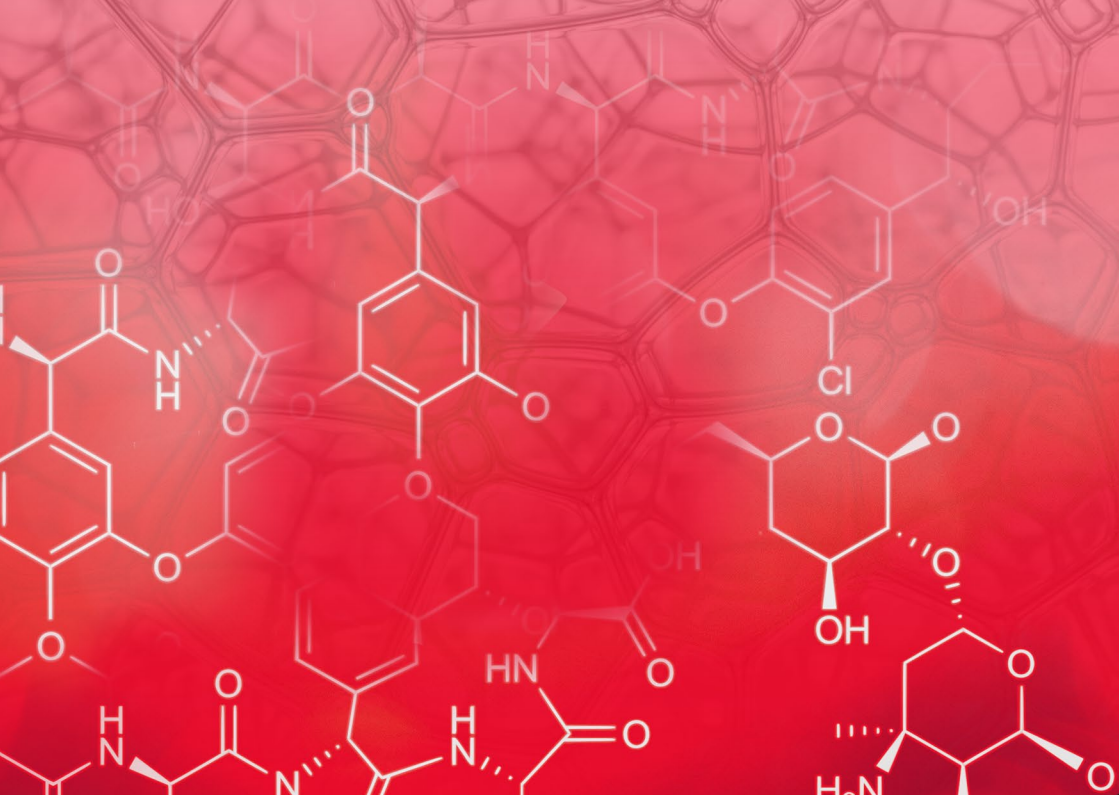




United Chemicals

Practical Information for the Leather Technologist





United Chemicals

Practical Information for the Leather Technologist

**PREPARED BY
Dr. İSMET HAKİMOĞLU**



Copyright © 2020 by United Chemicals Dış Ticaret A.Ş.

All rights reserved. This book or any portion thereof may not be reproduced or used in any manner whatsoever without the express written permission of the publisher except for the use of brief quotations in a book review.

Printed in Turkey
Second Printing, 2022

Çoraklar Mahallesi 5004 Sokak No. 23 Aliağa, İzmir 35540 TURKEY

www.unitedchemicals-co.com

P R E F A C E

This document contains selected information on different aspects of leather technology.

PART 1. gives a general view on the statistics of available livestock and raw material, animal diseases and general ante – post mortem defects. All wet process phases from soaking to dyeing shortly examined and vital data are included for each stage. In addition, additional data are given for the important tanning materials and auxiliaries widely used. A complete general finishing systems and products used are classified and evaluated for the users of this document. Also, in this part, the proprietary chemical products manufactured by the company are shortly mentioned in the appropriate process phases. More detailed information can be obtained from the “Technical Data Sheets (leaflets)” and pattern cards.

PART 2. contains definitions for old and less known leathers and information on tannery machinery, equivalences between different items, shrinkage temperatures of different leathers, worldwide produced leather distribution percentages are given with tannery costings. Relevant comparative subjects are included for interested users.

PART 3. is dedicated to practical tannery process control methods. Practical solutions by using basic reactive, indicators and classical laboratory equipment are explained which are selected from the different process phases.

PART 4. shortly explains the environmental current issues together with available types of wastes, waste treatment, safer processing methods and environmental protection and pollution controls. Discharged tannery water limits shortly evaluated.

PART 5. is dedicated to restricted chemicals used in leather industries.

PART 6. includes fundamental chemicals compounds, general data on preparation of buffer and indicator solutions are listed. Also, conversion tables relevant to densities, thicknesses and water hardness are given. Updated lists of chemical analysis and physical testing methods will be interesting for technologists. The requested limit values for different leathers are included. Selected books on leather technology and chemistry are added for curious and researcher readers. Finally, it was impossible to include many other practical information given in handbooks or manuals, due to limited paging of the document.

Table Of Contents

PART 1. LEATHER PROCESS PHASES AND RELEVANT SUBJECTS	8
1.1 World Livestock Population By Inventory	8
1.2 Common Defects Found In Alive And Slaughtered Animals	9
1.3 Factors Affecting The Wet-Processes	10
1.4 Soaking	12
1.5 Water - Importance And Usage	13
1.6 Unhairing (Depilation) And Liming	14
1.7 Deliming	15
1.8 Bating	16
1.9 Degreasing	17
1.10 Bactericides And Fungicides	18
1.11 Pickling	19
1.12 Tannins And Tanning Materials	21
1.13 Vegetable Tannins	23
1.14 Synthetic Tannins	24
1.15 Chrome Tanning	26
1.16 Neutralisation (Deacidification)	27
1.17 Retanning	28
1.18 Fatliquoring	30
1.19 Dyeing	32
1.20 Finishing	34
PART 2. COMPARATIVE AND INFORMATIVE LISTED SUBJECTS	37
2.1 Definitions Of Different Types Of Leathers	37
2.2 Equivalences As Weight Ratios Between Preservation Methods And Pelts At Different Phases	39
2.3 Tannery Machinery	40
2.4 The Leather Types Produced From Different Raw Material Sources	41
2.5 Worldwide Distribution Of "Finished" Leathers Produced From Available Raw Material Sources	41
2.6 Amounts Of Chemicals Necessary For Wet-Processes For Two Different leather Types	42
2.7 Shrinkage Temperature Values Of Different Leathers	42
2.8 Composition Of Green (Fresh) Raw Hide And Skin	43
2.9 Tannery Costing	43
2.10 Correlations Between The Tannery Parameters	43
PART 3. QUALITY AND PROCESS CONTROL METHODS	45
3.1 Examples For Practical Control Methods	46
3.2 Quality Control Of Leather Chemicals	51

PART 4. ENVIRONMENTAL ISSUES FOR LEATHER INDUSTRY	52
4.1 Sources Of Wastes And Treatment Methods	52
4.2 Advices For Safer Processes By Using Environmentally Friendly Chemicals	52
4.3 Advantages Of Partly Processed Leathers	53
4.4 Liquid Effluent Load (%) Distributions In Process Phases For Different Leathers ...	54
4.5 Hydrogen Sulphide Hazard And Remedies For The Prevention Of Accidents	54
4.6 Parameters And Limits For Discharged Tannery Water	54
4.7 Savings, Controls And Safety In The Tannery	55
PART 5. RESTRICTED CHEMICALS IN THE LEATHER INDUSTRY	57
PART 6. SELECTED DATA FOR THE TANNER	61
6.1 Chemical Compounds Used In Leather Industry	62
6.2 Preparation Of Buffer Solutions For Ph-Meters	62
6.3 Preparation Of Indicator Solutions.....	63
6.4 Conversion Table Of Specific Gravity, Barkometer And Beaume	63
6.5 Leather Thickness (Substance) Conversion Table	64
6.6 Comparison Between German, English And French Degrees Of Water Hardness	65
6.7 Chemical Analysis And Physical Testing Methods	65
6.8 Quality Requirements For Different Types Of Leathers	69
6.9 Books On Leather Science	72
6.10 Useful Conversion Factors And Measurement Systems	74
6.11 Useful Abbreviations	75

PART 1. LEATHER PROCESS PHASES AND RELEVANT SUBJECTS

1.1 WORLD LIVESTOCK POPULATION BY INVENTORY

The available world livestock as, Bovine, Ovine and Caprine animals for the production of raw hides and skins are given below.

Total alive bovine animals:	1.70 billion heads
Total alive ovine animals:	1.20 billion heads
Total alive caprine animals:	1.10 billion heads

Below 5 important breeding countries with numbers are given from each animal group.

BOVINE: cattle, calf, ox, buffalo

INDIA	340 million heads
BRASIL	210 million heads
CHINA	135 million heads
USA	110 million heads
ARGENTINA	58 million heads

Extra selected countries: Ethiopia, Pakistan, Australia

OVINE: sheep, lamb

CHINA	160 million heads
AUSTRALIA	73 million heads
INDIA	65 million heads
IRAN	55 million heads
NEW ZEALAND	44 million heads

Extra selected countries: Nigeria, Sudan, UK.

CAPRINE: goat, kid

CHINA	195 million heads
INDIA	140 million heads
NIGERIA	71 million heads
PAKISTAN	66 million heads
BANGLADESH	56 million heads

Extra selected countries: Sudan, Kenya, Iran

WORLD SLAUGHTER-SUPPLY OF HIDES AND SKINS

World leather industry consume the following amounts of raw material:

Total slaughtered hides amount:	450 million pieces
Total slaughtered sheep and lambskin amount:	650 million pieces
Total slaughtered goat and kid skin amount:	400 million pieces

Below 5 important supplier countries are given from each group of raw material source:

HIDES as cattle, cow, ox, buffalo:

CHINA	55 million pieces
INDIA	45 million pieces
USA	38 million pieces
BRASIL	36 million pieces
ARGENTINA	15 million pieces

SKINS as sheep and lamb:

CHINA	110 million pieces
NEW ZEALAND	35 million pieces
AUSTRALIA	33 million pieces
INDIA	30 million pieces
IRAN	23 million pieces

SKINS as goat and kid

CHINA	90 million pieces
INDIA	55 million pieces
PAKISTAN	23 million pieces
BANGLADESH	20 million pieces
NIGERIA	13 million pieces

1.2 COMMON DEFECTS FOUND IN ALIVE AND SLAUGHTERED ANIMALS

ANTE-MORTEM DEFECTS INVOLVING HUMAN ACTIVITIES:

Breeding factors	Cutaneous infection punctures
Barbed wire damage	Horn rake
Yoke marks	Dung and urine damage
Goad or prod marks	Brand Marks (hot/freeze)

ANTE-MORTEM DEFECTS FROM ARISING FROM DISEASE OR OTHER NATURAL CAUSES

Damages resulting from bacterial attack

- contagious acne
- mycotic dermatitis

Damages resulting from viral attack

- lumpy skin disease
- smallpox

Damages resulting from fungal attack

- ringworm

Damages resulting from protozoal attack

- globidiosis
- trypanosomiasis

Damages resulting from helminth attack

- summer sores
- filarial dermatitis
- hump sore

Damages resulting from arthropod parasite attack

- warble flies(foot-and-mouth-disease)
- screw worm fly
- fleece fly
- ked and louse infestation
- tick damage
- demodectic/follicular mange
- sarcoptic mange
- psoroptic mange

POST-MORTEM DEFECTS

Damages caused after slaughtering, flaying and wrong handling

- improper bleeding
- dragged grain
- butcher-flay cuts
- bad pattern
- inadequate cooling and cleaning
- inefficient fleshing and trimming
- overstretching and distortion
- folding damage
- curing faults
- damages associated with transport

Damages occur during storage

- red heat
- hair slippiness
- salt stains

- insect damage (beetle)
- rottenness (staling)
- metal (iron/copper) stains

CURING AND PRESERVATION OF HIDES AND SKINS

Air drying

- suspension drying
- line drying
- ground drying

Salting

- dry-salting
- wet-salting
- brining

Other methods

- pickling
- cooling (refrigeration)
- electron beam irradiation
- gamma radiation

1.3 FACTORS AFFECTING THE WET-PROCESSES

Most of the classical “wet-processes” have in common several factors which should be taken under consideration by the responsible technician/technologist. This normally starts with soaking and ends with dyeing/fatliquoring, i.e., just before dry-mechanical operations.

Also, in writing a recipe/formula these points should be considered.

MATERIAL: it should start with the statement on the available state of the material (substrate), such as: wet-salted goatskin
wet-blue split cow hides
crust sheepskin

The origin, weight, thickness and failures should be stated.

VESSEL TYPE: wet operations are performed in special vessels, such as: paddles, drums, mixers and Y-drums.

Basic data, on usable capacity, r.p.m. should be stated.

The batch amount(kg/ton) should be calculated in accordance with the needed amount of water to be used.

FLOAT / BATH WATER CONTENT: all wet processes need water and the necessary is calculated on the material(substrate) used and given as percentage (%). Expression on ratios is also possible, as 1 part material: 5 parts water Also, it can be given as g/l basis.

MECHANICAL ACTION: in vessels the created mechanical action aids the chemical reactions, penetration(exhaustion) and differ and depend on the process phase, material type and water/substrate ratio.

For example: in drum unhairing 2 – 4 r.p.m.

TEMPERATURE: the float/bath temperature is unique for each process and kept constant (stationary). Temperatures of the process stages are in accordance with the durability of the substrate.

CHEMICALS: the material in water is treated with selected chemicals in each process. Amounts, additions are stated in the recipe. In processes, with the given chemicals, either some components from the substrate are taken out (e.g. in soaking, liming) or bind-fix after penetration-distribution in the cut of the substrate (e.g. chrome tanning, dyeing).

TIME: each process stage needs a certain time for the completion of process reactions, such as, 60 mins., 2 hours. Timing mainly depends on material's thickness, percentage of the chemicals used, r.p.m. of vessel.

CONTROLS: at the end of each operation phase basic process controls should be done before passing the next stage.

Such as:

- pH of the bath and cut(section) of leather,
 - penetration observed for chemicals,
 - visual appearance / hand touch of grain and flesh sides
 - visual exhaustion of baths, i.e. colour of bath after dyeing.
- Info obtained from the practical controls and organoleptic evaluations give effectiveness and success level of the process done.

1.4 SOAKING

Initial wet process for all basic leather productions. The aim is to rehydrate the structure and removal of soluble proteins (interfibrillary), albumin, globulin, curing agents and adhering dirt.

FACTORS EFFECTING THE SOAKING PROCESS

The quality of flaying: available adhering fats, tissues prevent penetration of water, so, proper flaying is important.

Preservation method and efficiency: air or dry-salted raw material need longer period of soaking.

Mechanical action: may be necessary for rapid penetration of water. Besides, dry-drumming, pre-fleshing can be applied.

Temperature increase of the soaking bath can positively affect together with other factors.

Addition of chemicals:

- careful observation for putrefaction and decomposition is necessary before the start of soaking in order to decide the addition of bactericides,
- alkaline chemicals: preferred for dried hides and skins, sodium sulphide, sodium hydroxide, soda ash can be used. The pH of bath must not exceed over 11.0
- acidic chemicals: mainly for dried skins, hydrochloric acid, formic acid can be used.
- wetting agents: accelerate the penetration and decrease the soaking period.
- enzymes: are less dangerous and remove soluble proteins, etc.

UNISOL TSW has a high rehydration capacity in soaking process which have different curings, such as, air-dried and dry-salted raw materials. It is also suitable for wetting back of wet-blue and crust leather. The penetration force of **UNISOL TSW** enables the water to transfer into the cross-section by causing a rapid and uniform soaking and wetting.

1.5 WATER -- IMPORTANCE AND USAGE

Water is the main constituent in all types of leather productions.

CLASSIFICATION OF SOURCES

- rainwater,
- surface water (rivers, lakes),
- sea water,
- ground water,
- condensed water.

EXPECTED PROPERTIES OF WATER USED IN LEATHER PRODUCTIONS

- it should be clear, colourless and tasteless,
- total hardness should be lower than 150 German hardness,
- temporary hardness should be lower than 120 German hardness,
- iron content should be lower than 6 mg/l,
- sodium chloride should be lower than 100 mg/l,
- pH should be between 6.5 – 7.5,
- seasonal temperature variations should not be high.

SUBSTANCES AVAILABLE IN WATER

- soluble salts: sodium, potassium, calcium salts
- partial soluble salts: bicarbonates of calcium and magnesium, calcium sulphate
- dissolved gases: carbon dioxide, oxygen
- organic suspended solids.

WATER HARDNESS

Available calcium and magnesium compounds dissolved in water create the hardness.

CLASSIFICATION ACCORDING TO TOTAL HARDNESS

- 0 – 5 German degrees hardness: very soft water
- 6 – 10 German degrees hardness: soft water
- 11 – 15 German degrees hardness: medium soft water
- 16 – 20 German degrees hardness: medium hard water
- 21 – 30 German degrees hardness: hard water

WATER SOFTENING METHODS

- by precipitation
- by ion-exchange resins,
- by heating,
- by addition of complexing products

UNIXOL NPS helps decrease the hardness of the water and helps the penetration for chemicals into the leather.

1.6 UNHAIRING (DEPILATION) AND LIMING

The removal of hair, wool and epidermal layers and opening up of fibre structure with swelling and plumping. Liming is continuation of unhairing for better pelt formation for successive processes.

UNHAIRING METHODS

- lime painting: mixture of lime, sodium sulphide and thickeners applied on the flesh of grain side,
- unhairing in drum or paddle. by using lime and sodium sulphide/sulphydrate with auxiliary chemicals,
- oxidative unhairing: usage of chlorine dioxide or similar chemicals
- enzymatic unhairing: usage of special enzymes by decomposing the keratin,

CLASSIFICATION OF MAIN CHEMICALS USED

- sodium sulphide: available as 60 – 70% purity, as block or flake, sulphur content 25%, water of crystallisation is 35-40%
- sodium hydrosulphide (sulphydrate): available 65-75% purity, as flake, available sulphur 40-42%.
- organic sulphides (mercaptans): proprietary products, no swelling potential, readily oxidised and create less effluent.

- selected amines: dimethylamine and derivatives are suggested and have gentle swelling action.
- calcium hydroxide: produced from quicklime by treating with water, has low solubility

AUXILIARY CHEMICALS USED IN UNHAIRING AND LIMING

- for increasing the solubility of lime: molasses, sugar,
- for reducing the swelling: calcium chloride (lyotropic and hydrotropic effect),
- for increasing the swelling: caustic soda, salt (below 4%),
- improve the liming effects: emulsifiers, s.a.a.,
- additives to lime paints: kaolin, starch, lime.

1.7 DELIMING

Free and chemically bound alkaline chemicals are neutralised and removed. The pelt pH is prepared for bating and pickling processes. In order to lower down (decrease) the pelt pH several acids and acid salts are recommended.

UNICAL KG is a mixture of non-swelling organic acids. It has a rapid and regular delimiting action on hides and can be used for both long and short float systems. The dosage of **UNICAL KG** depends on several parameters, such as the content of alkaline products, thickness of the pelt, the desired delimiting degree, and the duration of the washing operation. **UNICAL KG** can be used in combination with other delimiting salts, such as ammonium sulphate and ammonium chloride.

IMPORTANT DEFINITIONS

Lime dissolving value: calcium hydroxide dissolved by the used delimiting agent.
 Delimiting value: The amount of delimiting chemical to neutralise 1 g calcium hydroxide.
 Buffering capacity: titration with 1 N caustic soda of the chosen agent up to pH 10.5

BASIC DELIMITING CHEMICALS

Hydrochloric acid: strong acid, forms soluble calcium chloride, may cause acid swelling.
 Formic acid: medium strong acid, less danger of swelling
 Boric acid: weak acid, good penetration ability, gives fine grain
 Acetic / lactic acids: mild acids, low swelling possibility, fine grain
 Ammonium sulphate: weak delimer, cheap, classical and common chemical, forms insoluble calcium sulphate.
 Ammonium sulphate: weak delimer, cheap, classical and common chemical, forms insoluble calcium sulphate.
 Sodium metabisulphite: weak chemical, less danger of acid swelling
 Dicarboxylic acids: non-swelling mild acids, faster penetration

AMOUNTS OF DELIMING CHEMICALS REQUIRED TO NEUTRALISE 1 KG CALCIUM OXIDE

- 3.5 kg hydrochloric acid (35%)
- 2.3 kg boric acid (100%)
- 1.9 kg formic acid (85%)
- 4.3 kg acetic acid (50%)
- 7.5 kg lactic acid (50%)
- 2.4 kg ammonium sulphate (100%)
- 1.9 kg ammonium chloride (100%)
- 3.8 kg sodium metabisulphite

1.8 BATING

Removal of hair roots, interfibrillary proteins (albumin, mucoid), scud, sebaceous/fat glands, elastin, keratose are achieved by usage of special enzymes in bating operation.

ENZYMES USED

Enzymes are biological catalysts which accelerate the reactions but, themselves are not changed.

- Enzyme active on protein is called protease
- Enzyme active on fat is called lipase
- Enzyme active on sugar is called amylase

THE SOURCES OF BASIC PROTEASES

- Pancreatic bates are obtained from pancreatic glands and contain trypsin, active at pH 8.0 – 8.6.
- Bacterial bates are obtained from selected bacteria, active pH 6.0 – 7.2.
- Mould –fungus protease is obtained from cultivated mould on suitable media, active pH is 3.5 – 5.0.
- The enzyme preparations contain wood-flour, delimiting/buffering salts which are mixed with enzyme.

ENZYME VALUE (LVU) AND UNIT

The enzyme value is the number of enzyme units in 1 g bating agent. Normally, fermentative capacity of 1 enzyme unit is equivalent to digested 1.725 mg casein.

Enzyme unit = LVU x 1.725

Necessary LVU values for different leathers:

- | | |
|--|-----------------|
| - weak bating agents (veg tan) | 700 – 1200 LVU |
| - medium-strong bating agents (upper/lining) | 1200 – 1600 LVU |
| - strong bating agents (glove/nappa) | 1600 – 2200 LVU |

UNILASE PEP-1000 is an excellent proteolytic enzyme sourced from animal and microbial organisms which is effective in removing interfibrillary proteins, elastin, Keratose and decompose fat cells for easier removal from hides and skins. The leathers treated with **UNILASE PEP-1000** gain more elastic grain and good scud loosening properties.

ENZYME USAGE IN OTHER PROCESS PHASES

In general enzymes are also used in soaking, liming, degreasing, besides bating operation:

- in soaking: lipase, amidase, phospholipase and protease are used to shorten the soaking period and the removal of interfibrillary proteins. Optimum range for activity is pH = 7.0 – 9.0
- in unhairing/liming: keratinase, elastinase, lipase and proteinase are used to eliminate the hair roots, epidermis, keratose, etc. Optimum range for activity is pH = over 10.
- degreasing / pickling: lipases are important, and used to eliminate the natural fats (grease), glands, etc. Optimum range for activity is pH = 3.0 – 5.0 or 6.0 – 8.0

UNILASE EBA is enzymatic product having a wide range of applications, which performs its efficient bating action in pH range of 3.0 – 5.0 and enables to use also during pickling and depickling processes. The bating action on the pelt is more delicate compared to relevant products working in alkaline medium. It also helps in the removal of wrinkles and opening of the fibre structure and removal of non-fibrous proteins are completed.

UNILASE EBA is compatible with polyphosphate salts and delimiting agents that can be used in the same float.

1.9 DEGREASING

Removal of high content (>10%) natural fat-grease from the structure by emulsification using selected degreasing agents, it is necessary for sheep, goat and pig skins.

UNISOL DA is an excellent solvent free degreasing agent which can be used in the removal high amount of natural grease from skins efficiently. **UNISOL DA** can be used either after bating or for stored pickle skins after depickling process. **UNISOL DA** is recommended also in soaking and liming processes for opening up of the fibres. **UNISOL DA** is compatible with all types of auxiliary chemicals and it is biologically degradable product.

METHODS APPLIED FOR DEGREASING (AFTER DELIMING OR PICKLING)

Dry degreasing: partly dried (low water content) and modified pelts- by pretanning operation is treated in closed system with selected solvents, effective system but need special machine and careful control.

Wet degreasing: treatment of pelts with a mixture of solvents and special emulsifiers, it is a classical method, applied in drums or mixers by using special solvents and s.a.a./emulsifiers; modern systems use only proprietary degreasing agents which easily remove > 90% of natural fat-grease and do not create pollution risk.

Squeezing method: the fatty skins are squeezed under high pressure press and extracted fat removed; but only partial removal is possible.

IMPORTANT DEGREASING SOLVENTS USED

	Boiling Point (°C)
Light gasoline	40 - 85
White spirit	150 - 200
Dichloromethane	40 - 44
Trichlorethylene	84 - 88
Perchlorethylene	118 - 120
Kerosene	160 - 260

1.10 BACTERICIDES AND FUNGICIDES

These chemical products consist an important group in leather processing. They prevent, inhibit the activities of bacteria and fungi available in different stages of leathers.

BACTERICIDES ARE MAINLY USED:

- in the preservation stage of raw materials
- in soaking,
- in bating
- for wet-blue chrome leather

UNIXOL BS is a biocide particularly suitable to control bacterial deterioration during beamhouse processes, such as soaking and degreasing. It is also recommended in wetting back, tannages, at final washings of retannages and in fatliquoring process phases. **UNIXOL BS** is highly effective on a quite wide range of bacteria families available in tanneries.

FUNGICIDES ARE MAINLY USED:

- in pickling process
- in preserved pickled stocks
- wet-blue chrome leather – for long term storage
- wet vegetable tanned sole/insole and also during drying and storage
- in long term stocking of crust or finished leathers,
- in some fatliquors, finishing products such as, pigment pastes and vegetable tannin liquors.

UNIXOL FN is highly efficient in the prevention of fungal growth. **UNIXOL FN** can be used for preservation and to prevent mould formation during the storage period of pickled pelts, wet-white, wet-blue and vegetable leathers. It is advisable to add **UNIXOL FN** in any process phase if a danger of mould formation is forecasted.

FUNGICIDES USED IN LEATHER INDUSTRY

	SOLUBILITY IN WATER (%)	USAGE LIMITS (%)
Ortho-phenyl-phenol (OPP)	9.3	0.2 – 1.0
Para-nitro phenol	1.6	0.1 – 0.4
Para-chloro meta cresol (PCMC)	4.0	0.3 – 0.8
Salicylanilide	1.0	0.1 – 1.0
2-(thiocyanomethylthio) benzothiazole (TCMB)	0.3	0.05 – 0.3
Methylene bis-thiocyanate (MBT)	0.3	0.05 – 0.3
Potassium N-hydromethyl N-methyl dithiocarbamate	Soluble	0.1 – 0.5
2-N-octylisothiazolin-3-one	Dispersion	0.2 – 0.5

BACTERICIDES USED IN LEATHER INDUSTRY

	SOLUBILITY IN WATER (%)	USAGE LIMITS (%)
Ortho-phenyl-phenol	0.7	0.2 – 1.0
PCMC	4.0	0.4 – 1.0
MBT	0.3	0.1 – 0.5
Lauryl-dimethylammonium chloride	Soluble	0.2 – 0.4
Boric acid	Soluble	1.0 – 5.0
Sodium silicofluoride	0.6	1.0 – 3.0
Zinc chloride	Soluble	1.0 – 3.0

1.11 PICKLING

The aim of pickling is to acidify the pelts to a planned pH range before entering the tanning (chrome, veg, wet-white) process. To prevent acid swelling of the pelt, sodium chloride added for adequate results.

IMPORTANT PICKLING ACIDS USED

	Density (g/ml)	
Sulphuric acid (96%)	1.84	strong acid
Hydrochloric acid (37%)	1.9	strong acid
Formic acid (85%)	1.20	strong acid
Acetic acid (60%)	1.12	weak acid
Lactic acid (80%)	1.20	weak acid

Glycolic acid (50%) 1.15 weak acid

Degree of swelling is an important factor in pickling process. Conventional acids used cause high degree of swelling of pelts. "Non-swelling acids" can be used to achieve controllable swelling.

Below several examples are given for safer pickling process:

	pH-VALUE	SWELLING (%)
Water	6.5 – 7.5	100
Sulphuric acid	1.2	235
Naphthalene-2,6-disulphonic acid	1.8	114
3,4 Dicarboxybenzene sulphonic acid	1.7	112
4-Hydroxybenzyl sulphonic acid	2.1	62
Naphthalene-2-hydroxy-3-sulphonic acid	2.1	60

1.12 TANNINS AND TANNING MATERIALS

Tanning is the backbone process for all leathers. By tanning the stabilisation of collagen structure is achieved and durable, consistent, long term usable leathers are obtained. Different "tannins" or "tanning materials/agents" are available for tanning processes. Selection and application and expectations depend on the producer and user.

CLASSIFICATION OF TANNINS AND TANNING AGENTS

There are 7 main groups which are used in the production of different leathers.

- Vegetable tannins
- Mineral (metal salt) tannins
- Synthetic tannins
- Polymeric and resin tannins
- Aldehyde tannins
- Oil tannins
- Other tannins

VEGETABLE TANNINS

The source of this group are vegetable tannins which are obtained from the wood, bark, leaves, fruits and roots of "tannin" containing trees.

Depending on their chemical structure they are divided into 2 main groups:

- condensed (catechol) tannins,
- hydrolysable (pyrogallol) tannins –these have 2 sub-groups:
 - a) gallic tannins
 - b) ellagic tannins

EXPLAINED UNDER SEPARATE HEADING.

MINERAL (METAL SALT) TANNING MATERIALS

Several metal salts have tanning capacity.

They are classified as:

- Chrome tanning materials

EXPLAINED UNDER SEPARATE HEADING.

- Aluminium tanning materials:

Aluminium salts are the oldest tanning group. Selected aluminium salts include alum, aluminium sulphate, aluminium chloride.

Basic salts of above is capable of tanning the collagen of hide. Due to inferiority against chrome salts, restricted usage is valid; mainly suggested in retannages of chrome leather; also used in double-face and fur skin tannages.

UNICHROME ALL is suitable in pretanning and retanning processes if it is accompanied with chrome salts, less chrome consumption is valid. **UNICHROME ALL** gives very fine grain and also increases buffing quality of suede, double-face and nubuck leathers. In double-face and suede leathers yields a lighter or whitish coloured stock. It is preferred as fixing agent for syntans and fatliquors, also quite suitable to use in the top dyeing fixations.

- Zirconium tannin

Most commonly used salt is zirconium sulphate; due to high price usage is limited and mainly for special articles and gives full and white leathers with high light fastness.

- Other minerals used

Iron and titanium are also advocated, but their usages are very limited.

SYNTHETIC TANNINS

These are man-made tanning materials that will be explained under a separate heading on Part 1.14 SYNTHETIC TANNINS.

POLYMERIC AND RESIN TANNINS

Acrylics belong to polymeric tannins and produced by polymerisation-condensation from selected monomers. Monomers used are acrylic acid, methyl acrylate, acrylonitrile, etc. They have good filling/glueing capacity at flanks. They are pH sensitive, proper adjustment is necessary and also, when using together with other tanning agents. Also, styrene-butadiene and styrene-maleic acid are other examples, but with less importance.

New polymeric softening, filling and retanning agents are also available for washable and water-resistant leathers. On the other hand, several chemicals when reacted with Formaldehyde give special resins used for leather. The used chemicals are urea, melamine and dicyandiamide. The obtained resin

tannins are good filling agents for the empty parts of hides and skins. They have restricted binding to collagen. Mainly used in retanning and preferably with other tanning materials.

ALDEHYDE BASED TANNINS

Several members of aldehyde chemical family can react with collagen and prevent putrefaction. The simplest is Formaldehyde gas – sold as 40% solution; it is historical tannin, nowadays restricted due to hazardous health properties. Glutaraldehyde is popular, commercially available at 50% conc. and has rapid irreversible tanning property; used in pretanning and retanning of selected leathers; improve perspiration and wash fastness properties of leathers.

OIL TANNINS

Several unsaturated marine oils with high iodine value when reacted with collagen, oxidised and binded (linked) to give a leathery effect. Chamois leather is a typical example which can be also dyed. Selected marine oils are cod liver oil, sardine oil.

OTHER TANNINS OR TANNING MATERIALS

These are less known and used for special purposes or conditions. Examples are polyurethanes, oxazolidines, epoxides and chinones.

1.13 VEGETABLE TANNINS

Historical and natural source of tannins exist in the appropriate countries of world flora. Although, raw sources are high numbered, but due to limited availability most of them “locally” consumed. Only some of them worldwide known and used. Only 8 extracts are worldwide usable and distributed.

RAW SOURCES OF VEGETABLE TANNING MATERIALS

1. WOODS

Oak wood (central Europe)	T: 5 – 10%
Quebracho wood (Argentina, Paraguay)	T: 15 – 30%
Chestnut wood (Italy, France, Slovenia)	T: 15 – 25%
Minor importance: Urunday, Tizera, Cutch	

2. BARKS

Mimosa bark (Brazil, S. Africa)	T: 25 – 35%
Mangrove bark (Tropical coasts)	T: 15 – 30%
Minor importance: Hemlock, Maletto,	

Bablah, Birch, Willow barks

3. FRUITS

Turkish oak-Valonea (Turkey, Greece)	T: 20 – 30%
Tara (Peru)	T: 35 – 55%
Myrobalan (India, sub-continent)	T: 25 – 45%
Minor importance: Algarobilla, Dividivi	

4. LEAVES AND GROWTHS

Sumac (Mediterranean countries)	T: 15 – 30%
Gambier (Indonesia, India)	T: 30 – 50%
Galls (China, Turkey)	T: 40 – 70%

5. ROOTS

Taran/Kermek (Russia, Turkey)	T: 15 – 22%
Badan (Russia)	T: 15 – 20%
Canaigre (Mexico, Algeria)	T: 20 – 25%
Rhubarb (China, Turkey)	T: 14 – 18%

AVAILABLE VEGETABLE TANNIN EXTRACTS

1. Major importance

Mimosa (sulphited)	T: 70-75%	pH: 4.5- 5.0
rapid pen. capacity, gives soft leathers, widely used		
Quebracho (sulphited)	T: 70-75%	pH: 4.5- 5.5
rapid pen. capacity, gives medium hard leathers, widely used		
Chestnut (sulphited)	T: 70-78%	pH: 3.3- 3.8
gives firm, full leathers, good pen., widely used		

2. Secondary importance

Myrobalan	T: 60-65%	pH: 3.0- 3.3
pen. problem, mixed and used with other extracts		
Valex	T: 64-67%	pH: 3.7- 3.8
gives firm and full leather		
Tara	T: 60-65%	pH: 3.5- 4.0
gives soft leather, mixed with other extracts, lightfast, recently popular		

3. Tertiary importance

Sumac	T: 55-64%	pH: 4.0- 4.5
gives soft leather, for special productions		
Gambier	T: 50-65%	pH: 4.2- 4.6
restricted usage, for high quality leathers		

Minor importance extracts: redpine bark, oak wood, cutch, mangrove extracts.
N.B: All given extracts are produced and marketed in "powder" form.

DEFINITIONS RELEVANT TO VEGETABLE TANNING

Binding capacity: shows the maximum amount of tanning material bound to the hide substance, also indicates the weight gain effect of the veg tanning agents. The tannin bound-fixed within a certain time shows the binding rate and resistance to repeated washing informs the binding strength.

Degree of tannage: is defined as the quantity of tannin bound to 100 parts hide substance.

Leather substance: is defined as the sum of % hide substance + %bound organic substances.

LEATHER TYPES FOR WHICH VEGETABLE TANNINS ARE USED

- sole, insole, belting: chestnut, quebracho, valex
- leathergoods: chestnut, quebracho
- lining: quebracho, mimosa, myrobalan
- chrome shoe-upper – in retannage: quebracho, mimosa
- chrome garment-nappa -- in retannage: mimosa, tara
- furniture, upholstery: mimosa, tara
- glazed-kid: quebracho, mimosa
- wet-white/chrome free/or specialty leathers: sumach, tara, gambier, root tannins.

1.14 SYNTHETIC TANNINS

These chemical products are a vital group in leather processing, and their applications are valid for different process phases

CLASSIFICATION OF SYNTHETIC TANNINS ("SYNTANS")

- Auxiliary syntans are mainly naphthalene based and used in different process phases in order to modify and accelerate the process.
- Replacement (Solo) syntans: phenol or sulphone based; replacement for veg tannins(self-tanning), have filling and softening effect.
- Dispersing (Levelling) syntans: can be used retanning and dyeing in order to achieve the faster penetration of other products; help and improve the distribution of veg tanning materials.
- Chrome syntans: these chrome complexed products are used in retannage of wet blues for better fullness and aid for better dyeing results.

- Pretanning syntans: they have the capacity to initiate tanning in veg tannages in order to ease and accelerate the penetration of veg tannins and helps paler colour and fine grain.
- Bleaching (White) syntans: have the effect of bleaching the grain of chrome or veg tanned leathers for lighter tones.
- Neutralisation syntans: preferred for the pH-regulation in neutralisation process and can be used together with other neutralisers.
- Amphoteric syntans: they show different tanning properties dependent on the pH and used in retannages; gives full level effects.
- Shrinking syntans: very astringent syntans; cause shrinkage on the grain; used only for special requirements.

UNITAN W is a suitable syntan for all types of white leathers and in retanning of chrome leathers to give paler-lighter colour. The leathers treated with **UNITAN W** result with full and compact with a fine grain. **UNITAN W** also advocated as a whitening agent for white and pastel shades. It is compatible with relevant synthetic and vegetable tannins.

BASIC CHEMICALS USED AND PREPARATION

The basic chemicals used in the preparation of syntans are naphthalene, phenol, crezols, beta-naphthol, aromatic ethers. In preparation sulphonation and condensation with formaldehyde results with unused formaldehyde in the finished syntan. Due to restrictions of formaldehyde, for condensation, sulphone or sulphonimide techniques are preferred.

1.15 CHROME TANNING

Basic chrome salts (Cr-3) have the ability to react with the carboxyl groups of the collagen and perform tanning

CHROME SALTS USED

The following chrome salts are used in the preparations of tanning agents:

- Sodium dichromate: most known and used salt, contains 50% Cr₂O₃
- Potassium dichromate: also preferred with 51.7% Cr₂O₃
- Chrome alum: not very popular due to low Cr₂O₃ – 15.2% -content
- Chrome sulphate: contains 21.2% Cr₂O₃

PREPARATIONS OF BASIC CHROME SALTS

Dichromates are hexavalent salts have no tanning effect. They are reduced by reducing agents in the presence of inorganic acids to basic Cr-3 salts. Reducing agents include, sulphur dioxide, sodium sulphite, glucose, molasses

MASKING OF CHROME TANNING SALTS

By masking we refer to the entrance of organic acid anions into the chrome sulphate complexes. Masking reduces the astringency, increase the resistance

to flocculation of complex and increase the penetration rate. Its effect to the tanned leather are fullness improve, shrinkage temperature, increases, touch-handle improved, and overall colour is lighter.

The preferred anions with high affinity are oxalate, citrate, phthalate and tartrate.

BASICITY AND BASICITY CALCULATIONS

Basicity is defined as the number of hydroxyl(basic) groups combined with one unit of chrome, expressed as a percentage of the maximum number that could combine to form chrome hydroxide. It is important for the calculations of tanning capacities.

General formula for the calculation of Basicity for reduced chrome liquors (Schorlemmer):

$$B = 133.3 - S$$

where, B = Basicity

S = kg sulphuric acid for 100 kg Potassium dichromate

BASICITY INCREASE OR DECREASE CALCULATIONS

Chrome tanning agents sometimes need to be re-adjustment for higher or lower basicity (e.g. 38%, 42%, 48%). The following formulations are suggested:

BASICITY INCREASE:

Several common alkalis can be used in the formula given below:

$$A = (B - C) \times D \times E \text{ where,}$$

A= amount of base to be used for 1 kg or L of tanning salt

B= required basicity

C= existing basicity

D= Cr₂O₃ content of 1 kg or L of tanning salt

E= factor, for soda ash(anhydrous)= 0.0209

for soda ash(crystal)= 0.0565

for sodium bicarbonate (100%) = 0.0332

for sodium hydroxide (100%) = 0.0158

BASICITY DECREASE:

Several common acids are used in the formula given below:

$$A = (B - C) \times D \times E \text{ where,}$$

A= amount of acid to be used for 1 kg or L tanning salt

B= existing basicity

C= required basicity

D= Cr₂O₃ content of 1 kg or L of tanning salt

E= factor, for sulphuric acid (98%) = 0.0198

for formic acid (85%) = 0.0214

for hydrochloric acid (35%) = 0.0381

AVAILABLE BASIC CHROME TANNING AGENTS

- Liquor: organic or inorganic reduced, contain 10 – 15% Cr₂O₃

- Powder: masked, uniform composition, normally contain 25 -- 26% Cr₂O₃

Basicity: 33% or higher

- self-basifying salts: better exhaustion properties, need lesser control, contains 20 – 22%Cr₂O₃, do not need basification.

DEFINITIONS RELEVANT TO CHROME TANNING

- Flocculation point: the pH value at which a permanent flocculation occurs during the basification of chrome tanning baths. Higher pH –values mean more stable tanning baths.

- Degree of olation: the proportion of olated hydroxyl groups to the theoretically possible total amount of hydroxyl groups per chrome atom. Higher the degree of olation means higher stability of solutions to acids.

1.16 NEUTRALISATION (DEACIDIFICATION)

Removal of acidity from the leathers by suitable alkaline chemicals. The cut pH to be reached depends on the retanning, dyeing and fatliquoring to be performed. Lower or higher pH-values create less uptake of process chemicals.

BASIC NEUTRALISATION CHEMICALS

Chemical	pH Range	Properties
Sodium carbonate (soda)	11.0 – 11.5	danger of over neutralisation
Borax	9.0 – 9.2	danger of over neutralisation
Sodium acetate	8.0 – 8.4	mild neutraliser, can be mixed with others
Ammonium bicarbonate	8.0 – 8.2	mild neutraliser, penetration is good
Sodium formate	8.0 – 9.5	mild and rapid penetrating agent cannot over neutralise, widely used
Sodium bicarbonate	7.8 – 8.3	mild neutraliser, widely used
Sodium sulphite	7.6 – 8.0	mild neutraliser, uniform distribution
Calcium formate	7.0 – 7.6	mild neutraliser, not effective, cause calcium sulphate formation

UNITANNS is a mixture synthetic tannins and organic salts, it is used alone for neutralisation and also together with other neutralisation agents. Due to its complexing property and rapid penetration capacity shortens the processing time and yields a homogeneous pH distribution.

1.17 RETANNING

Mainly important for chrome tanned shoe-upper, garment-nappa and relevant leathers. Required physical properties of the end product is obtained in retanning by necessary modifications. All main and secondary type of tanning agents are used for the retannings of different leathers.

CLASSIFICATION OF RETANNING TANNINS

- Vegetable tannin extracts: mimosa, quebracho, chestnut is used for filling and firmness; percentages adjusted according to required properties.
- Chrome and aluminium retannage can be advocated on special conditions to increase dyeing quality and brilliance.

UNICHROME CS can be used as a retanning agent alone or together with basic chrome salts. **UNICHROME CS** gives a very uniform colour distribution on the grain and cross-section, together with softness and fullness. It is also recommended for the production of pale or light-coloured leathers. **UNICHROME CS** increases the light fastness and mechanical stress of the leathers.

- Aldehydes: mainly glutaraldehyde is preferred; helps in developing physical properties of leather. New modified aldehydes are used for wet-white systems.
- Polymeric and resins: they are used together with other tannins; preferred for filling of empty-spongy parts of the structure.

UNISIN DSD is a retanning resin with selective filling properties for the loose areas of hides and skins, which results with filled bellies and flanks. The articles obtained show little elasticity, tight grain structure and uniform fullness throughout leather area. **UNISIN DSD** is suitable for shoe-upper, glazed kid and calf bag/purse type of leathers.

- Syntans: replacement and chromed types are widely used.
- Filling agents: these are mainly kaolin, talc, flour based and have limited capacity.

1.18 FATLIQUORING

Stationary softness, elasticity is obtained by the application of fatliquors with different chemical compositions. Majority of them are obtained by chemical modification of raw oils or fats of different origins.

BASIC RAW SOURCES OF OILS AND FATS

Two main groups are known:

Natural sources

- Vegetable oils – classified as in 3 sub-groups:
 - drying oils: linseed

semi-drying oils: rape, sunflower seed, soya, cotton seed

non-drying oils: castor, olive

- Animal oils – classified as in 2 sub-groups:

fish oils: whale, herring, cod, anchovy

land animal oils-fats: tallow, neatsfoot

Mineral – Synthetic oils

paraffin hydrocarbons, synthetic fatty acids/alcohols, chlorinated hydrocarbons, sulphochlorinated hydrocarbons, synthetic fatty esters.

CLASSIFICATION OF FATLIQUORS USED IN LEATHER PRODUCTIONS

1. Raw or natural oils: these are untreated oils and used directly
2. Emulsified oils: raw oils are mixed with suitable emulgators (e.g. non-ionic) and water miscible products are obtained.

UNIOIL LL is a perfectly emulsified mixture of fatliquor having strong lubrication properties and advocated as a main fatliquor for many types of leather products. **UNIOIL LL** is resistant to wide margin pH variations and hence proposed for vegetable and special leather productions. The leathers obtained have good softness, waxy handle, low specific weight and high light fastness properties. **UNIOIL LL** is compatible with all types of fatliquors and auxiliaries used in post-tanning processes.

3. Sulphonated/Sulphated oils: produced from the treatment of vegetable, fish or animal oils with sulphuric acid at low temperature, afterwards washing and neutralisation done; used for all types of leathers.

Examples: sulphated castor oil (Turkey red oil), sulphated cod oil

UNIOIL H-140 is a general-purpose fatliquoring agent designed for many types of articles where high fibre lubrication and good surface feel are desired. **UNIOIL H-140** is advised for garment and softy type of leathers, which need improved stitch and tear strength along with high grain crack properties.

4. Sulphited oils: obtained by treating with sodium metabisulphite and addition of oxygen; have high softening effect; inner- cut lubrication is effective; used for most leathers. Higher usage may cause emptiness/looseness; preferred usage together with sulphated/synthetic oils.

Example: sulphited sperm oil

5. Synthetic oils: their range is increasing; new age products have high fullness, high yellowing resistance, high washing fastness and low fogging properties., preference is increasing against natural based fatliquors.

UNIOIL ST is a multipurpose fatliquoring agent for different types of leathers and especially for double-face resulting with supple and soft leathers. It can be applied at a wide pH range, such as, in pickling, tanning and retanning due to its good electrostability against different agents. **UNIOIL ST** outstands with its excellent penetration capacity without creating greasy hair in double-face productions. It is compatible with all post-tanning agents, such as, syntans, resins and dyestuffs.

UNIOIL I-32 is a special electrolyte stable product that can be used in different process stages, such as, in pickling, tanning, and retanning and main fatliquoring. The combination of **UNIOIL I-32** with selected sulphited and sulphated fatliquors efficiently yields with the expected requirements under normal conditions. **UNIOIL I-32** is specially recommended for articles destined for wet-toggle drying.

6. Cationic oils: are made by mixing raw oil and a cationic emulsifying agent. In these emulsions the oils droplets formed have positive electrical charge; they have excellent stability to acids and mineral salts. Low percentages used and preferred for top fatliquoring.

DEFINITIONS RELEVANT TO RAW OILS-FATS

Important definitions relevant to examined raw oil-fats to be used in fatliquor preparations:

- Saponification value: the necessary amount of potassium hydroxide in mg for the neutralisation of 1 g fatty acid.
- Iodine value: gives info on the amount of unsaturated compounds in the oil.
- Acid value: gives info on the available fatty acids in the oil,
- Peroxide value: it is the measurement of peroxide bound to oxygen contained in the oil; gives info on the degree of oxidation,

1.19 DYEING

It is a colouration process for cut and grain for better appearance. Mainly done by using synthetic dyestuffs which have affinity to collagen.

CLASSES OF DYESTUFF USED

There are several classes available with different chemical structure and physical properties, the selection of the optimum dye type depends on the technician. Below short info is given for each class.

BASIC (CATIONIC) DYESTUFFS

The colour carrier part is cationic. Precipitates with anionic syntans, fatliquors. Doesn't have affinity to chrome leather and have restricted colour range. Good surface dyer with low light fastness(fading), but high fastness to perspiration.

ANIONIC DYESTUFFS

The colour carrier part is anionic. Classified as 3 main groups.

ACID DYESTUFFS: these are homopolar dyes and acidification is necessary for fixation. Wide spectrum of colour is available. Fastness to light and dry-cleaning is good, but, wash and perspiration fastnesses are not sufficient.

DIRECT DYESTUFFS: these are heteropolar dyes and have high molecular weights. Dyeing under neutral or weak acidic media is necessary. Fastnesses to light, washing and dry-cleaning is sufficient. During the last 10 years an important number is forbidden due to content of hazardous components.

PREMETALLISED DYESTUFFS: these are available under 2 sub-groups.

- 1:1 **PREMETALLISED DYES:** one metal atom is connected to 1 dye molecule. Chemically stable and suitable for chrome leathers. Fastnesses to light, washing and dry-cleaning is good. Light and medium tones of dyeing are preferred.

- 2:1 **PREMETALLISED DYES:** two dye molecules is connected to 1 metal atom. Chemically stable, but low penetration ability, good for surface dyeing.

OXIDATION DYESTUFFS:

Old class of dyes for wool dyeing. The main constituents are, p-phenylenediamine, o-aminophenol, resorcinol. Cannot dye directly, "killing and mordanting" by using metal salts before dyeing is applied. Colour formation and fixing is performed by hydrogen peroxide. They have limited colour range. Nowadays classified as hazardous for human and environment.

OTHER DYESTUFFS

Chrome-mordant, reactive, sulphur, vat dyestuffs are minor importance. These are used under special conditions and for selected leathers, such as, aldehyde tanned, chamois or crusted wet-white leathers.

AUXILIARIES USED IN DYEING

These products help in homogeneous dyeing, increase penetration and also, help in fixation.

- surface active agents: decrease surface tension cause better penetration, cationic are also used for fixation.
- syntans: increase dispersion, penetration and help homogeneous dyeing.

UNITAN NNF is suitable in the pretanning of vegetable tannage and for the neutralisation of chrome tanned leathers, together with other neutralisation agents. **UNITAN NNF** is a quite active neutral syntan having dispersion property and it doesn't add weight on leather. The usage of **UNITAN NNF** provides homogeneous distribution of fatliquors and dyestuffs throughout the cross-section of the leather.

- fixation agents: these are mainly cationic chemicals for anionic dye fixations, chrome and aluminium salts, cationic resins are used.

- complexing agents: prevent the hard water usage damages in dyeing; EDTA, polyphosphates are preferred.

COLOUR INDEX NO. AND NAME

Synthetic dyestuffs are classified according to their; chemical class, characteristic structural unit and dyeing class. In order to use these dyestuffs properly and prevent interferences; a simple international (universal) registration method had been developed. To each dye, firstly a Colour Index Number and Name is given. Several examples are given below:

C.I. No: 50315	C.I. Name: Acid Blue 53
C.I. No: 10415	C.I. Name: Acid Brown 103
C.I. No: 29160	C.I. Name: Direct Red 23

1.20 FINISHING

Finishing is the final stage for most leathers. The purpose of finishing is to increase the resistance by protective coats and add aesthetic properties to leathers. The main aims are:

- by changing the diffraction of light matt, shiny effects are given,
- the surface - grain can be easily cleaned,
- the failures on grain decreased or removed,
- increase in resistance to water penetration, abrasion and the adverse effects of acids, alkalis, solvents and soil are decreased,
- light and rub fastnesses and water repellence are increased,
- homogeneous coloured leather obtained by which the cutting value increased.

CLASSIFICATION OF FINISHING SYSTEMS ACCORDING TO THE EFFECTS, APPLIED TECHNIQUES AND MATERIALS USED

- Aniline finish: transparent coats with dyestuff solutions with thin/less binder and unpigmented topcoats,
- Corrected grain finish: buffed leathers embossed and covering films applied, Others are opaque, brush off, easy-care, antique, two-tone effect finishes.

EXAMPLES ACCORDING TO THE APPLIED FINISHING TECHNIQUE

- Curtain coating: overflow or slot-type curtain coater used; high coverage is obtained.
- Glace finish: application of thermoset binders and glazing machine; high gloss obtained.

Others are embossed, foam finishes

EXAMPLES ACCORDING TO FINISHING MATERIAL USED

- patent finish: polyurethane lacquer with high gloss,
- casein finish: natural casein or derivatives mixed with colourings, fixation and application of glazing/plating.

CLASSIFICATION OF LEATHER FINISHING PRODUCTS

The main product classes used in different finishing systems are explained below.

PIGMENT PASTES (P.P.)

- sub-classified as:
- with casein
 - casein free
 - cationic ranges
 - others

main component in the system, produced by dispersion of coloured pigments. inorganic pigments: titanium dioxide, lithopen, carbon black, ultramarine, iron oxides, chrome oxides, organic pigments: copper-phthalocyanine, indigo, para-red.

UNITONE range is an aqueous, anionic pigment paste series that doesn't include metals. Excellent tinting strength and fastnesses make **UNITONE** suitable for most valuable applications such as car seat, upholstery or the finishing of metal-free leathers.

BINDERS

sub-classified as: synthetic range:

- acrylic
- butadiene
- polyurethane
- copolymers
- compact
- cationic

natural (proteinic) range:

- casein
- albumin (blood/egg)
- others (shellac)

film forming with adhesion ability on leather surface, it contains also p.p. and waxes in the prepared coat mixture.

UNIBIN 5010 is advocated in the finishing of different type of leathers where high penetration and physical resistance is required such as garment, shoe-upper and upholstery finishes. It has very good dry milling properties and creates soft and elastic film without overloading the grain. **UNIBIN 5010** can be mixed with other **UNIBIN** range of binders in all ratios depending upon the leather type.

UNIPUR 5410 is a fine particle sized low viscous aliphatic polyurethane binder. The product forms clear, bright, medium soft films with medium tackiness and reasonable swelling resistance. The transparent film formed also gives deepness to the colour of the coat. **UNIPUR 5410** is proportionally advised in appropriate combinations for glazeable, polishable and in general finishing applications.

WAX EMULSIONS

- sub-classified as:
- plate releaser
 - combined (compact)
 - cationic
 - others

prevent adhesion of base coats to plate of the ironing press; improve also flow out of the coat mixture.

FILLERS AND THICKENERS

sub-classified as: - base coat fillers
- thickeners as additives
increase the density of coat mixture and help in the concealing of defects.

LACQUERS – SOLVENT BASED

sub-classified as: - N/C (clear, coloured, matt, etc.)
- P/U
- CAB
- others

classical top coating products for most leathers; dilution by thinners, sprayed; protective coat gives shininess.

LACQUERS – WATER BASED (EMULSION)

sub-classified as: - N/C
- P/U
- others

environmentally safer, but decreased fastness properties.

UNILAC MP 7020 is a polyether based aliphatic polyurethane and suitable as a matt topcoat with a pleasant touch. **UNILAC MP 7020** is a solvent-free product and it doesn't contain silica. It is suggested for the finishing of all articles that need high wet-dry rub fastness, such as, garment, upper and upholstery leathers. The product can be used as matt topcoat and due to resistance to mechanical operations, it doesn't lose its matting behaviour develop a whitish effect.

UNILAC W 9020 is an aqueous emulsion of nitrocellulose lacquer. It can be used as a final topcoat for garment, shoe-upper and leathersgoods (handbag/belt/purse) articles. It allows high gloss and efficient wet-dry rub fastness properties. **UNILAC W 9020** can be diluted with water miscible organic solvents, in order to increase the gloss of the topcoat film. **UNILAC W 9020** is readily compatible with aqueous agents and touch modifiers.

THINNERS

sub-classified as: - for N/C system

- for P/U system
- others

mixture of solvents and diluents; composition differ according to the lacquer to be used.

UNIWAX 3115 is particularly suitable for soft leather finishing and gives waxy and warm touch. It has excellent sealing effect, reducing the sticking of the finishing coats to hot ironing and during piling period. **UNIWAX 3115** is compatible with all types of binders and pigment dispersion.

PENETRATORS AND FLOW—IMPROVERS

sub-classified as: - for impregnation
- for base coats
- general purpose

decrease interfacial tension and increase penetration for effective results.

DYESTUFF SOLUTIONS (“ANILINE”)

sub-classified as: - solvent soluble
- water soluble

selected anionic/premetallized dyes, free from extenders are used; added in all coats for colouring, better than p.p.

TOUCH MODIFIER (HANDLE MODIFIER)

sub-classified as: - solvent based
- water based

used on topcoats, changes handling of leathers by, e.g. silky, waxy, slippery, oily touch effects.

DULLING—MATTING AGENTS

sub-classified as: - solvent based
- water based

cause in decrease of shininess of films, but appearance of faults is decreased

CROSSLINKING AGENTS

sub-classified as: - for film forming
- hardeners
- others

special selected chemicals for better linkage of film forming components, e.g. carbodiimides, aziridines.

PLASTICIZERS

sub-classified as: - non-gelatinizing: butyl stearate, castor/linseed oil
- gelatinizing: camphor, dibutyl-phthalate

added into N/C, P/U and CAB systems for increasing flexibility, plasticity and softness and for the prevention of drying or crackiness of films.

REPELLENTS

sub-classified as: - waterproofing (water-repellence) agents
- stain repellent and soil-proofing agents

they increase the durability of topcoats against water, food/beverage, alkali/acidic product stains; and help for long term safe usage.

UNIFIN 4107 can be used for different types of leathers to gain external water repellence. It can be applied directly before the finishing applications on the grain or together with topcoats during the finishing operation. If necessary, the penetration of **UNIFIN 4107** can be increased by addition of a water miscible solvent, such as isopropanol to the diluted mixture.

AUXILIARIES

- sub-classified as:
- shade deepening agents
 - stabilisers
 - levelling agents
 - defoamers
 - optical brighteners

added into the main composition of coat formulations to increase the performance and modify-enhance their activity.

TRANSFER SYSTEMS

- sub-classified as:
- laminates
 - foils
 - others

transfer of synthetic films onto the leather, applied by special equipment; new types even accept finishing.

EXPECTED PROPERTIES FROM BINDERS

Following properties are important for binders:

- adhesion strength,
- resistance to swelling
- rewettability,
- dry-wet rub fastness,
- flexing endurance,
- filling and penetration effect,
- cold crack stability.

EXPECTED PROPERTIES FROM PIGMENTS AND PIGMENT PASTES

Following properties are important for pigment and pigment pastes:

- staining power, tinting strength
- opacity/hiding power/covering power,
- oil absorption
- light fastness
- light absorption/light scattering power
- bleeding
- particle size/particle shape,
- specific gravity,
- chemical reactivity
- thermal stability.

SOLVENTS AND DILUENTS USED IN THINNER PREPARATIONS

	Boiling Point (°C)
Acetone	55 – 60
Ethylacetate	74 – 78
Methylethylketone	78 – 80
Isopropyl alcohol	80 – 82
Toluene	110 – 112
Buthylacetate	110 – 130
Buthylalcohol	115 – 117
Ethylglycol	132 – 136
Xylene	136 – 140
Amyl acetate	140 – 145
Cyclohexanone	150 – 155
Buthylglycol acetate	180 – 185

PART 2. COMPARATIVE AND INFORMATIVE LISTED SUBJECTS

2.1 DEFINITIONS OF DIFFERENT TYPES OF LEATHERS

Below a selected list given for the less known and rare manufactured leather types for the interested readers.

Alum leather: leather produced by alum tannage

Apron leather: for protection purposes, soft/mellow leather from cattle hide, veg or chrome tanned, stuffed; may need repellency and special finishing

Bark leather: leather tanned by tannin containing barks.

Baseball leather: basic aluminium/chrome tanned from suitable hide/skin

Belt leather: leather for waist belts from suitable hide/skin depending on the required thickness, veg or chrome or combination tanned.

Belting leather: used for transmitting power in machinery, using butts of hides by using veg or combination tannage.

Bookbinding leather: used for the binding of historical or important books or similar, by using skivers of goat, calf, etc. and using veg or chrome tannage. Special treatment necessary for the prevention of rotting,

Bridle leather: a harness finished strap leather.

Buckskin leather: leather from deer or elk, grain removed, used for gloves or clothing and dusted with talc or finely ground pigments.

Cabretta leather: leather made from hair sheep for gloving and shoe upper.

Carding/Roller/Picker band: leathers used for textile machines

Chamois leather: skivers of sheep or goat or similar skins, tanned with fishoil having high iodine value, nowadays combination tannage with aldehydes practised.

Chevrette leather: leather made from sheep or lambskin for upper as imitation of glazed kid.

Cordovan leather: originates from Cordoba-Spain, made from butt and shell of horse. Used for uppers.

Glove/gloving:

a) for dress gloves or sports--leather: from sheep, lamb, pig, kid skins, by aluminium, zirconium or special aldehyde and oil tannage; soft, elastic quality product natural colour

b) for daily usage made from sheep, kid, calf, chrome tanned, dyed and finished

c) for work-industrial purpose – from cattle or pig, or splits; mainly chrome tanned, for protective purposes

Gusset leather: a soft flexible leather used for gussets in shoes, bags and cases.

Harness / Saddlery leather: veg or chrome tanned, specially treated-fatliquor; made from cattle hides or similar.

Hydraulic leather: for industrial usage, from cattle hides, veg or combination tanned, special stuffing provided; used for pump valves, piston packings, gasket, bellows, etc.

Latigo leather: combination of alum and gambier, used for saddle strings, army accoutrements.

Mocha leather: made from kid and lambskins, formerly produced from glazed tanning buffed on the grain, in order to obtain velvety effect.

Morocco leather: vegetable-sumac- tanned goat leather, also boarding or graining., applied, used for leather goods and furniture.

Parchment: skins of lamb, goat, calf is used; mainly untanned, obtained by drying out of the degreased, delimed and cleansed pelt. With smooth surface and translucent or opaque. Used for writing manuscripts and other purposes.

Russet leather: veg tanned, heavily oiled from cattle hide, for special footwear for hiking, winter, army boot

Russian leather: veg tanned-with willow bark calfskin shoe and boot leather, dressed with birch oil and distinguished by its odour rather than its appearance, today, combination tanned with veg and chrome.

Vachette leather: cattle, buffalo origin, vegetable tanned, soft, for shoes; today, chrome tanned, soft, with high fastness properties, used for shoes, furniture, saddlery and leather goods.

Wallaby leather: tanned skin of a small or medium sized kangaroo.

Welting leather: veg tanned, stuffed leather, used for the welted models of men's shoes, dyed, good stitch tear, flexibility and waterproofness required.

2.2 EQUIVALENCES AS WEIGHT RATIOS BETWEEN PRESERVATION METHODS AND PELTS AT DIFFERENT PHASES

Wet-salted: Dry-salted 1 : 0.6 – 0.7

Wet-salted: Air-dried 1 : 0.4 – 0.5

Wet-salted: Pickled pelt 1 : 0.7 – 0.8

Wet-salted: Limed pelt 1 : 0.9 – 1.3

Dry-salted: Wet-salted 1 : 1.4 – 1.7

Dry-salted: Air-dried 1 : 0.75 – 0.85

Dry-salted: Pickled pelt 1 : 1.2 – 1.3

Dry-salted: Limed pelt 1 : 1.4 – 1.6

Air-dried: Wet-salted 1 : 2.0 – 2.5

Air-dried: Dry-salted 1 : 1.2 – 1.3

Air-dried: Pickled pelt 1 : 1.8 – 2.2

Air-dried: Limed pelt 1 : 1.8 – 2.5

Pickled pelt: Wet-salted 1 : 1.3 – 1.4

Pickled pelt: Dry-salted 1 : 0.75 – 0.85

Pickled pelt: Air-dried 1 : 0.45 – 0.55

Pickled pelt: Limed pelt 1 : 1.3 – 1.5

Limed pelt: Wet-salted	1 : 0.8 – 1.1
Limed pelt: Dry-salted	1 : 0.6 – 0.7
Limed pelt: Air-dried	1 : 0.4 – 0.5
Limed pelt: Pickled pelt	1 : 0.65 – 0.75

EXPLANATIONS:

- 1) Wet-salted preserved raw material, trimmed, Water content = 35 – 45%
- 2) Dry-salted preserved raw material, trimmed, Water content = 20 – 30%
- 3) Air-dried raw material, trimmed, Water content = 10 – 20%
- 4) Limed pelt, unhairing/liming done, fleshed, trimmed, Water content = 60 – 70%
- 5) Pickled pelt, pickled conventionally, Water content = 40 – 50%

2.3 TANNERY MACHINERY

Modern leather production systems need different machines and equipment for different physical and mechanical operations. The capacity, working width, precision, durability mainly depends on the type of the material to be used. Every tannery must calculate the number of the necessary machinery according to their daily production capacity.

Below, worldwide accepted, known and used classical tannery machines listed for information purposes:

- Deburring
- Unhairing
- Fleshing
- Shaving
- Samming
- Setting out
- Splitting
- Vacuum drying
- Paste drying unit
- Staking (Slocomb, rotary, vibration)
- Togglng unit
- Buffing / dedusting
- Glazing
- Polishing
- Boarding
- Hydraulic press
- Cylinder/rotary ironing
- Automatic spraying
- Curtain coating
- Roller coating
- Measuring

2.4 THE LEATHER TYPES PRODUCED FROM DIFFERENT RAW MATERIAL SOURCES

- shoe-upper(side) leathers: cattle, cow, ox, pig
- shoe-upper suede leathers: cow, calf, goat, pig,
- glazed-kid leathers: goat, kid,
- lining leathers: goat, kid, calf, sheep
- sole/insole/belting/welting/harness/textile leathers: cattle, ox, buffalo
- automotive/upholstery leathers: cattle, cow
- glove leathers: kid, lamb, sheep, calf, pig
- chamois leather: sheep, deer
- garment-nappa leather: lamb, sheep, goat
- garment-suede: kid, lamb, sheep, calf,
- double-face (fur-suede): lamb, sheep
- bookbinding leather: goat, kid,
- leather goods (bags, purses, luggage, cases, belts, etc.): cattle, calf, goat
- exotic/fancy leathers: lizard, crocodile, snake, fish, ostrich
- fur products: mink (vison), fox, beaver, chinchilla, lynx, sable, raccoon, rabbit.

2.5 WORLDWIDE DISTRIBUTION OF “FINISHED” LEATHERS PRODUCED FROM AVAILABLE RAW MATERIAL SOURCES

BOVINE: hides from cattle, cow, bull, ox, etc.

60 – 70%	Chrome tanned shoe-uppers
4 – 6%	Full veg sole/insole
5 – 10%	Chrome and veg tanned leather goods (bags, belts, accessories)
25 – 30%	Automotive/furniture/upholstery

OVINE: skins from sheep and lamb

60 – 70%	Chrome tanned garment-nappa
5 – 10%	Chrome tanned double-face(fur-suede) leathers
20 – 30%	Shoe-upper, lining and similar leathers,
7 – 10%	Wet-white, chrome free and special leathers

CAPRINE: skins from goat and kid

30 – 40%	Chrome tanned shoe- upper
5 – 10%	Chrome tanned garment nappa/suede
60 – 70%	Chrome, veg and combination tanned lining leathers

N.B.: The above, “wide limit percentages” are given due to the changes occurring on the “supply and demand chain” and price fluctuations of raw materials.

2.6 AMOUNTS OF CHEMICALS NECESSARY FOR WET-PROCESSES FOR TWO DIFFERENT LEATHER TYPES

	1000 kg wet-salted cattle hide for shoe-upper (KG)	1000 kg wet-salted sheepskin for garment-nappa (KG)
Soaking agents	10 – 20	10 – 20
Unhairing/Liming chemicals	30 – 50	60 – 100
Hydrated lime	30 – 60	80 – 120
Deliming agents	20 – 30	20 – 30
Bating agents	10 – 20	10 – 20
Degreasing agents	–	15 – 30
Pickling chemicals - SALT	80 – 120	60 – 80
ACIDS	10 – 15	10 – 15
Chrome tanning salts	60 – 100	60 – 80
Neutralisation chemicals	10 – 20	10 – 20
Vegetable tannins	20 – 50	10 – 20
Synthetic tannins	20 – 50	20 – 30
Polymers / Resins	10 – 20	10 – 15
Fatliquors	40 – 60	30 – 50
Dyestuffs	10 – 30	10 – 20
Bactericides /Fungicides	1 – 4	3 – 5

2.7 SHRINKAGE TEMPERATURE VALUES OF DIFFERENT LEATHERS

	TS (°C)
UNTANNED HIDE/SKIN	
Native collagen	55 – 60
Limed/pickled skin	40 – 50
TANNED HIDE/SKIN	
Chamois leather	68 – 72
Aluminium tanned leather	75 – 85
Synthetic tanned leather	75 – 82
Oxazolidine tanned leather	76 – 85
Wet-white tanned leather	78 – 85
Vegetable tanned leather	80 – 85
Glutaraldehyde tanned leather	80 – 85
Zirconium tanned leather	85 – 95
Titanium tanned leather	85 – 95
Veg - hydrolysable tannin + Oxazolidine	85 – 90
Veg tannin + Glutaraldehyde tanned	90 – 95
Veg tannin + Phosphonium salt (THPS) tanned	90 – 95
Veg tannin + Metal salt (Al / Ti / Zr)	90 – 100

Chrome tanned leather	> 100
Veg - condensed tannin + Oxazolidine	105 – 115

2.8 COMPOSITION OF GREEN (FRESH) RAW HIDE AND SKIN

	HIDE-cattle (%)	SKIN-sheep (%)	SKIN-goat (%)
Water	60.0 – 65.0	60.0 – 65.0	60.0 – 65.0
Structural (Fibrous)			
Collagen	30.0 – 33.0	20.0 – 25.0	28.0 – 33.0
Keratin (hair/wool)	2.0 – 4.0	3.0 – 6.0	3.0 – 5.0
Elastin	0.2 – 0.4	0.2 – 0.4	
Non-structural			
Albumen/Mucoids	1.0 – 3.0	0.5 – 1.5	1.0 – 3.0
Natural fat/grease	2.0 – 4.0	10.0 – 15.0	2.0 – 6.0
Mineral salts/other subs.	0.5 – 1.5	0.5 – 1.5	1.0 – 2.0

2.9 TANNERY COSTING

Every tannery should do overall costings of its production in order to know the total costs in order to decide and determine the selling prices of their saleable end products. Direct production costs involve raw material, labour, process chemicals, energy supplies (electricity fuel/coal), effluent treatment, etc. Indirect (Over-head) costs include administration, sales, insurance, depreciations (buildings/machines), etc. Below an example is given for a shoe-upper leather (from cattle hide) tannery:

Direct Production Costs:	Raw material	50 – 55%
	Process chemicals	10 – 15%
	Energy supplies	5 – 7%
	Labour	12 – 15%
	Wwt.p. costs	2 – 4%
Indirect Production Costs:	Administration/Management	5 – 8%
	Depreciations	2 – 4%
	Insurance/transport, etc.	6 – 8%
	Maintenance/spare parts	2 – 5%

For other types of leathers, such as, upholstery, double-face the main variable is the cost of raw materials. Significant changes are rare for other components.

2.10 CORRELATIONS BETWEEN THE TANNERY PARAMETERS

Below several tannery parameters are given for the existing tanneries and also new tanneries whose feasibility reports/studies are developing – in terms of efficient utilisation of labour, space, energy and water.

PARAMETER: OUTPUT

(A) Hide/skin (kg) necessary for per worker(labour)

The variations depend on the characteristics of the country (climate, comfort conditions, annual working hours/days of the worker) and the experience of the manpower employed.

EXAMPLE: for wet-salted hides of 20 -25 kg for shoe-upper, it is 30000-40000 kg per worker [per annum].

(B) Leather area produced (ft²) per worker

Average value for wet-salted hide as above, it may give 40000 – 50000 ft² per worker.

For sheepskin for nappa, it may be 50,000 – 60,000 ft² per worker [per annum]

Distribution of personnel in production departments (units):

Beamhouse	15 – 20%
End of tanning	15 – 20%
Post tanning ope.	20 – 25%
Mechanical ope.	20 – 25%
Finishing	25 – 30%

PARAMETER: YIELD

Finished leather produced (ft²) per wet-salted hide/skin (KG)

The yield depends on many factors, such as, preservation method, weight range, thickness, efficiency of mechanical operations.

EXAMPLE: Normally a 20 – 25 kg wet-salted hide gives ±1.5 sq. ft leather (grain) per KG.

But higher yield values can be obtained for dry-salted and lighter raw materials.

PARAMETER: FLOOR SPACE-AREA

Leather produced (ft²) per m² tannery floor space-area

Floor space includes production area, warehouses, maintenance shop, boiler house, lab.

Average value for shoe-upper tannery, it may be 1200 – 1500 ft² /m².

For sheepskin tannery for nappa, it may be 3000 – 4000 ft² /m².

The breakdown of floor space-area in a balanced tannery building is as follows:

Production depts.	70 – 75%
Raw mat. Warehouse	6 – 10%
Maintenance/atelier/boiler	5 – 8%
Laboratory	2 – 4%
Offices- Administration	15 – 20%
Labour Rest Rooms, etc.	5 – 10%

The breakdown of the floor space-area for production departments:

Beamhouse	25 – 30%
End of tanning	10 – 15%
Post tanning ope.	15 – 20%
Mechanical ope.	20 – 25%
Finishing	25 – 30%

PARAMETER: POWER FACTOR

Necessary leather produced (ft²) per installed kWh

This gives indication of the degree of mechanisation. The installed electricity power includes all tanning machinery/equipment - even lightning - in all sections of the tannery.

EXAMPLE: For a shoe-upper tannery, it may be 4,500 – 6,000 ft² / kWh [per annum]

The distribution of energy consumption in production departments:

Beamhouse processes	15 – 20%
Pickle/chrome tanning	10 – 15%
Post tanning processes	25 – 30%
Mechanical operations	25 – 30%
Finishing	15 – 25%

PARAMETER: CHEMICALS CONSUMPTION

Necessary chemicals (KG) per hide/skin (KG)

This coefficient must be regarded as indicative only. Each tannery has different recipes, techniques, so the total consumption of used chemicals show great alterations.

EXAMPLES: For each kg of w.s. hide for shoe-upper production – from soaking to the end of finishing - the chemical consumption is 0.5 – 0.7 KG.

Also, for each kg w.s. sheepskin for nappa leather production it is 0.4 – 0.6 KG.

PARAMETER: WATER CONSUMPTION

This parameter mainly depends on the technological level of the tannery. Decreased washings, rinsing and recirculation greatly lower down the consumed fresh water.

EXAMPLES: From soaking to the end of finishing operations:

Wet-salted hides for shoe-upper total amount can be 20 – 30 litres per KG.

Wet-salted sheepskins for nappa leather total amount can be 30 – 40 litres per KG. Besides above correlations, the technologist can look for similar in order to see and compare the effectiveness of his production system.

PART 3. QUALITY AND PROCESS CONTROL METHODS

Quality and process control systems or methods used in productions are important parts of leather technology. Depending on experience and applicability we can divide them into 4 different categories:

- CHEMICAL ANALYSIS: in chemical analysis, process liquors, processed leathers and chemicals used for productions are analysed and results are evaluated. Most of the procedures to be followed in analysis are given as national or international methods (ISO, IULTCS)

- PHYSICAL TESTING: physical testing mostly considers properties such as, tensile strength, elongation, tearing load and fastness properties such as, light, wet-dry rub, perspiration, etc. of semi or fully finished leathers or end products. The evaluations of analysis or test results are mostly done by comparing them with previously set-up standard limits, expressed as minimum or maximum values.

- MICROBIOLOGICAL METHODS: these methods deal with the structural behaviour of hides and skins. The application of staining techniques and use of microscopes is basic techniques.

- SENSORY-VISUAL METHODS (“ORGANOLEPTIC METHODS”): sensory-visual methods are practical and mostly non-destructive historical methods which are widely used all over the world. These depend on the practical experience and sometimes can tell us more than a complete physical testing. For example: the quality classifications of 1. grade, 2. grade, etc. are done using sensory-visual methods on pickled, wet-blue, crust and finished leathers. Accordingly, the detection of faulty sources or prevention of problems in leather production can be done by application of easy, rapid and cheap “in-house methods”. Most of them depend on qualitative estimations using special reagents, simple equipment and also utilise the above-mentioned methods. In this respect the reagents, apparatus and equipment used in the tanneries play an important role in the process control of leather production. For example: thickness gauge, thermometer, refractometer, pH-meter, indicators (paper + liquid), moisture meter, hydrometer, stereoscopic microscope, colorimeter, shrinkage temperature device, etc.

3.1 EXAMPLES FOR PRACTICAL CONTROL METHODS

Several selected practical and rapid control tests which are used in tanneries are explained below.

EXAMPLE NO.1 Colour, turbidity, pH-value say a lot about process water quality. Simple qualitative tests by using general reagents can give important information on the contaminants existing in water sources:

- fill a test tube with 10 ml water sample, add 2 ml 10% barium chloride, shake, a white ppt shows sulphate,

- fill a test tube with 10 ml water sample, the add drops of 10% potassium chromate and 2 ml 2% silver nitrate and shake, formation of red brown ppt shows chloride,

- fill a test tube with 10 ml water sample, add 2 ml 5% potassium or ammonium thiocyanate, shake, a red colouration shows iron contamination.

EXAMPLE NO.2 Ammonia odour, hair slip and red heat are the common clues

of bacterial damage to raw materials. Staleness or inadequate curing of hide/skin can be controlled by trying to puncture it with a suitable nail or a screwdriver. Undamaged hide/skin resist, but damaged material is more easily punctured.

EXAMPLE NO. 3 Enzymes which are produced by bacteria can be easily assimilated by gelatine. By using this phenomenon, the level of preservation can be estimated. A suitable portion of hide is cut off and squeezed by hand to remove 6 – 10 drops of “hide juice” onto a watch glass or Petri dish. Dilute with 2 – 3 ml distilled water and adjust the pH either with dilute alkali or acid to pH 7.0 ± 0.5 . A small piece of unfixed (unused) photographic film is taken and first wetted with water and afterwards the prepared solution is transferred to it. The film is put into an oven at $38 \pm 1^\circ\text{C}$ for about 45 minutes. Meanwhile the film should not be allowed to dry out. Afterwards the film is washed, dried and examined. Removal of gelatine (erosion) indicates the intensive bacterial activity.

EXAMPLE NO.4 The penetration of sodium sulphide or sulphhydrate during unhairing or lime painting can be checked by dropping 5% lead acetate solution on a cut of the hide/skin. Black colouration on the cross-section of the cut shows the distribution and penetration level of sulphide.

EXAMPLE NO.5 Damage to pelts in delimiting and bating are mainly due to the careless accidents with water (or steam) or high acidity in pickling which causes severe damage on the grain or even to the skin structure. A suspect of 5x10 cm is taken, squeezed and dehydrated with acetone and dried. Crackiness of grain shows above mentioned damages.

The loss of grain enamel due to mechanical or chemical causes can be detected by acetone dehydration and examination under a stereoscopic microscope.

EXAMPLE NO.6 Assessment of cross-sections of leathers during tanning or afterwards, for tannin penetration and fixation can be observed for chrome leathers as streaks of colour difference in samples taken from a thick part of the hide. For vegetable leathers, a cut piece of 1x2 cm is squeezed and put into concentrated acetic acid, i.e. for 30 minutes, drained and washed. Gel like appearance is seen in the untanned zones of the cut.

EXAMPLE NO.7 The contaminations of chrome tanned leathers with coloured metal salts can be detected as follows:

- pink colouration can be due to iron, a sample is taken, the grain is acidified with hydrochloric acid and 1 ml of 5% potassium ferrocyanide added a deep blue colour formation shows the presence of iron.

- green colouration can be due to the staining of copper, so, a leather sample is taken and 2 – 3 drops of 5% potassium cyanide is dropped on to the suspected stain, disappearance of stain shows the presence of copper.

EXAMPLE NO.8 The surface charges of tanned (dry or wet) leathers are important for estimation degree of the penetration of subsequent chemicals or to aid control of the adhesion of finish to the grain. In order to check the ionic charge, 3 to 5 drops of a special reagent is applied on to the same point

on the grain and left a few minutes. The formation of a blue-purple inner circle with a surrounding yellow ring, shows an anionic surface charge. If a yellow inner circle forms, surrounded by a blue-purple ring, this shows that the surface charge of the leather is cationic. Preparation of reagent: 0.05 g C.I. Acid Orange 61 dissolved in 10 ml distilled water and 0.0025 g Crystal Violet (C.I. Basic Violet 3) dissolved in 90 ml ethanol and mixed together.

EXAMPLE NO.9 Spew or spue formation on semi-finished or finished leathers are always a headache. The main causes for these are: a) migration of neutral salts (sodium chloride or sulphate), b) migration of fatty components, c) generation of fungi colonies due to organic residues.

The experiments below can give clues to the sources of spews/spues:

- with a knife scrape part of spue area and mix with 2 - 4 ml diethyl ether, if it dissolves easily, the test is positive for fatty components.
- smear with a knife a part of the contaminated area and well mix 3 - 5 ml distilled water, if it dissolves, the test is positive for neutral salts.
- if both above tests are negative, then the spew is most probably of fungal origin.
- use of stereoscopic microscope with 30x or 50x magnification can also be helpful on spew/spue identification.

EXAMPLE NO.10 In order to evaluate the rate of exhaustion of a retanning bath a gelatine test is necessary. Most of the syntans, resins and vegetable tannins give a reaction with gelatine. For testing, 10 ml filtered exhausted bath liquor is transferred to a test tube, add 1 ml gelatine reagent. Formation of a precipitate shows the existence of unbound or unpenetrated retanning agents. The density of the precipitate gives an idea of the quality of the process. Preparation of the reagent: take 1 g gelatine in 100 ml water, wait for 30 min., heat to 50°C, add 10 g sodium chloride, mix, lastly add 2 - 3 drops toluene or chloroform as preservative.

EXAMPLE NO. 11 Detection of fungicides in pickled pelts or in leathers:

Preparation of test sample take 10 - 15 g diced pelt or ground leather sample, transfer into a distillation flask, 100 ml distilled water and 10 ml 1M sulphuric acid are added. Heat until 50 ml distillate are collected. The following tests can then be tried:

- 5 ml distillate is taken in a test tube, 2-3 drops of Folin's and Ciocalteu's reagent is added, mixed and 2 ml 20% sodium carbonate solution added. Formation of a blue colour indicates the presence of a phenolic compound.
- 5 ml distillate is taken into a test tube, 2-3 drops of Folin's Ciocalteu's reagent added, mixed and 2 ml 20% sodium carbonate solution and 1 ml 1% ferric chloride are added, shaken. A reddish-violet colour shows the presence of paranitro phenol.
- 10 ml distillate is transferred into a 50 ml separating funnel and 10 ml chloroform is added, shaken and left for the separation of phases. The lower chloroform phase is taken into a test tube with addition of 10 ml water and 3-5 drops of

copper/pyridine reagent, shaken well and left.

If the chloroform phase shows a brown colour it denotes the presence of penta-chlorophenol or 2,4,6-trichlorophenol. (N.B. usage of these fungicides is banned in most countries.)

- diazotised sulphanic acid gives coloured reactions with phenolic fungicides (excluding chlorinated phenols), e.g. yellow orange colour with paranitro phenol, red with ortho-phenylphenol and para-chloro-meta-cresol.

EXAMPLE NO. 12 Detection of tanning components in leathers:

- 2-3 g ground leather (without finish) is put into a 20 ml 5M urea solution and shaken, left 24 hours. Brown colouration shows vegetable tannins, green colouration shows chrome.
- spot tests on the cut edge of leather for aluminium or zirconium detection can be done by dropping 1% Alizarin Red S indicator, aluminium gives orange and zirconium a red colouration.
- syntans can be detected according to their active groups as, with 1% uranyl acetate, sulphones give bright orange, naphthalene sulphonic acids yellow brown colour. With 1% azobenzene phenylhydrazine sulphonic acid gives a bright pink colour with cresol/sulphonic acids and cresol/phenol condensates. Sulphones give purple, cresol/phenol condensates a blue colour with 1% ferric chloride solution. Conc. nitric acid develops an orange colour with cresol/sulphonic syntans and light brown with naphthalene sulphonic acids.
- for the detection of urea-formaldehyde, hydrolyse a sample of ground leather with acid, neutralize (using bromphenol blue) and add urease, mix, a rise in pH indicates the resin.
- boil 1 g ground leather sample with 10 ml toluene for few minutes and pour into 20 ml ethanol, formation of a floc-precipitate shows the existence of acrylates.
- spot tests on cut edge of leather samples for the detection of vegetable tannins:

With conc. hydrochloric acid valex and chestnut give green-brown, mimosa gives red brown.

With perchloric acid and sulphuric acids (2:1) mixture, mimosa and quebracho develop a dark red colour.

U.V. light causes fluorescence with certain vegetable tannins, e.g. with quebracho and mimosa yellow; with mangrove brown and gambier shows a light green colour.

- 2-4 g ground leather is extracted with 15-20 ml warm water, the solution is transferred into a test tube and 1 ml aniline added, well shaken, formation of a precipitate shows sulphite cellulose (lignin sulphionate).

EXAMPLE NO.13 Each individual laboratory analysis result gives clues to the quality of the processing system or end product. Correlation or relationship between the results can be also a useful tool for practical quality evaluations.

Examples:

- ash and moisture content: laboratory analysis of wet-salted or brine cured hides can be evaluated as such. If the ash-moisture ratio is between $35 \pm 5\%$, it

means that the hide is properly cured.

- during chrome tanning: the values for pH and shrinkage temperature are directly proportional to the Cr₂O₃ content of leather.

60 ± 15%. Lower values show inferior tanning, higher values the possibility of over tanning.

EXAMPLE NO. 14 In order to decrease or make savings in the amounts of water used and to measure the effectiveness of washings or rinsing a rough estimation of the residual chemicals can be checked by “pass or fail” tests.

For example, an aliquot is taken from lime washings (for the control of selected maximum permitted residual sulphide) and reacted with a fixed amount of buffer and iodine solution and checked for the presence of persistent iodine. So, either the washing is complete or further one is necessary.

EXAMPLE NO. 15 Estimation of the exhaustion rates of coloured process baths can be made by the preparation of a series of standard solutions with different concentrations for visual comparison of colours. For example, the tannin content in colouring/pretanning baths or pits of vegetable tannins; residual dyes of double-face (fur-suede) in mixers, chrome oxide content of the exhaust baths can be estimated. In order to prevent the instability of some coloured standard solutions in the long term, suitable colours may be obtained by reacting the product with certain reagents.

EXAMPLE NO. 16 The quality of raw material has great effects on the value of end products, but it is not easy to estimate or detect the state of grain damage visually even after liming, pickling or tanning. Also, the faults caused by machines cannot be noticed during wet stages. So, in order to make the damage visible, a dark coloured pigment dispersion is applied by slicking (swabbing) to selected samples and afterwards the pigment is wiped off. The damaged areas are filled by the pigment and can be easily observed and the degree or distribution of damage like scratches, parasitic disease marks, etc are then recorded.

EXAMPLE NO.17 The pH measurements of cross-sections of cut pieces of pelts or leathers during wet processes depend on the limited precision of bromocresol green and phenolphthalein indicators. The supply and use of the following indicators are recommended for more reliable measurements: thymol blue or methyl orange for pickling; dimethyl yellow for basification; methyl red in neutralisation and phenol red or bromothymol blue in deliming bating.

The above practical tests are examples of long experience, but with the development of science and technology new and modern techniques are available. The new techniques are either presented as “test kits” or as sophisticated instrumental analysis equipment.

For example, test kits for water hardness, BOD/COD analysis are also used in other industries, it is possible to determine the concentration of ions in baths (e.g. chloride, sulphide, ammonium, etc.) with ion selective electrodes.

3.2 QUALITY CONTROL OF LEATHER CHEMICALS

Countless number of chemicals are used in leather processing. The quality control of them is important for obtaining efficient and optimum end results.

The leather chemicals can be looked and examined under 2 groups
GENERAL (BASIC) CHEMICALS: these being commodity chemicals, such as sodium sulphide, ammonium sulphate, formic acid mostly do not need “% active substance” control, but the control of impurities (or contaminations) might be necessary or important for safer usage, e.g. iron contaminations, existence of more moisture than expected. The control of specific gravity of acids or liquid chemicals is not always reliable, so checks for “cheap fillers” are necessary. Addition of molasses in lactic acid, sodium chloride to liquids are common tricks.

PROPRIETARY CHEMICALS: these chemical products are produced by special companies and have also “trade names” given by the manufacturing company. Suspected or newly marketed products may need more attention for qualitative or quantitative analysis for control purposes. If necessary, classical moisture, ash or solid matter content analysis, stability and viscosity tests or pH-value determination says a lot about the products expected performance on leather. It is mostly pointless to attempt to control sophisticated proprietary products with limited lab facilities and possibly lack of experience, e.g. enzyme preparations, biocides, dyeing auxiliaries, waterproofing agents, etc. Proprietary products manufactured under license mostly do not need lab control as basic information is given in their technical leaflets and safety- environmental issues are explained on their “material safety data sheets”. Below by given simple tests a satisfactory guidance can be obtained:

- fatliquors: odour, appearance, emulsion stability to acid/salts, charge control and yellowing test give enough information. Similar tests are also, valid for surface active agents, emulgators, etc.

- dyestuffs: “the blow out test” is common for checking the composition and solubility in water, stability to acid/bases/hardness, ash analysis (for inorganic filler) are common.

- synthetic tannins: ash analysis gives clues to the presence of fillers or buffer salts.

- finishing auxiliaries: in general, water or solid matter control, stability, compatibility with other components and specially film formation and yellowing tests are important for binders and lacquers.

Technological applications are the best way of evaluating the performance of post-tanning agents, e.g. for dyestuffs, colour tone, penetration; for synthetic tannins, tanning value/capacity; for fatliquors, softness, smell, handle is important aspects.

PART 4. ENVIRONMENTAL ISSUES FOR LEATHER

INDUSTRY

Below, a short view is given on the created tannery wastes, w.w.t. methods. Safer processes for environmental protection and pollution control advantages from partly processed leather examples are given.

4.1 SOURCES OF WASTES AND TREATMENT METHODS

Tanneries create 3 types of wastes during productions.

GASEOUS: these occur due to the release of fumes during pre-tanning processes, such as, hydrogen sulphide, ammonia, acids, etc.

In finishing operations evaporation of thinners and volatile compounds are seen. Treatment or reusage is expensive, so, the usage of evaporable hazardous chemicals should be restricted.

SOLIDS: main sources are trimmings from raw material, from limed pelts, fleshing and chrome shavings and buffing dust, crust trimmings

A certain part of them can be utilised for the production of value-added products, such as: limed fleshing can be used for gelatine, protein source, glue, fodder.

Chrome shavings and leather trimmings can be consumed for leather board and as chemical auxiliaries.

LIQUID: main source of pollutants are waste waters obtained from each process, all wastes are carried and exist in water as soluble or suspended forms. Major concern is the treatment of polluted-used water, before giving to the environment, e.g. to rivers, lakes.

CLASSICAL W.W.T. COVERS 3 MAIN STAGES

- mechanical treatment: separation of coarse particles and removal of fat-grease by decantation. Initial clarification is by settling the water and primary sludge formed is removed.

- chemical treatment: separation of dissolved pollutant components by using flocculating agents (polyelectrolites, Al-salts). The secondary sludge formed is removed.

- biological treatment: activated sludge, percolated filter, aeration, etc. methods are used. The sludge formed is removed.

4.2 ADVICES FOR SAFER PROCESSES BY USING ENVIRONMENTALLY FRIENDLY CHEMICALS

Soaking: usage of biodegradable surfactants / bactericides

Liming: selection of hair saving and low sulphide processes,
 Deliming / Bating: low ammonium usage, recycling of spent liquors,
 Pickling: usage of low salt and organic acids, recycling,
 Chrome tannage: apply higher exhaustion / fixation system, recycling of liquor by mending. Usage of low chrome; replacement-support of other tanning agents,

Retannage: low-HCHO and salt containing syntans, resins

Fatliquoring: use AOX –free products with high exhaustion and having low fogging values with neutral odour,

Dyeing: use liquid and dedusted dyes with good light and wash fastnesses and with effective fixing rate.

Finishing: prevent p.p. made from heavy metals, use low or free VOC systems,

Wet-white systems: usage of alternative tanning agents without chrome or aluminium which should give sufficient Shrinkage Temperature.

4.3 ADVANTAGES OF PARTLY PROCESSED LEATHERS

In order to minimise the effluents created from the productions, the below given partly processed leathers can be preferred where strict environmental restrictions are valid.

Initial stage

Pickled pelt: no pollution from beamhouse processes; medium term storage is possible,

Wet-white: no tanned waste created; flexible tannage and post-tanning processing possible,

Dry-white: as wet-white and reduced transport costs,

Wet-blue: high stability, long term storage possibility; easier and preferred commodity,

Undyed crust: low pollution, low transport costs and rapid response to orders,

Dyed crust: easy finishing and rapid response to orders.

4.4 LIQUID EFFLUENT LOAD (%) DISTRIBUTIONS IN PROCESS PHASES FOR DIFFERENT LEATHERS

	Wet-salted cattle hide for shoe -upper leather (%)	Wet-salted cattle coupon for sole leather (%)	Wet-salted sheepskin for nappa (%)
Soaking/Unhairing /Liming/Washing	40 – 50	40 – 50	35 – 45
Deliming/Bating	10 – 15	10 – 15	10 – 15
Degreasing/Washing	-	-	10 – 15

Pickling/Chrome tannage	15 – 20	-	15 – 20
Neutralisation/Retanning/ Dyeing/Fatliquoring	20 – 25	-	20 – 25
Full veg tannings (sole) and in relevant processes	-	40 – 50	-
Mec. ope. (samming) and finishing (wasted chemicals etc.)	3 – 5	1 – 2	3 – 5
General wastewater	5 – 10	5 – 10	5 – 10

4.5 HYDROGEN SULPHIDE HAZARD AND REMEDIES FOR THE PREVENTION OF ACCIDENTS

The use of sodium sulphide, sodium sulphhydrate and organic sulphides for unhairing operations mostly lead to the formation of poisonous gas – “hydrogen sulphide” due to the rapid lowering down of bath pH from 14. Inhalation of the gas may cause rapid poisoning, even 700 ppm can be dangerous

The following measures can be advised for reducing the occurrence of danger:

- before discharge washing of limed pelts,
- advocate low sulphide unhairing methods,
- addition of sodium bisulphite in deliming,
- practical ventilation of the working area,
- using special gasmasks while opening up of the drums.

4.6 PARAMETERS AND LIMITS FOR DISCHARGED TANNERY WATER

Legislations on wastewater discharges is becoming increasingly strict.

The establishment of wastewater treatment plants, either for individual tanneries or for common in clusters – or special zones – are going to be compulsory in most of the countries.

The legislations for the level of treatment (purification) and hence, the acceptable analysis limits of liquors mainly set by 3 sources:

- the municipalities involved – where general sewage treatment is compulsory,
- the national bodies involved – have stricter and sometimes have compulsory rules,
- the international bodies involved – give more elastic rules and act as advisory level.

Before discharge into the environment, the tannery waste liquors are treated by physical/chemical/biological methods and afterwards discharged to rivers or seas. The waste liquors given to sewer(sewage) systems, such as, to municipality, terminates in a joint effluent treatment(purification) plant. The main parameters with their corresponding limits are given below as for guidance purposes.

LIMIT – A is for discharge into the environment – surface waters (mg / litre)

LIMIT – B is for discharge into the public sewer treatment plant (mg / litre)

Parameter	LIMIT – A	LIMIT – B
pH-value	6.0 – 9.0	6.0 – 10.0
COD	200	1000
BOD	100	400
Suspended oils	100	600
Total kjeldahl Nitrogen	20	100
Phosphorus	2	20
Chloride	500	1000
Sulphide	1	2
Sulphate	500	1000
Chromium – 3	2	2
Chromium – 6	0.1	0.1
Aluminium	5	15
Phenol	0.1	1
Dissolved salts	1000	3000
Oils and greases	10	30
Hydrocarbons	10	20
AOX	2	5

4.7 SAVINGS, CONTROLS AND SAFETY IN THE TANNERY

Below a checklist is given for different aspects of energy and water conservation and safety concepts in the tannery and also in the office and service departments. The suggestions(advice) also leads to “money-cost saving” and refer to the respect to the environment:

- Check all energy use points day and night for possible waste.
- Cut out week-end overtime, limit it to certain evenings.
- Use battery powered(operated) lift trucks which can be recharged at low night periods.
- Lubricate machinery according to the manufacturers’ specifications.
- Check belt tensions.
- Maintain equipment according to operating hours, not calendar.
- Install more insulation on the ceiling and walls, mainly if winter and summer temperature degrees differences are high.
- Use air or canvas or similar where doors must be open.
- Clean heating and cooling units and filters regularly.
- Install heat recovery units on exhausts – especially on driers. Turn off process and drier exhausts when not in use.
- Recirculate heat from a high ceiling to a low level where space heating is required.
- Check boiler efficiency and note that for every 5°C increase in boiler feedwater temperature, boiler efficiency is increased by 1%.

- Match electric motors to supply voltage when ordering. Also match motors to average cycle loads not peaks.
- Use timers, pilot lights, float switches, temperature controllers, etc.
- Ensure all walls are light coloured and make maximum use of daylight and heat from the sun in the factory.
- Lower lights in high ceilinged media.
- Don't use air pressure higher than necessary.
- Install air compressors intakes in coolest location available.
- Redesign exhaust systems in order to improve their efficiency.
- Determine the lowest possible temperature for process liquors(baths) being left overnight or at weekends.
- Use warm wastewater to heat new solutions.
- Check throughout the tannery for water leaks.
- Reuse the water used by the vacuum driers.
- Control the flow of water in heat exchangers and clean them regularly.
- Adopt low float processes where applicable or practicable.
- Recycle or recirculate process liquors, save chemicals as well as water -- taking under consideration the adverse effects.
- The purified wastewater from the wastewater treatment plant can be used in certain beamhouse processes—this is can be more important where the scarcity of clean water is valid.
- As the conc. of pollutants is the basis for the effluent charge, a reduction in effluent emission will mean an increased conc. of pollutants, unless chemicals are being recovered and recycled. In these circumstances reduced emission could be counter cost productive.
- Care should be necessary for optimum temperature control in the raw material warehouse depending on the preservation methods and period of storage.
- The storage of vital spare parts of the tannery machinery is important for unexpected breakdowns or failures.
- Mechanical separation by sieves of solid particles such as, hair, pieces of trims, fleshes from the discharged waste liquors of the tannery help a lot to wwt.p.
- Separation of solid wastes as, limed fleshing/trimmings/chrome shavings are necessary for proper evaluation and hence for environmental respect.
- Filters/washings can be applied to decrease down the negative impact of the boiler exhaust gases.
- Flammable chemicals (thinners, lacquers) should be stored separately.
- Practical process quality controls should be done for each process phase in order to produce standard quality end products.
- The activities of the laboratory should be encouraged for basic chemical analysis of process liquors, pelts and certain chemicals.
- Periodical calibration should be done for the sake of precision of machinery and equipment, e.g., measuring machine, weight balances, etc.

PART 5. RESTRICTED CHEMICALS IN THE LEATHER INDUSTRY

Basic information is given on the banned (forbidden) and restricted hazardous chemicals -- used in the production of different leathers - which could be available (exist):

A) in the proprietary chemical products,

B) in semi-finished/finished leathers and "ready-made" leather garments

At the moment there are several problems between the producer-seller (exporter) and tanner-buyer (importer) on the following points:

A) The analysis methods of sophisticated chemicals have different precisions,

B) The permissible limits (accepted limits) of individual chemicals:

- in chemical products – sold to tanners

- in leather or leather end products (garment, footwear, leather goods) are variable in different countries.

There are strict limits for several chemicals, but an important part has a wide range of acceptability. For example:

BUYER A for X chemical accepts max 10 ppm.

BUYER B for X chemical accepts max 50 ppm.

For most of the hazardous or RSL products the limits accepted are very low - depending on the method – it refers to the detection limit of the reference sample.

The lowest available detectable limits mainly depend on the extraction method of the chemical and the precision of the instrumental analysis machine.

Besides international manufacturers, ECOLABEL, NGOs, ISO have their own analysis methods and limits and REACH on behalf of the EU acts in order to protect the member countries.

Nevertheless, negotiations continue for the limits which could be acceptable by the majority. Below important chemical groups are investigated for the degree of hazardous activity, properties explained, and proposed limits are given for better understanding the importance of the problem.

FORMALDEHYDE

It is the simplest, traditional and widely used aldehyde in different industries.

It mainly exists in syntans, resins as the unreacted component of the reaction.

Complete banning will not be possible due to compulsory wide usage in different industries besides leather industry. Such as in the production of UF / MF adhesives used in plywood and fibreboard, etc.

Restrictions are seen which differ in each country, current limits for leather garments/shoes is 20 ppm for children and for adults is 75 ppm.

Skin contact of leather and emission to the air are important aspects. For automotive upholstery, it is lowered down, as to max 10 ppm.

HEXAVALENT CHROME(Cr-6)

Hexavalent chrome is a carcinogenic and allergenic and focused on intensively during the last 10 years. It is formed after tanning with the basic Cr-3 salts. There are several factors effecting the formation of Cr-6 during storage and usage. Such as fatliquors-having unsaturated comp., oxidising agents which accelerate with the help of moisture and temperature. Prevention can be by using several proprietary products (antioxidant), vegetable tannins (tara, redpine bark ext.) The detection limit in the analysis is 2 ppm, but higher allowances are seen from different sources.

AROMATIC AMINES

Aromatic amines are sourced from azodyes, they are formed by break of the structure. At the moment about 30 aromatic amines are restricted due to their carcinogenic properties. Below several examples are given for information:

- 4-chloroaniline
- o-toluidine
- 4-aminodiphenyl
- 2-naphthylamine
- 3,3-dichlorobenzidine
- 3,3-dimethylbenzidine
- benzidine
- 4,4-thiodianiline
- 4,4-oxydianiline
- 2,5,5-trimethylaniline

There are several methods put forward, for analysis, but 20 ppm is given by EU Regulation and up to 200 ppm allowance is possible in the dyestuffs for each amine.

A long list of dyestuffs from Colour Index had been banned from production.

They are mainly Direct, Disperse and Basic class of dyestuffs.

BIOCIDES: BACTERICIDES AND FUNGICIDES

They are prepared and used widely; bactericides in preservation, soaking and fungicides in pickling, tanning, wet-leather storage, etc.

Nowadays, for the used biocides, such as, for PCMC the limit is max 300 ppm, for OIT max 100 ppm, for OPP max 300 ppm and for TCMTB max 500 ppm.

Biocides and pesticides also exist in w.w.t.p. and their treatment may be problematic. Also, mono/di/tri butyltin products used as biocide were banned years ago, but some sources give allowance as max 5 ppm.

CHLORINATED PARAFFINS

For short chain (C10 – C13) chlorinated paraffins restrictions are valid (0.1-1.0%), but, for medium chain (C14 - C17) and long chain (C18 - C30) no restrictions in ZDHC-MRSL list.

CHLORINATED PHENOLS

Classical chlorinated 3 different phenols used as fungicide were forbidden years ago, not only in leather but also at other industries These are:

PCP: pentachlorophenol

TeCP: tetra chlorophenol

TriCP: trichlorophenol

Still some sources accept and give as max 5 ppm limit.

CHLORINATED SOLVENTS

Chlorinated solvents are preferred mainly for degreasing purposes. For aqueous degreasing (together with emulsifiers) methylene chloride and trichloroethylene is used – and their allowance is max 5 ppm in leathers. Whereas, perchloroethylene (tetrachloroethylene) is used as degreasing in closed system solvent degreasing machines mainly for double-face – and allowed as max 40 ppm in leathers.

NONYLPHENOL ETHOXYLATES (NPEOs)

They belong to alkylphenol ethoxylate group. Their production restrictions began 20 years ago, but still widely used due to their cheap price. Being a non-ionic, they are used as surface active agent/emulsifier/degreaser, etc. depending on the ethylene oxide number in the molecule.

PHTHALATES

Phthalates are used for plastics as softening and in leather finishing as plasticiser.

At the moment the below given 6 phthalates are focused on:

- di-(2 ethyl hexyl) phthalate
- di-butyl phthalate
- benzyl butyl phthalate
- diisodecyl phthalate
- diisononyl phthalate
- di-n-octyl phthalate

The allowance in leather chemicals is 1000 ppm, but for footwear, it is max 500 ppm.

DIMETHYL FUMARATE (DMF)

Dimethyl fumarate is also used for furniture as fungicide. The sublimation characters of the chemical initiates and act as irritator and sensitizer to humans.

POLYCYCLIC AROMATIC HYDROCARBONS(PAH)

Naphthalene, pyrene, anthracene and phenanthrene are common PAHs and sometimes exist in leather chemicals. Allowance of max 5 to 30 ppm is given by several sources.

PERFLUORINATED AND POLYFLUORINATED CHEMICALS

These are historical chemicals, but still found in different products, such as PFOA, PFDA, PFNA, PFTA and more than 20 similar chemicals. Some sources already banned them due to their toxic effects. But, still, a max 2 ppm restriction is seen by bilateral agreements.

VOLATILE ORGANIC COMPOUNDS (VOC)

VOCs include solvents and diluents used in leather finishing phase and mainly cover the Boiling range 60 – 220 °C. VOC, normally emit to atmosphere due to the evaporation after the treatment (e.g. as thinner – with N/C, P/U lacquers). The allowance limits of VOC in chemical products are negotiable in RSL. For example, for xylene and o-/m-/p- cresols the limits are max 500 ppm. Cyclohexane, methylethylketone (MEK) have less allowed limits, as max 100 ppm.

HEAVY METALS

Restrictions of heavy metals in chemical products had started 50 years ago. But still their existence is seen, and limits set for them; cadmium 70 ppm, barium 1000 ppm, lead 80 ppm, selenium 400 ppm and antimony 70 ppm. Modern leather technology lead to the production of metal free leathers (inc. -wet-white systems) and decrease the usage of Cr-3, Al-3 tanning salts. But, due to the contaminations, important amount of heavy metals is traced in analysis which create problems.

SUBSTANCES OF VERY HIGH CONCERN (SVHC)

There are more than 170 different chemicals which are listed in SVHC, in near future the numbers will increase, mainly depending on the attitude of REACH and it will be focused on the leather products imported to EU member countries. At the moment max 1000 ppm allowance is given, but decrease of limits will occur inevitably.

SOME OTHER FOCUSED CHEMICALS

The following chemicals are also in the restricted lists:

- Boron containing chemicals: borax and boric acid
- Acetaldehyde
- N-methyl pyrrolidone (NMP) and N-ethyl pyrrolidone
- Halogenated (Brominated) flame retardants – TRIS, PBB, HBCD, BBMP, TBBPA.

PART 6. SELECTED DATA FOR THE TANNER

6.1 CHEMICAL COMPOUNDS USED IN LEATHER INDUSTRY

Name	Molecular Weight	Solubility (g/l in water)
Acetic acid	60.2	miscible
Acetone	58.2	miscible
Aluminium chloride	241.3	450
Aluminium oxide	102	insoluble
Aluminium sulphate	666.4	363
Ammonium hydroxide (Ammonia solution)	35	miscible
Ammonium chloride	53.5	370
Ammonium sulphate	132.1	750
Borax (Sodium tetraborate)	381.5	15
Boric acid	61.8	50
Calcium carbonate	100.1	insoluble
Calcium chloride (anhydrous)	111	readily sol.
Calcium chloride (cryst.)	19.1	750
Calcium formate	130	500
Calcium hydroxide	74.1	1.3
Chrome alum	499.5	240
Chromium chloride	158.5	readily sol.
Chromium hydroxide	103	insoluble
Chromium sulphate	716.5	120
Formic acid	46	miscible
Glucose	180.3	850
Glutaraldehyde	100.1	soluble
Glyoxal	58	soluble
Hexamethylene tetraamine	140.2	810
Hydrochloric acid	36.5	miscible
Hydrogen peroxide	34	miscible
Hydrogen sulphide	34.1	soluble
Iron alum	503.2	soluble
Iron (+3) chloride	270.4	519
Iron (+3) sulphate	562.1	440
Iron (+3) oxide	159.8	insoluble
Lactic acid	90.1	miscible
Magnesium chloride	203.3	542
Magnesium oxide	40.3	insoluble
Magnesium sulphate	246.5	350
Oxalic acid	90	97
Phthalic acid	146.1	6
Potash alum	474.4	115

Potassium carbonate	138.4	120
Potassium chloride	74.5	340
Potassium dichromate	294.2	125
Potassium hydroxide	56.1	???
Potassium permanganate	158	64
Sodium acetate	136.1	800
Sodium bicarbonate	84	96
Sodium dichromate	298	240
Sodium carbonate	106	readily soluble
Sodium carbonate (cryst.)	286.1	readily soluble
Sodium chloride	58.4	360
Sodium chlorite	90.4	600
Sodium formate	68	readily soluble
Sodium hexametaphosphate	611	soluble
Sodium hydrosulphite	210.2	250
Sodium hydroxide	40	1070
Sodium nitrite	69	830
Sodium phosphate (mono)	138	1100
Sodium phosphate (di)	358.2	700
Sodium phosphate (tri)	380.2	260
Sodium sulphate (anhydrous)	142.1	readily soluble
Sodium sulphate (cryst.)	322.2	190
Sodium sulphide	78.1	150
Sodium sulphite	126	readily soluble
Sodium sulphhydrate	56	readily soluble
Sodium thiosulphate	248.2	700
Sulphuric acid	98.1	miscible
Tartaric acid	150.1	140
Titanium dioxide	79.9	insoluble
Urea	60.1	800
Zirconium dioxide	123.1	insoluble
Zirconium sulphate	355.5	soluble

6.2 PREPARATION OF BUFFER SOLUTIONS FOR pH-METERS

BUFFER FOR	pH = 1.7	12.7 g/l	Potassium Tetroxalate
	pH = 2.0	1.0 g/l	Tartaric Acid
	pH = 3.56	Saturated solution of Potassium Hydrogen Tartrate	
	pH = 4.0	10.2 g/l	Potassium Hydrogen Phthalate
	pH = 7.0	3.4 g/l	Potassium Dihydrogen Phosphate
and			
	pH = 9.2	3.6 g/l	Disodium Hydrogen Phosphate
		19.2 g/l	Borax

Carbonate	pH = 10.0	4.7 g/l	Borax and 4.0 g/l Sodium
	pH = 12.0	0.4 g/l	Sodium Hydroxide (0.01M)
	pH = 12.6	Saturated solution of Calcium Hydroxide	
	pH = 13.0	4.0 g/l	Sodium Hydroxide (0.1M)
	pH = 14.0	40.0 g/l	Sodium Hydroxide (1.0M)

6.3 PREPARATION OF INDICATOR SOLUTIONS

Indicator	Effective pH Range	Colour Range	Preparation
Thymol blue	1.2 – 2.8	red – yellow	0.1% in 20% alcohol
Bromophenol blue	3.0 – 4.6	yellow – blue	0.1% in 20% alcohol
Methyl orange	3.1 – 4.4	red – orange/yellow	0.1% in water
Bromocresol green	3.8 – 5.4	yellow – blue	0.1% in 90% alcohol
Methyl red	4.4 – 6.2	red – yellow	0.2% in 90% alcohol
Bromocresol purple	5.2 – 6.8	yellow – purple/red	0.05% in 90% alcohol
Bromothymol blue	6.0 – 7.6	yellow – blue	0.1% in 20% alcohol
Phenol red	6.8 – 8.4	yellow – red	0.04% in 90% alcohol
Phenolphthalein	8.0 – 10.0	colourless – red	1.0% in 50% alcohol
Thymol violet	9.0 – 13.0	yellow/green – violet	0.2% in 50% alcohol
Thymolphthalein	9.3 – 10.5	colourless – blue	1.0% in 90% alcohol

“UNIVERSAL INDICATOR” can be prepared by mixing the following indicators:

- 1 pt. Methyl red
- 1 pt. Phenolphthalein
- 2 pt. Thymol blue
- 2 pt. Bromothymol blue

Colour Range of Universal Indicator:

pH-Value	3	4	5	6	7	8	9	10
	Red	Orange	Orange	Yellow	Yellow	Green	Blue	Violet
		-red			-green		-green	

6.4 CONVERSION TABLE OF SPECIFIC GRAVITY, BARKOMETER AND BEAUME

SPECIFIC GRAVITY (g/cm ³)	DEGREES BARKOMETER (°B _K)	DEGREES BEAUME (°B _e)
1.0007	0.7	0.1
1.0069	6.9	1.0
1.0138	13.8	2.0

1.0280	28.0	4.0	1.5	1.88	2.69
1.0353	35.3	5.0	2.0	2.50	3.58
1.0501	50.1	7.0	2.5	3.13	4.48
1.0653	65.3	9.0	3.0	3.70	5.37
1.0731	73.1	10.0	3.5	4.38	6.27
1.0890	89.0	12.0	4.0	5.00	7.17
1.1054	105.4	14.0	4.5	5.63	8.06
1.1223	122.3	16.0	5.0	6.25	8.95
1.1398	139.8	18.0	5.5	6.88	9.85
1.1578	157.8	20.0	6.0	7.50	10.74
1.1763	176.3	22.0	6.5	8.13	11.64
1.1955	195.5	24.0	7.0	8.75	12.55
1.2153	215.3	26.0	8.0	10.00	14.30
1.2357	235.7	28.0	9.0	11.25	16.08
1.2569	256.9	30.0	10.0	12.50	17.90
			11.0	13.75	19.68
			12.0	15.00	21.50
			13.0	16.25	23.27
			14.0	17.50	25.06
			15.0	18.75	26.85

6.5 LEATHER THICKNESS (SUBSTANCE) CONVERSION TABLE

INCH	OUNCE (1/64")	IRON (1/48")	MILIMETER (0.03937)	
1/64	0.016	1	3/4	0.4
1/32	0.031	2	1 1/2	0.8
3/64	0.047	3	2 1/4	1.2
1/16	0.063	4	3	1.6
5/64	0.078	5	3 3/4	2.0
3/32	0.094	6	4 1/2	2.4
7/64	0.109	7	5 1/4	2.8
1/8	0.125	8	6	3.2
9/64	0.141	9	6 3/4	3.6
5/32	0.156	10	7 1/2	4.0
11/64	0.172	11	8 1/2	4.4
3/16	0.188	12	9	4.8
13/64	0.203	13	9 3/4	5.2
7/32	0.218	14	10 1/2	5.6
15/64	0.234	15	11 1/4	6.0

6.6 COMPARISON BETWEEN GERMAN, ENGLISH AND FRENCH DEGREES OF WATER HARDNESS

German (°G)	English (°E)	French (°F)
0.5	0.62	0.90
0.7	0.87	1.26
1.0	1.25	1.79

CONVERSION OF HARDNESSES:

1 German Degree of Hardness (°G)	= 1 part CaO	in	100,000	parts
of water				
1 English Degree of Hardness (°E)	= 1 part CaCO ₃	in	70,000	parts
of water				
1 French Degree of Hardness (°F)	= 1 part CaCO ₃	in	100,000	parts
of water				
10 USA Degree of Hardness (°US)	= 1°F			
1°G = 1.79°F = 1.25°E = 17.9 ppm (°US)				

6.7 CHEMICAL ANALYSIS AND PHYSICAL TESTING METHODS

The IULTCS through the "IULTCS Testing Commissions (IUC, IUP, IUF) provides help and protection for the leather tanning industry worldwide by developing and publishing test methods that are explicitly relevant to leather manufacture and leather usage. Without the work of IU Commissions which develop these methods, the leather industry could be open to having to meet performance standards of other materials that bear no relationship to the reality of working with leather. The IULTCS test methods are accepted ISO and following agreements in 1990 and 2005, ISO recognises IULTCS as international standardising body.

IULTCS AND ISO OFFICIAL CHEMICAL ANALYSIS METHODS

IUC / ISO NO.	METHOD NAME
IUC1	General comments
IUC2 / ISO 2418	Sampling location
IUC3 / ISO 4044	Preparation of chemical test samples
IUC4 / ISO 4048	Determination of matter soluble in dichloromethane
IUC5 / ISO 4684	Determination of volatile matter
IUC6 / ISO 4098	Determination of water-soluble matter
IUC7 / ISO 4047	Determination of sulphated ash
IUC8 / ISO 5398	Determination of chromic oxide content
IUC9 / ISO 5399	Determination of water-soluble magnesium salts
IUC10 / ISO 5397	Determination of nitrogen and hide substance
IUC11 / ISO 4046	Determination of pH and difference figure
IUC13	Determination of zirconium
IUC15	Determination of phosphorus
IUC16	Determination of aluminium
IUC17	Determination of hydroxyproline in collagen
IUC18 / ISO 17075	Determination of hexavalent chromium content
IUC19 / ISO 17226	Determination of formaldehyde content
IUC20 / ISO 17234	Determination of certain azo colorants
IUC21	Method for the detection of certain azo colorants
IUC22	Determination of aluminium oxide in aluminium tans
IUC24	Determination of basicity of aluminium tanning agents
IUC25 / ISO 17070	Determination of TCP, DCP, PCP contents
IUC26 / ISO 27587	Determination of free formaldehyde content
IUC27 / ISO17072	Chemical determination of metal content
IUC28 / ISO 18218	Determination of ethoxylated alkylphenols in leather
IUC29 / ISO13365	Determination of TCMTB, OPP, CMK, OIT in leather
IUC30 / ISO 18219	Determination of chlorinated hydrocarbons in leather
IUC32 / ISO 14088 method	Quantitative analysis of tanning agents by filter
IUC33 / ISO 17489	Determination of tan content in synthetic tannins
IUC34 / ISO 19070	Determination of N-methylpyrrolidone in leather
IUC35 / ISO 19071	Determination of Cr-6 in leather
IUC36 / ISO 20137	Guidelines for testing critical chemicals in leather
IUC37 / ISO 20136	Determination of degradability by microorganisms

IULTCS AND ISO OFFICIAL PHYSICAL TESTING METHODS

IUP / ISO NO.	METHOD NAME
IUP1,3 / ISO 2419	Sample preparation and conditioning
IUP2 / ISO 2418	Sampling location
IUP4 / ISO 2589	Measurement of thickness

IUP5 / ISO 2420	Measurement of apparent density
IUP6 / ISO 3376	Measurement of tensile strength
IUP7 / ISO 2417	Measurement of static absorption of water
IUP8 / ISO 3377	Measurement of tear load – double edge tear
IUP9 / ISO 3379	Measurement of distension and strength of grain
IUP10 / ISO 5403	Water resistance of flexible leather
IUP11 / ISO 5404	Measurement of water resistance of heavy leather
IUP12 / ISO 3378	Measurement of resistance to grain cracking
IUP13	Measurement of two-dimensional extension
IUP14	Measurement of waterproofness of gloving leather
IUP15 / ISO 14266	Measurement of water vapour permeability
IUP16 / ISO 3380	Measurement of shrinkage temperature
IUP17	Assessment of resistance of air-dry insole leather
IUP18	Resistance of air-dry lining leather to heat
IUP19	Resistance of air-dry upper leather to heat
IUP20 / ISO 5402	Determination of flex resistance
IUP21	Measurement of set in lasting
IUP22	Assessment of scuff resistance by viewing box
IUP23	Measurement of scuff damage
IUP24	Measurement of surface shrinkage
IUP26	Measurement of resistance to abrasion of heavy leather
IUP28	Measurement of resistance to bending of heavy leather
IUP29 / ISO 17233	Measurement of cold crack temperature of surface coatings
IUP30	Measurement of water vapour absorption and desorption
IUP32 / ISO 11646	Measurement of area
IUP35 / ISO 17227	Determination of dimensional stability of leather
IUP36 / ISO 17235	Measurement of leather softness
IUP37 / ISO 17231	Measurement of water repellence of garment leather
IUP38 / ISO 17232	Measurement of heat resistance of patent leather
IUP39 / ISO 5402	Determination of flex resistance – Part 2
IUP40 / ISO 3377	Measurement of tear load – Single edge tear
IUP41 / ISO 17186	Measurement of surface coating thickness
IUP42 / ISO 17229	Measurement of water vapour absorption
IUP43 / ISO17236	Measurement of extension set
IUP44 / ISO 23910	Measurement of stitch tear resistance
IUP45 / ISO 17230	Measurement of water penetration pressure
IUP46 / ISO 17071	Measurement of fogging characteristics
IUP47 / ISO 17074	Measurement of resistance to horizontal spread of flame
IUP48 / ISO 17076	Measurement of abrasion resistance
IUP 49	Measurement of bagginess
IUP51	Measurement of surface friction
IUP52	Measurement of compressibility
IUP53 / ISO 26082	Determination of soiling
IUP54 / ISO 14087	Determination of flexural properties

IUP55 / ISO 17130	Determination of dimensional change
IUP56 / ISO 17131	Identification of leather with microscopy
IUP57 / ISO 19074	Determination of water absorption by capillary action
IUP58 / ISO 19076	Measurement of leather surface – by electronic techniques

IULTCS AND ISO OFFICIAL FASTNESS TEST METHODS

IUF / ISO NO.	METHOD NAME
IUF105	Numbering code for fastness tests
IUF110 / ISO 2588	Leather –Sampling – Number of items for gross sample
IUF120 / ISO105-A01	General principles of colour fastness testing of leather
IUF 131 / ISO105-A02	Grey scale for assessing change in colour
IUF132 / ISO105-A03	Grey scale for assessing staining
IUF151 / ISO151	Preparation of storable Standard chrome grain leather for dyeing
IUF201	Approximate determination of the solubility of leather dyes
IUF 202	Fastness to acid of dye solutions
IUF203	Stability to acid of dye solutions
IUF205	Stability to hardness of dye solutions
IUF401 / ISO105-B01	Colour fastness of leather to light: Daylight
IUF402 / ISO105-B02	Colour fastness of leather to light: Xenon lamp
IUF412 / ISO17228	Change of colour with accelerated ageing
IUF420 / ISO15700	Colour fastness to water spotting
IUF421 / ISO11642	Colour fastness to water
IUF423 / ISO15703	Colour fastness to mild washing
IUF426 / ISO11641	Colour fastness to perspiration
IUF427 / ISO20701	Colour fastness to saliva
IUF434 / ISO11643	Colour fastness of small samples to solvents
IUF435 / ISO15702	Colour fastness to machine washing
IUF441	Colour fastness in respect of staining raw crepe rubber
IUF442 / ISO15701	Colour fastness to migration into polymeric materials
IUF450 / ISO11640	Colour fastness to cycles of to-and-fro rubbing
IUF452 / ISO20433	Colour fastness to crocking
IUF454	Fastness to buffing of dyed leather
IUF458	Colour fastness of leather to ironing
IUF470 / ISO11644	Leather – Test for adhesion of finish
IUF472 / ISO17502	Leather – Determination of surface reflection

6.8 QUALITY REQUIREMENTS FOR DIFFERENT TYPES OF LEATHERS

SHOE-UPPER LEATHERS

ANALYSIS/TEST METHOD		GRAIN/BOX SIDE	GLACED OR SIMILAR
IUC4	%	3.0 – 12.0	4.0 – 10.0
IUC5	%	<18	<18
IUC6	%	<1.5	<1.5
IUC7	%	<2.0	<2.0
IUC8	%	>2.5	>2.5
IUC10	%	>60	>60
IUC11	-	>3.5	>3.5
IUP6	N/mm ²	>20	>15
	e.a.b., %	<75	<75
IUP7	2 h, %	<60	<60
IUP9	g.c., N:mm	>200:>7	>150:>7
IUP10 -1	w.p., min	>30	>30
	w.a., %	<30	<30
IUP15	mg/cm ² .h	>1.0	>1.0
IUP16	°C	>100	>100
IUP20	dry		
	wet	>50000	>20000
		>20000	>5000
IUP29	°C	<(-20)	<(-15)
IUP30/42	mg/cm ² (after 8 hours)	>10	>10
IUP8/40	N/mm	>40	>30
IUP44	N	>100	>80
IUF401/402	B.W.S	>5	>4
IUF450	dry, 50 rub, G.S.	>4/3	>4/3
	wet, 50 rub, G.S.	>3/3	>3/3
IUF458	°C	>80	>80
IUF470	dry, N/cm	>4.0	>3.0
	wet, N/cm	>3.0	>2.0

CLOTHING / GARMENT LEATHERS

ANALYSIS/TEST METHOD	NAPPA	SUEDE	DOUBLE-FACE
IUC4	%	6.0 – 14.0	8.0 – 16.0
IUC5	%	<18	<18
IUC6	%	<1.5	<1.5
IUC7	%	<2.0	<2.0
IUC8	%	>2.5	>2.5
IUC10	%	>60	>60
IUC11	-	>3.5	>3.5
IUP6	N/mm ²	>10	>6
	e.a.b., %	<60	<60
IUP9	g.c., N:mm	>150:<7	-

IUP10 -1	w.p., min	>20	>10	>10
	w.a., %	<15	<20	<20
IUP15	mg/cm2.h	>1.0	-	-
IUP16	°C	>100	>100	>100
IUP20	dry	>50000	-	-
	wet	>20000	-	-
IUP29	°C	<(-20)	-	-
IUP30/42				
	mg/cm2 (after 8 hours)	>10	-	-
IUP8/40	N/mm	>35	>25	>20
IUP44	N	>100	>100	>50
IUF401/402	B.W.S	>5	>6	>6
IUF450	dry, 50 rub, G.S.	>4/4 >3/3	-	-
	wet, 50 rub, G.S.			
IUF458	°C	>80	-	-
IUF470	dry, N/cm	>5.0	-	-
	wet, N/cm	>4.0		

SHOE LINING LEATHERS

	ANALYSIS /TEST METHOD	VEG TANNED	COMBINED TANNED	CHROME TANNED
IUC4	%	4.0 – 8.0	5.0 – 10.0	5.0 – 10.0
IUC5	%	<18	<18	<18
IUC6	%	<6.0	<4.0	<2.0
IUC7	%	<3.0	<2.0	<2.0
IUC8	%	-	>1.0	>1.5
IUC11	-	>3.5	>3.5	>3.5
IUP6	N/mm2 e.a.b., %	>15 <70	>15 <100	>15 <100
IUP7	2 h	>75	>75	>75
IUP15	mg/cm2.h	>2.0	>2.0	>2.0
IUP16	°C	>80	>90	>95
IUP30/42	mg/cm2 (after 8 hours)	>20	>20	>20
IUF450	dry, 50 rub, G.S.	>4/4 >3/3	>4/4 >3/3	>4/4 >3/3

	wet, 50 rub, G.S.			
IUF470	dry, N/mm	>4.4	>4.4	>4.4
	wet, N/mm	>3.0	>3.0	>3.0

FURNITURE AND UPHOLSTERY LEATHERS

ANALYSIS/TEST METHODS

ANALYSIS/TEST METHODS

IUC4	%	<16
IUC5	%	<18
IUC6	%	<1.5
IUC7	%	<2.0
IUC8	%	<2.5
IUC11	-	>3.5
IUP6	N/mm2 e.a.b., %	>15 <50
IUP9	g.c., N:mm	>200:>7
IUP15	mg/cm2 .h	>1.0
IUP16	°C	>100
IUP20	dry	>100000
	wet	>50000
IUP8/40	N/mm	>40
IUP44	N	>100
IUF401/402	B.W.S	>6
IUF450	dry, 500 rub, G.S wet, 200 rub, G.S	>4/4 >4/4
IUF458	°C	>100
IUF470	dry, N/cm wet, N/cm	>5.0 >5.0

VEGETABLE TANNED HEAVY LEATHERS

ANALYSIS/TEST METHOD	FULL VEG SOLE	FULL VEG INSOLE	COMBINED TANNED SOLE
IUC4	%	2.0 – 4.0	4.0 – 6.0
IUC5	%	<18	<18
IUC6	%	<10	<10
IUC7	%	<3.0	<4.0
IUC8	%	-	>1.0
IUC9	%	<2.0	<2.0
IUC10	%	>35	>35

IUC11	-	>3.5	>3.5	>3.5
FIXED TANNIN				
DEGREE OF TANNAGE	%	>24	>24	>24
IUP6	N/mm ²	>25	>20	>25
	e.a.b., %	>30	>30	>30
IUP7	2 h	<35	>35	<35
	24 h	<50	-	<50
IUP11	min	>30	-	>30
	%	<30	-	<30
IUP16	°C	>80	>80	>90
IUP30/42				
mg/cm ² (after 8 hours)		-	>20	-
IUP8/40	N/mm	-	>60	-
IUF44	g/cm ³	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1

EXPLANATIONS:

1) ABBREVIATIONS:

- e.a.b. elongation at break
- G.S. Grey Scale
- B.W.S. Blue Wool Scale
- min minute
- h hour
- g.c. grain crack
- w.p. water penetration
- w.a. water absorption

6.9 BOOKS ON LEATHER SCIENCE

Below a selected textbooks list are given on leather technology, leather chemistry and relevant subjects available in German and English languages.

Gerbereichemie und Gerbereitechnologie
F. Stather
4. Auflage 1967, Akademie Verlag - Berlin

Bibliothek des Leders, Band 1 – 9
Herausgeber Prof.Dr. Hans Herfeld
1. Auflage 1981 – 1990, Umschau Verlag – Frankfurt

Leather Technician's Handbook
J.H. Sharpouse
2. Edition 1975, Leather Producers Ass. - London

The Chemistry and Technology of Leather
F.O'Flaherty, W.T. Roddy, R.M.Lollar
2. Edition 1976, Krieger Pub. Co. - Florida

Practical Leather Technology
T.C. Thorstensen
2. Edition 1976, Reinhold Pub. Corp. - NewYork

Gloving, clothing and special leathers
P.S. Briggs
1. Edition 1981, Tropical Products Institute – London

The manufacture of upper leathers
D.H. Tuck
1. Edition 1981, Tropical Products Institute - London

Physical Chemistry of Leather Making
K. Bienkiewicz
1. Edition 1983, R.E.Krieger Pub. Co. - Malabar, Florida

Introduction to the Principles of Leather Manufacture
S.S. Dutta
2. Edition 1983, Indian Leather Tech. Ass. - Calcutta

Theory and Practice of Leather Manufacture
K.T. Sarkar
3. Edition 1985, M.Sharif Pub. – Madras
Fundamentals of Leather Manufacturing
Prof.Dr. E.Heidemann
1.Edition 1993, Eduard Roether KG – Darmstadt

Possible Defects in Leather Production
Gerhard John
1.Edition 1996, Druck Partner Rubelmann GmbH - Hemsbach

Tanning Chemistry – The Science of Leather
Prof.Dr. A.D. Covington
1. Edition 2009, Royal Society of Chemistry - Cambridge

6.10 USEFUL CONVERSION FACTORS AND MEASUREMENT SYSTEMS

CONVERSION FACTORS: BRITISH AND SI METRIC SYSTEMS

	TO CONVERT:	TO:	MULTIPLY BY:
LENGTH	Inches	Centimetres	2.54

	Feet	Metres	0.3048
	Centimetres	Inches	0.3937
	Metres	Feet	3.2808
AREA	Square inches	Square centimetres	6.4516
	Square feet	Square metres	0.0929
	Square centimetres	Square inches	0.1550
Square	metres	Square feet	10.7639
VOLUME	Cubic inches	Cubic centimetres	16.3871
	Cubic feet	Cubic metres	0.0283
	Cubic centimetres	Cubic inches	0.0610
	Cubic metres	Cubic feet	35.3147
	Cubic feet	Litres	28.3161
	Litres	Cubic feet	0.0353
	Fluid ounces	Cubic inches	1.7339
	Cubic inches	Fluid ounces	0.5767
WEIGHT	Ounces	Grams	28.3495
	Pounds	Kilograms	0.4536
	Grams	Ounces	0.0353
	Kilograms	Pounds	2.2046
IMPORTANT FORCE	CORRELATIONS		
	1 N = 0.1020 kp (kilogram force)		
	1 kp = approx. 10 N = 10 daN		
PRESSURE	1 bar = 0.1 MPa		
	1 atm = 101.32 KN/m ²		
	1 kg/cm ² = 98.06 KN/m ²		
ENERGY	MJ (megajoule) = 106 J		
	1 Kcal = 4,1868 KJ		
	J = 0.2388 cal		
POWER	1 hp (horsepower) = 745,70 W		

SURFACE TENSION 1 DYNE/CM = 0.001 N/m

AREA	1 ft ² (square feet) = 9,29 dm ² (square decimetre)
	1 dm ² = 0,1076 ft ²

6.11 USEFUL ABBREVIATIONS

AOX	Absorbable Organic Halogenated Hydrocarbons
av.	Average
BOD	Biological Oxygen demand

COD	Chemical Oxygen demand
conc.	Concentrate / Concentrated
ex/ext	Vegetable Tannin Extract
IUF	Fastness Test Methods (IULTCS)
IUP	Physical Test Methods (IULTCS)
l/l	Litre
MAK	Maximum Admissible Concentration
MSDS	Material Safety Data Sheet
N/C	Nitrocellulose
NOX	Oxides of Nitrogen
PCP	Pentachlorophenol
Pdr	Powder
P/U	Polyurethane
ppt	Precipitate
RSL	Restricted Substances in Leather
r.p.m.	Revolution Per Minute
T	Tannin
Ts	Shrinkage Temperature
TDS	Technical Data Sheet
temp	Temperature.
s.a.a.	Surface active agent
s.g.	Specific Gravity
veg	Vegetable
VOC	Volatile Organic Compound
Wt	Weight
ZDHC	Zero Discharge for Hazardous Chemicals



United Chemicals

United Chemicals Dış Tic. A.Ş.

Çoraklar Mah. 5004 Sokak No. 23 Aliođa / İzmir Türkiye 35800

t: +90 232 425 42 58 | f: +90 232 621 50 67

unitedchemicals-co.com