PROCESSING DIFFERENCES REQUIRED FOR DIFFERENT LEATHERS CURING

Curing is the process of dehydrating the hide without disturbing the skin structure. This is necessary because within hours of slaughter, decay begins. Hides and skins need to be protected against excessive heat, humidity, rain and pests during the curing process. Preparing hides begins by curing them with salt or any other method appropriate for the area. Curing is employed to check putrefaction of the protein substance (Collagen) because of the chance of bacterial infection due to the time lag that might occur from procuring it to processing it. It removes the excess water from the hides and skins where water flows from inside because of difference in osmotic pressure. Thus the moisture content of hides and skins get greatly reduced. In wet-salting, the hides are heavily salted, then pressed into packs for about 21 days. In brine-curing the hides are agitated in a salt water bath for about 16 hours. Methods employed for curing greatly make the chance of bacterial growth unfavorable. Curing is also done by preserving the hides and skins at a very low temperature.

Before starting the processing, the hides and skins are sorted preferably of uniform grade, weight or size and having been packed and the number on each pack noted. Attention should be given to factory safety precautions and personnel must be made aware of dangers of infections such as anthrax by display of notices emphasizing initial symptoms which can lead to rapid diagnosis.

Water

Tanneries use large quantities of water and are not only with problems of an adequate of clean cold water but also with the disposal of large quantities of dirty water (effluent). Approximately 50% of the water used is for washing purposes. Modern drums and hide processors can reduce materially this usage.

Tannery water is supplied by municipal mains supply, springs, bore-holes, wells, rivers, lakes or ponds. These are seldom pure. River or surface water may be badly contaminated with bacteria, mould and fungus spores and dirt which may subsequently infect the skins in such processes as soaking and washing

Soaking

Introduction

Correct soaking of the raw hides and skins is the foundation of beamhouse processing. This process must be optimized for the condition and origin of the hides or skins being worked. Errors or omissions made here will give rise to basic faults such as draw, poor grain and handle characteristics which cannot be corrected later in the leather making process. Soaking is the process of rehydrating the cured Hides in water to return them to their original flaccid condition,

remove dirt, salt and some soluble proteins. The purpose of soaking hides and skins before liming is more than just the simple rehydration of the raw material.

The raw hide as presented to the tanner will consist of the following

- Dirt, blood
- Epidermis, hair
- Collagen
- Elastin
- Subcutaneous tissue
- Non-structural proteins
- Fat
- Water
- Salt in the case of salted or brined hides/skins other preserving agents may also be present.

The purpose of soaking

- Rehydration of the hide
- Removal of preserving salts
- Removal of dirt and blood
- Removal of unstructured proteins and proteoglycans
- Attack on epidermis structures
- Slackening of the subcutis
- Optimum preparation of the hide for the subsequent process

Good soaking is a vital precursor to unhairing and liming. It is an important factor in optimizing the fibre opening up characteristics during liming resulting in flatter pelts with clean grain and increased area yield.

Liming

The purpose of liming is to uniformly open up the fibre structure and to remove the hair and epidermis. Correct liming procedure is vital for the production of flat, tight and mellow leathers. Incorrect procedure will produce leathers with excessive draw, deep growth marks and uneven tanning and post tanning processes. Liming produces an effluent which is obnoxious and expensive to treat.

The liming process is so important that it opens up the collagen fibre by the alkaline swelling of the structure and further pulping of the hair/epidermal protein (keratin) occurs by the reduction of the disulphide bridges under the influence of alkali. This should be achieved without producing undesirable effects like looseness in the belly areas. Hair root is expected to be loose and can be easily removed later during deliming and bating operations. The liming process should also optimize substance and area yield within the possibilities of raw stock being worked.

Process vessels for liming and vessel loading parameters

The choice of the vessels should be the same as for soaking with drums and mixers being favoured over paddles because of lower water requirements. A good liming vessel should;

- Be easy to load and unload
- Be automated
- Be easy to be inspected regularly

Control of temperature is important in liming. The liming temperature should not exceed 28°C with 25°C-26°C being normal. Higher temperatures in liming will reduce physical properties such as tear and grain strength and in extreme cases result in leather which is unusable. In some areas, the incoming water exceeds these recommended temperatures and it is recommended that ice is added to the vessel to reduce the temperature. Liming at temperatures below 25°C-26°C will show an increasing tendency to scuddy and drawn grains.

For the liming process, the vessel loading should be such that the bulk of the goods are covered during the stationery process periods. Under the influence of the alkali, the hide or skin will swell absorbing water and reducing the effective float level and this should be taken into account when checking float levels. Practice indicates that a final float level of around 120-150% on wet salted hides and 200-300% on wet salted skins is required to achieve the condition depending on vessel type and shape. The ideal conditions of any vessel are best arrived at by trial as the indicated maximum physical capacity of a given vessel is not always the optimum processing capacity taking into account different hide weight and area ratios.

The aim of most tanners is to achieve the best possible limed pelt in as short a time as possible, usually 24hrs including soak time. The use of simple recipe such as 2.5% sodium sulfide and 3% lime will perform the basic requirements, removal of hair/epidermis by pulping or hair burning, and plumping or swelling of the hide structure. However direct and uncontrolled application of these chemicals over a short period of time will cause rapid and premature swelling of the grain resulting in trapped hair root and wrinkles or lime draw. The following options should be considered when there is need to improve the quality of liming process;

- Extend time of process, reduce offer of chemicals and make additions over longer periods of time to reduce alkali shock to the grain.
- Reducing alkalinity by use of sodium hydrosulfide to replace all or part of the sodium sulfide offer thus reducing the caustic alkalinity and the effects of rapid alkalinity increase.

- The use of liming auxiliaries to control alkali swelling and to improve the solubility of the lime producing more uniform swelling and opening up of the fibre structure resulting in a smoother, flatter and cleaner limed pelt.
- The use of suitable surfactant/emulsifiers to prevent fat deposits on the grain which prevent uniform lime penetration leading to drawn grain. Emulsifiers also promote scud release helping produce clean bright wet blue.
- Special enzyme preparations able to work at high pH to accelerate fibre opening up and also disrupt sebaceous grease layer resulting in faster, more uniform penetration of lime and subsequent process chemicals.
- Combination of some of the above options together with a hair saving liming procedure.

A hair pulping liming process which will meet the demand of modern leather fashion i.e. soft tight and smooth grained leathers with good strength may be achieved with a combination of the above stated options and enzymatic soaking.

Process	%	Chemical	Temp.	Time/mins	pН	
Load + Dirt soak	150	H ₂ O	28°C	30-60		Drain
Main soak	120	H ₂ O	28°C			
	0.5	Sodium carbonate				
	0.25	Non-ionic emulsifier				
	XX	Enzymatic soak agent		240-360	9.5-10.5	Drain
Wash	100	H ₂ O	26°C	10		Drain
Lime	100	H ₂ O	26°C			
	1.0	Liming auxiliary				
	1.0	Sodium hydrosulfide 72%		45		
	0.2	Non-ionic emulsifier		60		
	50	H ₂ O	26°C			
	2	Lime		30		
Run on automatic stop - 50mins/run 10mins for 12-14hrs						Drain
Wash	100	H ₂ O	26°C	15		Drain
Wash	100	H ₂ O	26°C	10		Drain
Take out for fleshing						1

Typical soak and lime process for wet salted hides. % based on wet salted weight.

The whole including soaking, fitting into a 24hr cycle, shorter liming times may be possible but in general 24hr processes fit into most tannery working schedules. The objective of these procedures is to produce a process in which the increase in alkalinity are gradual and controlled avoiding sudden jumps in pH but at the same time producing a fully opened up structure and clean smooth grain. Control of the alkali swelling is the function of the liming auxiliary and many such products are available. In addition, the use of sodium hydrosulfide is favoured to replace fully or partially the sodium sulfide and thus reduce the caustic alkalinity available from the dissociation of sodium sulfide in water. A small addition of sodium carbonate or sodium sulfide may be made together with the final lime can be used to check and control the final degree of swelling achieved depending on the type of leather being produced.

Hair saving liming

The hair saving type of liming is normally done to address the environmental demands made on the tanner to have to look for more fully at processes which produce less waste water contamination (COD, sulfide, nitrogen) without compromising the quality of the limed pelt. In this process, the hair is immunized i.e. transformation of the cystine into lanthionine by pretreatment with alkali, normally lime and at the same time the hair root area is prepared for destruction by an auxiliary product.



This has the effect of rendering the hair shaft keratin resistant to reduction by sulfide but the presence of the auxiliary prevents accidental immunization of the root area in the event of breakdown etc. smaller additions of reducing agent then attack only the prepared root area causing the rest of the immunized hair shaft to be released intact. This intact hair may continually be taken out of the vessel by circulation through a screening system. The resulting hair may be used for composting in fertilizer compounds or dumped to landfill.

Process	%	Chemical	Temp.	Time/mins	pН	
Load + Dirt soak	150	H ₂ O	28°C	30-60		Drain
Main soak	120	H ₂ O	28°C			
	0.5	Sodium carbonate				
	0.25	Non-ionic emulsifier				
	XX	Enzymatic soak agent		240-360	9.5-10.5	Drain
Wash	100	H ₂ O	26°C	10		Drain
Immunize	120	H ₂ O	26°C			
	1.0	Liming auxiliary				
	1.5	lime		60		
Hair release	1.0	Sodium hydrosulfide 72%				
	0.2	Non-ionic emulsifier		20 stop, 90		
Lime	30	H ₂ O	26°C			
	1.5	Lime				
	0.5	Sodium sulfide 62%		30		
Run on automatic stop	- 50mins/	run 10mins for 12-14	hrs			Drain
Wash	100	H ₂ O	26°C	15		Drain
Wash	100	H ₂ O	26°C	10		Drain
Take out for fleshing	1	1	1	l	I	1

Paint unhairing.

The washed, deburred or soaked skins are piled to drain off surplus water. The amount of water in the material can be critical. Too little impedes the action of the paint whilst too much reduces the viscosity of the paint, dilutes the chemical therein and, when these contain or produce caustic soda, causes swelling of the skin and possible grain distortion or weakness. Allow the mixture to age overnight to reach a state of equilibrium whereby the lime particles become fully hydrated and finely dispersed. This increases the viscosity of the paint to a suitable consistency for application

0.1 - 0.15 alkali-stable non ionic dispersant	Make a paste for every 10 parts of water (8°-
5 – 20% Sodium sulfide	15°Be). Coat on the flesh side using nylon
5 – 20% hydrated lime	brush resistant to paint chemical.

The painted skins are then piled until such time as the hair or wool loosens. With sheepskins, it is important that the valuable wool is not contaminated with paint which may pulp the wool or, at least spoil its strength and feel. Woolskins may be paired flesh to flesh, stacking the pairs 3-4

feet high. Too high piles may lead to overheating due to bacterial activity from dirt on the wool. Temperatures in the pile of over 30°C will cause grain damage and skin weakness. Each painted skin may be folded along the backbone, flesh in, and then piled. After piling, the wool is pulled, usually by hand and graded. This process of separating wool is usually carried out by separate establishments known as fellmongeries or pulleries. In case of hair not for use it may be scrapped off with a curved blunt unhairing knife on the beam or by an unhairing machine.

The unhaired pelts must then undergo a modified liming to remove unwanted proteins and prepare them for fleshing. The liming liquor is prepared without the unhairing chemicals.

Deliming and Bating

Deliming; The purpose

Process	%	Chemical	Temp.	Time/mins	рН	
Wash	120	H ₂ O	30°C	20		Drain
Wash	120	H ₂ O	30°C	20		Drain
Wash	120	H ₂ O	30°C	20		Drain
Delime	30	H ₂ O	30°C			
	1.5	Ammonium sulfate				
	0.1	Non ionic surfactant				
	0.3	Sodium bisulfite		45		Drain
Delime	50	H ₂ O				
	3.0	Ammonium sulfate				
	0.2	Non ionic surfactant		90	8.0-9.0	
If pH is higher than 9.	0, add mo	re ammonium sulfate.	. If pH is	good but pen	etration is	Drain
poor, run for longer tir	ne. If cond	lition is satisfactory, c	ontinue	to bating		
Bate	80	H ₂ O	35°C			
	XX	bate				Drain
Wash	100-200	H ₂ O	>26°C	10		Drain

Weigh the fleshed material

Pickle

The purpose is to reduce the pH of the pelt for a subsequent chrome penetration.

Pickling basic types

- a) Equilibrium pickling
- b) Light pickle
- c) Short pickle

Pickle (drum)	30-40	H ₂ O	<26°C			Check
	7	Sodium chloride		10		8°Be
	0.3	Formic acid (1:10)		15		
	0.8	$H_2SO_4(1:10)$		60-90	2.5-2.8	
Tan	3	Chrome (33% basic)				
	0.4	Electrolyte stable fat		30		
	3	Chrome (33% basic)				
	0.7-1	Sodium phthalate		120		
	0.3	Magnesium oxide				
	0.4	Sodium acetate (1:5)		120		
	0.4	Sodium acetate (1:5)		120	Float 3.8	

The leather may now remain in drum overnight. The following morning the bath may be flooded with 30-40% water at 40°C and the stock run for 30mins before piling. Instead of overnight tanning, the process may be continued by flooding the bath with 30-40% water at 35°C and drumming continued for another 60-90 minutes.

If the wet blues are expected to be stored in the tan yard for a longer period, it is advisable to add some disinfectants (0.05-0.2) to the flooded bath. The stock is finally piled. The float pH at the end of tanning is 3.8-3.9 and the final bath temperature is approximately 40° C.

Magnesium oxide basification has the advantage of sparing the efforts by the tanners to fix chrome salts by periodic additions of alkalis to the bath. Owing to their limited solubility magnesium oxide, dolomite (MgO, CaCO₃), when added in calculated amounts will adjust the end pH of the tanning bath to very near the desired level. There are however, other mild acting alkaline salts which are equally effective for the grain leather e.g., a solution of sodium bicarbonate (0.5-1.0%) buffered with sodium acetate (1.0-1.5%) or sodium sulfite (0.5-1.0%) or sodium formate. These basifying salts are dissolved in water (5-10 times on the salt weight) and the solutions added to the chrome bath in 2-3 portions at an interval of 10-15 minutes. A mixture of equal parts of sodium phthalate, sodium formate and sodium bicarbonate can also be used with excellent results. The objective of the chrome basification is to gradually raise the original pickle pH of the bath from 2.6 uniformly to 3.8 or up to 4 depending on the type of finished leather in view, e.g., a grain leather or suede.

AFTER TANNAGE

Removal of surplus tan liquor – It is common to allow excess tan liquor to drain from the hides or skins after tannage, and to stand them in a damp condition for a day or more. With most tannges, further fixation and setting of the fibres occur. Common methods are;

1. Horsing up – Traditionally made of wood but may be made of light non corrosive, non staining material (e.g. plastic) and it may sometimes be on wheels for easy movement. It

is commonly used for skins and side leathers. The pack is usually covered to prevent surface soiling and drying

 Piling or cessing – The butts or bends for sole and heavy leathers are piled on a wooden stillage or pallet and often covered to prevent over drying of the surface or the edges of the pile.

Sammying and Setting – Water content is reduced to about 40% with the use of a combined sammying and Setting out machine which stretches out the leather, smooth the grain side and reduces the water content.

Reducing thickness – Depending on the intended use of the tanned leather, thickness is reduced to produce different layers which can be used differently or simply reducing the thickness. Reduction is done to reduce the excess usage of chemicals in the proceeding processes on parts which will not be used. Different methods of reducing the thickness are by;

- 1. Splitting Done using a band knife splitter
- 2. Shaving Done on the uneven thickness of hides or skins to make them even

RETANNAGE

Shaving or splitting to substance 1.2 - 1.7mm

Process	%	Chemical	Temp.	Time/mins	pН	
Wash	200	H ₂ O	50°C			
	0.2-0.3	Non ionic degreasing and		10		Drain
		dispersant agent				
Retan	100	H ₂ O	50°C			
	1	Cr ₂ O ₃ 50% basic		30	4.0/4.2	
	2	Phenolic syntan			neutr to 6.5	
	1	Sod. Formate			using Sod	
	2	Mimosa extract		20	acetate	
				20		
	1	Electrolyte stable				
		fatl (60% fat)		25	4.5-4.8	Drain
Wash	200	H ₂ O	50°C	10		Drain
Dye	150	H ₂ O	60°C			
	0.5	Dye leveling syntan				
	1	Dye stuff				
Fatliquor	4.5-8.5	Fatliquor		45	4.2/4.3	
If necessary adjust the pH and exhaust the fatliquor by adding 0.1-0.15% formic acid. Increase						
mimosa extract from 2% to 4% for corrected grain leathers. After fatliquor, the leathers are						
rinsed with cold water for 5 mins and horsed up or piled.						

The following morning, set out, vacuum dry for 1.5 mins at 80°C, toggle dry for complete drying, stake, condition and vacuum dry again for half a minute at 80°C. The leathers are now ready for finishing or grain correction as the case may be.

Preparation of leather before finishing

Before finishing, the leathers should be sorted out to examine their nature in order that correct formulation of leather finish, the application method and the drying conditions are carefully determined. The desirable characteristics of leather prior to finish are:

- 1. The leather should have a flat, smooth grain with a fine break, tight flanks and even substance.
- 2. The grain surface should not be excessively greasy. Greasy grains will cause inadequate anchorage of the finish, poor coverage and streaky appearance. In addition, the fat migrates to the finish layer when the leather is subsequently hot plated.
- 3. The leather meant for corrected-grain finish should have a uniform buffed surface.
- 4. The leather should not be too absorptive.
- 5. The leathers must be well laid out to facilitate brushing, padding and spraying operations

Buffing – The purpose of grain buffing technically known as grain-correction is to refine the grain by buffing off the upper layer of the grain. In this way the large craters of the hair follicles are leveled to the extent that they become flatter and smaller.

Accumulated fatty materials on the grain during fatliquoring usually cause trouble which a finisher often encounters in the finishing room. These fatty matters adversely affect the adhesion and evenness of the subsequent finish film. Anionic clearing coat consisting of liquor ammonia, methylated spirit, anionic wetting and dispersing agents, plasticicers etc. may be used. Heavily greased leather may require further addition of ethyl glycol or methylated spirit or any other suitable alcohol.

Typical examples are:

1. Sealing coat for corrected grain leather;

a)	Cationic oil emulsion	75 – 100parts
	Basic dyestuffs (if necessary)	0-5 parts
	Water	900
b)	Suitable anionic dyestuff	0 - 20parts
	Dissolved in water	300parts
	Cellosive (ethylene glycol monoethyle ether)	25 - 200parts
	50% turkey red oil	20 - 50parts
	10% wax emulsion	0 – 50parts
	Acrylic resin binder (soft type)	30 - 150parts
	Water to make	1000

2. Cleansing coat for full grain leather

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Preparation of the finishes

Leather finishing comprises a series of operations done towards the concluding stages of leather manufacture and are meant to impart such essential qualities which qualify them to be defined as finished leathers. These elaborate operations dress up the leathers to suit varying requirements of the end product.

There are a number of auxiliary finishing chemicals which are added to the prepared dispersion of pigments, dyes and binders. The principal function of these added auxiliaries is to modify the finish to aid uniform application and to achieve those characteristic qualities which mostly appeal to the sense of comfort, feel and handle giving an added value to the leather. The most important among the auxiliaries are:

- a) Wetting, leveling and flow controlling agents (especially water-based finishes)
- b) Finish thickeners (methyl cellulose or other polymer resins) mostly required for controlled penetration of finishes
- c) Auxiliary additives which modify the feel and handle of the leather in order to give an appealing sense of touch. These auxiliaries are mostly based on oils, waxes, silicones in an emulsified form.

Finishes should be prepared in the following order of additions

- a) Pigment pastes and aniline dyes
- b) Plasticicers of the soluble oil type
- c) Protein binder thoroughly mixed with wax emulsion when desired
- d) Mucilage, thickeners (if desired)
- e) Water for dilution (preferably and demineralized water)
- f) Resin dispersion binders
- g) Fixatives (formaldehydes)
- h) Preservatives (para-chlor-meta-cresol.)

The water for dilution should be added with constant stirring, starting with very small amounts. When the finishing solution has been prepared, it should be strained through a tightly woven nylon filter cloth or through a brass sieve of 0.08mm mesh. The finish is now ready for application

Preparation of desired quality of leather

Shoe upper, waterproof 1.6mm (acrylic syntan retanning)

Raw material; wet blue bovine hides, shaved to 1.5-1.6mm

Process	%	Chemical	Temp.	Time/mins	pН	Action
Wash	200	H ₂ O	35			
	0.2	Formic acid		10		Drain
Neutralize	100	H ₂ O	35			
	1.7	Sod. Tetraphosphate				
	0.1	Sod. bicarbonate		90	4.5	Drain
Wash	200	H ₂ O	35	10		Drain
Retan/Dye & fatliquor	50	H ₂ O	35			

% based on shaved weight

Pg462

Recipe for full chrome gloving leather

Raw material – Wet Salted Wool sheepskins 28" – 36"

Determine raw weight of the materials

Pre-soak	Add		
	400%	Water@25 [°] C	In pit. 1-2hrs, drain bath, pile to drain
			excess water
Main soak	400%	Water@25 [°] C	In pit
	0.2%	Soaking auxiliary	
	0.2%	Sodium	Overnight in bath, break over the beam.
		trichlorophenate	Take soaked weight
Painting	1 part	Na_2S conc.	28^{0} Be'; The lime paste is applied on the
	2 parts	Slaked lime	flesh, folded along the backbone and
	3parts	China clay	piled 4-5 hrs.
	8parts	Water	Dewool
Liming	500%	Water	
	0.5%	Sodium sulfide conc.	2 days in pit or paddle, turning skins for
	5%	Slaked lime	5mins, morning and evening. The
			percentages are calculated on soaked
			weight. scud
Plumping	300%	Fresh water	3 days in pit or paddle, turning skins for
Relime	150%	Previous lime liquor	5mins, morning and evening. The

	3%	Slaked lime	percentages are on soaked weight. Flesh,
	0.2%	Non ionic emulsifier	scud & rinse in soft water for 15mins.
			Determine pelt weight.
Deliming & bating	250%	Water	
	0.7%	Lactic acid (80%)	Drum 10mins
	1.5%	Suitable bate	The temperature of the bath should be
	50%	Water	35° C. The pH during bating period
			should be maintained @7.8-8.2 for 3-
			4hrs; if preferred, overnight bating in
			which case the temp. of bath should be
			between $28-30^{\circ}$ C. Drain and rinse
Diabilina	200/	Water@25 ⁰ C	10mins.Scud if necessary
Pickling	80%		Run 10mins.
	10%	Salt	Run 10mins.
	0.8%	Sulfuric acid (1:8)	
	1.2%	Acetic acid	Deep Ohne with stanlafe with Orescher
Decement	20%	Water	Run 2hrs, pile, stock for 1-2weeksRun 30mins
Degreasing	20%	Kerosene oil	
	100%	Water@35 [°] C	ispersing surfactant – Run 1hr
	6%	Salt	Run 30mins then drain float
Brine wash 1	100%	Water	Run Sommis then dram noat
Dille wash i	6%	Salt	Run 30mins then drain float
Brine wash 1	Repeat as 1	San	
Chrome tanning	60%	Water	
Chrome taining	3%	Salt	Run 10mins.
	6%	Chrome alum	
	20%	Water	
	0.3%	Formaldehyde (40%)	Run 45mins.
	0.7%	Soda ash	
	15%	Water	Run 45mins.
	6%	Chrome alum	
	20%	Water	
	0.9%	Soda ash	Run 45mins.
	0.25%	Soda ash	Added in 2 feeds at 30mins interval. Run
	5%	Water	6hrs end pH 4.0 Pile 48hrs. Shave
			0.6mm. Determine shaved weight
Wash			30mins in water
Neutralize	200%	Water	
	1%	Sodium acetate	Run 30mins
	0.7%	Sodium bicarbonate	Run 30mins
	1%	Natural syntan (Naphtha	alene based) – Run 30mins
Wash			10mins in water
Fatliquor	100%	Water @50 [°] C	
	1%	Sulfited fish oil (deoduc	
	4%	Sulfited sperm substitut	*
	2%	Neatsfoot oil	Run 30mins
	2%	Egg yolk	
	1%	China clay (colloidal)	Run 30mins, drain, horse up, set out air
			dry, saw dust, stake, buff with paper
			320/400 on flesh. Wet back, dye and
			fatliquor as usual

Gloving leather

For centuries gloves have been made using leather, and it certainly is no exception today. But, Gloving leathers have dramatically changed in the last few years. Today leather can be created with multiple technologies within them, something that synthetic materials cannot achieve. It is now possible to create gloving leathers with the following properties

- i. High levels of water and perspiration (sweat) resistance,
- ii. Extremely high levels of colourfastness,
- iii. Fire retardance,
- iv. Antimicrobial properties,
- v. Soil and dirt resistance properties

Top priority should be the correct selection of raw material substrate to use. The leathers which are suitable for glove production must always be pliable, soft, and fine. Furthermore, the leather must be able to breathe to avoid humidity in the glove. The particular properties of the skins of lean, scrawny animals are normally best. Hence, most glove leather comes from dry warm countries which have limited vegetation - Ethiopia, for example. These skins very often have small scars, caused by thorns and insect bites, which are evidence of the animals' free-range life. Typically a choice of cabretta [hairsheep], goatskin, kangaroo or pigskin is preferred, the required grading characteristics to gain the correct cutting coefficiencies and ensuring quality assurance levels has to be maintained throughout the manufacturing of Gloving leathers. Bovine leathers could also be used but has a problem of reduced tear strength properties when shaving the cowhide so thin.

Types of gloving leathers in the market

- i. Baseball batting gloves,
- ii. Baseball catchers mitts,
- iii. Cycling gloves,
- iv. Dress & Fashion gloves,
- v. Golf gloves,
- vi. Law Enforcement gloves,
- vii. Military gloves,
- viii. Ski gloves,
- ix. Snowboarding gloves etc

Requirements for water proof shoe upper leather

Shoe upper leather is used for making shoes which if not water proof will get soaked with sweat when worn for a long time. In contrast, the trekking boot is made of state-of-the-art waterproof leather. Ramblers can walk quite long distances in these shoes and the feet stay comfortable in spite of perspiration even in the rain, even when walking in a meadow moist with dew, which is a very harsh test for the water resistance of shoes. The aim of processing waterproof leather is to produce leather which has an appealing appearance and results in shoes or motorbike garments etc with high wearing comfort even under wet and cold conditions. Leather should act as a second breathing skin. The skin protects humans against external influences. However, it also allows the body to regulate its temperature by perspiration. Waterproof leather literally stands for leather which water doesn't penetrate. However, the leather should allow additionally high water vapour permeability and some reversible water up-take to remove perspiration from the foot. The leather should insulate against heat and cold and be lightweight.

The common testing procedure for waterproofness

- i. The static tests of the life time of a water droplet,
- ii. Kubelka water up-take and the soaking up test
- iii. The dynamic tests, Bally penetrometer and Maeser value

Leather which has absorbed too much water loses its ability to insulate against heat and cold. Therefore, waterproof leather should not take up more than 25-30% of water. The dynamic tests Maeser flexometer and Bally penetrometer and their comparability are intricate because - depending upon the customer requirements - different modifications are done. Often the customers' needs deviate from the official testing procedure. This request might come from the experience that waterproof values sometimes break down after buffing or finishing combined with the need for a reasonable 15-40,000 flexes in the final article.

Some general thoughts about waterproofing. If we understand how the wetting of leather takes place, then we will understand more easily how we can slow down or completely prevent this process. The wetting of leather takes place in a four-step process. The water spreads over and wets the leather surface. Then the water penetrates the leather and, thereafter, the water wets the fibre network; in other words, it wets the internal surface of the leather. Finally, due to attractive interactions between water and the leather network the leather gets soaked with water. The collagen, tanning agents, dye molecules, salts etc, which are present in the leather network, might be involved in these interactions. This chain of process steps must be interrupted to prevent the wetting of leather. A closed waterproof film can be applied in finishing. The spreading of water over the surface is prevented by the film and the leather cannot be wetted at least under static conditions. However, such films even with most modern technologies

drastically reduce the water vapour permeability. The gaps in the leather can be filled in two complete different ways: firstly, impregnation and secondly, hydrophilic waterproofing. Firstly, impregnation is a treatment of leather by molten waxes. The filling of the gaps with wax prevents the penetration of the water into the fibre network. The disadvantage is that the leather is extremely heavy and completely prevents any air and water vapour permeability. Secondly, hydrophilic waterproofing is achieved by application of certain surfactants, eg sulphosuccinates which bind to the leather and make the leather absorb a certain quantity of water. The surfactants and the water form a water-in-oil emulsion, which fill the gaps in the fibre network. Additionally, these micelles are hydrophobic on their outer side and, therefore, the gaps are filled with a hydrophobic material. Shoes, which are made of this leather, might have an excellent wearing comfort directly after being put on because the leather is absorbing sweat. However, unfavourably, the leather weight increases drastically. In addition, the breathability of this leather will cease when water has been taken up. Afterwards the shoe will be dried and the water will be removed completely and the leather will return to its original state.

Open waterproofing is the smartest approach to make waterproof leather. The internal surface of the leather is coated by a waterproof agent that binds to the fibres and fibrils through its functional groups. Waterproof agents are more efficient as the surface tension is lower. The larger the surface and the higher the surface tension is, more surface energy must be spent. A very thin coat of the internal surface is formed by waterproofing agents, which have a very low surface tension. Water vapour permeates always from the side with higher water vapour concentration to the reverse side with lower concentration, from the side with higher temperature to the side with lower temperature. Therefore, in hot and humid conditions, for example in a tropical rain forest, waterproof boots loose the ability to emit moisture. The open waterproof effect can be visualised by an example from nature. Water striders can walk and jump over water. Their tarsus is covered with numerous fine hydrophobic hairs that cannot submerge allowing the water striders to stay on water. If we put soap into this water, the surface tension of the water would decrease and water striders would sink. Similarly, waterproof leather cannot be wetted. However, surfactants cause the leather to be wetted quickly and should be strictly avoided. Actually, the presence of all kinds of hydrophilic substances within the leather might negatively influence the waterproof values of this leather by varying degrees. However, the use of dyes, synthetic and vegetable retaining agents is required to obtain the desired article with a pleasing appearance. Appropriate products and application processes ensure that the hydrophilicity, which is an inherent part of all kinds of leather treatment agents, will be masked in the final article. Salts originating from the neutralisation are hydrophilic and, therefore, their presence will increase the water absorption of the final leather article. In addition, during the processing of waterproof leather, these salts might be harmful as they could cause the breaking

of the emulsion of the waterproof agent and, hence, prevent even distribution through the crosssection. Consequently, waterproof leather should be washed well after neutralisation. Likewise, retanning agents, which are huge and bulky molecules, might influence the waterproof values negatively. Therefore, vegetable tanning agents should be selected carefully. Sweetened vegetable tanning agents have to be strictly avoided because they are even more hydrophilic. Normally synthetic retaining agents cause fewer problems and can be applied in normal quantities. Polyacrylates are flexible molecules, which usually do not harm the waterproofness at all. The hydrophilic parts are supposed to bind to the internal surface, the hydrophobic parts are directed into the gaps of the fibre network. Despite their hydrophilicity, certain polymers and nitrogen containing aromatic syntans support the waterproof effect for several reasons. Firstly, these chemicals are anionic and, therefore, the charge of the cationic wet-blue will be changed into a weakly charged or even anionic substrate. In other words the isoelectric point of the leather will be reduced by the presence of syntans and polymers. This is a precondition for the penetration of the anionic waterproofing agents into the inner section of the leather. In addition, specially designed nitrogen containing functional syntans support the even distribution of the waterproofing agent through the cross-section due to their dispersing power without negatively affecting the tightness of the wet-blue. The use of such products is highly recommended when heavy substance wet-blue is processed, when wet-blue which is not uniform over the hide, when wet-blue from different origins are processed together, or when wet-blue is processed which cannot be neutralised too strongly because the tightness would be negatively affected by strong neutralisation. Likewise, special polymers improve the waterproofness as they disperse the waterproofing agents and support the penetration through the cross-section. The use of such polymers in the beginning of the waterproofing step is almost always recommended.

The production of waterproof leathers showing excellent leather properties and wearing comfort requires both appropriate products and application know-how. Both products and application process must be adapted to the requirements for the final article and to the processed wet-blue. Here, the character of the leather, the charge and the degree of olation has to be considered.

Masking in mineral tannage

Masking and masked solutions:

Anions which are firmly held in a complex retard penetration of OH ligands. Therefore they may prevent formation of large olated and insoluble complexes. This action is known as masking. Entry of masking agents into the chrome complexes in solutions of basic chromium sulphate appears to depend on:

- a) relative amounts of masking agent and Cr
- **b**) absolute concentration of Cr

- c) presence of other competing ligands (sulphate, chloride, hydroxyl)
- d) whether competing ligands are added together or separately
- e) pH
- f) Temperature
- g) time
- h) whether ligand is added as free acid or salt;
 - i. with monocarboxylic acid



ii. with dicarboxylic acids



if less than 2 carbons separate COO groups (ie. oxalic acid chelate ring structure of extreme stability, therefore use of oxalate ions in quantitative estimation of Cr ions)



tartrate complex



Masking action of geometrical isomers (cis/trans) maleic and fumaric acid:

Addition of sodium fumarate to a basic chromium liquor leads eventually to formation of an insoluble polymer.





whilst maleic anions give



When used under controlled conditions, the chain forming dibasic acids are of great technical importance, eg. Where large amounts of fixed chromium are needed to fill the loose flank regions of a hide.

Rate of reaction will depend on the nature of the ligands already present in the chrome complex. If large amounts of very stable masking ligands such as oxalate ions are present, no tannage will occur, since these cannot be displaced by carboxyl groups (a small amount is O.K.). When using masked liquors in industrial level, the aim is to prevent excessive and rapid reaction in the grain and flesh regions of the pelt, allowing adequate amounts of Cr to penetrate into central regions where collagen carboxyl groups can react with complexes.

Pretannage operations of liming and deliming leaves the pelt collagen at a pH 5-6. Not far removed from the iso-electric condition.

With basic chromium sulphates, reaction with the pelt would be very rapid and lead to overtanning of outermost surface unless special precaution is taken. One approach is to used masked tanning salt. Another approach is to discharge the carboxyl groups of pelt collagen by back titration with strong acid. Unionized carboxyl groups are inactive in forming complex with the Cr (tanning action completely prevented) and hence penetration of the pelt by the chrome liquor may be achieved. The subsequent addition of alkali or highly basic Cr salt raises the pH

value and tannage takes place. Excessive swelling of the pelt by acid is prevented by adding neutral salt to the pickle liquor (Balanced conditions require skill).

Particle size of Cr complexes is also of importance. It is thought that polynuclear complexes of 2 to 7 Cr atoms are present in solutions of chromium sulphate of basicity 33-50. It was found that at 40 % overall basicity the addition of carboxylic acid masking agents could increase the particle size twofold. At higher basicities, insoluble masked complexes and aggregation takes place. Particle sizes are obtained by rates of diffusion of complex ions.

The chromium sulphates used in leather industry are predominantly cationic at concentrations normally (2 % Cr_2O_3 solutions) used. Concentrated stock liquors (11-15 % Cr_2O_3) and dry powders (25-33 % Cr_2O_3) when freshly diluted may be non-ionic or even anionic in character. Conversion to cationic character is always favored by aging of dilute solutions. With more easily displaced sulphate ligands, the chromium complexes will revert to the cationic form more rapidly than when organic anions are involved.

Little is known, of the rate of reaction between particular chromium complex ions and competing ligands, whether in solution or in actual tannage of pelt. Following reaction sequence suggested:



Conditions are likely to be most complex, overall reaction rate being influenced by factors such as:

- a) compactness of pelt structure (affect diffusion rates) sizes of Cr complexes
- b) rate of over-all-coordination
- c) pH
- d) Temperature
- e) relative concentration of reactants
- f) nature of ligands in complexes
- g) nature and addition sequence of competing ligands

Olation in chrome tannage

In chemistry, olation can be described as the process by which metal ions form polymeric oxides in aqueous solution. The phenomenon is important to understand the relationship between metal ions in aqueous solution and metal oxides, which are represented by many minerals.

At low pH, many metal ions exist in aqueous solution as aqua coordination complexes, often with the formula $[M(H_2O)_6]^{3+}$. As the pH increases, one O-H bond ionizes to give the hydroxide complex, the conjugate base of the parent hexa-aqua complex:

Olation and oxolation in leather tanning

One application where olation is important is leather tanning using chromium(III) sulfate. This salt dissolves to give hexa-aquachromium(III), $[Cr(H_2O)_6]^{3+}$ and sulfate anions. $[Cr(H_2O)_6]^{3+}$ acts as an acid according to the reaction

$$[Cr(H_2O)_6]^{3+}$$
 $[Cr(H_2O)_5OH]^{2+} + H^+; K_{eq} \sim 10^{-4} M$

Thus, higher pH favors $[Cr(H_2O)_5OH]^{2+}$. This hydroxy complex can undergo olation:

$$[Cr(H_2O)_6]^{3+} + [Cr(H_2O)_5OH]^{2+} \rightarrow [(Cr(H_2O)_5)_2(\mu-OH)]^{5+} + H_2O^{2}$$

2[Cr(H_2O)_5OH]^{2+} $\rightarrow [(Cr(H_2O)_4)_2(\mu-OH)_2]^{4+} + 2H_2O^{2}$

The "diol" (second reaction) is favored and is accelerated by heat and high pH. The balance of these two factors, temperature and pH of the solution, along with the concentration of chromium(III), influence the continued polymerization of $[(Cr(H_2O)_4)_2(\mu-OH)_2]^{4+}$. The chromium(III) hydroxide is susceptible to oxolation:

 $[(Cr(H_2O)_4)_2(\mu\text{-}OH)_2]^{4+} \rightarrow [(Cr(H_2O)_4)_2(\mu\text{-}O)_2]^{2+} + 2 H^+$

Products of oxolation are less susceptible to acidic cleavage than the hydroxy bridge. The resulting clusters are active in cross-linking the protein in tanning which essentially involves the cross-linking of the collagen subunits. The actual chemistry of $[Cr(H_2O)_6]^{3+}$ is more complex in the tanning bath rather than in water due to the presence of a variety of ligands. Some ligands include the sulfate anion, the collagen's carboxyl groups, amine groups from the side chains of the amino acids, as well as "masking agents." Masking agents are carboxylic acids, such as acetic acid, used to suppress formation of polychromium(III) chains. Masking agents allow the tanner to further increase the pH to increase collagen's reactivity without inhibiting the penetration of the chromium(III) complexes.

Effects of acids and salts in vegetable tanning

Vegetable tannins are dervatives of phenol(with several OH groups). Phenols are more acidic than alcohols (pKa~10), but are weak acids therefore form salts only with strong bases. Solubility of phenol ~7% in cold water. But the sodium salt is soluble. Vegetable tannins react with atmospheric oxygen, particularly at high pH values to form quinones (for OH groups that are ortho-para to one another).

Vegetable tanning liquors are very complex and continually changing physically, chemically and biologically. They are partly colloidal but easily aggregate and will then sediment. Yiests moulds and bacteria can grow in the liquors, the main consequence being the fermentation of sugars to acids.

Tannins are not the only constituents of vegetable tanning liquors. The non-tans include, apart from the sugars, acids and their salts, hemicelluloses, pectin and lignin, as well as compounds containing nitrogen and phosphorus. The acids and their salts are the most important for the tanner. Apart from the nature of the tannins themselves, the acids and salts are the principal means of controlling the astringency of liquors and whole process of vegetable tannage. Several acids, such as gallic, oxalic, citric, tartaric, and phosphoric are present in the original tanning material and sugar fermentation can yield carbonic, acetic and lactic acid. Gallic and other phenolic acids can arise from the breakdown of tannins. Polyuronic acids, whether from hemicellulose or pectin, contribute to the acidity.

There are mainly two classifications for vegetable tannins:

1) catechol tans (condensed tans)- they are similar to catechol, usually give red-brown color and are astringent. Condensed tannins are not decomposed by acids. They gradually polymerize becoming phlobaphenes, insoluble derivatives. On dilution and standing, they deposit a thick, reddish sludge called "reds" (phlobaphanes). In order to prevent "reds" the extract is solubilized by heating under pressure with sodium bisulphite (3-8 % on the extract) at 98 0 C.

Mimosa(or Wattle)bark	natural pH= 4.8
Mimosa(or Wattle)extract	natural pH= 4.8
Sulphited Mimost Extract	natural pH= 4.8
Quebracho	natural pH= 4.9

Quebracho is obtained from the heart-wood of the quebracho tree which grows in south America chiefly in Argentina and Paraguay.Ordinary- or warm soluble Quebracho is the natural extract rich in condensed tannins(phlobaphenes) and is not easily soluble. Its use is therefore limited to tannage of sole-leather according to the process known as "hot-pitting".It results in a red-brown color and excellent water-proofness.

Sulphited Quebracho; natural pH = 4.9

Ordinary extract is subjected to sulphitation process which transforms it into soluble tannins. The main properties are: rapid penetration into the pelt, a high tannin and low non-tannin content. The rather low acid and medium salt content characterize them as mild tanning agent(can also be deduced from their pH values).

Sulfiting as applied to the condensed tannins consists in treating their solutions with a mixture of sodium sulfite and hydrosulfite. A part of the bonds in tannin is then split. Initially phlobaphanes

dissolve, then not only the size of the tannin molecule decreases but changes in the molecule occur.

Mangrove Bark	natural pH= 4.0
Pine Bark	natural pH= 4.5
Hemlock Bark	natural pH= 3.5
Gambier	natural pH= 4.0

Gambier is a solid extract(cubes) obtained from the leaves and stems of Uncaria Gambier, a plant which occurs both wild and cultivated in the Malayan region. Besides the predominent catechol tannins it also contains sugar, salts, waxes, oils, and even mineral substances. If used alone, it tends to give a rather flabby leather. When used in retannage, it imparts suppleness and a smooth feel. A peculiarity of gambier is to give leathers an excellent capacity of being glazed and very glossy dyeings.

A lot is known about the tannins of spruce bark. These consist of polyphenols mainly in the form of glucosides. The principal polyphenol is called piceatannol. Glucosidic groups are known to be associated with reduced tanning power and thus spruce bark is a relatively poor tanning material. Stilbenes and their glucosides have also been found in wandoo, an extract of eucalypt.

The poor tanning properties of glucosidic groups is explained by the ease with which a glucon is oxidated. Piceatannol in an oxygen free medium does not cause a Ts increase. In presence of oxygen, like in other flavanols, quinone systems appear which are bound irriversibly to the pelt. Tanning consists of oxidizing piceatannol to its quinone and then addition of free collagen amino groups in the 1,4 position via covalent bonds. Glycosides of piceatannol do not have tanning capacity.

The great majority of condensed tanning materials contain compounds derived from flavan. Flavones, such as quercetin, are fairly stable, almost insoluble substances are known to be a frequent source of yellow colors in nature. The closely related but colorless and soluble catechin was found in gambier leaves. It is not a tannin but during the commercial preperation of the extract it is converted into tannins, the liquor darkening at the same time. (+)-catechin is also widely distributed in nature and constitutes a minor component of wattle bark and heartwood, chesnut bark, spruce bark, oak bark,quebracho bark, tea and cola. Compounds related to catechins occur in small amounts in some tanning materials. (+)-gallocatechin, which has an extra hydroxy group at the 5'-position, is present in the barks of chesnut, wattle, and oak, as well as in tea, and wattle bark also contains some (-)-robinetinidol, which is (+)-catechin without the 5-hydroxy group.

Most of the red and blue colors of flowers are due to other derivatives of flavan, the anthocyanins such as cyanidin and delphinidin chlorides. In some flowers and fruits colorless

substances occur, which on treatment with strong acids give red colors due to anthocyanidines. The simplest representatives of these colorless compounds are flavan-3,4-diols. Thus wattle heartwood contains a small amount of (+)-mollisacacidin, whereas in quebracho sapwood there is almost 2 % of the (-) enantiomer. In oak bark 0.5 % leucodelphinidin is present and 8-10 % of an isomer in karada. Leucocyanidines have been isolated from some species of mangrove. To the tanner it is more important to know the constitution of the tannins present in condensed liquors than to know the formula for the relatively simple compounds since these are present only in small amount, except in quickly and very carefully prepared extracts of freshly gathered material. Condensed tannins are formed by condensation of these simpler compounds and it is of importance whether they are a result of acid condensation or of oxidative condensation.

2) pyrogallols (**hydrolysable tans**) - esters of glucose and gallic acid (glucoside tannins) and its derivatives which are easily hydrolizable. Hydrolizible tannins, having a polyester structure, easily hydrolize to the respective sugar or polyhydric alcohol and polyhydric phenol with carboxyl group. Hydrolysis products my be classified into gallotannins, derivatives of gallic acid, and ellagitannins, derivatives of ellagic acid. These are more yellow-brown than catechols. Their sugar content may lead to acid fermentation during long tannage, when a deposit of sand colored sludge known as "bloom" is also formed. The later is a result of enzyme action causing hydrolysis of the ester link, releasing insoluble acids, eg. Ellagic, chebulinic from the tannins. They are usually less astringent than catechol tans.

Myrobalans natural pH = 3.2

Myrobalans has been extensively studied. There up to 12 % chebulinic acid and 2 % chebulagic acid, two tannins which have been isolated in crystalline form. Chebulagic acid is identical with chebulinic acid, except for an additional link between the positions marked.

Divi-divi contains about 2.5% chebulagic acid and 5% corilagin. Tannins of algarobilla contain other related structural units, namely the quinone of 4,4',5,5',6,6'- hexahydroxydiphenic acid and brevifolincarboxylic acid. The quinone is yellow and similar components may account for the color of some myrobalans tannins also.

Chestnut wood natural pH = 2.8

Chestnut extract contains a convenient quantity of soluble organic non-tannins and of organic acids of natural origin and others which develop during manufacturing proces and is characterized by considerable astringency. Such astringency manifests itself in a relatively low speed of penetration of the tanning matters into the pelts and in the property in which these tanning substances possess of fixing themselves irreversibly and in large amount to the hide.

These properties make Chestnut extract especially suitable for the tannage of heavy hides and of sole leather in particular, as by its use it is possible to obtain a firm and compact yet flexible

leather of good color, light resistant with low water absorption. Sweetened Chestnut is a chestnut extract with varied astringency therefore different behaviour in the tanning process.

Valonia natural pH = 3.6

Sumac natural pH = 4.0

It is obtained from the leaves of Sumac(Rhus Coriaria). It is the purest among vegetables hydrolizable tannins. Using sumac as the only tannin a full and even leather of yellow-hazel color is obtained. In dyeing with both anionic and basic dyestuffs an excellent color levelness is achieved

Oak bark natural pH = 3.4

Tara

The tannin of Caesalpinia Tinctoria(bear the fruits called pods) has pyrogallic character but small quantities of catechol derivatives also occur in it. It contains practically no coloring substances therefore permits very bright and light-resistant leathers. Tara gives leather fullness and softness and at the same time a fine, closed grain. In leathers tanned with tara the grain resistance to breaking load is higher than that achieved with any other vegetable tannin.

Tannin obtained from Chinese galls contains apart from tannin, galic, m-digallic and trigallic acids. On hydrolysis gives D-glucose and gallic acid in a molecular proportin of roughly 1:10. It is thought that m-digalloyl groups are attached to each of the five free hydroxy groups of glucose, but it is possible that some of them are simple galloyl ones, whereas others are trigalloyl ones.

Tannins of Turkish galls and Sumac are similar, but with a lower proportion of gallic acid to glucose. Tannins such as these which yield only gallic acid and sugar on hydrolysis are called gallotannins.

Ellagitannins give on hydrolysis a precipitate of ellagic acid. Ellagic acid is not present as such in tannin molecules, but is derived from hexahydroxydiphenic acid.

Lignins:

Lignins constitute the material that fills out the spaces between the microfibrils of the cellulose in certain plant cells and stiffens the cell structure. They are the charasteristic constituents of wood, but are also present in bark and straw. In young tissue of trees, coniferin ie. coniferyl-4-b -D-glucoside, is present; a b-glucosidase liberates coniferyl alcohol from it in the wood and bark and lignin is formed in situ. Deposition of lignin brings about the physiological death of the cells. Lignins are insoluble in water, organic solvents and even sulphuric acid. They contain 59-67% carbon, some methoxy groups, can be oxidized to give up to about 25 % aromatic aldehydes and react with sodium bisulphite, sodium hydrosulphide and thioglycollic acid, HSCH₂COOH. It is known that coniferol alcohol can be polymerized to give a number of intermediate products, such as dehydrodiconiferyl alcohol, a-guaiacyl glycerol b-coniferyl ether and pinoresinol.

Sulphiting:

In paper production, lignin has to be removed from the cellulose fibers, and one way of achieving this is by treatment with bisulphite under pressure, which solubilizes the lignin, leaving the cellulose unaffected. In the process, the hydroxy groups of aromatic side groups can be replaced by sulphonic groups to give RSO_3H , SO_2 can add to double bonds to give RSO_3H and ethers may split to give $-OH + H_3OS$. Such sulphite cellulose, lignocellulose or ligninsulphonicacid liquors have low tanning power but are very cheap. They are sold alone or as blends with syntans and tanning extracts. Their main function is to solubilize the less soluble components, to speed up tannage, and to act as a filler.Condensed tanning materials are subjected to the sulphiting process in order to solubilize the less soluble fractions, when reactions similar to those with lignin occur. Theory of tannage with vegetable and synthic tannins:

The first step in tanning is the binding of hydroxyls of vegetable tannins to the active collagen centers. The next step- the binding of further tanning molecules continues until the interfibriller spaces are filled. The collagen active centers which react with vegetable tannins are various functional groups of its side chains and peptide bonds as well. This stage ends when collagen has absorbed ½ of its weight of vegetable tannins. The difference between Cr and vegetable tanning becomes striking here, since 3% of Cr tanning agent is sufficient to form stable bonds between collagen and tanning agent. Tanning is carried invariably under acid conditions, although it can be done at pH 1-9. The reason lies in the fact that liquors containing vegetable or synthetic tannins are naturally acidic (at higher pH s polyphenols may oxidize and dark colors may dye the leather).

Below pH 5, limed collagen is + charged, charges on basic side chains. Vegetable tannins normally carry negative charges due to dissociation of their carboxy and phenolic groups. Tannage therefore involves ionic interaction between collagen and tan.

Collagen-NH₃⁺ + tannate⁻ --> collagen-NH₃⁺tannate⁻

In pelt, structure can cause difficulty with accesability. Because of "case hardening" (rapid overtannage of outermost layers), pelts are not readily penetrated. It is important to distinguish between penetration and fixation. Apart from ionic interaction that brings the tans close to collagen fibres, other factors like H-bonds and van der Waals attractions must be involved since polyamides such as nylon can bind tannins via their -CO-NH- groups. The weak character of such binding forces could well account for the relatively low shrinkage temperature of vegetable-tanned leather. Some firmer covalent bonds (crosslinking collagen chains- and so contributing to tanning) may arise from quinones and possible aldehydes formed by the oxidation of polyphenols.

Much of the tannin may be physically held within the leather structure and be independent of specific chemical bonding to the collagen, since electronmicrographs of vegetable tanned leather

clearly show the presence of large aggregates of tannin, lying between hide fibers. Undoubtly this accounts for the well known "filling" action of vegetable tannage and the physical properties of roundness and fullness associated with this tannage.

Effects of finish materials on the leather end use

The main purpose of finishing is to provide different types of leather with characteristics that satisfy the requirements of a continously evolving global market. These characteristics include the following:

- Colour
- Brightness
- Matting
- Feel
- Softness
- print pattern
- water resistance
- special physical properties

Almost all types of hides and skins can be finished. The final uses of the different leathers is wide and includes shoe uppers, furniture and automotive upholstery, garments and leather goods. It is therefore very important for finishing in the best way. The range of chemical products used in finishing is considerable, and combinations of these products can produce almost any effect or property. These auxiliaries can be divided into the following groups:

Binders

Acrylic binders

These represent the most widely used polymer group for leather finishing and can be used in all stages of finishing, from impregnation to top coats. They generally provide a finish film with good flexiblity, adhesion and lightfastness. There are also self cross-linking acrylic polymers, or binders with free reactive groups. These can be successively cross-linked to obtain better fastness properties.

Polyurethane binders

The second largest polymer group used in finishing is polyurethanes. There is a wide variety of this type of binders, which can be divided into two principal groups:

Aliphatic polyurethane:

These products are widely used as their properties satisfy nearly all requirements. Their range is extended from extremely small particle-sized binders to products with extraordinary covering power. It can be stated that polyurethane binders posses the best physical and mechnical properties found in finishing polymers.

Aromatic polyurethane:

These are generally more economical in use. Although they provide excellent adhesion, the light fastness is poor.

Butadiene binders

These binders provide particularly high covering power and therefore find applications mainly on buffed leathers and splits. Their use is limited on long life articles, such as upholstery and automotive leathers, or on white leathers because of their reduced light fastness.

Protein binders

Protein binders are used on a large scale in the leather industry, and are based on casein, albumin and synthetic polyamides. They belong to the group of non-thermoplastic binders so they do not soften when temperatures are increased in finishing. Leathers can therefore be plated and embossed at high temperature without becoming tacky. In addition these binders can be used to provide a strong glazing effect. When used with acrylic, butiene or polyure thane binders, the natural tackiness that these products exhibit is reduced. Protein binders with stand the hot iron test, but in order to enhace the fastness to wet rub, crosslinking with formalde hyde or polyaziridine is required.

Crosslinkers

Crosslinkers are chemical substances that react with various binders, improving physical properties such as resistance to dry and wet flexing, fastness to wet rub, water and solvent resistance. Other characteristics are modified, such as embossing behaviour. Normal crosslinking eliminates or reduces print cut, while excessive crosslinking prevents a good retention.

There are different types of crosslinkers. Zinc oxide is mainly used for butadienic resins, whereas formaldehyde, together with polyaziridine, is the principal crosslinker for protein binders. Carbodiimides, epoxides, polyisocyanates and polyaziridines, being products with different characteristics and reaction rates, interact with different polymers thus changing their properties.

When using crosslinkers in finishing formulations, it is important to consider the reduced pot-life of the blend. This depends not only on the type of crosslinkers used, but also on the type of binder. All crosslinkers, except zinc oxide, are considered harmful and must therefore be handles with grat care and with strict regard to health and safety.

Matting agents

Matting agents are mainly used to modify the degree of gloss of the finish, both in base coats and in top coats. These products are supplied in water or, in order to obtain a higher matting effect, on silica. They are generally mixed with different binders - acrylates, polyurethanes, protein and cellulose acetate butyrate.

The addiction of matting agents to finishing formulations results in a drier, less tacky surface. It is important not to use large amounts of matting agents because a white break coloration can develop in the finish film.

Fillers

Fillers are finishing auxiliaries usually added to formulations in order to increase covering power, fullness, the embossability of the finish, and to reduce tackiness.

Waxes

Both natural and synthetic waxes are used in finishing for a variety of purposes. The tackiness of thermoplastic binders can be reduced, polishing can be produced more easily, a particular feel can be developed, or darkening effects in "burnished" finishes can be ajusted. When waxes are used, particular attention must be paid to the adhesion of the finish to the leather and between finish coats, especially when used in large amounts.

Wetting and penetrating agents

These auxiliaries are maily used to improve the penetration of the finish into the leather surface. These products are based on surface-active substances and/or solvents. Their main application is in impregnation and in spray dyeing, and for improving adhesion in pre-bottom and first bottom coats. They also improve the flow properties of the finishing during application, but excessive use generally reduces wet fastness resistance.

Thickening agents

Often finish blends require an increase in viscosity or thickening. This may be in mixtures applied by roller coat, curtain coat machines, pad coats, spray coats on buffed leather or for foam finishes to prevent an excessive penetration of the mixture. For a good final result, such as when applying aqueous dull top coats for upholstery and automotive leathers, it is very important to be able to spray with exact and constant viscosity. To meet these needs there are thickeners that are pH-dependent, and thicken at certain pH values of the mix.

Emulsion and solvent based products

Nitro-cellulose lacquers and emulsions

These can be divided into aqueous NC-emulsions and solvent-borne NC-lacquers. Both are used as light top coats or intermediate coats to facilitate embossing. There are gloss and dull versions, which allow flexibility and provide good rub resistance and water fastness. The degree of softness and elasticity can vary widely, depending on the quantity of plasticiser used in the mixture. Because of their limited lightfastness, nitrocellulose lacquers should not be used in white leather finishes or on upholstery leathers. After a period of time, plasticisers can migrate from the surface causing a brittleness of the film.

Cellulose acetobutryrate (CAB) lacquers and emulsions

There are two product types - aqueous emulsions and solvent-borne solutions. When compared with NC-lacquers, CAB-lacquers have extremely good heat and light resistance. Because of these properties they are applied as final top coats for white leathers, particularly when used for sport shoes. They can also be used in combination with other laquers, such as in top coats for upholstery and automotive leathers. CAB-lacquers can be supplied in gloss, dull and white pigmented versions.

Mono and two component solvent-borne polyurethanes

There are two types of products that are mainly used as top coats for leathers with high physical fastness properties.

Mono-component polyurethanes:

These can be applied without any crosslinker (polyisocyanate) because they form a highly resistant film after solvent evaporation. With aliphatic compounds this film provides very good light and heat resistance.

Two-component polyurethanes:

These products need a suitable quantity of polyisocyanates to react. After crosslinking the fastness properties developed are generally higher than those obtained using mono-coponent polyurethanes.

Aqueous and solvent-born silicones

These are used to modify the feel of the finishing, which can vary from a greasy and waxy feel to an extremely smooth and silky texture. Silicones are also used to improve some physical properties of the finishing such as resistance to abrasion on automotive leather. It is always very important to check the "overcoating properties" in order to ensure the adhesion of any following coats.

Fluoring derivatives

These products are used in both the aqueous and solvent phases, their major use being to provide oil and water repellent properties to leathers. They can be sprayed alone on to aniline or nubuck leathers, or added to the top coat of finishing formulations.

Pigments

Pigment blends can be divided into two principal groups:

Inorganic pigments:

These include white pigments (titanium dioxide based), and various colours from ochre to brown (iron dioxide based). These provide very good covering power and excellent light and heat fastness.

Organic pigments:

These are brighter, provide less cover and present some difficulties in establishing the right shade. Black pigments are based on carbon black. Pigment blends can be supplied as dispersed

products which include casein or are casein-free. As casein-free products are more concentrated, these pigments are more finely dispersed to avoid the risk of excessive pigmentation. Anionic pigments are employed in anionic finishes and cationic pigments are available for use in cationic finishes. Non-ionic pigments can be applied both in anionic and in cationic formulations.

Liquid dyestuffs

Dye solutions are generally of the metal-complex type in water-miscible solvents. They are used in spray dyeing, base coat mixtures and for two-tone effects. They also provide brightness to the finish when used in top coats. The lightfastness is lower than that of pigments, so these products should not be used for upholstery or automotive leathers. An important item for consideration and evaluation when selecting a liquid dyestuff is the tendency for some spray dyed leathers to show rings when spotted with water. Another consideration is the tendency for these dyes to migrate into plasticised PVC, causing light coloration on plastic soles when used in shoe construction.

The evolution of finish application systems

The development of machine technology has radically changed the traditional application of finishing products. Once, applications with pads, sponges and air pressured spray guns were standard. Nowadays, althought manual work has not completely disappeared, finishing is rationalised wherever possible to save time, products, and reduce air emissions.

Finish applications

Spray technology guns have made great progress since the introduction of high volume low pressure (HVLP) and compliant spray systems. These can produce the same technical results but allow a drastic reduction of products used, and a smaller number of applications. Further improvements are expected by the development of electrostatic spray systems, currently under consideration.

Remarkable progress has also been made using through-feed roller coating applications, where waste is almoust completely eliminated. Another optimised and widely used system is curtain coating, especially for grain tightening impregnation, covering base coats and special lacquers. Immersion systems are also being investigated where crust leathers are passed through a dye solution as an alternative to traditional spray dyeing methods.

Leather modification

Although leather has a number of desirable properties such as thermal stability and fire retardancey, in addition to high toughness, it has a few drawbacks such as weight, high water absorption, poor soil and rot resistance, and non-uniformity. If these defects are overcome, leather's usefulness would be further enhanced and its competitive position with respect to synthetics would increase. This is the reason for the need for leather modification to fit into the intended use. Some finishes and mechanical operations partly help in solving the problems.

Mechanical operations – softening

After the process of setting, which is the removal of excess water and spreading the hide out prior to drying. There are several methods of drying depending on the type of leather being produced. Upholstery leather is normally toggle dried (spreading the leather over expanding frames held by toggles or clips) Staking is the mechanical softening of the leather after drying. Staking is a process which makes the leather softer and more flexible by massaging it to separate the fibres. Leather is staked to make it pliable. In combination with the correct fat-liquoring treatment, staking governs the final firmness or softness of the leather.

Dry milling

The hides may also be softened by milling which is dry tumbling with atomized moisture injected into the tumbler. The hides are placed in a large dry drum and tumbled until the desired softness is obtained.

Finishing consists of placing a series of coatings on the surface of the leather. These coatings are designed to protect the leather and produce surface effects pleasing to the eye and hand. Finishing today reflects the latest technology in the use of coating materials. Various mechanical operations are necessary to obtain the desired effect. Hydraulic presses, printing, embossing machines, automatic spray applicators and vacuum driers are a few of the machines used in the finishing process. The end use of the leather determines the type of finish process to be applied. Each type requires different physical properties in the finish. Flexibility and resistance to water and wear are a few of the required properties in the finish.

Improvement of rub fastness

The measures you may take to improve fastness to perspiration will also improve the fastness to rubbing. The general rules are:

- The retaining should not reduce excessively the fixation of the dye on the leather fiber: leather should not be too anionic. Retaining with chromium or aluminum may help to improve these fastness.
- The dyes should be selected very carefully so they have very good affinity for the leather fiber. When a high % of dyes are applied it will be harder to achieve good fastness, this is especially true for intense nubuck black dyeings. Use specially fast dyes for the last additions, usually the liquid form is better than the powder form.
- Avoid fatliquors that leave a greasy surface and those that are sensitive to acids.
- Dye fixation is very important. High dye offers need a high % of formic acid to fix them and the pH should be lowered very slowly to avoid dye precipitation. The fixation time should be long enough that the end pH is well established in the whole cut of the leather. High end temperature also helps as well as a cationic fixing agent usually applied in a new bath.

PROPERTIES OF DIFFERENT TYPES OF LEATHERS

Gloving leather

This material offers all the features required, its thin tough structure giving strength and maximum dexterity to make a product which is both hard wearing and comfortable – dyed all the way through for a superior feel and colour depth.

Properties

- 1. Good tear strength
- 2. Hard wearing but comfortable
- 3. Dyed all the way through for a superior feel and colour depth.
- 4. Sweat resistant for moisture management
- 5. Textured grain for grip enhancement
- 6. Smooth surface for classic touch
- 7. Water resistance for improved comfort

Garment leathers

The properties of leather vary considerably depending upon the type and quality of both the skins and the tanning process. Every piece of leather has individual markings which relate to its origins and add character to each skin.

Relative to virtually all man-made textiles, leather is very strong and has a high resistance level to tears and punctures. The comfort provided by most leather goods is due in part to leather's ability to combine breathing and insulating properties. You may have heard... "Leather is hot in summer and cold in winter." In reality, leather adjusts constantly to its environment. Because it is a natural product, leather "breathes" freely, maintaining a comfort level in all seasons.

Properties

Like a fine wine, a good quality leather garment should improve with age.

- 1. It should be comfortable to feel and be resistant to stitch and tear
- 2. The natural elasticity of each hide means it is flexible and will stretch and return to its original shape.
- 3. Leather also has a natural tendency to repel liquids and resist staining.
- 4. It's also fire resistant, and
- 5. It should emit no toxic fumes, even when exposed to intense heat.

Types of Garment Leather.

Cowhide is the most common leather used in the making of garments, furniture and leathergoods. Cowhide as a category covers a wide spectrum of textures and quality, but generally, it is quite durable, easy to care for and resistant to water and dirt. Cowhide leather will maintain its integrity, taking on the shape of the wearer, making it more comfortable with everyday use. This affordable, functional leather offers fashion, value and endless colours and

style.

Lambskin is very soft, luxurious leather. Its natural lightweight layers give it a distinctive, velvety touch, which suites form fitting jackets, pants, skirts as well as coats. But don't let its delicate texture discourage you. With a little extra care, lambskin is very wearable and the ultimate luxury.

Pigskin is by far the most popular and versatile, easily transformed into fashion's most current looks. When tanned on the outside, it produces smooth napa finish, often used for jackets and accessories. Tanning on the inside results in a silky suede finish. The natural, lightweight structure of pigskin produces delicate patterns, textures and silky soft naps, perfect for sportswear, shirts and blazers.

Wool-on sheepskin refers to the cover of a sheep used with the wool still attached. Usually, the wool side faces into the garment or accessory, but it can also be made reversible. The wool can be ironed, which means straightened to yield a smooth, fur-like appearance, or it can be left naturally curly. Whichever way the wool is styled, this is the warmest leather available. Shearling is quite similar in appearance to sheepskin; the term shearling refers to skins from lambs which are generally much lighter in weight than ordinary sheepskin and much softer. Although they may be lighter, shearling coats are just as warm as the heavier sheepskin. They are an elegant alternative to a fur coat.

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Properties of finish

- 1. Protect grain and give desired colour pleasant to look at.
- 2. Grain improvement to feel and touch.
- 3. Improve colour fastness.
- 4. Improve softness as per the intended use.
- 5. Improve light fastness
- 6. Retain embossing and printing patterns.

Leather Properties

- 1. The physical properties which make leather a unique and valuable material for upholstery purposes includes:
- 2. High tensile strength
- 3. Resistance to tear
- 4. High resistance to flexing
- 5. High resistance to puncture
- 6. Good heat insulation

Leather contains a great deal of air, which is a poor conductor of heat. This is an important comfort consideration.

Permeability to water vapour

Leather fibres will hold large quantities of water vapour. This property enables leather to absorb perspiration, which is later dissipated - significant factor in comfort.

Thermostatic properties = Leather is warm in winter and cool in summer.

Mouldability – Leather can be moulded and will retain its new shape. It has both elastic and plastic properties in wear.

Resistance to wet and dry abrasion – These properties, concerned with wear and maintenance, are controlled by the tannage and surface finish. These have now reached high levels of excellence.

Resistance to fire – Leather is inherently resistant to heat and flame.

Resistance to fungi – Leather is resistant to mildew.

Resistance to chemical attack – The atmosphere of modern cities is polluted from the burning of carbon fuels with sulphur dioxide gas, which can accelerate the deterioration of leather. Modern leathers are tanned and dressed to resist these harmful chemicals.

Sheepskins

Like wool is classed, sheepskins are graded for their strength, durability, wool quality, density, thickness of pelt etc. Generally lower graded sheepskins are thinner in the pelt and will stretch much more so. These are to be avoided as these skins can tear more easily.

Lambskin Leather.

Many fashion items are made from lambskin due its lightweight, soft and supple texture. Accessories like gloves, small purses and light jackets are popular lambskin garments because of its silky fine texture. The leather is thin, but it still does a great job of keeping the cold out, explaining why many winter garments are made of lambskin. What differentiates this type of leather to others is its ability to be processed down to such a thin texture without tearing or spoiling the skin.

Aside from apparel, this luxury leather is used to line seats in super cars, personal items and expensive furnishings. Although delicate, soft and elegant, lambskin can stretch over time, meaning you probably shouldn't buy items made from this leather for rough or daily use. It is also ideal for the production of shoe upper linings but not ideal for shoe uppers due to its thinness

Sheepskin Leather

Sheepskin is light and smooth. Products made by sheepskin leather are usually still attached to wool and they make stylish jackets, coats and hats. Sheepskin garments are really warm and will keep you warm throughout the harsh winters. Their behavior is similar to lambskins.

Goatskin Leather

Goat leather is water resistant, making it useful material for products. This leather was used back in the day to make traditional wine containers called 'bota bags'. Due to its properties, larger goatskin is used mostly for shoes due to its thickness, coats and weathering jackets. Thinner and smaller goatskins are not ideal for shoe uppers but are equally ideal for shoe linings. Goatskin is still soft, just like sheep and lambskin, due to something called 'lanolin' or wool wax. This waxy substance is stored in the glands of the animal and it protects and conditions the skin. Other than its use in fashion, goatskin is also used for bookbinding.

Buffalo & Young Bovine Leather

This type of leather is thick and heavy, yet soft to touch. Buffalo leather will make a perfect biker jacket, and any kind of jacket made from this will probably last a lifetime! Buffalo leather is not stretched during the tanning process – doing so would ruin the unique grain of the leather. Naturally hardwearing and durable leather like this is good for shoes and furnishings, such as sofas and rugs. Not only are they fashionable when worn, but are also practical due to its breathability. Air passes easily through the pores of buffalo leather, keeping you cool during the warmer weather and cozy in the winter.

Chamois and Antelope Leather

Chamois or antelope leather is very soft and porous but is not often used anymore because it is hard to work with. Nowadays, culled sheepskin is used to imitate the aesthetics of antelope or chamois leather.

Ostrich Leather

Ostrich leather is unique for its bumpy quill patterns and is expensive to make, as the production process is very specialized and intricate. Ostrich leather is usually used for belts, wallets, boots and bags.

Crocodile Leather

Crocodile leather is luxurious and lavish. The leather is extracted from the crocodile's stomach and the value lies in the interesting patterns of scales on the skin. Crocodile skin is used for expensive belts, shoes and bags.

Snakeskin Leather

Snakeskin is a very extravagant leather. Anaconda and cobra leathers are rare, and in particular, python material is more expensive because these leather goods are produced from wild python snakes. Snake leathers are often used on the same luxury items as crocodile leather.

Fish Skin Leather

Fish leather is surprisingly strong – shark leather is 5 times stronger than cow skin leather! Fish leather is used to make jewellery, accessories, wallets and bags. Salmon skin is thin, which is good for making accessories and jewellery. Sea bass leather is thick and very strong. Unlike other traditional fabrics, it does not ravel.

Leathers are highly prized status symbols but have caused much controversy, especially in the fashion industry, where millions of animals are killed every year. Animals face the dangers of extinction and raised animals are put in terrible living conditions. Many international celebrities

such as Eva Mendes and Pink have supported organizations like PETA's campaign against animals used for clothing. However, it's not all nightmares and murder. Many reputable leather makers in Europe produce their goods without the use of harsh chemicals and pledge not to treat animals in an inhumane way, so make sure you lookout for where your leather item is produced.