Back to Basics: Leather Manufacture

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WTP

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Part 1

Raw material and preservation

Introduction to "Back to Basics"

The intention of this publication is to provide insight into a very complex and changing industry. Each tannery develops techniques according to its customers' requirements, raw material availability, plant limitations and, increasingly, environmental restraints. In practical manufacture the "text book rules" are often modified both through necessity and technical ingenuity, and this applies to all types of leathers.

The appearance of finished leathers – colour and texture – is driven by fashion, hence the finishing operations are subject to rapid change to meet market demands. However, many changes also take place in the earlier stages of leather manufacture, via the use of chemicals, production techniques and through improved machinery. In addition to customer needs, major changes are now driven by specification, legislation and environmental demands, and processes, therefore, will continue to evolve.

In this publication, leather making technology is set out as the main subject matter. There are, however, many associated issues that merit discussion, so these are presented in a series of panels. Where a topic is raised in the main text that is discussed in greater detail in some other part of the feature, a reference is given in the text.

Finally, it must be borne in mind that the technology applied in leather manufacture must build on the characteristics of the raw materials available and meet the consumer end use. This publication therefore provides an overview of the basics of leather making, designed both as an introduction to the industry as well as a refresher.

The structure of skin

To understand leather making principles, it is helpful to appreciate some details of the structure of skin *(Panel 1)*.

THE GRAIN LAYER

The grain bears a hard outer layer known as the epidermis, and the animal hair (scales in reptiles and fish) being embedded in follicles reaching down into the skin structure. With all types of leather, except fur or wool skins, the hair and epidermis are chemically removed in the first stages of the leather making process.

The basic substance of the grain is a densely interwoven fibrous tissue made from the protein collagen. This provides a fine, firm and sensitive structure that is the key to good leather quality and the characteristic appearance of each leather type.

THE CORIUM

The corium supports the grain layer and is relatively thick. The structure is fibrous, strongly interwoven but coarse. Made from collagen, it also contains veins, fats and non-fibrous proteins.

The denseness and interlacing of this tissue varies according to the different parts of the skin. The angle of weave of these fibres strongly influences the hardness and stretch characteristics of the leather, and provides basic strength, although these properties are modified during leather manufacture.

THE FLESH

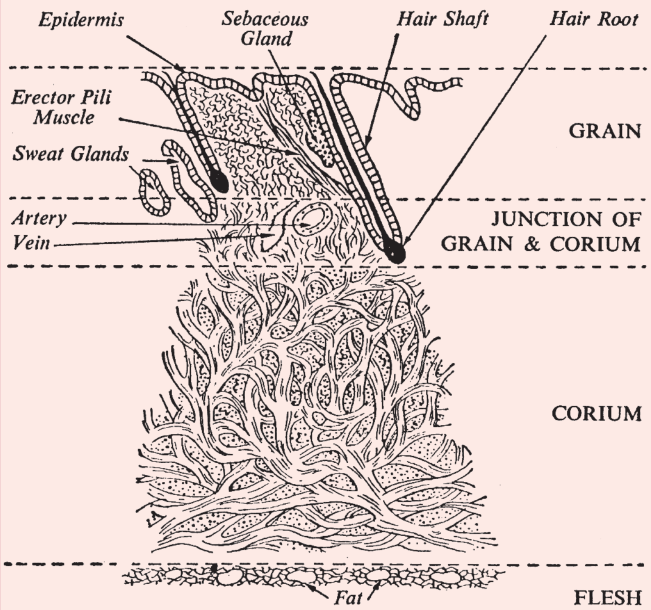
Flesh tissues are of no use to the tanner and are cut away by machine before tannage.

VARIATIONS IN HIDE AND SKIN STRUCTURE

There are considerable variations between individual hides or skins depending on the breed, geo-climatic conditions and husbandry, type of feed stuff, time of year, sex and age of the animal. The structure also varies across the area of each skin. For example, the butt area is relatively thick and has a densely woven fibre structure, whereas the belly area is thinner, less dense and will stretch more readily. With bovine hides there is a low natural fat content, although this varies according to feed. With sheep and pigs this can be as high as 30% of the skin weight and, when removed, can leave weakening spaces in the structure.

Panel 1

Cross section of skin



The skin section comprises three main layers: Grain, Corium & Flesh. Courtesy: Leather Technician's Handbook: J.H.Sharphouse

The basic raw material

The basic raw materials for the leather manufacturer are hides and skins, being by-products of the meat industry. Quality can be diminished by many factors including:

ANIMAL HUSBANDRY

Poor animal husbandry can cause significant damage to the living skin. Poor feed, disease, infestation, adhering dung (dung-cladding), branding, prod marks, cuts, scratches, and abrasions all reduce the potential quality and cutting values. This reduces both demand and outlets for leathers carrying these defects.

TRANSPORT & PRE-SLAUGHTER MANAGEMENT

Skin damage such as scratches and bruising can occur through poor conditions in transit to abattoirs. Discoloration and vein marks can also be found in leathers due to increased blood levels in the skin in the period before slaughter as a result of unnecessary animal stress.

Animal slaughter

As part of slaughter procedures the carcass is hoisted by the hind legs and bled from a throat incision. This improves the colour of the meat and skin, and also removes a component that can readily putrefy. Cuts are carefully made in the skin (marking) to assist in separating the hide from the carcass (flaying), and to maintain a uniform hide/skin shape. The hide is removed from the carcass by mechanical pulling, or by hand flay. Skin damage can result from excessive tension caused by pulling smaller animals, while hand flaying requires a considerable amount of lateral cutting while separating the skin from the meat and fat. Flay damage can include deep cuts and gouges in the flesh side of the skin, and even holes. The depth of these cuts affects the potential thickness (substance) that can be obtained from the final leather and can seriously affect values.

Panel 2

Raw materials trading

In addition to purchases of raw materials preserved as described, there is considerable movement of hides and skins in a semi-processed state. The most common forms are in the wet blue (chrome tanned) *(Part 4)*, and the crust condition (dry, pre-finished) *(Part 8)*. Some leathers are sold part vegetable tanned and dried (veg tanned crust) *(Part 4)*, and sheepskins can be sold in the pickled condition *(Part 4)*. There are other conditions, where the skins are preserved, stabilised or part-tanned, which will develop in the future.

Preservation of the skin

The skin of the living animal is protected against putrefaction, but this ceases from the moment of slaughter. Bacterial attack of the skin or decomposition readily occur, so under ideal conditions this is addressed directly after flay.

MEDIUM TERM PRESERVATION: WET SALTING & AIR DRYING

As bacterial action is temperature sensitive, under ideal conditions the skins are sprayed with chilled water to cool the skin. The skins can then be preserved using a technique called wet salting, where the hides are covered with salt and stacked in piles. The salt absorbs water from the skin, which drains away as a brine solution causing partial drying. Liberal application of salt ensures good water removal and inhibited bacterial activity, thus safeguarding the skin against further bacterial action.

Another quality technique is to circulate the hides in concentrated salt solution. This requires specialised plant but is commonly used in the US and is known as brining.

However, in many instances hides are simply washed after slaughter, to remove blood and dirt, and salted or collected by dealers who salt and grade elsewhere. Delays before preservation run increasing risks of bacterial damage, especially to the sensitive and valuable grain layer.

Another method of preservation, practised in tropical countries if salt is not readily available, is to stretch out the hides or skins on frames to dry in the shade. This is known as air drying, and as bacteria cannot exist without water it is possible to keep these skins for long periods without deterioration. If the skins are dried too rapidly, say in the direct heat of the sun, chemical changes will occur in the skin proteins that result in a thin, hard leather. If dried out too slowly, partial decomposition may occur, giving a pitted appearance and weakening the final leather. The quality is never as good as with salt preservation.

SHORT TERM PRESERVATION & HIDE PROCESSING

Due to environmental problems associated with salt, short term preservation is also being used, mainly through chilling by the direct application of ice to the fresh hide. Other techniques are possible including bactericide preparations, ice containing bactericides, air chilling and refrigerated transport, as well as hide irradiation. To maintain raw material quality, these various methods of preservation need reinforcing by good storage conditions at the tannery.

Rationalisation has also led to tanneries being coupled with large slaughter houses to avoid the expense of preservation, transport and losses through hide deterioration. In some situations hides are directly conveyed from the slaughter line to the tannery for brining or conversion to the tanned (wet blue) state. Delays before processing can therefore be reduced to less than one hour.

Part 2

Preparation for Tanning (i)

The soaking process

The first leather making operation is to soak the skins in water with the objective of:

- Rehydrating the skin/protein structure, to return the skin to the condition it was in before preservation.
- To remove salt, dirt, dung and blood from the skin.

Soaking time can vary from a few hours for wet salted hides, to several days for some types of air dried hides. Bactericides are used to prevent decay of the skin, and wetting agents (detergents), alkalis, and selected enzymes *(Panel 4)* can be used to accelerate the soak.

Unhairing and Liming processes

DISSOLVING HAIR

Under alkaline conditions, the chemicals sodium sulfide and hydrosulfide can break down the protein keratin, being the main component of hair, whereas under controlled conditions the main skin structure (collagen) remains intact. It is therefore possible to safely remove hair from the skin without causing damage to the sensitive grain layer.

If the hair is of no commercial value then the unhairing and liming processes are carried out together. Sodium sulfide/hydrosulfide is offered to the skins while being moved in the process water (the float), followed by lime as the source of alkali. The hair readily breaks down into solution, this often being called a hair burning process.

RECOVERING HAIR AND WOOL WITH VALUE

If the hair on the skin is of value (wool from sheepskin, bristles from pigskin for brushes), unhairing and liming are carried out separately.

In this situation the hair is removed by applying an alkaline paste of sodium sulfide and lime to the flesh side of the skin. The sulfide solution penetrates through the skin structure to the hair root and epidermis which then breaks down leaving the hair shaft intact. The hair may then be removed by hand or machine, washed, dried and sold. The skins are then limed and any remaining hair or stubble is removed chemically.

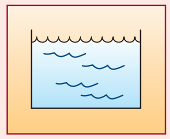
"HAIR SAVING" PROCESSES

For environmental reasons, hair is also removed from the hide largely intact with a combined unhairing liming process instead of simple dissolution. The technique is performed in a way somewhat similar to the hair dissolving system, but the hair shaft is first made chemically immune to breakdown by pre-alkali treatment. The hair root is then dissolved, the released hair being filtered from the float using specialised filtration equipment fitted to modified drums or hide processors. The recovered hair is partially broken down, matted and of negligible value. It can be composted with other organic waste, although value adding alternatives are being sought.

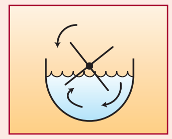
Panel 3

Vessels for wet processing

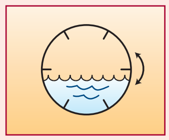
For good processing there should be uniform contact between water, chemicals, hides and skins. There are several options:



PITS: Occasionally used in manufacture.

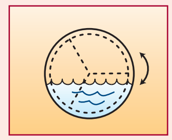


PADDLES: Used for moving hides and sensitive skins.



DRUMS: The major vessel used in leather processing.

HIDE PROCESSORS: Also used for processing hides.



Y–SECTION VESSELS: Found together with drums in dyeing and fatliquoring processes (Part 7).

THE LIMING PROCESS

Liming has a decisive effect on the character of the leather produced. Slaked lime is the most widely used agent as it is only sparingly soluble in water. Excess quantities are used so that a saturated solution is maintained within a float, keeping the alkalinity of the solution constant.

In addition to providing a source of alkali to assist in the removal of hair and epidermis, liming is carried out with two major objectives:

- Alkali swelling of the skin, to open the structure of the collagen fibres and modify the skin for the reception of chemicals used in tanning.
- To break down non-structured proteins, complex sugars and combination products situated within the collagen structure that would harden the final leather, unless removed before tanning. There is also partial hydrolysis of natural greases within the structure, which assists in their removal.

Flesh residues also become swollen in this process and this helps in their removal at a later stage during the fleshing operation *(Part 3)*.

Sodium sulfide and hydrosulfide are normally part of the liming process. Sodium sulfide may be seen as combining with water to produce sodium hydrosulfide which removes the epidermis and hair (as described), and sodium hydroxide (caustic soda) which makes the solution more alkaline and accelerates the liming process.

As a general rule the more alkaline the liming, or the longer the liming time, the softer and looser the characteristics of the final leather.

The liming process can be performed by treating the skin with these chemical solutions in pits, paddles, but generally wooden drums, the vessel used being dependent in part on the type of skin being limed. Liming is usually a one-day operation but varies depending on the type of skin, and the required type of leather.

Part 3

Preparation for Tanning (ii)

The fleshing operation

When the unhairing and liming process is complete, and after washing, the skins are removed from their processing vessel. Occasionally hides are cut along the backbone to form two 'sides' for easier handling, but normally they remain intact.

At this stage the skins are slippery, alkaline swollen and translucent. Residual flesh and tissue remaining from flaying can readily be cut away from the corium using a fleshing machine.

Fleshing

This operation leaves a clean skin section for good presentation to the splitting operation, and in preparation for the tanning process.

Lime fleshing also squeezes dirt and debris from within the grain layer, and causes a general relaxation of the hide. However, fleshing can be carried out after removal of the skin from the carcass before preservation, or after soaking before liming and unhairing. The operation is particularly important for the mechanical removal of grease from skins with a high natural fat content such as pigs and sheep, and in this event can even take place in the pickled state *(Part 4)*.

The splitting operation

Splitting

Hides have considerable variations in thickness between the butt, shoulders, neck and belly areas, and between individual hides. These variations can be rectified by the lime splitting operation. By feeding the hide against a moving band knife, the hide can be split into two layers, the top grain layer being the required thickness or substance.

The most important section is the grain layer. The lower layer, termed flesh split, carries the variation in substance, and can be processed separately to produce lower quality industrial gloving leather, shoe linings, suede leathers and laminates. Splitting also causes a relaxation of the grain split so that the area increases. In addition, the thinner skin section means that chemicals used in subsequent processing penetrate the hide more rapidly. This can shorten the time required for processing, and minimise both chemical offers and waste.

Splitting is often omitted in the limed state, but performed after the tanning operation and, in this event, the splitting accuracy is improved.

When processing sheepskins for bookbinding and chamois leathers, splitting is performed on pickled stock. Bovine leathers are occasionally resplit in the dry state (crust) to correct substance before finishing.

Deliming and Bating

These processes are frequently carried out together and follow unhairing and liming.

Deliming is necessary to de-swell the skins, gently releasing soluble non-structured protein residues from within the skin that would otherwise cement the fibre structure on drying and harden the leather. It is also part of a gradual change from the strongly alkaline (high pH) liming condition towards the acid state (low pH) that is normal for most tanning methods. Ammonium sulphate is used in this process although this is being replaced in many tanneries by carbon dioxide gas to reduce the ammonia levels in waste waters.

Bating is a mild form of enzymatic cleaning action and helps relax the skin and produce a softer type of leather. Specialised enzymes *(Panel 4)* from pancreatic trypsin or bacterial proteases that best perform at the pH levels found in deliming are used to remove degraded protein residues.

The normal practice is to completely delime and bate skins, but occasionally this is restricted to the outer section producing very firm leathers.

Sometimes, after deliming and bating, the grain of sheepskins is cleaned by hand or machine operation. Known as scudding, the operation squeezes hair roots, pigmentation and proteinous residues from the skin, leaving a very clean grain.

Degreasing

When fatty skins are being processed, such as sheepskins and pigskins, it is important to remove as much grease from the skin as possible. Multi-stage fleshing and detergents used during soaking, liming, deliming and bating assist in this removal. More recently specialised enzymes have been introduced into these processes to rupture fat cell membranes and thus assist in the fat release.

With very greasy skins, after the pickling process *(Part 4)*, the skins can be drummed with paraffin to soften the grease, together with detergents to disperse and emulsify the grease in water. Environmentally, this is a difficult operation, so aqueous degreasing is far more common. In this process the shrinkage temperature of the skin is raised by a pre-tannage *(Part 4 & 5)*, so that warm water (45°C) can be used to melt the grease. This is easily dispersed using emulsifying agents, then washed from the skins.

Panel 4

Enzymes in manufacture

Enzymes have huge potential in manufacturing industry as they can target, digest or modify very specific organic components. This shifts the processing from often difficult and inefficient chemical processing, to an energy efficient, bio-chemical reaction with minimum environmental impact.

Uses are established in leather manufacture to assist soaking, liming, and bating processes via the digestion of non-structured proteins. Other uses include breaking fat cells for fat and grease release. Recent applications include the removal of non-tanned components in the grain of chrome tanned leathers for relaxation and area gain, and the breakdown of dung-cladding pre-slaughter. Focus is now on the unhairing process.

Part 4

The Tanning Process (i)

The objective of tanning is to modify the chemical structure of the skin collagen to provide resistance to putrefaction and stability under conditions of heat and moisture. Many tanning materials are in common use, applied either alone or in combination with other agents to target leather qualities *(Panel 5)*.

The predominant tanning technique in the world is chrome tannage (approximately 85%) but a significant quantity of vegetable tanned leathers are also made. A growing volume - often termed "wet white" - is part-tanned or pre-tanned, *(Part 5)*, before committing to specialised tannage.

Pickling process

After deliming and bating the skins are mildly alkaline (about pH 8.5), but almost all tannages require the skins to be in a moderately acid state. If these conditions are not met, then a very rapid fixation of the tanning agent can occur on the skin surface, and the centre remains raw. Different tannages requires different levels of acidity or pH.

The skins are therefore pre-treated in a process called pickling, generally using sulphuric and formic acid, to ensure a controlled tannage. Common salt must also be included to prevent the skins from swelling under acid conditions.

The process is generally carried out in drums, but sheepskins that retain the wool and fur skins are treated in paddles to prevent felting of the hair. Using very acid pickling systems, sheepskins can be preserved for long periods of time and are sometimes sold in this state.

Chrome tannage

Chrome tanning materials are based on chromium sulphate and are supplied in varying 'basicities'. The more basic the chrome, the more rapidly it combines with the skin collagen and the less it penetrates before tanning. The higher the basicity, the plumper, softer and looser the leather produced. Chrome tanning agents can be modified or masked within the tanning operation by other chemicals, usually organic acid salts such as formates. This produces softer, lighter and less chemically reactive leathers.

The more acid the skins are, the slower the reaction between the collagen and the chrome, and the deeper the penetration into the skin structure before fixation. However, after penetration of the chrome through the skin structure, usually by a combination of acid conditions and masking, the tanning system is made slightly less acidic by the controlled addition of mild alkalis. This increases the reaction or fixation of the chromium compounds with the carboxyl groups of the collagen. Known as wet blue, the leathers are a light blue in colour, resistant to putrefaction, exhibit a shrinkage temperature >100°C, and are very versatile.

The length of time in chemical process between commencing deliming until the end of tannage is usually around 15 hours.

Vegetable tannage

Vegetable tanning materials are extracted from shredded bark, wood, leaves and fruits of trees and bushes by leaching with water. The source of the extract gives each type of vegetable tannin a distinct character and this is reflected in the final leather produced in terms of colour, plumpness, tightness and firmness. These extracts can also be chemically modified, normally by sulfiting, to increase the solubility of the tannin, and to produce a lighter colour.

To help achieve the required leather characteristics it is usual to blend several types of vegetable extracts together. The most common extracts are mimosa based, followed by quebracho and chestnut, although there are many other products available.

The solutions have a colloidal nature and contain tannins in a range of particle sizes. The smaller molecular clusters penetrate the skin rapidly and help disperse the larger particles. The smaller clusters possess weak tanning properties giving thin leather, whereas larger particles penetrate more slowly, giving a fuller leather.

Vegetable tanning is the normal method for tanning shoe sole leathers. This was once achieved by suspending the skin in pits containing diluted vegetable extracts, and gradually increasing the concentration of the solution until tanning was complete, traditionally taking up to one year! Techniques used today can reduce the time to about ten days, but drum tannages for similar leathers can reduce the time drastically.

Leathers for shoe uppers and lining are tanned by drumming skins, usually pre-tanned with synthetic tanning materials (syntans), in vegetable extracts until penetration and fixation of the extract to the collagen. With low substance skins this can be as little as eight hours.

Panel 5

General properties of different tannages

Tannage	General properties
Chrome	Multi-purpose leather. Blue green in colour, thin, and hard if dried out without further processing. High shrinkage temperature (for forming in footwear construction) and good dyeing properties. Does not absorb water easily.
Vegetable	Cream to dark brown in colour but darkens on ageing. Shrinks at approx. 85°C, good shape retention and perspiration resistance. Leathers are water absorbent, but when dry feel warm and "natural".
Synthetic	Similar to vegetable but thinner and light in colour. No darkening on ageing, but poor dyeing properties.
Cod oil	Sheepskins and certain game skins (like deerskins) for chamois leathers. Characteristic yellow colour, very soft and stretchy, very water absorbent. Shrinks at 50°C.
Glutar-aldehyde	Light yellow/brown to natural in colour. Shrinks at 75°C, poor shape retention but provides high perspiration resistance. Main use is for pre-tanning or "wet white" processing as part of process rationalisation. *(Part 5)*.
Alum	Little used except for white speciality leathers. Can be thin and hard. Shrinks at 65-85°C.

Part 5

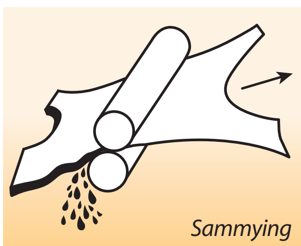
The Tanning Process (ii)

Pre-tanning for specialised processing

In addition to the major tanning techniques described in Part 4, hides and skins are being pre-tanned or stabilised after pickle, using low offers of lightly coloured tanning agents. These agents are usually modified forms of gluteraldehyde, but can include poly-phosphates, forms of silica, and specific syntans and resins. The intent is to raise the shrinkage temperature of the fibre structure sufficiently to enable shaving to a precise substance before tanning, and to provide moderate resistance to putrefaction. This product is often termed "wet white".

This pre-tanning treatment provides a substrate that does not exhibit strong characteristics. It can therefore be tanned with any combination of synthetic or vegetable tanning agent and auxiliary products to achieve very specific leather properties *(Part 7: Panel 8)*. Bovine, ovine and other types of quality skins are being processed using this technique, although the major outlets are as chrome-free leathers for automotive use. The technique, however, can also be used for chrome and vegetable tanned leathers. This rationalisation enables better chemical use and wider outlets for solid waste, making this route of considerable environmental interest *(Panel 6)*.

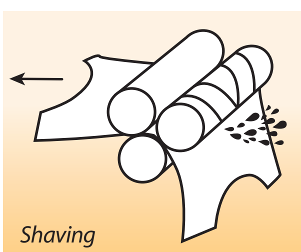
Sammying, blue splitting & shaving


Sammying

After tannage (or part-tannage) the leather is unloaded from the processing vessel, and surplus water squeezed from the hides or skins by the sammying operation.

This is generally a through-feed squeezing operation, but spin drying can be used for small skins and wool-sheepskins. The damp leather is then examined, sorted and graded for potential thickness and quality.

Often lime splitting *(Part 3)* has been omitted to leave the greatest leather substance, hence versatility at this stage. In this event, after selection, the leathers are split in the wet blue state to provide a grain section that shows only a small variation in thickness across the skin. The thickness is again slightly reduced in a precision operation known as shaving where leather substrate is cut from the inner section of the skin by the action of very sharp spiral knives mounted on a rotating cylinder.


Shaving

The substance of this shaved grain section can be very uniform, and accurate to 0.1mm. With thin skins the splitting operation is often omitted.

The skins are now ready for dyeing, retanning and softening processing.

Panel 6

Process control, the environment and sustainability

Process control

Consistent processing is key to leather uniformity, and the main control factors are: temperature, degree of acidity or alkalinity (pH), quantity of chemicals offered, the amount of water or float used in process, mechanical action, and process time.

Attention to these points ensures the most effective use of chemicals. Their uptake is, however, restricted by raw material limitations. Raw skin is damaged at temperatures greater than 38°C, while conditions of high alkalinity (pH 12.4) in liming and unhairing restrict temperatures to a maximum of 29°C. Similarly there are limits in pickling, tanning, and within other areas of processing.

Clean technology

Hair dissolving processes are being replaced by hair saving processes. This leaves hair as a compact solid for disposal, composting, or as a 'new raw material', thus avoiding effluent treatment.

New enzyme applications can speed reactions and reduce the quantities of chemicals used. The environmental problems created by ammonium salts traditionally used in deliming can be avoided by changing to carbon dioxide, and chemicals that more readily biodegrade are finding greater use. The level of salt in waste waters is being reduced by alternative methods of preservation, recycling of pickle liquors, and use of chemicals from which neutral salts have been removed. Solvent based systems have been almost completely replaced by water based systems, especially in finishing operations.

Considerable quantities of water are being saved by a combination of good control, clean technology and recycling, and chemical wastage minimised by reuse. Floats from chrome tannage can be recycled to the next tanning batch to make use of residual chrome. Similarly, it is possible to recycle liming liquors to the next batch and, through advances in membrane filtration, the technology is expanding to other areas. Regeneration is also possible. Classically, residual chrome can be precipitated, then processed into new tanning materials.

The environment

Physical, chemical and biological treatment systems are well-established for treating tannery effluents and remaining problems are being closely addressed. The objective for the future is the closed loop where even water from the waste treatment plant is completely reused in process.

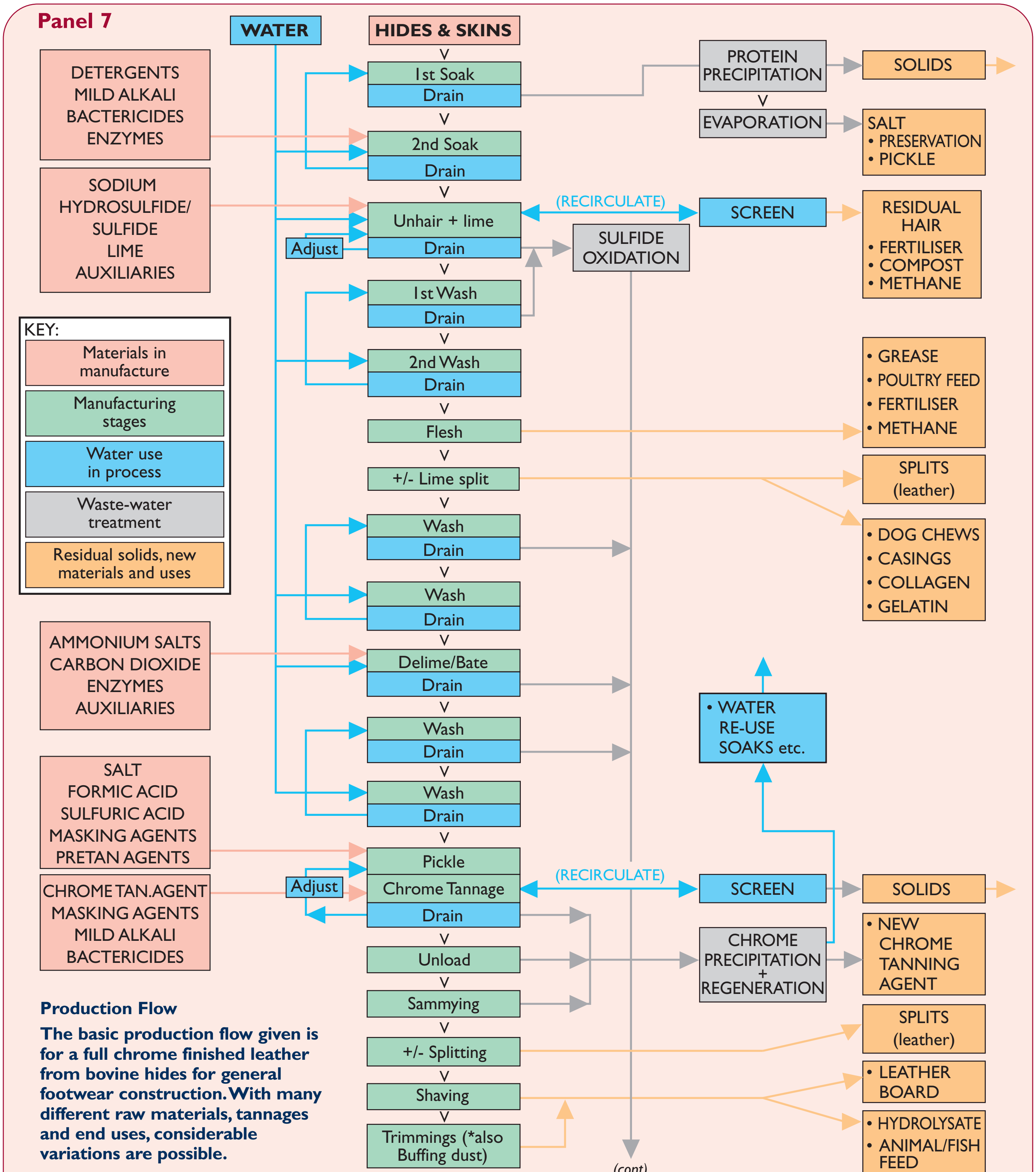
Outlets for waste as new raw materials are being pursued: as the cost of disposal increases, and legislation becomes more stringent, this route inevitably becomes more cost effective.

Hair and non-tanned residues, including shaving from pre-tanned skins and sludges from effluent treatment, are being composted commercially. This is extending to leather products at the end of their useful life, and driving developments in the area of new chrome-free tannages. Tanned shavings/trimmings are being converted into leatherboard and hydrolysates. Gasification and pyrolysis of solid waste are also being applied. Energy can be released for power generation, with chemicals, such as chrome, reprocessed from the residual ash, or locked in a fused slag for aggregate or landfill.

Best Available Technology (BAT) is moving leather manufacture toward the target of sustainability *(also see Part 6: Panel 7)*.

Part 6

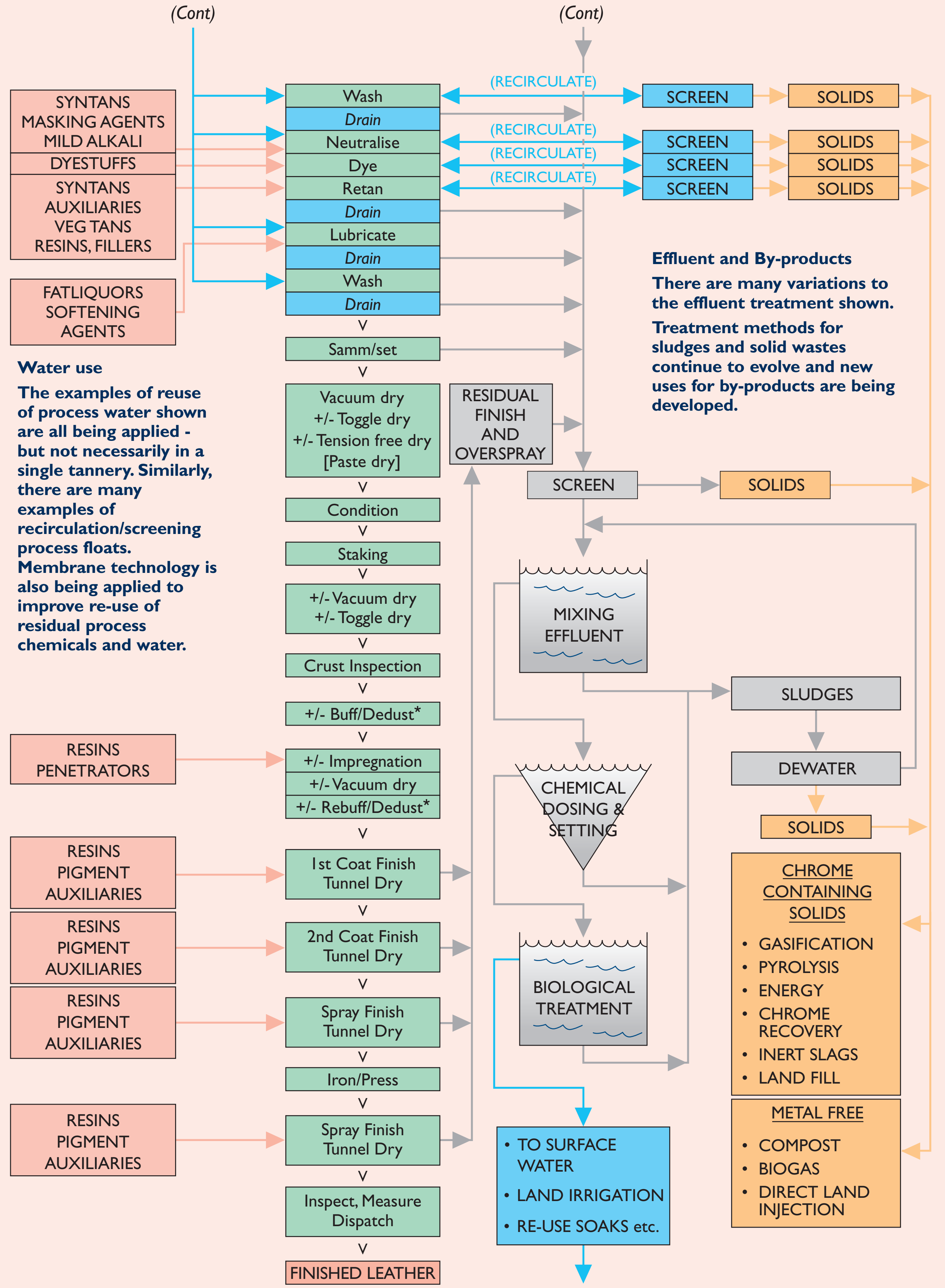
Production flow and materials use



Production Flow

The basic production flow given is for a full chrome finished leather from bovine hides for general footwear construction. With many different raw materials, tannages and end uses, considerable variations are possible.

Panel 7



Water use

The examples of reuse of process water shown are all being applied - but not necessarily in a single tannery. Similarly, there are many examples of recirculation/screening process floats. Membrane technology is also being applied to improve re-use of residual process chemicals and water.

Effluent and By-products

There are many variations to the effluent treatment shown.

Treatment methods for sludges and solid wastes continue to evolve and new uses for by-products are being developed.

Part 7

Retanning, Dyeing and Softening

It is not possible to build the exact properties required into the leathers during the tanning operation. This applies in particular to chrome leathers, so it is common practice to develop the leather character by further wet processing of the shaved goods.

Neutralisation

This treatment prepares the leather for dyeing, retanning, and softening. In this first stage of often complex processing, mild alkalis are added to the leather to reduce the moderate acidity (pH) of the leather. This is to enable deep penetration of reactive chemicals and agents into the leather structure in subsequent processes. The reactivity of the leather can also be modified by masking agents such as formates, and specialised products of low molecular size known as auxiliary syntans.

The dyeing process

There are many types of dyestuffs but anionic dyes are the most frequently used. Acid and direct dyes are used for penetration, surface dyeings and selected fastness properties, and 1:2 premetallised dyes mainly for lightfastness.

Whole ranges of colour are covered by these dyestuffs and thus the tanner is able to dye accurately to a pattern. The dye can be added to the processing vessel either pre-dissolved or as a dry powder. The dyeing process can be on neutralised leather, or after a suitable retannage. Several additions can be made according to the intensity of colour required or dye penetration into the leather. The dyes are usually fixed by acidification or the use of specialised fixatives. Sometimes specialised pigments are included, mainly for black and white leathers.

Special dyestuffs are available for dyeing wool-sheepskins and furs.

The retanning process

Selected materials are applied to the neutralised leather to combine with and modify the leather structure. Normally these products are vegetable tanning materials, synthetic tanning agents, acrylic resins and fillers. These provide very specific properties to the final leather and it is normal to apply several different retanning agents together. Their combined effects can make the leather feel softer, and fuller - especially in the more empty belly areas - to level and improve embossability. The products can also selectively fill the grain and the junction between the grain and corium to improve the leather break. The characteristic colour of the tannage is changed by these products, and the leather grain made more uniform in preparation for finishing operations.

Leather softening

A variety of products are used for fibre lubrication and softening by preventing the leather fibres sticking together on drying.

THE FATLIQUORING PROCESS

A fatliquor is an oil, chemically treated so that it will emulsify with water to penetrate and lubricate the leather fibre structure. The deeper this penetration the softer the leather, but the greater the tendency for a coarse break. However, these leather making properties are strongly dependent upon the raw oils used - synthetic, fish, vegetable, animal, tallow and even greases. These oils are generally sulfonated or sulfited to ensure good self-emulsification.

A leather with a soft, plump chrome tannage will not require as much fatliquor as leather produced by a firm tannage. Vegetable tanned leathers need little fatliquor for softening when compared with chrome leathers.

POLYMERIC SOFTENING

Water soluble acrylic polymers of high molecular weight can be modified for leather softening. These products can be made chemically active so as to combine with collagen, providing good light fastness, heat resistance and improved physical properties. In practice they are used in combination with reduced offers of fatliquors.

WATERPROOFING

Modified acrylic polymers with long molecular side chains can be used to soften and develop waterproofing properties in suitably prepared leathers. These products often incorporate silicon oils in their structure, but under carefully controlled conditions can form an emulsion in water and penetrate the leather structure. Acidification deactivates the emulsion, and the water repellent properties normally substantiated by chrome fixation.

Special effects and process variations

Specific properties can be introduced. For heavy duty walking boots hot waxes and grease can be drummed into the leather. Complete dye penetration or two tone effects can be managed. Very level dyeings are possible by processing the leather to the dry state, then after sorting and grading, re-wetting and re-dyeing.

The sequence given can also be broken. Fatliquors can be added both with and before retannage. Sometimes neutralisation and dyeing are performed together, and can include retanning agents. Different floats can be used with each process stage, or multi-addition processes used.

Panel 8

Processing pre-tanned hides & skins

After being shaved to substance, the processing of pre-tanned hides and skins *(Part 5)* can be completed by a combination tannage process that includes dyeing and softening. For chrome-free automotive leathers high levels of specialised syntans and acrylic resins are often used, together with vegetable tanning materials, fatliquors and polymeric softening agents. Chemical offers tend to be high, but the processing time is shorter than required for normal tanning as the skin structure is relatively thin and enables rapid chemical penetration.

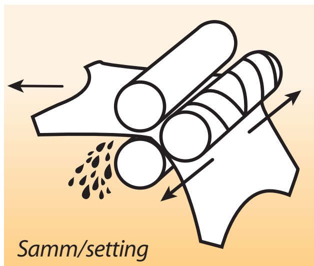
High offers of vegetable tanning extracts and lower levels of the other components can produce leathers showing typical vegetable tanned characteristics.

Chrome leathers may be produced by a rapid chrome tannage, followed by conventional retanning and softening.

Part 8

Drying and Pre-finishing Operations

After the retanning, dyeing and softening processes, the leathers are removed from the processing vessel, stacked to avoid creases, and water allowed to drain from the skins. In preparation for drying, excess moisture is mechanically removed. Hides of high substance are sometimes offered to a sammying operation *(Part 5)* to squeeze water from the leather, and sometimes small skins are centrifuged. This dewatering is then followed by the setting operation, where the damp leather is stretched using the action of blunt, angled blades mounted on a rotating cylinder to remove pleats and creases.



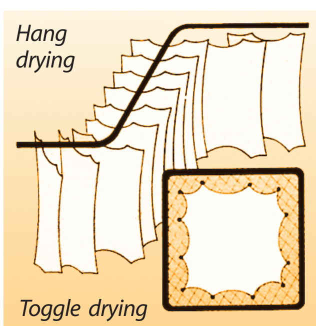
Samm/setting

The most commonly used method, however, known as samm/setting, combines a light sammying with the setting operations.

Drying leathers

The techniques used in drying leathers, and the associated mechanical operations, need to be in harmony with the techniques used in the earlier wet processing stages to create a well balanced leather. There are several key factors to take into account:

- Rapid drying will tend to give a harder product and slow drying will give a softer, more mellow leather.
- The greater the tension applied to the leather in drying the firmer the leather.
- The greater the compression of the leather (either created before drying or during drying) the firmer the leather.
- More gentle conditions assist an improved grain break.
- Tension maintained in drying is conducive to a greater area yield.



Hang drying

Toggle drying

HANG DRYING

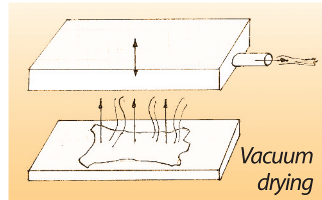
A tension-free suspension with a slow drying will produce a very soft leather, with a tight break, but a significant reduction in area.

TOGGLE DRYING

If the leather is to be firmer and show better shape retention the leather can be dried out under tension. This may be done by stretching the leathers on a wire frame and holding in position with clips, a process known as toggling. The greater the tension and the faster the drying, the firmer the leather.

VACUUM DRYING

Leathers are placed grain down onto a smooth, heated, stainless steel plate and an air tight seal formed with a mechanical hood. The air pressure is reduced using a vacuum pump causing the water to boil rapidly out of the leather at a reduced temperature.



Vacuum drying

This method produces leather with a smooth grain; however, unless the vacuum drying temperatures are low (45°C), the leathers can become hard and thin. It is therefore normal practice to part vacuum dry the leathers, completing the drying either by tension-free hanging or light toggling.

PASTE DRYING

A method successfully used with some lower quality cattle hides is known as paste drying. The leather is applied grain side to a glass plate covered with adhesive to hold the leather, then dried. The rate of drying is carefully controlled by regulating both the temperature and relative humidity in the drying chambers. When dry the leather is peeled from the glass frames.

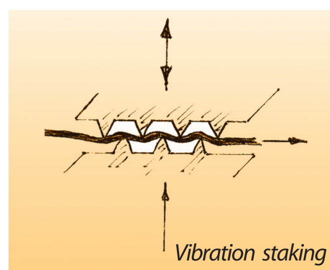
Conditioning and staking

After drying, the leathers often lie for one to two days to reach an equilibrium. There is a relaxation of the structure and migration of free moisture and oils in this 'ageing' period. The properties of the fatliquors and softening agents used significantly affect the degree of migration during drying and in this period.

The drying causes a bringing together of the structure resulting in fibre-sticking, so a mechanical softening processes is needed for almost all leathers. Normally the leather is slightly damped, usually by a water spray, and stacked in piles and left to achieve moisture equilibrium through the leather. This operation is known as 'conditioning' and usually increases the moisture content to 25/30% in preparation for softening.

This operation is carried out using a staking machine where a strong flexing/stretching action is applied to the leather. This flexing loosens the sticking fibres to provide the softness needed in the final material.

In the staking operation the moisture in the leather acts as a fibre lubricant and helps to prevent damage to the leather structure. A slow drying follows, either under tension or tension-free, often using a vacuum drier to produce a smooth surface, reducing the moisture content to about 16%.



Vibration staking

Leathers are normally inspected and graded after these operations according to quality of grain, softness, colour, and suitability for customers' specification. This is termed crust sorting and the leathers are now ready for the finishing processes.

Part 9

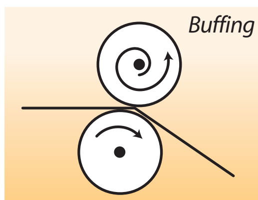
Leather Finishing

Leathers are finished to enhance their appearance, and to offer a higher degree of grain layer protection when in use as clothing, footwear, leathergoods or upholstery.

Full grain and corrected grain leathers

Where the grain is of good quality, the finish can be directly applied, perhaps after a vacuum drying for grain flattening. These leathers are known as “full grain” and are generally lightly finished so that the grain characteristics are developed as opposed to covered.

Bovine leathers for shoe uppers or automotive use that have a poor quality grain are often buffed to form a surface of improved uniformity and are termed corrected grain leathers. Buffing is carried out by feeding the leather grain against a rotating cylinder covered with emery paper. This operation buffs away the top layer of the grain and any small irregularities, producing a smooth surface for finishing.



Dust produced by buffing must be removed from the leather either by a brushing machine or by air blast.

Normally a colourless emulsion of soft acrylic resin is applied to the buffed grain to penetrate deep into the grain layer. This process is known as impregnation, and fills and supports the grain to improve the break. After drying, plating and a light re-buffing, a uniform surface is formed that enables heavy finish applications. Impregnation can also be used for improving full grain leathers, although the finish application remains light.

Nubuck leathers are also buffed on the grain, and suede leathers on the flesh side of the skin. The coarseness of the emery paper largely determines the length and fineness of the fibres, which is called the ‘nap’. Chamois leathers receive a similar type of treatment known as dry wheeling, and this is performed on the flesh side of clothing leathers for softening and cleaning.

Aniline and pigmented finishes

Many leathers have simple finishing techniques: suede and nubuck leathers may be sprayed with special dye solutions to match a colour pattern and treated with water repellent agents for protection against water spotting. Leathers for a waxy texture may be treated with blends of oils, waxes or greases to give a specified feel to the leather, and sole leathers may be rolled under pressure to compress the fibres.

Aniline finishes consist of a transparent film containing dyestuffs to adjust the shade to pattern. It is essential to be able to see the grain of the leather through the finish and retain the natural appearance of the leather so no pigments (insoluble colouring materials) may be used in the finished formulation.

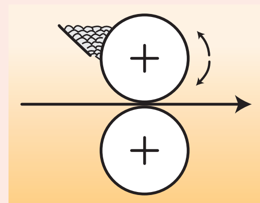
Some leathers are not entirely suited for this type of finish although they may be of reasonably high quality. In this instance

Panel 9

The mechanics of finishing

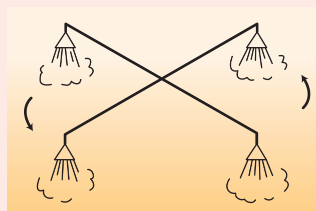
Finishes are sometimes applied to leathers on flat tables using labour intensive hand padding operations. However, almost all finish applications use two types of precision machine for accurate dispensing:

The roll coater



These operate on the principle of transferring the finishing material offered to an engraved roller onto the leather. The leather is presented to the roller by a feed-belt, with the finish application determined by the depth of engraving, the setting of a doctor blade and direction of rotation of the top roller. Special effects - shading, tipping and clouding - can also be developed by forward roll coating.

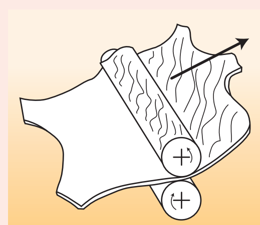
The spraying machine



The leather is conveyed under a series of spray guns, with micro processor devices ensuring that the spraying only occurs when the leather is positioned under the spray area. The systems employ either 4, 8 or 12 guns carried on rotating arms, or 2 or 4 guns reciprocating in a straight line. The feed systems and machine controls can ensure repeatability of a given process.

Both roll coating and spraying are feed through systems, and each application stage is completed by a controlled tunnel drying. These operations can be rationalised, and often there is more than one unit in a line, with the leathers being handled at take-off by stacking machines.

Ram and roll pressing



Hot roll pressing or ironing is used to press the leather grain during finishing. The finish film, being thermoplastic, softens and flows forming a smooth flat surface on the grain of the leather. Ram pressing employing a large heated plate is an alternative technique, although it does not provide the advantages of a feed through operation. The smooth rollers or plates can be changed for engraved ones so that a huge range of patterns can be printed or embossed into the leather grain.

Panel 10

Leather specifications

There are many applications for leathers, and each use demands its own specification. Although many agreed standards and limits are established, additional requirements are commonly set by the individual leather product manufacturer. These are mainly in line with traditional values expected of leather items, including properties needed in the manufacture of goods, but increasingly they address consumer or marketing based concerns or demands.

However, leather is increasingly being used in multi-fabric construction, so that added properties are needed to synergise with other materials - i.e. colour fastness or non-migration when combined with clothing fabrics.

Other uses are found as basic components in direct competition with alternative materials i.e., in the automotive sector. In this situation the leather properties are strongly influenced both by the physical properties offered by these competitive materials, and the unusual demands expected by owners of very high value products - not by values that might first be associated with leathers.

Panel 11

Changes in finishing technology

Finishing techniques are subject to rapid change, so generalisations often become outdated. For example, rapid changes in fashion and intense competition have demanded softer shoe upper leathers with greater emphasis on texture and tactile properties. These softer, higher substance leathers cannot carry a high degree of finish without a reduction in the 'break' of the leather. To enable a lighter finish for a high value natural look, the accuracy of dyeing and quality of colour matching has developed to the niche standards previously found with high quality clothing leathers. However, these lighter finishes are also expected to perform to the standards expected of traditional upper leathers which were more heavily finished, thus creating new challenges in leather and finishing technology.

The physical properties of automotive leathers have now been driven to levels that until recently would have been considered very extreme. Engineering demands have stimulated finishing technology for leathers that are highly durable, precisely colour matched, totally uniform, and fully compatible within multi-fabric automotive seat construction.

a small quantity of pigments of ultra-fine particle size are added to the finish formulation. These partially cover or mask minor blemishes and leave the skin with a natural appearance. This is termed semi-aniline or aniline assisted finishing.

Heavier finishes are usually applied to lower quality full and corrected grain leathers. The film formed mainly consists of pigments and binders thus providing good cover. The binders lock the pigments within the film, bond with the grain layer, and provide protection.

Finishes to meet customer needs

Most finishing techniques are, however, more involved and developed to suit precise marketing requirements. The final leather must match a standard pattern in colour, texture and brightness of finish. Good standards need to be met, so the finish must be stable under wet and dry conditions and have good scuff resistance. The finish must be able to stretch with the leather and be compatible with the demands of footwear, clothing, leathergoods, furniture and automotive manufacture and consumer use.

After suitable preparation, the first coat of the water based finish is applied to the grain by roller coater or spraying machine. This coat is dried to form a continuous film, and a second or third coat applied. After drying, this finish may be hot rolled, pressed or plated to develop a very smooth surface.

Each film developed within the finish may differ from others within the formulation. Usually the first film is relatively soft with good adhesion, each layer becoming progressively harder so that the top coat provides good wear resistance. Plating may occur between finish coats, and be varied so that patterns may be embossed into the leather to give numerous effects and grain textures.

This is generally followed by spraying a top finish to improve wear resistance. Specialised top sprays of waxes or silicones may be given to enhance the feel, handle or tactile characteristics of the grain surface. There are also many auxiliary products included in the formulation to assist in finishing operations and develop specific properties in the finish film.

Finishing technology

Finishes are available from specialist suppliers. The binders available can include proteins and resins based on polyurethanes, acrylates and butadiene. Polyurethanes are very durable, and are used chiefly for upholstery, clothing leather and high property shoe leathers. Nitro-cellulose finishes are also employed to form hard wearing, high gloss top coats. Sometimes solvent soluble, these are now largely replaced by specialised water based finishes for environmental reasons.

Cross linking systems are also highly developed, where catalytic agents activated by high temperature or ageing are added to the system. The reactions between the resins and catalysts improve the properties of the finish to develop very high resistance to abrasion under both dry and wet conditions.

Foam based finishes are also available. The finish contains acrylic and polyurethane products, and the foam is usually mechanically generated. Because of the low water content, comparatively large amounts of finish can be applied without wetting the leather, thus maintaining a soft handle. Alternatively, chemically generated foams can be used to apply exceptionally heavy coating of cross linking finish for very high cover and abrasion resistance.

Conformity and dispatch

The final stage of leather manufacture comprises inspection against standard patterns, with conformity to standards, and grading for quality. Some manufacturers, such as automotive suppliers, provide leathers as cut and graded components, but generally leathers are measured for the selling area and dispatched for delivery.

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