mixtures • High-exhausting to reduce the COD as much as possible
Finishing agents for topcoats, binders (resins) and cross-linking agents	• Binders based on polymeric emulsions with low monomer content • Cadmium- and lead-free pigments and finishing systems
Others: - Water repellent agents - Brominated and antimony-containing flame retardant	• Free of agents building up AOX - Exception: waterproof leathers • Applied in organic solvent-free mixtures or, when not possible, low organic solvent mixtures • Free of metal salts - Exception: waterproof leathers • Phosphate-based flame retardants

source: IPPC study European Commission 2003

The key issue is to provide a good "SELECTION" upstream discharges that can ensure effective management of downstream discharges



GLOSSARY

Vat	**Aspo**	Particolare reattore per il trattamento in acqua delle pelli.
Float (liquor)	**Bagno (liquore)**	Soluzione contenente i prodotti chimici richiesti per una specifica azione, in cui vengono immerse le pelli.
Drum	**Bottale**	Contenitore cilindrico chiuso ruotante attorno all'asse.
Liming	**Calcinazione**	Processo per rimuovere il pelo, l'epidermide ed altri materiali contenuti nella pelle che causa un'idrolisi alcalina controllata del collagene e conferisce, quindi, una certa flessibilità alla pelle.
Fleshings	**Carniccio**	Pezzo di tessuto sottocutaneo, grasso e carne separati dalla pelle durante la scarnatura.
Collagen	**Collagene**	Principale proteina fibrosa costituente il derma della pelle che viene stabilizzato durante il processo di concia.
Tanning	**Concia**	Processo di stabilizzazione irreversibile del collagene della pelle che, mediante l'uso di agenti concianti, la rende imputrescibile.
Mineral tanning	**Concia minerale**	Processo di concia in cui gli agenti concianti sono sali minerali (es. sali di alluminio, cromo, zirconio).
Vegetable tanning	**Concia vegetale**	Processo di concia mediante l'uso di tannini vegetali estratti dal legno, corteccia, foglie, radici, ecc.
Conditioning	**Condizionamento**	Introduzione di un quantitativo controllato di umidità nella pelle asciutta per conferirle un determinato grado di morbidezza.
Curing	**Conservazione**	Operazione che ha lo scopo di prevenire la decomposizione della pelle nel tempo che intercorre tra la scuoiatura dell'animale e le operazioni di riviera.
Split	**Crosta**	Parte inferiore della pelle ottenuta in seguito a spaccatura.

Leather	**Cuoio, pelle**	Termine generico per definire la pelle nella sua originale struttura fibrosa più o meno intatta, che è stata trattata per essere imputrescibile.
Deliming	**Decalcinazione**	Rimozione della calce dalla pelle prima del processo di concia attraverso l'azione di acidi organici o inorganici deboli o di sali di questi acidi. Tale operazione permette inoltre di ridurre il pH e il rigonfiamento della pelle.
Fellmongeries	**Delanatori**	Addetti alla lavorazione di pelli caprine e ovine fino allo stadio di piclato.
Painting	**Depilazione con pasta (o per allattamento)**	Depilazione mediante l'azione di una pasta depilante (pasta di calce) applicata sul lato carne. La pasta depilante è composta da acqua, calce, solfuro di sodio e un agente addensante.
Grain	**Fiore**	Può significare: a. La parte esterna lato pelo della pelle che è stata spaccata in più strati. b. Il disegno visibile sulla superficie esterna della pelle dopo la rimozione del pelo o della lana.
Fatliquoring	**Ingrassaggio**	Incorporazione di grasso nella pelle che permette di conferire flessibilità e morbidezza.
Rinsing	**Lavaggio**	Processo condotto dopo ogni trattamento mediante un continuo afflusso e deflusso di acqua nello stesso impianto in cui è avvenuto il trattamento.
Length of (liquor) float	**Lunghezza del bagno (liquore)**	Volume di un bagno espresso come percentuale relativa al peso della pelle in lavorazione.
Bating	**Macerazione**	Fase di lavorazione che segue la decalcinazione e precede il piclaggio. Ha lo scopo di pulire il fiore, ridurre il rigonfiamento, peptizzare le fibre e rimuovere i prodotti di degradazione delle proteine.
Neutralisation	**Neutralizzazione**	Processo che consente di portare il pH della pelle al valore ottimale per le successive fase di riconcia, tintura e ingrasso.
Staking	**Palissonatura**	Ammorbidimento e stiramento della pelle.
Aniline leather	**Pelle anilina**	Pelle che è stata tinta solamente con coloranti all'anilina e che è stata sottoposta a poca o nessuna rifinizione per mantenere un aspetto naturale.

Hide	**Pelle di animale di grande taglia**	Pelle non conciata di un grande animale (es. mucca, cavallo).
Skin	**Pelle di animale di piccola taglia**	Pelle non conciata di un animale di piccola taglia (es. vitellino, maiale, pecora).
Bovine	**Pelle bovina**	Pelle di bue, vacca, vitello e bufalo.
Limed hide or skin	**Pelle calcinata**	Pelle risultante dopo l'eliminazione del pelo, epidermide e tessuto sottocutaneo. Nome usato per le pelli dopo la calcinazione.
Crust leather	**Pelle in crosta**	Pelle che ha subito un processo di essicazione dopo le fasi di concia, riconcia e tintura senza rifinizione.
Ovine	**Pelle ovina**	Pelle di pecora.
Upholstery leather	**Pelle per rivestimento**	Termine utilizzato per le pelli destinate all'arredamento e agli interni dei veicoli.
Calf skin	**Pelle di vitello**	Pelle di un animale bovino giovane e inferiore ad un certo peso.
Pickling	**Piclaggio**	Processo che segue la macerazione, durante il quale la pelle è portata ad un pH acido per immersione in una soluzione salina acida.
Pickled pelt	**Pelle piclata**	Pelle derivante dalla fase di piclaggio. Prodotto commerciabile.
Shavings	**Rasatura**	Residuo derivante dalla livellazione dello spessore della pelle condotta mediante un cilindro munito di lame taglienti.
Beamhouse/Limeyard	**Reparto Riviera/Calce**	Reparti della conceria in cui le pelli vengono lavate, calcinate, scarnate e depilate, quando necessario, prima del processo di concia.
Retanning	**Riconcia**	Processo mediante il quale la pelle che è stata precedentemente conciata viene sottoposta ad un secondo trattamento conciante effettuato con prodotti chimici analoghi o, più frequentemente, diversi.
Trimming	**Rifilatura**	Eliminazione delle parti marginali della pelle: es. zampe, coda, faccia, mammelle ecc. su pelli grezze o rinverdite; sfilacciature, ritagli e parti danneggiate dopo le operazioni meccaniche (scarnatura, spaccatura ecc.).
Trimmings	**Rifilature**	Residui derivanti dal processo di rifilatura.

Finishing	**Rifinizione**	a. Operazioni meccaniche volte al miglioramento dell'aspetto estetico e del tatto della pelle; es.:condizionamento, palissonatura, smerigliatura, follonatura, lucidatura, stampaggio. b. Applicazione di uno strato superficiale più o meno pigmentato e/o fissativo.
Soaking	**Rinverdimento**	Primo trattamento a cui viene sottoposto la pelle volto alla reidratazione e al lavaggio della pelle stessa.
Brining	**Salatura in salamoia**	Conservazione delle pelli tramite impregnazione in una soluzione satura di sale.
Fleshing	**Scarnatura**	Eliminazione del tessuto sottocutaneo, del grasso e della carne attaccata alla pelle attraverso l'azione meccanica di un cilindro munito di lame taglienti.
Lime fleshing	**Scarnatura in calce**	Scarnatura effettuata dopo la calcinazione e depilazione.
Green fleshing	**Scarnatura in verde**	Scarnatura effettuata prima della depilazione e calcinazione.
Degreasing	**Sgrassaggio**	Eliminazione, per quanto possibile, del contenuto di grasso naturale nella pelle.
Dewooling	**Slanatura**	Separazione della lana dalle pelli ovine.
Buffing	**Smerigliatura**	Trattamento abrasivo della superficie della pelle. Se tale operazione viene condotta sul lato carne, si ottiene una pelle scamosciata; se è interessato il lato fiore, si ottiene una pelle a fiore corretto o nabuck.
Plating/embossing	**Stiratura/Stampaggio**	Appiattimento e stampaggio di un disegno sulla pelle.
Splitting	**Spaccatura**	Spaccatura orizzontale della pelle con l'ottenimento di uno strato fiore e, se la pelle è sufficientemente spessa, di uno strato carne. Tale operazione è condotta con macchine apposite munite di un nastro particolare e può interessare pelli calcinate o conciate.
Dyeing	**Tintura**	Operazione che permette di conferire alle pelli la colorazione desiderata attraverso l'uso di coloranti naturali o sintetici.
Wet-blue	**Wet-blue**	Pelle conciata al cromo allo stato umido.
Wet-white	**Wet-white**	Pelle (pre-)conciata con prodotti alternativi al cromo di colorazione bianca allo stato umido.

ABBREVIATIONS

AOX	**Absorbable organic halogenated compounds**	Composti organici alogenati adsorbibili
BOD	**Biochemical oxygen demand**	Fabbisogno biochimico di ossigeno
BREF	**Bat Reference Document**	Documento di riferimento per le BAT
COD	**Chemical oxygen demand**	Fabbisogno chimico di ossigeno
COV	**Volatile organic compounds (VOC)**	Composti organici volatili
NOAC	**No observed acute effect concentration**	Concentrazioni prive di effetti acuti osservati
NOEC	**No observed effect concentration**	Concentrazioni prive di effetti osservati
IPA	**Polycyclic aromatic hydrocarbons (PAHs)**	Idrocarburi policiclici aromatici
PCDD **PCDF**	**polychlorinated dibenzo-dioxin** **polychlorinated dibenzo-furan**	Policlorodibenzodiossina Policlorodibenzofurano
SS	**Suspended solids**	Solidi sospesi
TDS	**Total dissolved solids**	Solidi totali disciolti
TKN	**Total kieldhal nitrogen**	Azoto totale kieldhal

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