

Gerhard John

**Possible defects
in
leather production**

**Definitions,
causes, consequences,
remedies
and
types of leather**

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Preface

While studying the available literature on tanning I discovered that there are only occasional references to possible sources of defects in leather manufacturing in the respective specialist books. For this reason I have tried to present in this manual a comprehensive look at possible problems as well as their remedies.

During 47 years of working in the leather industry, including 30 years in the leather department of BASF in Ludwigshafen, I was confronted with the smaller or more serious production problems of many leather factories both in Germany and abroad. In most cases it was possible to identify and pin-point the problems and also to remedy them. However, in some cases correction of defects was not possible as the skin and leather material had suffered irreversible damage.

Every responsible leather specialist is familiar with the many influences to which the entire manufacturing process is subject. Therefore, he should always adhere strictly to the formula developed for each respective type of leather at all stages of the production process in order to produce leather of consistently high quality. When changing the production method, only one change should be introduced at a time and its effect thoroughly examined before adding another step which might prove necessary.

I hope that this manual provides quick informative help for practitioners, engineers, leather merchants and all those involved in the interesting matter "leather". However, due to further product developments and technical progress in the field of leather making, it will not be possible to prevent other new sources of defects in future.

Lampertheim, April 1997

Gerhard John

Foreword

This book by Mr Gerhard John fills a gap in an area which has not been thoroughly covered until now by providing a detailed description of possible defects in the complex and complicated subject of leather technology.

A book of this kind can be written only by someone who, like Mr John, has many years of practical experience as a leather specialist. His survey is of special value in that it deals with all fields of leather technology in the same detail. This was possible because he formerly worked for BASF, a leading company in all fields of leather technology. For instance, he was able to include his experience with a very wide range of chemical products. However, the subject can only be adequately treated using the respective technical terms for the manifold processes. This book therefore provides at the same time an introduction to leather vocabulary and the concepts of leather technology.

This book is addressed above all to experts and aspiring experts. Even specialists should find it useful to consult the "Big John" when researching into the causes of problems. They might find many a solution which they have never thought of or had not considered in a particular situation. The book is therefore a screening aid.

Moreover, the second part of the book provides an excellent survey of methods for leather testing, a description of the many kinds of leather and fundamental information on leather production and leather characteristics. With their systematic arrangement, commendable brevity and accuracy the final chapters are highly recommended as a reference for people with less experience in leather manufacture, namely leather processors and merchants.

Seeheim-Jugenheim,
April 1997

Professor Dr.
E. Heidemann
(retired)

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The "natural product leather"

Leather and fur making is one of the oldest trades of mankind. In the early days, the skins of animals killed for food were made fast to putrefaction by kneading them with grease, which also made them supple and soft. In addition, the skins were smoked over an open fire to prevent them from rotting. The skins treated in this way, complete with coat of hair, were mainly used as a fur garment to protect the wearer against the adversities of the weather. Over the centuries, further methods were developed, often as a result of chance discoveries. It was found that the hair could be loosened by wood ash and burnt limestone rocks. This made the manufacture of leather possible. A further discovery was that the skins could be made more resistant if they were treated with leaves and barks containing tannin, and later the tanning effect of alum salts. Vegetable dyestuffs were even used in ancient history for colouring purposes.

Through the migrations of peoples, the art of leather and fur making gradually spread and by the Middle Ages it had developed into a highly-sophisticated craft. Initial scientific research which was then carried out led to the further advancement of the manufacturing methods and to the use of new products in leather making. The fabrication of efficient tanning machines and further systematic research relating to the raw skins and hides, the manufacturing processes, the products and auxiliaries soon made industrial-scale production feasible. New discoveries about the chemical and physical properties of the final product, leather, and the development of quality guidelines for each type of leather have channelled the production process in a precisely defined way in order to promote functional properties.

Nowadays, leather production is largely based on the utilization of the raw hides and skins which occur as a "waste" product in the slaughtering of domesticated animals that are kept for meat. From an ecological point of view, the tanner is therefore an "important utilizer" of putrescible matters which would otherwise contribute to an immediate increase in the release of CO₂ into the atmosphere and the much discussed heating up of the earth's climate.

To obtain high quality leather, efforts are undertaken to minimize the defects present in the raw hides and skins caused by improper livestock breeding, incorrect flaying of the skins or insufficient preservation by providing appropriate instructions and further information.

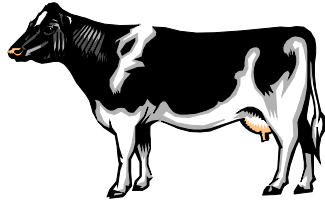
No defects at all should be introduced as a result of the beamhouse, tannery, dye-house, after-tanning, fatliquoring and finishing operations. In view of constantly increasing vessel capacities and loading weights, working must not be inaccurate, and continuous inspections of the work process are absolutely essential. Shorter production processes, which are often the result of arbitrary decisions, should be avoided because this could increase the defect phenomena even further.

The growing tendency to consider ecological requirements will in future place heavy demands on the leather manufacturer, but also on the producers of chemicals and auxiliaries. These issues are no doubt resolvable, so that we can look forward to having the natural product leather and its excellent wearing properties, for which there is still no perfect substitute, for a long time to come.

Leather is always leather!

Mainly used raw hides and skins ¹

Horned cattle



Livestock of the world ²:

1,434 million

Annual slaughtering rate:

15 - 25 % (varies considerably in the different countries)

Including calves,
water buffalos and zebus

About two thirds (65-70 %) of this kind of rawstock are processed for the total annual world leather production. It is thus by far the largest source of supply of all raw hides and skins available for the leather industry.

Types:

Milk calf skins, calf skins, veal calf skins, grasser skins up to cow hides, including the types: cow (female), bull, steer (male, not emasculated), ox (male, castrated). They are suitable for making almost all types of leathers.

Structural composition:

Race and provenance, age and sex, nutrition, climate, type of rearing (in stalls or wild), surface area, thickness, weight class, deposition of fat cells, sweat glands and blood vessels as well as density of hair largely determine the texture of the skin and thus the serviceability and the properties of the leather.

The total thickness of the flayed cattle hide is about 3-12 mm depending on the species. The corium, i.e. the actual material used for leather making, consists of about 10-20 % of a loose papillary layer and 70-80 % of a tighter reticular layer (main carrier of the skin's mechanical properties) which is a particularly favourable ratio for the quality of the leather to be produced. The epidermis (outer layer) comprising about 0.5-1 % and the subcutis (hydrodermis) comprising about 5-15 % of the total thickness of the raw hide is removed in mechanical beamhouse operations.

The size of the raw hide varies between 2.0-5.5 m² depending on its provenance and age.

Calf skins have a similar structure to cow hides, however their composition and fibre texture is finer. The skin has a total thickness of 1.5-3.5 mm and is made up of the papillary layer (25-30 %), reticular layer (50-60 %), epidermis (1 %) and hydrodermis (10-20 %).

Due to the very fine hair pores and the tighter surface of the cutis they have a very fine appearance of grain. The younger the animal, the more striking is the appearance of the grain.

Therefore these skins are particularly suitable for making high-quality shoe uppers and fancy leathers.

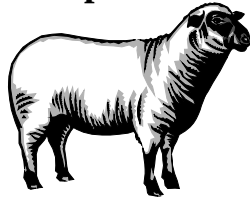
Milk calf skins have a useful area of about 0.6-1 m², veal calf skins of about 0.9-1.7 m² and grassers of about 1.5-2.2 m².

Zebu hides are obtained from zebras living in South Asia, particularly in India. They are also called "kips". The most striking characteristic of this race is the fatty lump between neck and shoulder, whereas the hide structure is similar to that of cattle hide. In some cases the prominent bulge of the fatty lump makes the manufacture of a smooth and even leather more difficult.

Buffalo hides, especially water buffalo hides, come from India, Nepal, China, Indonesia and sometimes from Asia Minor.

Being a cattle subspecies they have a markedly rustic, coarse appearance of grain and a considerably thicker skin with partially loose fibre texture.

They are made into technical leathers, and have also been used in the manufacture of special furniture leathers for some time. If they are 4-8 mm thick they are also used as heavy unlined covers for chairs.

Sheep

Including lambs

Livestock of the world ²:

1,213 million

Annual slaughtering rate:

25 - 45 % (varies considerably in the different countries)

Account for about 10-12 % of the total leather production.

Types:

Slinks (animals only a few days old), small lamb skins, lamb skins (especially: Karakul lamb skins for Persian lamb production) and sheep skins. They are supplied in long, medium and short wool lengths, and in shearling qualities. There is no clear-cut dividing line between fine (merino quality) and coarse quality and hair sheep quality.

These skins are made into garment, fancy, bookbinding and lining leathers. Skins with a tighter texture are used for shoe uppers, so-called chevrettes, the smaller skins for making glove leathers. A large part of lamb and sheep skins is used for fur skin production.

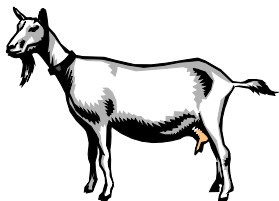
Structural composition:

The main objective of breeding is to produce a high wool quality. The finer and denser the wool fleece, the looser is the skin texture and thus the poorer the leather properties.

The total thickness of lamb and sheep skins is about 1-3 mm. 40-60 % of the corium consists of a papillary layer, part of which is considerably loosened up by sebaceous and sweat glands and deeper wool pores. The firmness of the reticular layer, which accounts for about 25-40 %, is also greatly reduced by adipose tissue which in many cases contains up to 30 % of fat in relation to the weight of the skin.

Lamb skins are of a similar composition, but they generally have a finer and firmer texture.

The average size of sheep skins is about 0.4-0.9 m², of lamb skins about 0.3-0.7 m² and of slinks 0.2-0.4 m².

Goats

Including kids

Livestock of the world ²:

569 million

Annual slaughtering rate:

20 - 40 % (varies considerably in the different countries)

Account for about 8-10 % of the total leather production.

Types:

Sucklings (skins of the youngest animals), young goats (skins of older sucklings), springers, young female goats, female and male goats.

Diverse applications in leather manufacturing. The best sorts are made into chevreaux (high-quality shoe uppers). Other applications include hard-wearing clothing, bookbinding, fancy and lining leathers. Suckling skins are used to make fine glove leathers.

Structural composition:

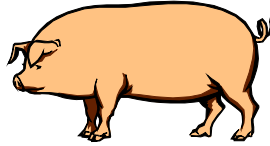
Differences in quality depending on race, country of origin, age and nutrition. However, overall they are of much greater firmness compared to sheep skins.

The papillary layer represents about 30-40 %, and the reticular layer about 40-50 % of the total thickness of 1-2 mm of goat skins. Both layers are tightly connected with each other such that loose grain, as found frequently in sheep skins, is less often observed. Since there are only a few sebaceous and sweat glands and little adipose tissue the fibre texture is relatively coarse, especially in the reticular layer. The crescent-shaped hair follicles create a very nice, characteristic appearance of the grain.

Suckling skins are of a similar structural composition, but have a finer fibre texture and finer appearance of the grain.

The size of goat skins is about 0.5-0.9 m² and that of suckling skins about 0.2-0.5 m².

Pigs



without piglets (insignificant for leather production).

Livestock of the world ²:

840 million

Annual slaughtering rate:

≈ 100 % (use of the skin only in some countries)

Account for about 3-5 % of the total leather production.

Types:

Domestic pig (mostly butts, seldom entire skins), sometimes used for shoe uppers, garment, pocket-book and lining leather as well as insole leather.

Wild boar (mostly whole skins), sometimes used for rugs or wall hangings.

South American navel pig, called peccary;

Water pig called carpincho.

The whole skins of these two wild species are made into special smooth glove leathers, to a lesser extent into garment leathers. In some cases the skins have severe defects so that only part can be used.

Structural composition:

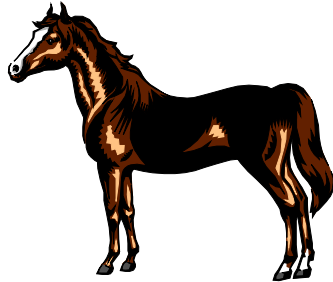
In contrast to the skins of other mammals a special histological feature of pig skins is that they have no reticular layer.

The papillary layer makes up about 80-90 % of the total skin thickness of 2-5 mm and is of a very tight texture in the butt area. The side parts are of looser texture. The epidermis makes up about 5 % of the total thickness, the hydrodermis, consisting of pure fatty tissue, makes up about 10-20%.

The hair roots penetrate through the entire cross-section of the skin and the open holes of the bristles are still visible in the lower split.

When processing the butt the usable size of the skin is about 0.6-0.9 m² and when processing butt with side parts it is 1.2-1.5 m².

Horses



Livestock of the world ²:

66 million

Annual slaughtering rate:

Yield of hides varies considerably in the single countries.

Including foals

Types:

As with cattle hides a distinction is made between domestic and wild hides.

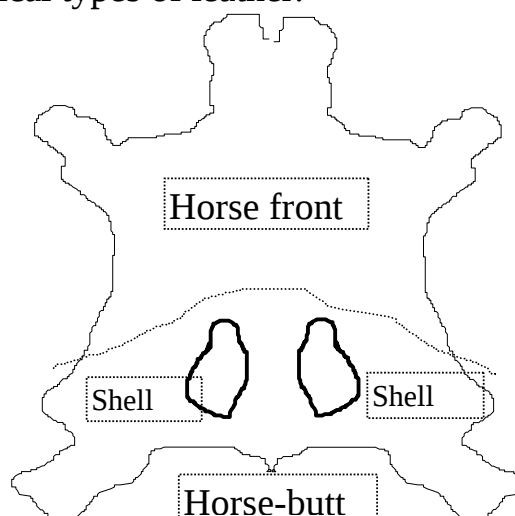
Heavy-horse races are predominant in moderate climatic zones, thoroughbred horses are found mainly in warmer climates.

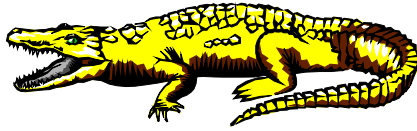
Zebras and donkeys also belong to the species of solipeds, but are of minor importance.

Structural composition:

Compared to cattle hides the horse hide has a loose papillary layer and a thinner reticular layer of fine fibre texture. The hide is divided into horse shoulder and horse butt, the latter comprising the so-called horse shell, a densely fibrous, very firm connective tissue matrix.

The horse shoulder exhibits an appearance of grain similar to that of goats and is therefore also called horse chevreaux and is used for upper leathers. Due to this fine texture it is also used for garment leathers. The horse shell is used for manufacturing stronger sole leathers or technical types of leather.



Reptiles**Occurrence:**

Equatorial zones of the earth. Bred to an increased extent on farms.

The Washington Agreement on Preservation of Species must be observed when processing reptile skins.

Account for less than 0.2 % of the total leather production.

Types:

Crocodiles, alligators, caymans, ³
turtles,
lizards, snakes,
bullfrogs.

Structural composition:

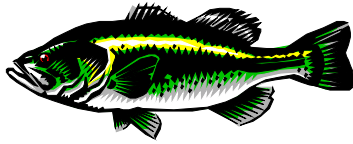
In the outer epidermis crocodile skin consists of a distinct horny layer of very little flexibility. The older the animal, the more pronounced are these horny shells. The corium has only a two-dimensional fibre texture which inhibits its elasticity. Therefore it is not suitable for making stretchy leather qualities, however it has the advantage of having a very good stability of shape.

The belly of the skins of younger animals is mainly used to produce pocket-book, fancy and upper leather qualities. Hides with a thick horny layer, mostly from older animals, are sometimes used as wall hangings.

Turtle flanks have similar characteristics of grain to those of younger crocodile skins.

Lizard and snake skins have the most varied appearance of grain and grain patterns owing to the large number of species.

Bullfrog skins are distinguished by interesting wart elevations on the grain side.

Fish**Use:**

Of minor significance world-wide.

Account for less than 0.1 % of the total leather production.

Types:

Different sharks, rays, seals, different dolphins, cod, pollack, haddock, eels.

Structural composition:

The scales in the epidermis of many fish have to be removed during the course of leather production. The same applies to many species of shark which have a tough siliceous layer.

Many fish skins are sensitive to high temperatures and the addition of concentrated chemicals (increased decomposition of protein).

Other types of hides**Use:**

Various

Account for less than 1.0 % of the total leather production.

Types:

Red deer (stag, roe), chamois, antelopes, reindeer, elks, camels, kangaroos, dogs, hares and rabbits, ostrich.

Structural composition:

Epidermis of different thickness and varying proportions of papillary and reticular layers in the total thickness of the corium.

Raw hide magazine

General structural conditions

1. Sufficient insulation of walls and roof against heat.
2. Minimum number of doors and windows in order to ensure a constant temperature level.
3. Strong floor covering, corrosion-proof and accessible by vehicles.
4. Installation of aeration and ventilation fans.
5. Cool basements or flat buildings are most suitable. In warmer climates it is necessary to install refrigerating sets if the raw hides are stored for a longer period of time.
6. For efficient handling the rawstock should be stored on pallets in multi-level racks.

Storage conditions for raw hides

Salted rawstock:

1. Storage at a temperature less than 15 °C and a relative humidity of 70 % (80 % as a maximum).
2. If the hides are stored in stacks, keep to a maximum stacking height of 1.00 - 1.20 m in order to avoid overheating the rawstock. Temperature control is necessary in the case of long-time storage.
3. It is most important to install drains to remove brine.
4. Every six months it is recommended that the walls be sprayed with disinfectants in order to avoid mould and bacterial growth. The disinfectant should be changed from time to time because the strains of bacteria might become resistant.

Dry rawstock:

1. Avoid excessive humidity.
2. See item 4 (salted rawstock).

Raw hide and skin defects

Defects in the living animals

Brand-marks	Produced by branding letters, numbers or figures by means of a red-hot stamping iron mainly in the butt, seldom in the forehead, neck or jaw. Several marks are often found. Visible, most severe scarrings on the finished leather, frequently going through the entire cross-section of the skin. These sections cannot be used as leather.
Cockle	Formation of nodules on the grain of sheep skins, mostly in the neck or shoulder area. Spot-like deposits of fat, mostly as a result of fattening; may also be caused by parasites.
Damage caused by the warble fly	Larvae of the warble fly which result from the bite of the warble fly and which eat their way from inside the animal through the skin, producing open or scarred holes, the so-called warble marks. Control is by mechanically removing eggs and larvae, treatment with special phosphoric esters or contact insecticides.
Scratches caused by thorns, barbed wire scratches	Open or scarred, irregular scratches caused when grazing animals chafe their bodies against thorn-bushes or barbed wire. Can be avoided by fencing the pasture with smooth electric fences.
Eczemas	More or less pronounced scale formation on the hair side of the skin which may completely destroy the grain.
Colour mark stains	May be caused by the use of highly acidic or alkaline colours for marking which can etch the grain, making it rough or matt.

Defects in the living animal

Freeze brands	Defects of the grain caused by marking with freezing mixtures at excessively low temperatures and long exposure. However, they are less severe than the defects caused by brand-marks.
Defects caused by awns	Defects of varying depth in the grain caused by sharp awns of plants, fruits or hard grasses.
Defects caused by trichodectes	Parasites which lodge in the hair coat and can destroy the skin down to the corium.
Skin diseases	Called dermatomycoses or cattle ringworm, subdivided into Microsporia and Trichophyton infection (qv).
Sponginess of the skin	Structural changes of the skin fibre texture due to excessive fattening. The affected sections are spongy and the firmness is greatly reduced.
Injuries caused by horns	Mainly occur during pasturing and transportation and cause deeper defects of the grain.
Hyperkeratosis	Pathological wavy thickening of the grain layer, in some cases accompanied by a loosening of the corium.
Defects caused by lice	Injuries caused by infestation with blood-sucking lice, with partial destruction of the grain layer.
Microsporia infection	Skin defect caused by trichomycetes which damages the grain surface by the formation of pinholes.
Defects caused by mites (mange, scabies)	Parasitic hair follicle mites which invade cattle, goats and sheep, but also pigs and dogs. They cause recessions or holes with formation of pustules in the grain tissue. Can be avoided by clean indoor livestock husbandry.

Defects in the living animal

Defects caused by dung and urine	Resulting from unclean indoor livestock husbandry. Etching of the grain occurs in soiled sections, in particular near the claws and on the belly, producing matt sections and blind or rough grain. According to statistics this still represents a considerable percentage of skin defects.
Defects caused by pitchfork stings and prod damage	Round spots in the grain which are caused during loading and unloading of the animals for transportation, or by driving cattle, or also during cleaning of the sheds.
Damage caused by nematodes	Skin defects caused by nematodes in the form of holes or scars and elevations in the grain.
Damage caused by smallpox	Typical skin diseases on pig skins. They result in spotty grain defects of the epidermis and formation of scarring.
Chafe marks, pressure marks, curry-comb scratches	Grain defects caused in livestock husbandry and transportation which can be avoided by proper livestock keeping .
Damage caused by radiation	X-rays or gamma rays used in veterinary medicine or ultraviolet rays of sunlight can cause defects of the skin.
Trichophyton infection	Trichomycetes, in particular in young animals, cause pitting of the grain. It can occur on the surface or in deeper skin.
Warts, sores	Defective grain or corium caused by virus infections.
Tick marks	The mouth parts of blood-sucking parasites cause holes or round recesses which in most cases reach down into the corium.

Flaying damage

Gouges	Unintentional cutting of flat pieces of skin out of the reticular layer when the skin is flayed. These sections result in a thinner quality of the finished leather.
Damage caused by setting out	Manual setting out using unsuitable tools may lead to overstretching of the grain, particularly in the case of skins of younger animals. This so-called cracking of the grain reduces the value of the skin. Cracking of the grain may also result from mechanical flaying.
Blood stains ⁴	If soiled and blood-stained skins are not washed adequately these incrustations may produce brownish stains on the raw hide. In the lime they lead to very dark iron stains and during vegetable tannage to blue-black stains.
Scald damage	Incorrect scalding of pig skins at excessive temperatures or for too long leads to liquor edges, i.e. in these areas the grain layer is damaged and roughened, or nubuked.
Butcher cuts	Cuts in the skin layers caused by uncareful skinning using a flaying knife. If the cuts are very deep they are also visible in the grain.
Kosher cuts	These neck cuts are made during ritual slaughtering of unstunned animals to enable quick bleeding. Kosher cuts produce two wide cuts through the skin.
Inadequate bleeding of the hide	Blood residues which remain in the veins encourage the development of microorganisms and thus increased putrefaction along the blood veins. This leads to a veiny appearance on the leather (grooves).

Damage caused by preservation

General

1. After flaying the skin should be cured after 12 - 24 hours at most, depending on the climatic conditions, otherwise *post mortem* changes, i.e. hydrolytic protein and/or tissue decomposition will occur.
2. Before curing is performed, adhering dung should be removed from the skin by washing in order to inhibit bacterial growth. Dung causes protein decomposition and even putrefaction, depending on the time of exposure. Higher temperatures accelerate bacterial growth.
3. After flaying it is necessary to cool down the hides quickly. This is achieved by very cold washing water, cooling with ice or hanging the hides up individually in cold stores.
4. Fleshing is recommended before curing because curing is quicker and more effective after residues of flesh and fat have been removed.

1. Fresh hides

Bacterial hide defects

Avoided by:

1. Quickest possible transportation of the flayed hides to the leather factory and immediate soaking.
2. If the time until further processing of the hides is longer than 12-24 hours, they should be transported in refrigerated containers and stored in cold stores.

Damage caused by preservation**2. Salted rawstock**

Lead stains	Lead compounds are contained as denaturing agents in curing salts, used mostly in overseas countries. They produce similar stains as iron.
Iron stains	Contact of the hides with iron parts or rusty iron compounds. They produce brownish stains which are further intensified by liming chemicals or tanning agents containing phenol. In many cases it is possible to eliminate them by a treatment with complexing agents.
Rottenness	If curing is inadequate or is performed too late and if the hides are stored too long at excessive temperatures in the salt, an increased development of microorganisms occurs on the skin. It starts with slimy smears on the surface, followed by hair-slippiness and at an advanced stage a loosening of the grain layer in some sections and destruction of the skin by the formation of holes.
Flesh side discolouration	Noticeable through red, blue or violet discolouration on the flesh side. These stains are caused by colour-forming bacteria which result in matt to rough grains and hair-slip, and also attack the hide substance. Can be avoided by increased addition of soda and addition of naphthalene to the curing salt.
Copper stains	Brown stains caused by copper compounds or copper-containing colours used for marking.
Naphthalene stains	Brown to red discolouration due to the use of unpurified phenolic naphthalene in the curing salt or by sprinkling the wool of dried sheep skins to protect it against ravage by insects.

Damage caused by preservation**Salt stains**

Mineral granular deposits in all skin layers, analysed mainly as insoluble calcium compounds. Caused by increased contamination of calcium and magnesium salts in the curing salt. These incrustations are probably promoted by increased bacterial activity, skin impurities, protein decomposition products, humidity and temperature fluctuations during storage. They result in callouses of the grain, crackiness of the grain and reduced diffusion of many application chemicals, tanning agents and dyestuffs during leather production.

Salt specks

Small to large patches of elevations the size of a pinhead due to salt incrustation, and occurring mainly in the grain. Similar to salt stains they are caused through contamination of the curing salt with calcium and magnesium compounds.

Prevention is possible by using common salt and by washing the hides thoroughly.

Mould stains

May occur in all types of curing. The stains or coatings of different colours (green, red, brown, yellow, orange, white, black) occur in patches or over large areas, depending on the type of mould spore infestation. In the case of prolonged infestation the mould stains will also be visible in the leather.

Prevention is possible by using disinfectants during curing. Mould which has already been produced can be removed to a large extent by brushing or washing.

Damage caused by preservation**3. Dried hides****Heat damage:
blistering**

Quick drying with exposure to excessive heat dries out the outer layers and makes them horny. The inner zone remains moist because it cannot give off water. During processing in the soak or in the lime the putrefactive inner zone dissolves and the hide is split into two skin layers.

Sunburn

The surface of the skin can be denatured by direct sunshine or by drying at high temperatures such that resoaking of the damaged sections is no longer possible. As a consequence the leather is hard and tinny in these sections.

**Damage caused by
beetles and
insects**

Infestation with various types of beetles, insects, flies and moths is possible especially in tropical and subtropical countries. They, and also their larvae, produce considerable defects on the skins. Apart from the affected sections, holes are drilled into the skin substance.

Preventive treatment and control is by sprinkling with naphthalene or spraying with bactericidal substances.

Heavily infested rawstock should be treated by gassing with potassium cyanide compounds whereby utmost precautions should be taken.

Breaking patches

Cracked grain may be produced if the hides are moved and bent without due care in the rawstock warehouses or during transportation.

Damage caused by preservation**4. Freeze drying**

Frost damage In the frozen state hides are sensitive to bending and plying. This sort of stress should be avoided because it leads to severe damage to the grain or deeply cracked grain.

5. Pickling pelts

Pressure folds Pressure folds may be caused by storing the hides for a prolonged period of time, in particular by storing hides of small animals in larger drums. The pressure folds are visible in the leather and reduce the yield of the assortment.

Upon delivery the pickling pelts should therefore be removed from the drums and stored in stacks of low height. Pickling pelts already showing pressure folds should be depickled to the neutral point and then refleshed mechanically in order to remove the folds.

Mould stains May occur in particular if the hides are pickled in only a weakly acid solution. Therefore the pickle used for storage should have a pH value of under 3 if possible.

Rancidity Decomposition of the natural fat may occur especially in the case of sheep skins which are rich in fat and stored at excessive temperatures in a weakly acid pickling solution. This process produces an unpleasant smell which may still be noticed in the leather.

Prevention is by careful fleshing in the country of origin, cold storage and pickling in a more acid solution.

Reduced tensile strength Can occur if the hides are stored too long or at excessive temperatures.

Water quality

Classification according to source:

1. *Rain water*

Of little importance for tannage, as it occurs only sporadically. However, as a medium, it has ideal characteristics for leather production as it is free of mineral substances, dissolved gases and impurities.

2. *Surface water* (rivers, streams, lakes)

Besides different quantities of mineral matters it contains organic substances, suspended solids and microorganisms. It shows considerable temperature fluctuations, depending on the climatic conditions. In many cases purification, filtration or softening is required.

3. *Sea water*

Despite its high content of salt and mineral matters of about 4 - 6 °Bé it can be used to some extent. Used for soaking, rinsing processes after the lime and for pickle floats which are discharged before chrome tannage is started.

4. *Ground water* (wells)

Mainly used in tanneries. Constant temperatures of about 8 - 15 °C are an advantage. High contents of mineral matters are possible, depending on which strata the water has passed.

Possible defects due to substances contained in the water

Microorganisms	Increased risk of putrefaction in the soak. <i>Prevention</i> by increased addition of disinfectants.
Suspended solids	React with tanning agents, auxiliary agents and dyes to produce precipitation or flocculation and result in stains in the leather. <i>Removal</i> by filtration.
Iron content ⁵	In the case of vegetable or some synthetic tanning or re-tanning processes results in grey or blue staining over the entire surface of the leather or in patches. <i>Removal</i> is possible by means of special complexing agents.

Possible defects due to substances contained in the water**Calcium salts,⁶
magnesium salts**

React with vegetable tanning agents or also synthetic phenolic tanning agents to produce insoluble precipitation compounds. Lead to stains in the leather which cannot be dyed, and also to crackiness of the grain in these parts.

Removal is by treatment of the water with ion exchangers.

**Carbonate
hardness**

The poorly soluble calcium carbonate is the main interfering factor. It can lead to precipitations, colour changes, retarded reactions and staining in many processes of leather production such as soaking, liming, rinsing and washing floats, bating, manufacture of vegetable tanning agents, during vegetable tanning, dyeing and fat-liquoring. It also causes dangerous scale formation in steam boilers.

Removal by precipitation and separation with calcium or sodium hydroxide or demineralization by means of ion exchangers.

Carbon dioxide

Occurs as dissolved gas in water. It reacts with lime to produce calcium carbonate. Carbon dioxide, especially in the rinsing water after liming, is likely to cause the so-called "lime blasts". Furthermore a high content of free carbonic acid has a destructive effect upon iron parts.

Removal is possible by heating.

**Chlorides,
sulphates**

Only in higher concentrations can these "permanent hardness constituents" cause a retardation of reaction or precipitations. They may also lead to the destruction of cement pipes or cement vessels by corrosion.

Removal by distillation (uneconomical) or demineralization with complexing agents.

Soaking

How to determine when soaking has been completed by checking the condition of the hide:

1. Restoration of the natural swollen condition of the hide
2. Good pliability in all sections of the hide
3. Slightly slippery handle of the flesh-side (particularly when soaking dried skins)
4. Complete removal of residual dirt, blood and dung.

Controls during the soaking process:

Operational:

1. Regular temperature measurements (especially in warm climates and if soaking is performed at higher temperatures).
2. Regular pH measurements (especially when using soaking liquors sharpened with alkalies).
3. Determination of the specific weight of skins and hides cured by means of salt. This indicates the progress of demineralization and shows whether the water should be changed.
4. Determination of the soaked weight. Enables a check in relation to the green weight and of the water absorption.

Analytical:

1. Determination of the total nitrogen content of the liquor. It provides information on possible loss of hide substance.
2. Determination of the ammoniac content of the liquor. Increase = degradation of hide substance.
3. Bacterial analysis of the soaking liquor if impaired due to microbial activity.
4. If soaking liquors are used several times, the content of common salt should be determined in order to avoid an excessive content. A high amount of common salt has a soak-inhibiting effect.

Soaking defects**Short, inadequate duration of soaking**

Is a particular source of defects for dried and partly dried, salted skins and hides. Results in a hard, tinny texture of the leather of hides or hide sections which have not been adequately soaked. This is due to different diffusion of the subsequent treatment chemicals into the skin fibres which are still partly stuck together.

A perfect soak is obtained by the addition of wetting agents and alkaline sharpeners. Mechanical drumming or stretching on blunt fleshing machines also promotes the soaking effect.

Low soaking temperatures (< 15 °C)

Lower temperatures of the liquor slow down and inhibit the soaking process. The water absorption of the skin is reduced. Furthermore a certain hardness or firmness of the skins is evident.

Excessive soaking temperatures (> 28 °C)

Soaking temperatures exceeding 28 °C can lead to undesired high bacterial growth and furthermore to greater hydrolytic degradation of skin substance, resulting in a flat and tinny leather quality. Prevention is only possible by adding higher amounts of disinfectants.

Damage caused by mechanical processing

In particular when soaking dried hides or partly dried, salted hides the grain may become cracky as a consequence of inadequate preliminary soaking followed too quickly by the subsequent treatment, or due to an excessive rotational speed of the drums.

Rollers in the mixer

Caused by overloading and inadequate soaking.

Soaking defects**Damage caused by microbial activity**

Minor damage due to putrefaction	Not visible on the soaked hide. Noticeable by putrid smell and matt, lustreless or blind sections in the grain of the leather.
Serious bacterial damage	Noticeable on the soaked hide by initial signs of hair-slippiness and/or slippery surface. Is revealed in the leather by loose grain and reduced firmness.
Heavy putrefaction	Noticeable on the soaked hide by pitting, holes, putrefaction marks on the grain and also by complete loosening of the grain layer.

All the above damage can be avoided by addition of bactericidal agents and by reduction of the soaking temperature.

Soaking of pickled pelts

Acid swelling	Irreversible damage of the fibres is caused by soaking with a common salt addition of less than 6 °Bé.
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Soaking of fish skins

Decomposition of skin substance	Increased protein decomposition is possible in many sorts. Therefore the soaking temperatures should be below 20 °C and only products with a neutral reaction should be used if an addition of wetting agents is necessary.
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Depilation and opening up the skin

General

The *type, concentration and duration of immersion* of the depilation methods as well as of the liming and sulphiding chemicals influence the future properties of the leather with regard to softness and strength.

Controls of the liming process

Operational:

1. Temperature measurements, especially when working with higher temperatures (not >28 °C) and for enzymatic liming or sweating treatments.
2. Test of the hair-slippiness.
3. Check of the degree of swelling and plumping by touch test.
4. Check of penetration by means of cross-section test (especially in the case of thicker hides).

Analytical:

1. Determination of total alkalinity.
2. Determination of sulphide sulphur.
3. Determination of efficient alkalinity.
4. Determination of ammonia content. Particularly recommended when using a recirculation liming process. If the content is too high, the liquor should be changed.

Test of the liming chemicals

Analytical:

1. Determination of purity and concentration should always be performed as an incoming inspection, in particular if suppliers change, in order to ensure a uniform process.
2. Determination of the iron content of sulphides and hydrosulphides. The cheapest products tend to contain high quantities, which cause blue-black iron sulphide liming stains.

Depilation and opening up the skin

Lime painting methods

Painting on the flesh side	Good draining of the soaked rawstock and a lime paint consistency that is not too thin are necessary to obtain an impeccable wool quality without defects.
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Grain lime painting (drum painting, Darmstadt through-feed method)	Specially suitable for sensitive hides, hides with prominent growth marks and/or very flat substance. Gives smooth pelts, without wrinkled or loosed grain.
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Liming methods

Pure hydrated lime pit

Depending on the rawstock, hair loosening occurs in 6 - 10 days with good opening up of the skin. If using slaked lime check for insoluble components which can damage the grain. Old lime liquors tend to contain uncontrollable decomposition products which may result in increased microbial activity and thus cause loose grain, greater loss of skin substance or spongy leathers. However, in these old lime liquors the hair loosening effect is more intensive than in freshly prepared limes.

If the lime pit is used for reliming, the slipperiness of the pelts caused by sulphide lime liquors is reduced and thus a drifting of the skins in the splitting machine is avoided. Furthermore, it is used to improve opening up of the skin.

Pure sulphide lime pit

Mainly used for hard goat skins to produce fine-pored, crack-resistant chevreaux leathers. Also used for veal skins or small cattle skins to obtain nubuk and suède leathers with a tight fibre texture. This method is also chosen for rapid hair loosening, poor opening up of the skin and to ensure the yield.

Sulphide/hydrated lime pit

Still the most commonly used liming method for leather production. Lime liquor concentrations with over 0.2 % Na_2S cause damage to the hair, more than 0.5 % Na_2S will destroy the hair (however, the amount of liquor, temperature and the ratio of hair coat to skin substance are influencing factors). If the pH value is below 11.0 the hair is not attacked or loosened up.

Any desired liming effect can be achieved by adjusting the parameters: proportioning and concentration of chemicals, amount of liquor, temperature, drumming intensity, duration and also the preliminary soaking method.

Sulphydrate/hydrated lime pit

Pure NaSH solutions do not result in depilation. Only the addition of $\text{Ca}(\text{OH})_2$ or NaOH achieves a similar effect to that of sulphide lime. This liming process causes a slight swelling of the pelts, reduces the accentuation of growth marks, grooves and wrinkleness. The fact that the leathers are flatter and firmer has to be taken into account in the subsequent processing steps.

Sulphide/sulphydrate/hydrated lime pit

A method which is gradually being used more often. Excessive lime swelling is reduced by replacing sulphide with sulphydrate, however, only if the content of NaSH prevails. An initial addition of NaSH is also advantageous.

Organic sulphydryl compounds

The most commonly used compounds are hydroxymercaptans or thioalcohols, especially 2-mercapto ethanol as alkali salt. They have a very high further oxidation speed and therefore do not contaminate the waste water and waste water treatment plants. If they are used alone, rapid mixing in the lime pit is necessary.

Due to their higher price they are mostly used with a low content of sulphide. These lime liquors lead to even less swelling than the use of sulphydrate and thus to a good area yield.

Amine lime pit

Dimethylamine or aminodimethylsulphate with the necessary addition of alkalines, mainly sodium hydroxide solution and calcium chloride as Ca donor, are used in most cases. Depending on concentration and temperature, it is possible to adjust hair-preserving or hair-destroying sulphide-free limes. These liming systems are no longer used due to the formation of nitrosamine.

Oxidative lime pit

Depilation by the action of chlorine dioxide was introduced for a short time only. The chemical used was sodium chlorite which forms oxidative chlorine dioxide in reaction with hydrochloric acid, sulphuric acid or glycolic acid. Advantages of this method were depilation in a weakly acid range, pigment-free clean pelts, compact leathers with a tight fibre texture and low accentuation of flanks. As the leather becomes too firm in most cases, this method has not been successful in practice.

Immunization method

The aim is to obtain a controlled, weak immunization of the hair coat by evacuation and filtration of the hairs from the liming liquor in order to reduce contamination of the effluent. Weak immunization is achieved by preliminary alkaline soaking and/or by an initial addition of hydrated lime before adding a reduced amount of sodium sulphide or sulphydrate. For this method it is important that the time of immersion, concentration of chemicals and amount of liquor are observed. This is especially important for rawstock with a hair coat of varying thickness and length.

One variant of this method is the so-called *sirolime method* (Australia). This involves a pretreatment with sodium sulphydrate, after which the liquor is discharged and recycled, washed in a washing bath in an intermediate stage and recycled again. For further oxidation of the sulphide some chlorinated lime is added, and hydrated lime is added to loosen up the hair. The hairs are then filtered off by recirculation. Reliming is necessary for complete removal of the scud. In the first phase attention should be paid to increased formation of hydrogen sulphide.

Enzymatic processes

The treatment of sheep skins in sweating rooms is the oldest method for obtaining undamaged wool or hair. It is a process brought about deliberately to form microorganisms which effect hair-loosening.

1.1 Cold sweating

Hanging of the soaked hides in rooms saturated with water steam at a temperature of 10 - 15 °C for about 8 - 12 days.

1.2 Warm sweating

Hanging of the soaked hides in rooms at a temperature of 20 - 25 °C for about 1 - 2 days. This method is difficult to control. Hair-slippery hides should be removed at once, otherwise serious skin defects occur due to putrefaction. Reliming is necessary to open up the skin.

2.1 Enzymatic liming

The chemicals used are specially isolated bacterial or fungal proteinases, which are also used in combination. Preliminary alkaline soaking or preliminary treatments and/or addition of activating salts such as sodium hydrogen carbonate, sodium bisulphite or sodium sulphite promote loosening of the hair. Fat residues or defective sections of skin and scars have an inhibiting effect. Reliming is necessary in most cases.

2.2 Enzymatic painting

Sprinkling with enzymatic preparations on the flesh side has proven a good method for sheep skins. Hair loosening occurs in about 18 - 24 hours. Reliming is necessary.

In general, further improvements of these enzymatic treatments can be expected as a result of new research findings because these methods considerably reduce ecological harm caused by chemicals.

Liming defects

Inadequate loosening of hair

Possible causes: Liming time too short, concentration of liming chemicals too low, inadequate soaking, excessive swelling of the skin at liming temperatures that were too low or immunization of the hair coat in an alkaline soak treatment for too long.

Effects: Short hairs are not removed. Results in a rough and uneven grain surface. May also damage the grain if depilation is done with excessive force.

Inadequate liming effect

Possible causes: Liming time too short, low concentration of liming chemicals, inadequate liming temperatures.

Effects: Lack of softness and crack-resistance, tinny leather, hard brittle condition of the grain, loose grain, reduced absorbing capacity for tanning agents and inadequate saponification of the skin fat.

Overliming (excessive opening up of the skin)

Possible causes: Liming time too long, high temperatures, use of recycled lime liquors for too long.

Effects: Loose fibre texture, often up to sponginess of the leather in pieces of poor substance, loose grain, running grain, excessive elasticity, insufficient resistance of the grain, reduced firmness and poor handle of the leather.

Bulging veins

Veins not bled during flaying, with bacterial damage. Intensive liming makes them even more prominent. The remedy is to choose a retanning process which has a good filling effect.

Liming defects**Lime stains,
lime blasts**

Deposits of insoluble calcium compounds on the skin.

Cause: Skins left carelessly in the open air for too long or inadequately covered by the liming liquor.

Use of water with bicarbonate hardness or free carbonic acid.

Effect: Rough to brittle grain, uneven absorption of tanning agent and receptivity for dyes. In vegetable tanning dark stains are caused by lime tanning compounds.

If the hides have not been stored too long it is possible to remove or weaken the stains by acid pickles of higher concentration. Staining can also be prevented by the addition of complexing agents and polyphosphates in the last washing water.

Lime soap formation

May occur when the skins and hides have a high natural fat content. The high alkalinity in the lime liquor promotes the action on the fat cells and fat is removed from the skin by partial saponification. The addition of surfactants or emulsifiers intensifies the effect. With a high fat content poorly soluble lime soaps may form with the lime and result in smudges and stains.

Prevention by thorough fleshing of fatty rawstock.

Sulphide stains

Prevention: Possible by using iron-free liming chemicals and by not introducing rust or iron particles into the lime liquor.

Liming defects**Short-hair and scud not removed**

Causes: Immunization of the hair coat by excessive alkalinity of the soak. Inadequate concentration of hair-destroying liming chemicals. Lime floats too short, resulting in overloading and delayed mixing of the chemicals. If the lime temperatures are too low, swelling of the skins is increased and the removal of short hair is reduced. Insufficient liming time and/or inadequate drumming movement. A high natural fat content can also result in stains caused by short-hair and scud.

Effects: Uneven receptivity for dyes and very harsh grain in some sections.

Remedy: Additional treatment by reliming. Thorough deliming and possibly the addition of special surfactants to promote the removal of short hair and scud. Mechanical scudding is necessary for strongly immunized skins.

Enlarged flanks and loose grain

Causes: Not only depending on the lime liquor, but also on the provenance of the rawstock. Excessive opening up through liming, high temperatures, prolonged drumming and liming time, inadequate amounts of liquor, additional reliming or even residual flesh and fat in some sections intensify this type of defect. Excessive stress such as scudding or depilation also have an unfavourable effect on the firmness of grain.

Improper deliming and bating are further important factors.

Liming defects**Increased formation of growth marks and/or wrinkled grain**

Causes: Differences of texture in single sections of the skin, promoted in particular by the world-wide increase in fattening methods. Uneven curing effect. Overloaded liming drums or insufficient liquor and therefore formation of false backs. Also due to insufficient removal of adhering dung, long hair, residues of flesh and fat in some sections, high concentrations of liming chemicals, intensive swelling at low temperatures.

Remedy: Preliminary fleshing, mild liming process by addition of liming chemicals in gradual portions or replacement of sulphide by sulphydrates, higher liming temperature, extended float, reliming or mechanical slating if growth marks or wrinkled grain are particularly prominent. A preliminary painting treatment also reduces these defects in the grain surface.

Cracked grain

Cause: Excessive swelling of the skin or low liming temperatures.

Remedy: Replacement of sodium sulphide by sulphydrate or mercaptan and/or addition of products containing amine to promote complete penetration of the lime.

Immunization of the hair/wool

Often caused by excessive amounts or excessive exposure to alkalies, such as sodium hydroxide solution, hydrated lime or soda, before liming. Removal of the hair is not possible or only possible with difficulty.

Excessive swelling

Reduces diffusion of liming chemicals into the skin and the removal of residual short-hair.

Deliming

Mostly used as a preliminary treatment with subsequent bating in the same bath. The process serves to remove the lime introduced during the liming process (capillary lime, mechanically deposited or chemically bound lime) and to deplete the skin. Inadequate deliming may give rise to an increase of basicity during chrome tannage and cause wrinkled grain, hardness, loose grain or cracky grain.

Furthermore, formation of gypsum may occur in pure sulphate liquors and result in lime stains. Lime tannates may form in vegetable tannage and also cause staining or cracky grain. Inadequate depleting will result in fixation of swelling during tannage and thus in unelastic, cracky leathers.

Control of the deliming process

- Operational:**
1. The deliming bath liquid is mixed with phenolphthalein, thymolphthalein or methyl red in a test tube. With good neutralization of the calcium hydrate the phenolphthalein should remain colourless (pH range 8). With products that do not contain ammonium salt thymolphthalein should also remain colourless (pH 9.4). In the case of acid bacterial protease bates the methyl red should remain yellow (pH 6.2); a red colour indicates that the liquid is too acid = risk of acid swelling.
 2. Cutting test in different sections of the skin using phenolphthalein. The progression of deliming is indicated by the red colour becoming less intensive.

Test of the deliming chemicals

- Analytical:**
1. Determination of the degree of purity and concentration of the products used.
 2. If necessary, determination of deliming value, buffering capacity and lime dissolving value.

Commonly used deliming products

1. *Strong deliming acids* (dissociation constant $> 2 \cdot 10^{-6}$)

Hydrochloric acid, sulphuric acid	High risk of acid swelling if added in quick sequence and in excessive amounts. Hydrochloric acid may peptize, sulphuric acid may cause gypsum stains.
Formic, acetic, lactic acid	The risk of acid swelling is less, but also possible. Lactic acid produces a finer grain due to the formation of lactates.

2. *Weak deliming acids* (dissociation constant $< 2 \cdot 10^{-6}$)

Boric acid, carbonic acid ^{7,8}	Suitable for nitrogen-free deliming. No risk of acid swelling. Carbonic acid, used as CO ₂ , causes problems as regards thorough deliming of thicker skins ⁹ .
Sodium hydrogen sulphite	Mostly used in compounds with ammonium salts. Has a bleaching effect, therefore suitable for light-coloured leathers.

3. *Ammonium salts*

Ammonium chloride, ammonium sulphate	The most commonly used products because they are inexpensive and have a rapid deliming effect. Chloride should not be used in large quantities because of its peptizing effect.
Ammonium acetate, lactate, formate	Have a favourable effect, but are expensive.

4. *Organic esters compounds*

Cyclic esters	Effect similar to that of CO ₂ deliming, nitrogen-free.
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5. *Commercially available products with special effects*

Mostly mixtures or polydicarboxylic acids	Application and mode of action are described in the suppliers' technical information.
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Deliming methods**1. Deliming in the float**

The more thorough and complete the deliming process, the softer and less cracky is the leather.

Quantity of liquor	50 - 200 %. The longer the float, the slower is the diffusion of deliming agents into the inner skin layers, and salts which have formed dissolve more quickly.
Temperature	25 - 35 °C. As the temperature increases (up to 35 °C) the swelling of the skin recedes.
Quantity of deliming products and duration	Depends on the intensity of liming, the amount of lime compounds, the type of deliming product used, the desired degree of deliming and on the texture and thickness of the skin. The duration may be reduced by a preliminary thorough rinsing process.
Addition of agent	Strong deliming acids should always be added slowly in order to prevent acid swelling or fixation of scud or scurf.

2. Dry deliming

In this process the limed and washed pelts are treated - without liquor - with ammonium salts or also with small quantities of polydicarboxylic acids. A short float of 20 - 30 % forms because the skin is quickly depleted. Due to this rapid depletion the deliming rate is very high and the deliming time can be considerably reduced with this method, especially when deliming thick hides. The process is intensified by the use of deliming agents which form readily soluble calcium salts such as ammonium chloride.

Deliming defects

Inadequate deliming	Results in a leather quality that is too tight and too hard and influences diffusion of the subsequent process chemicals, in particular tanning agents.
Damage to the grain	<i>Causes:</i> Action of hot water, addition of excessive quantities of acid or chafe marks due to vessels operating at too high a speed. <i>Effect:</i> Damaged grain, cracky grain, stained grain or reduced breaking strength.
Loose grain and flank accentuation	<i>Causes:</i> Excessive drumming times, uneven deliming effect and high salt deposits in different sections of the skin.
Lime stains	<i>Causes:</i> Use of water with high bicarbonate hardness and/or free carbonic acid.
Soiled pelts, rough grain	<i>Causes:</i> Inadequate removal of scud and scurf by fixation, and formation of gypsum due to high sulphate concentrations. Occurs mostly if the pH value drops briefly to <5 during the process.
High formation of hydrogen sulphides	Formation of this dangerous lethal gas is promoted in particular with dry deliming methods, short-float deliming and excessive loading of the vessels, and already occurs at pH values < 9. <i>Remedy:</i> Deliming in closed vessels which can be aerated and ventilated. Use of sulphide-free liming systems. Performance of catalytic oxidation of the remaining sulphide by means of manganese salts before deliming, in a closed washing bath.

Bating

Is mostly performed in the same bath as deliming and is a treatment with enzymatic systems of the pancreas, bacterial strains or cultures of fungi. It effects a further opening up of the collagen fibres, depleting of the skin material, loosening of scud and scurf and splitting of the natural fat by the presence of lipases.

The more intense the bating process, the softer and less wrinkled is the leather.

Determining the final stage of bating

1. Thumb test: The impression should remain on the grain surface for some time.
2. Palpation of the skin: All areas should be uniformly slender and slippery to the touch.
3. On well-bated pelts residual scud and scurf should be easily removable (thumb nail test).
4. Especially in the case of thin skins the permeability to air is tested by pleating the skin like a bag and pressing the trapped air through the skin. The degree of porosity is a measure of the attained bating intensity.

Controls of the bating process

- Operational:**
1. Performance of pH value tests because the respective bating preparations have different optimum ranges of action.
Pancreas protease base approx. pH 7 – 9
Bacteria protease base approx. pH 6 - 7.5
Mould fungus protease base approx. pH 3.5 - 6.
 2. Temperature measurements:
Temperatures of > 38 °C should not be exceeded as the pelts are particularly sensitive to heat in this condition.

Test of the bating agents

Bating agents of different suppliers have different enzyme concentrations and efficiencies. The technical information sheets of the suppliers indicate the respective strength in enzyme units. There are weak, medium and strong product classes depending on their respective efficiency.

Different methods ¹⁰ are used to determine the effectiveness of enzymes:

1. Method according to Löhlein-Volhard (most commonly used) or older methods according to Fuld-Groß or Kubelka-Wagner with casein as substance to be analysed.
2. Method according to Anson (haemoglobine as substance to be analysed).
3. Method according to Kunitz (casein-photometric).
4. Hidepowder Azure Method, BLMRA / UK (measurable colouring of hide powder degradation products).

Bating intensity

Depends on the type of leather to be produced, on the type and condition of the rawstock, on the opening up of the skin in the preceding lime process and on deliming efficiency. Furthermore, it is influenced by the efficiency of the bating preparations used, time of immersion, machine movements, quantity of liquor, temperature and pH value.

1. Goat skins, kips and pig skins, horse butts or reptiles require a higher bating intensity than cattle, veal or sheep pelts.
2. Dried skins should be bated more intensely than salted hides, and the latter more intensely than green hides which have been directly supplied.

Bating defects**Inadequate bating**

Causes: Bating time too short, use of low enzyme concentrations, pH values which are not in the optimum range, bating temperature too low, inadequate preliminary soaking, liming and deliming.

Effect: Insufficient removal of scud and scurf, hard to brittle grain, loose grain (if the grain has been bated correctly, but the inner layers have not been bated), poor penetration of tanning agent and staining.

Overbating of pelts

Causes: Bating time too short, enzyme concentrations too high, excessive bating temperatures or storing of cured rawstock for too long.

Effects: Overloosening of the fibre texture results in loose grain, excessive drawing of the grain and spongy leathers. Furthermore the strength and fullness of the leather is reduced (tinny). Extreme overbating may result in a matt and blind to defective grain (bate pinholes, bating stains). Often these cannot be distinguished from defects caused by soaking, putrefaction or liming.

In order to avoid overbating it is better to bate for a longer time with lower enzyme concentrations and at a lower temperature.

High grain

"Goose-flesh grain" is caused on goat skins if hot-bated pelts are put into cold water directly. This results in shrinking of the grain and is particularly evident in sensitive types of rawstock.

Degreasing

A high content of natural fat, especially in sheep and lamb skins, some kinds of goat skins, pig skins and many cattle hides due to increased fattening practices disturb the leather production process and produce eruptions and staining of the leather. Therefore most of the natural fat has to be removed or, with a lower fat content, be distributed over the cross-section of the skin.

This process is often executed after bating by a treatment with surface-active substances, mostly by adding fat-dissolving organic degreasing agents. Degreasing of pickled pelts is more efficient, especially for sheep and lamp skins. In the case of pig skins the "defatting process" is performed after soaking, prior to liming.

Defects due to inadequate degreasing

Fatty spew

Definition: Fine white, crystalline coating or light film occurring on dried or finished leathers, mainly on chrome-tanned leathers, after a short or prolonged period of storage. In most cases distributed over the entire leather surface, sometimes occurring only in parts. Encouraged by alternate cold and warm storage, high humidity, on leathers that have not been neutralized completely and by the action of bacteria and mould fungi. Contact with an open flame will melt this coating and it can thus be distinguished from efflorescence of salt.

Cause: If the content of natural fat is high, especially with mainly free fatty acid components such as palmitic or stearic acid, these fats crystallize on the grain surface.

Defects due to inadequate degreasing

	<i>Remedy:</i> Besides thorough degreasing, fatty spew can be rubbed off with a cloth soaked in fat solvent, petroleum or kerosene. Subsequent application of mineral oil or chlorinated paraffin reduces the formation of fatty spew. However, re-occurrence cannot be entirely prevented.
Fat stains	<i>Definition:</i> Formation of oily dark-coloured irregular fat stains may occur in the renal region, on the neck and back part of sheep and lamb skins, some kinds of goat skins, pig skins and cattle hides, in particular if the rawstock comes from fattened animals. In most cases they are due to the excretion of liquid fatty substances. These unpleasant fat stains can no longer be removed if they form insoluble soaps with lime, chrome or aluminium salts.
Fat grooves	Found in fine-wooled and some coarse-wooled sheep skins, mainly in the neck or shoulder region. They occur as raised parallel strips running from the back towards the flanks and containing increased deposits of fat. Furthermore these sections are often loose-grained and result in callouses on the grain in the leather due to an inadequate penetration of tannin. <i>Remedy:</i> Attenuation is not possible if the grooves are very prominent. Intensive degreasing is necessary.
Fat soaps	High contents of natural fat react with cationic metallic salt such as chrome, aluminium, zirconium tanning agents to form insoluble soaps and result in heavy staining. <i>Remedy:</i> Intensive degreasing and elimination of the emulsified fatty matters before tanning.

Mechanical processes in the beamhouse

Vessels

Chafe marks

(sore grain, scratches, rips, nubuked grain)

Causes: Excessive rotational speed, insufficient floats, excessive swelling of the hide material due to high alkali content or low temperatures, prolonged drumming times, insoluble impurities in the liming chemicals, deposits on the walls of the vessel or damaged metal parts in the vessels.

Remedy: Besides remedying the above-mentioned possible causes, addition of high-molecular slip additives on a copolymer basis.

False back

(sore grain, nubuked grain, wrinkles)

Narrow elongated pressure marks which run parallel to the back line and are caused by pleating or rolling up the hides with the hair coat on the outside and by chafing against the walls of the vessel.

Causes and remedies: Add slip additives and on bends perform cuts along the back line.

Fleshing machine

Inadequate fleshing of loosely structured sections

Noticeable in particular on hides of poor substance.

Remedy: Reduce the pneumatic pressure in the middle of the pressure hose and increase it in the outer parts.

Cut marks, gouges, inverted pleats

Placing the skin material onto the transport roll with creases; occurs in particular on flabby skins and hides of small animals.

Transport groove squeezes

Caused on sensitive skins by sharp-edged transport rolls.

Splitting machine**Uneven
split thickness**

Causes: Different setting of top and bottom pressure, insufficient fine adjustment, band knife guide not straight, poor sharpening of the band knife, knife guide too loose due to wear, incorrect position of the knife-edge with regard to the center line.

**Gouges, holes,
formation of stairs**

Produced on the skin by adhering foreign matters or by dirt accumulation on the section roll. The skin may also run off the knife in the running direction due to insufficient top or bottom pressure or too slippery pelts.

**Transport groove
squeezes**

Profiles of the transport rolls too sharp-edged or top or bottom pressure of the pressure rolls too strong.

Unhairing, slating and scudding machine**Sore grain**

Excessive pressure during unhairing, slating and scudding.

**Grain defects in some
sections**

Ragged blade cylinders, foreign matters of granular nature or formation of pleats on the pelts.

Inadequate cleaning

Causes staining, hardness in some sections, brittleness and harshness of the grain.

Rinsing or washing processes

Rinsing and washing processes are absolutely necessary in almost all beamhouse operations. Where possible, the rinsing processes - which are mostly uncontrollable and require large amounts of water - should be replaced by the more economical washing baths.

Soaking The preliminary soak, or first soaking bath, should always be removed because it contains a high accumulation of constituents such as salt, dirt, soluble proteins and also preserving agents.

Liming After depilation and opening up of the skin it is imperative that the lime liquor be drained and followed by a washing bath. Liming chemicals not used up, dissolved residues of keratin and hair, and fat saponification products must be removed. The subsequent washing bath serves to make the slippery surface of the limed pelts easier to handle in the following mechanical treatment processes such as fleshing and splitting. Often an intermediate reliming process is performed at this stage, depending on the type of leather, or cream of lime is added to the washing bath in order to avoid lime blasts through the action of air.

Deliming and bating The addition of deliming agents causes the formation of readily or slightly soluble calcium salts which have to be removed from the process, as do the unused enzymes contained in the bate in order to avoid refermentation. A washing bath is essential.

Degreasing After degreasing a washing bath is required so that all fatty matters which have been emulsified by means of surfactants and fat solvents are removed from the skin.

Pickling

The pelt is acidified to a pH value < 3.8 by a treatment with salt and acid to prevent basification of chrome tanning salts during subsequent chrome tannage due to the remaining alkalinity of the bate and deliming agent and any existing calcium salts, as this would result in surface tanning and lead to changes of the grain or handle of the leather.

One variant is preservation pickle or storage pickle which contains larger amounts of acid and higher additions of common salt. Small quantities of disinfectants are added in most cases. The pelt is acidified to a pH value < 2.5 . This type of pickle is mainly used for dewooled sheep and lamb skins as well as for grain split, so-called pickle skivers. These pickled pelts can be stored for many months if the storage conditions are adequate.

Control of the pickling process

- Operational:**
1. Determination of the salt content of the pickling float prior to the addition of acid. It should be at least 6 ° Bé.
 2. Testing the final pH value of the float.
 3. Testing a cross-section of the hide by means of bromcresol green in order to determine the depth of penetration of the pickling acid and thus the progression of pickling.
 4. Temperature measurement of the pickling float.

- Analytical:**
1. Determination of the moisture content of the common salt. Should be done especially if the salt is coarse-grained and stored loosely.
 2. Determination of the concentration of the pickling acids used.

Parameters of the pickle

Pickling salts	Sodium chloride (common salt) is most commonly used, followed by sodium sulphate (Glauber salt) and the salts of the organic acids sodium formate and sodium acetate. Combined applications are also common. In the above order they reduce swelling of the skin.
Pickling acids	Commonly used pickling acids are sulphuric acid, formic acid, hydrochloric acid, less frequently lactic acid and glycolic acid, sulphophthalic and dicarboxylic acids. Beta naphthalenesulphonic acid has proven useful for low-salt or salt-free pickling systems.
Float	To save water, reduce pollution and enable quicker penetration of the pickling acids the pickling systems used today are mainly short floats of 30 - 70 %, and about 20 - 30 % in the case of low-salt or salt-free pickling systems. Furthermore, continuation of tannage in the pickling bath has gained acceptance.
Duration	Depending on the skin material, thickness of skin and desired penetration, pickling takes about 1 - 3 hours, and is now rarely done over night. 5 - 10 minutes are sufficient with beta naphthalene-sulphonic acid pickles.
Temperature	The best range is 20 - 30 °C. Temperatures below 20 °C should be avoided because of the risk of low-temperature swelling, and temperatures exceeding 30 °C because of possible damage to the grain.
Pickling additives	<i>Glutaraldehyde, modified glutaraldehyde:</i> Improve handle, fullness and perspiration resistance. <i>Formaldehyde:</i> To obtain flat leathers and promote penetration of the pickling acid. <i>Potash alum, aluminium sulphate:</i> Improve the fineness and tightness of the grain, increase the degree of exhaustion of chrome tanning agents. <i>Syntans:</i> Promote the distribution of chrome and brighten the chrome tannage colour. <i>Sodium chlorite:</i> Bleaches out pigment stains.

Pickling defects

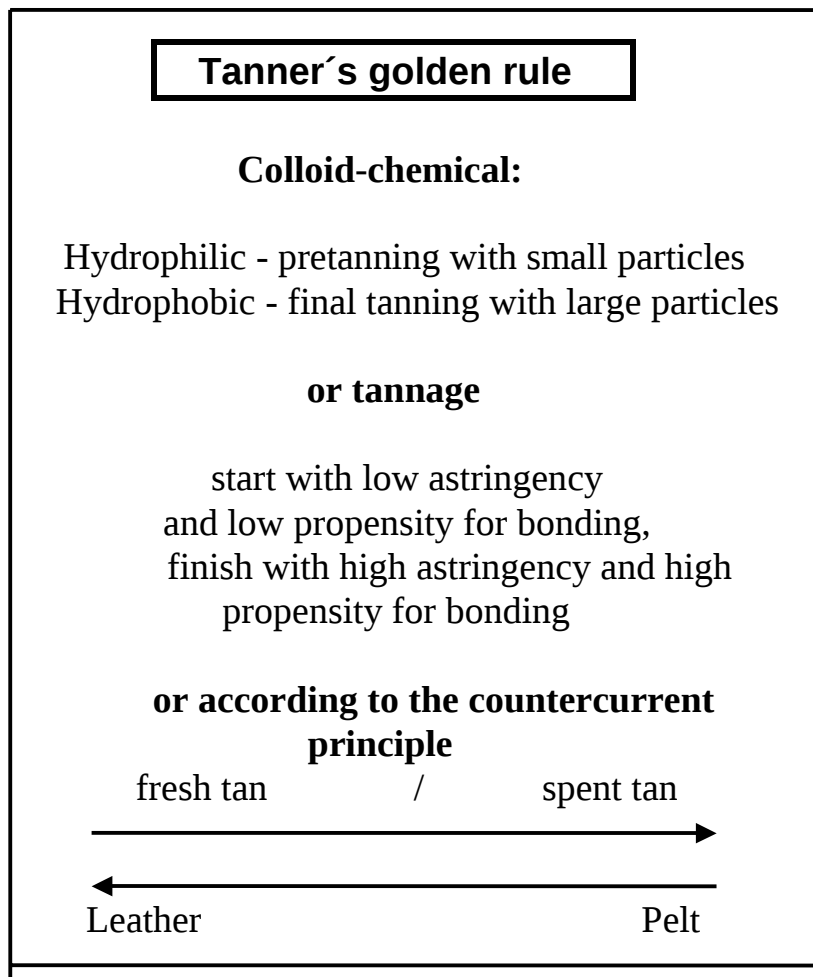
Salt content too low	Results in irreversible acid swelling of the skin. A hydrometer test must be performed. The minimum salt content should be 6 °Bé. In determining the percentage the water absorbed by the skin and the moisture content of the salt should be taken into consideration.
Excessive salt content	Not as serious. However, excessive dehydration of the skin could result in flat, thin leathers.
Pickling pH value too low	If the pH value is <3.2, penetration of the chrome tanning agent is quicker, however larger quantities of basifying agent have to be added.
Pickling pH value too high	If the pH value is >3.8 - 4.0, superficial precipitations may occur, especially with unmasked tanning agents, which produce stains and make complete penetration of the tannin more difficult.
Grain too rough	Here formic acid should be used in corresponding proportions instead of sulphuric acid, or sodium formate or sodium acetate should be additionally used. Additions of aluminium salts or also polyphosphates result in a finer grain.
Cracking of the grain	Beginning of acid swelling due to a large amount of acid, low salt content or low float temperature.
Leathers too flat	Common salt should be replaced by sodium sulphate (Glauber salt). The use of glutaraldehyde is good for fullness. Fuller leathers are also obtained by using a low-salt or salt-free pickle with beta naphthalenesulphonic acid. At the same time this has the advantage of reducing pollution of the waste water because of the lower salt content.

**Every tannage is an irreversible stabilization of the hide
which is prone to putrefaction**

This is achieved by "tanning matters" which cross-link with the collagen through different types of bonds without modifying the natural fibre texture. In this transformation process of the animal skin, which is freed of hair and subcutaneous tissue, the pelt is converted into "leather" which has been valued for thousands of years.

Certain general principles should be observed in order to avoid possible defects by an incorrect tanning process.

The so-called "golden tanner rule" which was established many decades ago is relevant the tanner.



Failure to observe this rule results in case hardening, i.e. clogging of the capillaries, so that the inner zones are not tanned.

Chrome tannage

Tannage by means of chrome salts is still the most common tanning method world-wide. Most types of leathers can be produced by this method as nearly any desired leather quality can be obtained due to the many retanning possibilities. Apart from enabling economical and efficient production it is suitable for integration into automated work processes. Consequently, the production of wet-blue leathers has become popular and is gaining significance in those countries which traditionally delivered raw skins only.

Controls of chrome tannage

- Operational:**
1. Determination of the final pH value of the tannage. It should be in the range 3.6 - 4.0.
 2. Measurement of the final float temperature: 28 °C as a minimum, 38 - 40 °C as a maximum.
 3. Cut tests at thicker sections of the skin to verify the penetration of tanning agent.
 4. Test of the tanned leather for resistance to boiling. A thicker piece of the leather is put into boiling water for 1 minute, and the degree of shrinking compared to the original size is determined. An extended theory on boilfast tannage was developed by E. Heidemann¹¹.
- Analytical:**
1. Determination of the chrome content of the residual float to verify the degree of exhaustion.
 2. The salt content should be checked regularly in the case of recycling chrome floats.

Testing the chrome tanning agents

- Analytical:**
1. Chromoxide content
 2. Insoluble constituents (cold-solubility, hot-solubility)
 3. Determination of basicity
 4. Masking agents
 5. Neutral salt content

One-bath tanning process**1. *Tannage with soluble chrome sulphates:***

Formerly the most common procedure. Is now less used due to rationalization and the progress of automation.

2. *Insoluble chrome tannage:*

Addition of the entire tanning agent in powder form. Basification may be started after only 30 - 60 minutes without risk of precipitations. The advantages of this method are uniform tanning, high operational reliability and efficiency.

3. *Tannage with self-basifying chrome tanning agents:*

They mostly contain magnesium oxide or dolomite which dissolves during the tanning process and effects a uniform increase in basicity. A minimum duration of 6 hours and a final temperature of 35 °C should be observed in order to avoid secondary reactions.

4. *Tannage with organically masked chrome tanning agents:*

Contain formates, acetates and recently dicarboxylic acid or their salts as masking agents. Good exhaustion of the float is achieved with a pH of 3.9 - 4.0. Preferred for thin, soft, light leathers.

5. *Tannage with self-reduced chrome liquors:*

In view of the great number of specially formulated, commercially available chromium(III) tanning salts individual production in the factory has decreased considerably. This is also due to the cancerogenity of the chromium(VI) compounds used.

6. *Tannage with chrome alum:*

Now only a special application, expensive and rarely used. The product has no initial basicity and has to be basified in advance or during tannage.

Two-bath tanning process

Practically of no more importance because of the strict safety measures which apply to the hexavalent potassium and sodium dichromates. This method was used especially for producing chevreaux, to obtain fine grains and good fullness by means of sulphur deposits.

Increase of basicity, basification

The basicity of the chrome tannage should be in a range of about 50 - 60 % (Schorlemmer) in order to achieve the best possible tanning effect and sufficient resistance to boiling, and also to attain a good bonding to the skin fibres and a high degree of exhaustion of the tan liquor.

This is done by means of products with an alkaline reaction during or at the end of the tanning process.

Products used:

Sodium carbonate (soda), sodium hydrogen carbonate, magnesium oxide, calcium carbonate, dolomite, polymetaphosphate and alkali aluminium silicates.

In most cases they are also combined with masking products (qv).

It is very important that the products be added slowly and in portions in order to avoid sudden pH changes or precipitations, especially of products with an alkaline reaction. Automatic dropping devices are recommended.

Masking, masking agents

"Masking" refers to the incorporation of anionic acid radicals into the complex of chrome tanning agents. The complex affinity of the acid anions has been fixed in a sequence. Each succeeding anion displaces the preceding one from the chromium complex (only valid for equivalent quantities and identical conditions regarding temperature, pH and neutral salt):

Water←chlorate←nitrate←chloride←sulphate←sulphite←formate
←acetate←collagenate←adipinate←sulphophthalate←succinate
←tartrate←glycolate←phthalate←sulphosalicylate←maleinate
←malonate←lactate←citrate←resorcylate←oxalate←hydroxide

The masking products mainly used in practice are sodium and calcium formate, sodium acetate, sodium hydrogensulphite, sodium sulphite, salts of the dicarboxylic acids or also salts of condensation products of aromatic sulpho acids.

By means of such masking processes it is possible to influence the properties of the tanning agent and also of the leather in a special way.

- | | |
|-----------------------|--|
| Tanning agent: | <ol style="list-style-type: none"> 1. Slows down bonding in order to achieve complete penetration of tannin. 2. Weakens the positive charge activity up to an anionic complex. 3. Increases the resistance to flocculation by alkalies. 4. Improves the degree of exhaustion of the chrome bath. |
| Leather: | <ol style="list-style-type: none"> 1. Improves fullness. 2. Achieves a finer appearance of grain and reduces pronounced growth marks. 3. Smoother handle. 4. Change of the tanning colour (lightened, more blue). 5. Even distribution of chrome in the cross-section of the leather. |

Defects caused in chrome tannage

- | | |
|-------------------------------|---|
| Flat leathers | <p><i>Causes:</i> Excessive amounts of neutral salts in the pickle or during the course of chrome tannage, insufficient supply of chrome oxide, pH value of the pickle too low and inadequate basification or excessive masking.</p> <p><i>Remedy:</i> Do not use hydrochloric acid in the pickle and replace common salt by sodium sulphate or use salt-free pickle with beta naphthalenesulphonic acid.</p> |
| Loose, spongy leathers | <p><i>Causes:</i> Excessive basic final tanning, rotary speed of drum too high or drum running times too long.</p> <p><i>Remedy:</i> Avoid the causes and also use appropriate quantities of aluminium tanning agents, glutaraldehyde, polymeric or synthetic tanning agents.</p> |

Defects caused in chrome tannage

Staining	<i>Causes:</i> Basifying agents were added too quickly, in concentrated form or too hot, pH value during final tanning was too high. No final reaction in the case of self-basifying chrome tanning agents, or abrupt pH changes due to large quantities of readily soluble magnesium oxide. <i>Remedy:</i> Avoid the causes.
Coarse, drawn grain	<i>Causes:</i> Initial pH value of tannage too high, inadequate amount of liquor and rotational speed of drums too high. Excessive temperatures, >38 °C, during final tanning. <i>Remedy:</i> Avoid the causes. Masking agents should be used for basification.
Cracking of the grain	<i>Causes:</i> Salt content too low or time of immersion in the new liquor after pickling too long before chrome tanning agents are added. When using unmasked chrome tanning agents, caused by basification to an excessive final pH value. Erroneous addition of hot water. <i>Remedy:</i> Avoid the causes.
Inadequate exhaustion of the float	<i>Causes:</i> Excessive amount of float, tanning temperatures too low, inadequate basification, excessive supply of chrome tanning agents, degree of masking too high, inadequate processing time. <i>Remedy:</i> The degree of exhaustion is improved by the addition of aluminium or zirconium tanning agents, glutaraldehyde or condensation products of aromatic sulpho acids.
Inadequate resistance to boiling	<i>Causes:</i> Mostly due to inadequate and incomplete basification and thus insufficient cross-linkage of the tanning agent with the hide substance. Despite a good tanning action and correct dosage of the basifying agents full or sufficient resistance to boiling cannot be achieved with an inadequate chrome supply, incomplete penetration of tannin or even special formulations of tanning agents.

Defects caused in chrome tannage

	In many cases a satisfactory resistance to boiling is only achieved after thorough and complete deacidification or after several days of storage. The resistance to boiling must never be overestimated.
Uneven distribution of chrome in the hide	<i>Causes:</i> Caused by inadequate deliming and also by preliminary tanning using excessively basified tanning agents. This is often desired for firm leathers. However, a uniform chrome distribution is essential for supple, soft leathers. <i>Remedy:</i> Addition of masking agents such as sodium formate, sodium acetate or oxalates.
Chrome fat soaps	<i>Causes:</i> High natural fat contents in the tanning bath or free fatty acids due to inadequate degreasing or fat which has not been dissolved in preceding beamhouse processes form stains of insoluble fat soaps. They are not penetrated by retanning chemicals and cannot be coloured by dyes. <i>Remedy:</i> Avoid the causes.
Formation of chromium-VI compounds	With oxidation bleaching using sodium chlorite in the pickling bath to remove stubborn pigment stains it is necessary to neutralize the excessive sodium chlorite still present in the bath by means of reducing substances such as sodium hydrogensulphite or sodium thiosulphate before starting chrome tannage. If this is not done thoroughly the chromium-III salts produce dangerous hexavalent chrome compounds. Apart from being carcinogenic they reduce the tanning effect and possibly the breaking strength of the leathers. The decomposition of sodium chlorite is checked by means of potassium-iodide starch paper.

Wet blue production

Chrome-tanned wet leathers, designated "wet blue", are becoming more important in the leather trade. Due to their economic and ecological advantages many suppliers have specialized in the production of these leathers, which are then sold to other leather factories for further processing.

For these commercial transactions the International Contract No. 6 - Hides & Skins, Annex C - was issued by the *"International Council of Hides, Skins & Leather Trader`s Associations and the International Council of Tanners"*. It contains regulations on all important trading aspects.

Standard for wet blue

Chrome oxide	The chrome oxide content should not be less than 2 % Cr_2O_3 and should not vary too much from lot to lot.
pH value	The pH value should be in the final range of 3.5 - 4.0, which is normal for chrome-tanned leathers, and should not vary significantly.
Preservation	In the case of prolonged shipment and prolonged storage the goods should contain preserving agents in order to prevent the formation of mould and bacterial growth.
Workmanship	When shipped, the leathers should be as smooth and creaseless as possible. Pressure marks fixed by tanning cannot be removed or only with difficulty.
Dry spots	Drying at the edges of the leathers should be avoided. Dry, not fatliquored sections of chrome leather can hardly be resoaked.
Efflorescence of salt	At the end of wet blue production a washing bath is absolutely necessary in order to reduce high salt concentrations.

Aluminium tannage

The oldest methods of tanning with potassium, simple aluminium chlorides and aluminium sulphates are now only seldom applied as they do not result in real tannage and can easily be washed out with water.

Since the chemical industry succeeded in making highly basic and partly masked aluminium chloride tanning agents which produce stable tanning results these products are used to make white leathers with a very good resistance to light. Optical bleaching agents can be used for subsequent treatment in order to intensify the white effect. However, they have gained more significance as pretanning, retanning and combination tanning agents and also as mixed-complex tanning agents with chrome and aluminium as base products. If used as retanning agents they improve the receptivity for dyes by providing full shades with high brilliance. Furthermore, they are very suitable for the production of nubuk and suède leathers as they improve the density of the fibre texture and thus the buffing properties. In full-grained leathers they reduce the propensity for loose grain and excessive formation of flanks.

Parameters of aluminium tanning agents

1. Increased hydrolysis formation in aqueous solution compared to chrome salts. If possible, tanning should be performed in shorter floats and the neutral salt content in the float should be observed.
2. Considerably increased precipitability, even with relatively low quantities of alkali additives.
3. Bonding with the skin fibre occurs more quickly, and in combination with chrome tanning agents is greater at the surface.
4. The shrinking temperature of aluminium-tanned leathers is lower than that of chrome-tanned leathers (about 80 - 90 °C).
5. If added to the chrome tan liquor they improve the degree of chrome exhaustion of the residual float.
6. In the case of pure aluminium tannage it is good to work with short floats in order to obtain an even absorption and bonding of the tanning agent.

Wet white production

Due to ecological legislation in many countries, which can be expected to increase in future, it will become more difficult to dispose of chrome-containing waste at economical prices.

Therefore procedures have been developed in the last few years in order to reduce or eliminate the large quantities of chrome shavings and thus to avoid their disposal on dumps for hazardous waste.¹²

This has been achieved by chrome-free preliminary tanning and by a shrinking temperature which is adequate for perfect shaving in the wet condition.

The leathers produced by such a procedure are called "wet white" leathers.

Procedure

The pelts which have been processed by the standard procedure including bating are washed as usual and thoroughly pickled through the cross-section of the skin, in most cases with sulphuric acid. A treatment with chrome-free products such as glutaraldehyde, polymer and/or aluminium tanning agents or also small quantities of synthetic alum tanning agents then follows in the same bath. After adjusting the pH value to about 3.8 - 4.5 the leathers are intermediately stored for at least 24 hours, sammed and subsequently shaved.

The leathers produced by this procedure can then be processed by any main tanning method.

Wet white production with sodium aluminium silicate¹³ or acrylic sulpho acid products¹⁴ is also possible.

Zirconium tannage

The most commonly used tanning agent is zirconium sulphate or its basicification. Their chemical behaviour is similar to that of chrome and aluminium tanning agents.

Like aluminium tanning agents they result in leathers with a pure-white cross-section and neutral-white surface having excellent lightfastness. Tanning is more compact and fuller and improves the density of fibre texture, and therefore they are specially suitable for treating loose and spongy raw hides. Full, clear and brilliant shades are achieved by dyeing with anionic dyes as in the case of leathers tanned by means of aluminium salts.

Parameters of zirconium tanning agents

1. Compared to chrome and aluminium tanning agents they have better hydrolysis properties. Therefore tanning should be performed in short floats and by adding neutral salt in order to avoid acid swellings.
2. The pickling pH should be reduced by at least one pH unit ($< \text{pH } 3.0$).
3. The tanning agent may be added to the pickling bath. In order to achieve quicker penetration of the tannin it is good to use a very short float and a tanning agent in powder form.
4. The penetration of tannin is tested by placing a piece of leather in water for a short time. If penetration is incomplete the inner zone has a glassy appearance. In this case the tanning time should be extended. Basicification should reach a final pH value of 3.2 - 3.5.
5. Due to the slower release of acid compared to chrome leather the leathers should be neutralized more intensely and during a longer period of time in order to avoid problems during retanning, dyeing and fat-liquoring as a result of inadequate diffusion or even precipitations.

Iron tannage

For reasons of economy or when there is a shortage of chromium, and recently also due to environmental legislation concerning the disposal of chromium, tanning with ferric salts has become a relevant issue. Recent trends and findings¹⁵ show that iron tannage is very suitable for preliminary tannage in the production of chrome-free leathers (wet brown, wet iron).

Iron(II)-tanned leathers have similar handle properties as chrome leathers. In order to obtain resistance to boiling they should be retanned using vegetable, synthetic or chrome tanning agents.

Parameters of iron tannage

1. The starting material consists of pelts which have been pickled in a pickling bath at a pH of <2.5.
2. It is better to use iron(II) sulphate as tanning agent. This is cheaper and results in a quicker penetration of tannin than the trivalent ferrous salts.
3. As a matter of principle, masking agents such as tartaric acid or sulphophthalic acid should be used for stabilization of the iron tanning liquors.
4. In order to avoid staining during storage on trestles it is advisable to use glucose or oxidants such as potassium permanganate.
5. Basification should be performed slowly with soda. It is better to use magnesium oxide.
6. Fullness, handle, firmness of grain and dyeing properties can be favourably influenced by suitable retanning with chrome, aluminium or syntan tanning agents.
7. Shavings tanned with ferrous salts cannot be processed to obtain gelatine. Therefore they have to be disposed of on dump sites.

Sulphur tannage

This method of treatment has no real tanning effect. The term "sulphur tannage" is therefore not correct, although very common. Used alone, this method is of minor importance and is used in some cases to make special technical leathers such as picker bands, lace or belt leathers. The advantage of this treatment consists in the deposition of colloidal sulphur in the interfibrillar spaces which effects excellent firmness, high pliability and elasticity of the skin. It is mainly used in combination with other tanning agents. When retanning by means of vegetable tanning agents penetration of the latter is accelerated and absorption and bonding of the tanning agents are increased.

In the case of two-bath chrome tannage, which is now only seldom used, the deposition of sulphur increases the fullness, softness and firmness of grain of the leathers.

This method is also used in combination with fat tanning agents, in particular with unsaturated fish-oil. Leathers of very good toughness, firmness and dense fibre texture are achieved by this method.

Procedure of sulphur tannage

The delimed and pickled pelts are treated with a highly acid, penetrative pickle, mainly with hydrochloric acid, followed by slow addition of 15 - 20 % sodium sulphate solution in portions. Fine colloidal sulphur forms at this stage and is deposited in the interfibrillar spaces of the hide fibre texture.

Vegetable / synthetic tannage

With the industrial application of chrome tannage rapidly advancing since the end of the last century, vegetable tannage has been ousted from its predominant position into second place.

Moreover, synthetic tanning agents were invented in 1911 by the condensation of phenols with formaldehyde and further developed with a great number of aromatics. In the past decades syntans having very particular properties have been produced. In many cases they improved the vegetable tanning agents in terms of tanning technique and were sometimes even superior. This led to a great number of combinations of vegetable tanning agents with syntans, which modified the tanning methods and also the properties of the leather.

Vegetable tanning materials ¹⁶

There is a worldwide abundance of woods, barks, leaves, fruits, roots or growths (gall-nuts) containing usable tannin. Plants with a particularly high content of tannin are native to the tropical and subtropical regions of the world. Most of them are therefore only significant for leather production at local or national level.

In crushed form they are only still used in small craftsman's establishments or as dusting material in the layer or handler in sole leather production. For international trading the tannin content is concentrated by extraction. It is mostly shipped as spray-dried powder, less often as viscous extracts or in blocks in order to reduce the shipping costs.

Vegetable tanning agents most commonly used worldwide:

Barks: Mimosa, mangrove, acacia negra, eucalyptus
Pine

Woods: Quebracho, chestnut, oak

Fruits: Myrobalans, valonea

Leaves: Sumac, gambir

Manufacture of tannin extract

Today tannin extract is mainly produced by specialized industrial companies and rarely by leather factories.

1. Disintegration of the dried tanning material by cutting, rasping, crushing or coarse grinding.
2. Extraction of the disintegrated bark by means of water according to the counter-current principle in extractor boilers, mostly of stainless steel, in order to prevent ferrous impurities. By the pumping action the weakest liquor moves towards the fresh bark and the tannin content in the liquor gradually increases. This process requires temperatures of 80 - 130 °C, sometimes under pressure, depending on the tanning material. In some cases (mostly when using quebracho and mimosa) sodium sulphite or sodium hydrogensulphite is added in order to improve solubility. Cold-soluble extracts are produced which give pale leathers. However, dosing should not be excessive in order not to reduce bonding of the tannin to the hide fibre. With chestnut extracts the pH value is increased to improve the tanning effect. So-called "sweetened" extracts are obtained. The addition of dispersing agents or auxiliary synthetic tanning agents improves the colour and reduces sludging.
3. The liquors obtained are purified by sedimenting, filtering or centrifugating and further concentrated in vacuum evaporators.
4. For reasons of transportation and to improve handling in the leather factory the extracts are now mainly supplied in powder form. The powder is obtained by spray drying, drum drying or occasionally by granulate drying. The products are sold with a 60 - 80 % content of pure tannin.

Lignin extracts

These extracts are inevitably produced during paper and pulp production in the form of spent sulphite liquor. They cannot be used separately, but are suitable as dispersing and bleaching agent or for the production of syntan.

Tanning properties of the most important tanning agents

1. *Hydrolysable tanning agents* (pyrogallol = acid former)

	Colour	Fullness	Tannage	Other
Oak	yellow brown, dark cut	full	very firm	acid-forming
Chestnut	pale yellow, olive tinge	full	firm	Bloom-forming
Myrobalan	pale-coloured	medium	little strength	strongly sludging
Sumac	almost white tanning	medium	soft, supple	good lightfastness
Valonea	grey-brown, pale-coloured	medium-full	tough, firm	low content of insoluble matters

2. *Condensable tanning materials* (catechol = phlobaphene former)

	Colour	Fullness	Tannage	Other
Pine	pale brown-brown	medium-full	firm-hard	becomes darker on exposure to light
Mangrove	intensive red-brown	medium	loose, spongy	strongly sludging
Mimosa, untreated	pale, slightly reddish tinge	full	quick, firm, supple	becomes darker on exposure to light
Mimosa, sulphited	bleaching, dull beige	medium-full	medium firm, fine grain	bleaching, readily soluble
Quebracho-ordinary	very intensive reddish tinge	full	slightly softer than mimosa	strongly sludging
Quebracho-sulphited	intensive reddish tinge	medium-full	slightly softer than mimosa	cold-soluble

Production of syntans

The base products are mononuclear and polynuclear phenols, naphthalene and their derivatives cresoles, naphtols, aromatic ethers and spent sulphite liquors. They are condensed, also as mixtures, mostly with formaldehyde and sulphonated by the introduction of water-solubilizing groups, usually containing sulphuric acid. They exist mainly in the form of sodium or ammonium salts. By varying the products and procedures it is possible to manufacture the most diverse syntans having particular properties. Most syntans are anionic, a few are amphoteric. Technical information and leaflets concerning the exact properties of these products are available from specialized suppliers.

Classification and properties

1. *Replacement tanning agents*

As they possess an equivalent self-tanning capacity these products can replace vegetable tanning agents or portions of them without problems and, if desired, give the leathers to be tanned particular properties.

2. *White-tanning agents*

In most cases this type of tanning agent can be classified as a replacement tanning agent. They generally exhibit a reduced filling capacity if they have a good white effect and high light-fastness.

3. *Shrinking tanning agents*

These tanning agents are highly astringent and acidified in order to achieve an astringing effect on the grain and thus a high shrinking grain. Besides phenolic tanning agents glutaraldehyde has also been used for many years to obtain line shrinking effects.

4. *Pretanning agents*

They have been developed to improve the diffusion of highly concentrated tanning agents with large-sized particles and thus to accelerate or reduce the tanning times.

5. *Retanning agents*

There is a great variety of products. Mainly used for subsequent treatment of chrome-tanned leathers in order to obtain special effects and properties such as fine grain, firm grain and good handle, softness or toughness, fullness, pastel shades or level dyeing properties, good buffing properties, lightfastness or resistance to ageing and improved physical properties.

6. *Auxiliary tanning agents*

These products serve to support tannage with specific objectives such as dissolution of sludge in vegetable tanning liquors, distribution of tanning agents or pH value adjustments.

7. *Bleaching tanning agents*

Are used for bleaching or correcting the colour of vegetably tanned leathers and simultaneously cleaning the grain surface.

8. *Dispersing tanning agents*

Are used with vegetable, untreated tannin extracts which penetrate slowly and with difficulty such as quebracho. In this way additions of large quantities of sulphite are avoided.

9. *Filling tanning agents*

Serve to fill heavy leathers or to upholster flat leathers during retannage. Besides syntans and some polymer tanning agents the resin tanning agents with their selective filling effect for hide sections of loose texture can be mentioned.

10. *Neutralizing tanning agents*

These products are used during deacidification because of their strong buffering capacity, low sensitivity to acids and good lightfastness. They have a neutralizing effect as well as a slight retanning effect. There is no risk of overneutralizing.

Tanning methods

1. *Slow pit tannage*

Now only used in isolated cases. Tannage, lasting about 12 - 18 months, is performed according to the counter-current principle with thin tanning liquors in the colour pit, followed by handler (1-3) and finally lay away (1-3). This tanning method gives a good quality leather. The label "old pit tanned" means tanning with oak and pine bark which provides a specially compact and firm sole leather having a low content of substances removable by washing. The disadvantage of these tanning methods consists in their prolonged duration, which ties up capital and also involves a high loss of tanning agents by decomposition due to oxidation and hydrolysis.

2. *Accelerated tannage with tan solutions of higher concentration*

Final tanning is performed by further increasing the concentration using higher-percentage tanning agents and tan liquors of higher concentration, in the handler and lay-away respectively, and by additional mechanical agitation in the drum. The duration of tannage is reduced to about 2 - 6 months depending on the method used. Compared to the slow method, bonding of tannin is slightly reduced and the content of substances removable by washing is considerably higher.

3. *Quick tanning methods*

These methods serve the purpose of reducing the duration of tannage. They are all based on the principle of increased concentration, mechanical agitation, increased temperature and pH variation. Furthermore they include the most diverse kinds of pretanning processes and the use of dispersing tanning agents. The duration of tannage is reduced to 4 - 20 days, depending on the operational conditions and type of leather.

Known methods ¹⁷:

1. West German Tanner School, Reutlingen
2. Italian method
3. English hot pit method
4. Igualada method
5. Four-step method
6. Liritan method

4. *Rapid tanning methods*

These are powder tanning substances without float. The best known methods are:

1. RFP process of BAYER
2. Rapitan process of BASF.

They reduce the duration of tannage to 2 - 3 days.

The hides should be well prepared for these tanning methods and the vessels should be suitable in order to reduce possible errors and avoid case-hardening.

**Tanning
process:**

1. Complete soaking and liming.
2. Complete removal of the subcutaneous tissue by thorough fleshing.
3. Complete deliming of all sections of the skin. Dry deliming and the addition of sodium hydrogensulphite as well as aromatic sulpho acids is good for thick pelts.
4. The formation of false backs is avoided by slashing the butts along the backbone line.
5. Pretannage with small-particle synthetic pretanning agents of low astringency. Also preliminary treatment with glutaraldehyde, polyphosphates or pickles containing chrome salts or chromiferous syntans.
6. Thorough washing after pretannage and good draining of the residual liquor.
7. Addition of the powder tanning agents for final tanning in 2 - 3 portions and addition of dispersing tanning agents in appropriate quantities. Temperature rise not exceeding 38 °C.
8. Addition of a slip additive or untreated oil to reduce friction.

Apparatus:

1. Drums equipped with strong transmissions.
2. Multistep transmission with change-over switch.
3. Checking device for temperature measurements during the tanning process.

Bleaching, filling, fixation of vegetably tanned leathers

Bleaching

Is applied for levelling, lightening or changing the tan colour, mostly after final tannage.

Mainly bleaching syntans, highly sulphited mimosa or quebracho extracts, specially formulated synthetic bleaching tanning agents and less frequently bleaching oils are used for this purpose. Acid bleaching, which was often used in the past, can no longer be recommended because defects to the fibre were caused by the presence of strong free acids.

Filling

Is used for heavy leathers to improve firmness and toughness of the sections of skin which are of poor substance, to improve abrasion resistance and also to improve the yield of sole leathers.

Untreated, liquid or powdery tanning extracts are used. Sulphited tanning agents should not be used as they increase the water absorption of the leathers.

However, excessive filling is not advised due to the high content of washing-out substances. Deposits of water-soluble loading agents such as barium sulphate or magnesium sulphate should also be avoided. When the shoe comes into contact with water they produce efflorescence of salt due to migration on the upper leather.

Fixation

The unbound tanning agent in the interfibrillar spaces of the leather, which is removable by washing, is precipitated and thus converted into an insoluble form which cannot be removed by washing.

Skin glue, casein, magnesium sulphate (bitter salt), aluminium sulphate or urea formaldehyde condensation products and hexamethylenetetramine are used, whereby the latter two are preferable because they achieve better bonding. They should always be dosed and used carefully, otherwise fixation is only superficial and may result in a greasy grain surface and flesh side. Crackiness of grain may also occur.

Controls of vegetable tannage

- Operational:**
1. Continuous concentration measurements by determination of the density or the Bé degree of the tanning floats in the application vessels.
 2. Temperature measurements, in particular during final tannage.
 3. Determination of the pH value by means of indicators or by means of electrometric measuring units.
 4. Test for complete penetration of colour into the pelts by regular cuts at thicker sections in order to verify the penetration depth of the tanning agents.
 5. Test for complete tannage by cutting off a narrow strip of the leather to be checked and putting it into 10-20 percent acetic acid. The untanned or insufficiently tanned zone swells to a greater or lesser degree. If light falls through that area it appears wax-like and shiny.
- Analytical:**
1. Determination of the acid and salt content ¹⁸ of tan liquors or tan solutions. Is determined by titration with 0.05 n sodium hydroxide solution before and after the liquor has run through an ion-exchange column which has been filled with a cationic resin.

Testing vegetable and synthetic tanning agents

- Analytical:**
1. Quantitative determination of the tanning agent according to the filter or shake method. Includes determination of water content, content of insoluble tanning agents, content of non-tannin and content of dry substance.
 2. Determination of tanning and binding value.
 3. Determination of ash content.
 4. Determination of the pH value.
 5. Determination of the acid value.

Defects by vegetable tannage

- Tanning stains** *Effect:* Irregular pale stains.
Causes: Are caused by packed suspension of the hides in the rounds of suspenders. Tanning is less intense where the hides are touching each other.
Remedy: Can be avoided by lifting and rocking the hides from time to time.
- Tanning agent stains** *Effect:* Small to large dark brown stains on the grain surface and on the flesh side.
Causes: Are caused by irregular deposits of unbound tanning agent.
Remedy: Reduce the use of tanning agents having a high content of insoluble or poorly soluble substances and avoid flocculation in tanning liquors, creasing of the leather and excessive air in the vessels. No uneven drying at excessive temperatures. Stained leathers should be washed or soaked and fixed.
- Iron stains** *Effect:* Grey, deep dark blue or blue-black stains of irregular distribution and size. May also cause crackiness of grain in these sections.
Causes: Tanning material soiled by iron particles, iron chips from splitting or shaving, rust particles of pipes, drum fittings or conveyors.
Remedy: Remove by a treatment with bleaching tanning agents, oxalic or hydrochloric acid solutions or complexing agents.
- Copper stains** *Effect:* Greenish, irregular stains.
Causes: Soiling of the tanning material or by pipe lines and drum fittings.
Remedy: As in the case of iron stains.
- Slime stains** *Effect:* Whitish, irregular stains.
Causes: Slimy substances caused by bacterial attack in tanning liquors and soaking liquors, particularly in old rounds of suspenders.
Remedy: Discard the affected liquors and add disinfectants.

Mould stains	<i>Effect:</i> Whitish, coloured or black coat occurring in some sections or all over the surface, producing irregular stains on the leather. <i>Causes:</i> May occur at all stages of leather production. Increased formation of mould is possible if the leathers are stored under humid and warm conditions. <i>Remedy:</i> Impossible or very difficult to remove. Can be prevented by using disinfectants during processing, on the factory premises and in the vessels.
Stains through formation of blooms (mud)	<i>Effect:</i> Light yellow to brownish deposits of ellagic and chebulinic acid which produce map-like stains. Was formerly a quality mark of sole leathers, not desired for leathers to be dyed. <i>Causes:</i> Separation products of bloom-forming tanning agents such as myrobalans, valonea, chestnut and oak. <i>Remedy:</i> Wiping or washing the leathers, treatment by means of bleaching tanning agents.
Grey-tinge leather colour	<i>Causes:</i> Use of process water containing iron or finely dispersed iron salts in the tanning liquors. <i>Remedy:</i> Use condensed water or treated water and complexing agents, change the tanning liquors.
Inadequate penetration of tannin	<i>Effect:</i> Hard tinny condition of the leather and inadequate elasticity, loose grain and wrinkled grain. <i>Causes:</i> Incorrect pretanning with extremely astringent tanning agents, insufficient tanning times, increasing the concentrations too quickly during tanning and retanning. <i>Remedy:</i> Observation of the Tanner's Golden Rule and regular checks for complete penetration of tannin. The pH value should not be too low for preliminary tanning, the drumming process should be long enough.
Case hardening	<i>Effect:</i> Hard, tinny leathers. <i>Causes and remedy:</i> as under inadequate penetration of tannin.

Brittle cracked grain	<i>Causes:</i> Overtannage of the grain by deposits of excessive quantities of unbound tannin, loading agents or incorrect fixation. Use of excessive quantities of bleaching agents. <i>Remedy:</i> Thorough washing or soaking after final tanning. Oiling of the grain.
Crumbly crackiness of grain	<i>Causes:</i> Damage due to the action of strong free acids. <i>Remedy:</i> Avoid or reduce the use of mineral acids or excessive quantities of oxalic acids and acid bleaching tanning agents.
Drawn grain	<i>Causes:</i> Pretanning with extremely astringent tanning liquors or agents, inadequate quantity of liquor, rotational speed of the tanning vessels too high. <i>Remedy:</i> Avoid the causes.
False back	<i>Effect:</i> Permanent creases along the backbone line, chafe marks with defective grain. <i>Causes:</i> Rolling up the hides, mostly butts, with the grain on the outside. <i>Remedy:</i> Short cuts along the backbone line and addition of highly polymeric slip additives during drum tanning.
Loose grain	<i>Causes:</i> Uneven deposition of the tanning agents, excessive stress by drumming. <i>Remedy:</i> Avoid the causes.
Efflorescence of mineral salts rash	<i>Effect:</i> Whitish, grey coat on the grain surface. Visible above all if shoes are exposed to moisture. Deposited salts will then migrate into the upper leather. <i>Causes:</i> Use of excessive quantities of loading agents (bitter salts) or use of synthetic tanning agents which have a high content of extenders consisting of mineral salts or kaolin. <i>Remedy:</i> Avoid the causes. Wipe shoes several times with a wet cloth.

Reactive tanning agents

Used mainly for retanning and less for preliminary tanning. They have not gained acceptance as self-tanning agents. The starting materials are melamine, urea and dicyandiamide which are mostly condensed with formaldehyde. A wide range of products having special properties are produced by modification with other substances which react with formaldehyde. Filling materials, buffering or neutralizing substances are often added.

Resin tanning agents

1. *Reactive resin tanning agents*

Initially, the starting material was applied to the hide and condensed during the course of the tanning process. As the final reactions were incomplete, postcondensation often occurred during storage of such leathers and resulted in hardness and cracked grain. Therefore this method was discontinued.

2. *Condensed resin tanning agents*

Anionic products have mainly gained acceptance as retanning agents. The particular advantages of these products are their selective filling effect in the loosely structured parts of the skin, firmness of grain, good buffing and milling properties. In particular, they considerably increased the number of pieces that could be cut out of the leather in the production of shoe upper leathers. Furthermore, their excellent filling effect meant that a good area yield was achieved in paste drying in the production of corrected grain side leather.

Cationic resin tanning agents are used for charge reversal according to the sandwich method (anionic-cationic-anionic) in order to increase bonding of fatty substances or to improve level dyeing properties. Excessive amounts should be avoided on all account because this would cause precipitations.

Condensation products of methylol compounds with phenol and dispersing agents may be used as pretanning agents for vegetable tanning, as levelling agents for dyeing applications or in order to improve buffing properties.

Aldehyde tannage

This class of product is seldom used for self-tanning, but for pretanning and retanning treatments. Glutaraldehyde and its modifications have gained more importance.

Formaldehyde

Optimum tanning effect is only achieved in pH ranges above 6.5 to 8.5. Binding to the hide substance is cancelled by acid solutions. Excessive formaldehyde should be removed by washing in order to avoid callouses on the grain. A further disadvantage consists in the increased water-absorption of leathers treated with formaldehyde. However, a pure white colour of leather and a fine, closed appearance of grain are obtained.

Glutaraldehyde

The use of glutaraldehyde and its modifications has gradually become more common because it produces a softer condition of the leather, greater fullness and increased fastness to perspiration, heat, washing and alkalies. The tanning effect occurs already at a pH of 2.5. Exhaustion of the tanning agents is improved when used in pickling or in chrome tannage, which makes it possible to reduce the amount of chromium. Moreover, a finer appearance of the grain is obtained. If glutaraldehyde is used for pretanning of leathers to be vegetably tanned, final tanning is accelerated and the fixation of tannin is improved. Used as a retanning agent it improves the softness as well as levelness of dyeing processes without having a bleaching effect. Line shrinking effects are possible if the liquor is slightly alkaline.

The slight tinge of yellow must be taken into consideration when tanning pure white leathers. However, certain modifications which have no yellow tinge have been developed. Furthermore, products for use in degreasing baths, especially for pickled pelts, are available and permit processing without salts and solvents.

Bad odours caused by unbonded aldehyde in the bath or leather can be reduced by adding small amounts of sulphite.

Tannage with polymers

The use of polymer tanning agents has increased during the last decade. Without exception they are used as pretanning and retanning agents as their self-tanning effect has not proven adequate up to now. The starting products are polymers of acrylic acid and methacrylic acid and their ethyl esters or methyl esters, styrene maleic acid, copolymers of different monomers and also oligomers from polyurethane chemistry¹⁹. The products have a different degree of polymerization and thus different molecular size depending on their application. This is decisive for penetrativeness into the fibre texture and for the fullness and handle properties of the leathers. These types of products will be further developed in future as they also have ecological advantages.²⁰

Polymer tanning agents

1. *Anionic products*

Most products are unstable with chrome or aluminium tanning agents, cationic products and high acid concentrations. However, there are special formulations in which these products are stable in such media and improve the fullness of loosely structured hide sections.

All polymer tanning agents based on acrylate are characterized by high lightfastness and improve fullness without overloading the grain. They do not change the leather properties significantly. Furthermore they improve the adhesion of the finishing.

If they are used as retanning agents, the quantities of phenolic syntans can be reduced. In the pretanning process of vegetably tanned leathers they accelerate the penetration of tannin.

2. *Amphoteric products*²¹

Retanning with products of this class improves fullness by means of pH variations. Furthermore, they improve the depth of shade of dyeings.

Polyphosphates

Metaphosphates^{22 23} are chiefly used. In practice they are not used for self-tanning. The optimum bonding pH value for these products is between 2.5 and 3.5. Hydrotopic swelling occurs at a pH value of 5 to 7.

Areas of application of these products are:

Pretannage	Bleaching of vegetably tanned leathers.
Depickling	Improvement of refreshing and reduction of the salt content by hydrotopic swelling.
Pickling, chrome tannage	Reduce the salt content in the pickle, improve chrome absorption and give a finer grain. Their disadvantage consists in the clearly greener chrome tanning colour.
Deacidification	High complex affinity, subsequent acidification of the leathers is avoided.
Complexing	Specially for water softening.

Aluminium silicates

The products used are sodium aluminium silicates.^{24 25} They are insoluble at pH values exceeding 7.0. Hydrolysis into aluminium salts and small-particle polysilicic acids occurs only with a pH value exceeding 5.0.

Areas of application of these products are:

Pretannage	Performed with glutaraldehyde, dicarboxylic acid and A1 silicate, followed by vegetable-synthetic final tanning in order to obtain chrome-free leathers.
Depickling, degreasing	Pretreatment with A1 silicate increases the shrinking temperature and enables solvent-free degreasing at 40 - 45 °C.
Final basification, chrome-retanning	Good exhaustion of the chrome, fullness and firmness of grain is achieved after preliminary basification by means of magnesium oxide and dicarboxylic acid to a pH of 4.2.
Deacidification	Improves fullness, firmness of grain and provides good buffing properties.
Ion-exchange resin	Binds especially calcium ions.

Tanning with fatty substances

Tanning with fatty substances is one of the oldest tanning methods. Real tanning requires the presence of reactive double bonds in the fatty substances. They are found in the oil of different marine animals and fish.

Chamois tannage

Is used to make wash leathers from sheep and lamb skins and garment leathers, especially leather for Tyrol trousers, from the skins of red deer, chamois, reindeer and elks.

The fish oil is beaten into the interior of well drained pelts by means of hammer stocks. Afterwards the pelts are stored in hot air chambers or in stacks to allow oxidation of the fish oil. Temperature control is very important. The temperature must not exceed 45 °C as otherwise damage to the fibre might be caused by burning. In large factories these two processes take place in a temperature-controlled hot air drum, followed by scouring of excessive fish oil, drying and finishing.

In new chamois tanning formaldehyde was used as a pretanning agent to accelerate tannage. Today it is mostly replaced by glutaraldehyde which gives more softness and also has the yellowish colour of chamois leather.

Tannage with sulphochlorides

The tanning effect by means of paraffin sulphochlorides is achieved by attachment to the amino groups of the collagen. They are also used to accelerate fish-oil tannage. They give pure white leathers having the properties of chamois leather. They are mainly combined with aluminium tanning agents.

Tannage with fatty alcohol sulphates

These have no self-tanning effect. However, in conjunction with mineral tanning agents they give very soft, elastic leathers. Disadvantage: Bleaching of dye shade and increased wettability.

Requirements on pretannage

1. Reduced tanning time.
2. Increased shrinking temperature.
3. Removal of water from the fibre texture.
4. Improvement of the penetration power and uniform binding of the subsequent tanning agents of the main tanning process.
5. Avoidance of case hardening.
6. Adjustment of the pH value required for final tanning.
7. Prevention of loose grain, wrinkled grain or formation of a coarse grain.
8. No change of the desired leather character as regards handle, softness or physical properties.

Possible types of pretannage

1. *Chrome tannage* (often carried out in the pickling bath)

Pretannage with:	Improvement:
Glutaraldehyde:	Cr absorption, fastness to perspiration
Polymer tanning agents:	Filling, fine grain, lightfastness
Syntans:	Bleaching, filling
Alumin. tanning agents:	Bleaching, firm grain
Resin tanning agents	Filling, firm grain, buffing properties
Alumin. sodium silicates:	Filling, firm grain, exhaustion

2. *Vegetable/synthetic tannage*

Pretannage with:	Improvement:
Syntans with small-sized particles:	Penetration of tannin , grain elasticity
Chrome syntans:	Penetration of tannin, flexibility
Cr tanning agents:	Penetr. of tannin, resistance to heat
Alumin. tanning agents:	Bleaching, absorption of tannin
Glutaraldehyde:	Flexibility, fastness to perspiration
Polymer tanning agents:	Penetr. of tannin, filling, lightfastness
Polyphosphates:	Bleaching, abrasion
Resin tanning agents:	Filling, firm grain

3. *Aluminium tannage*

Pretannage with:	Improvement:
Glutaraldehyde:	Softness, fastness to perspiration
Polymer tanning agents:	Shrinking temperature, handle

Definition of retanning

Retanning is a subsequent treatment with the most different tanning agents following the main tanning process in order to give the leather special, optimum properties for use.

Due to the great variety of retanning agents available on the world market any desired character of the leather can be achieved for practically all sorts of leather by the process of retanning ²⁶. In special corrective formulations retanning agents enable industrial production and increase the utility value of leathers, e.g. by selective filling of poor-quality rawstock, equalization of lots tanned in different quality, incorporation of special effects for mechanical processing, increase of yield, enhanced firmness of grain, modification of the handle properties and flexibility of the leather or improvement of the hygienic properties of garment leathers.

The most important retanning methods**1. Chrome-tanned leathers**

Retanning with:	Improvement:
Vegetable and syntans:	Filling, firmness, non-elasticity, handle
White-tanning agents:	Tan colour, fineness of grain, handle
Chrome tanning agents:	Dyeing propert., grain, resistance to heat
Polymer tanning agents:	Softness, handle, filling, chrome fixation
Aluminium/zirconium:	Fibre texture, fineness of grain, brilliance
Resin tanning agents:	Selective filling, firmness of grain
Glutaraldehyde:	Fine grain, resistance to perspiration

2. Vegetably/synthetically tanned leathers

Retanning with:	Improvement:
Vegetable and syntans:	Yield, tan colour, levelness of colour
Chrome tanning agents:	Temperat. resistance, dyeing properties
Bleach. tanning agents:	Tan colour, fixation
Resin tanning agents:	Filling, alkali and heat resistance
Aluminium/zirconium:	Buffing, dyeing properties, tan colour

3. Aluminium-tanned leathers

Retanning with:	Improvement:
Glutaraldehyde:	Resistance to perspiration, softness
Polymer tanning agents:	Softness, handle, filling

Definition of combination tanning

These are tanning methods carried out by the use of two or several chemically different tanning agents in the same tanning process or in tanning processes which follow each other immediately. Generally, the prevailing tanning process determines the character of the leather.

Possible types of combination tanning

Aluminium/ fat tannage	Referred to as "Glacé tanning". Is performed on lamb and kid skins by means of alum and egg yolk. The washable "nappa" leathers are obtained by subsequent treatment with vegetable tanning agents.
Aluminium/ vegetable tannage	Called "Dongola tanning". Alum tanned veal, goat and sheep leathers are thoroughly tanned with gambier extract. For the production of bottom leather the absorption of vegetable tanning agents is accelerated by aluminium.
Aluminium/ polymer tannage	This chrome-free combination tannage is gradually gaining importance (wet white production).
Aldehyde/ fish oil tannage	Referred to as "new chamois tanning". The aldehyde treatment accelerates penetration of the fish oil due to increased removal of water and improves resistance to alkalies.
Fish oil/paraffin sulphochloride tannage	Paraffin sulphochloride accelerates fish oil oxidation. Furthermore, the quantity of fish oil used can be reduced.
Chrome/ aluminium tannage	The combined use of chrome and aluminium tanning agents promotes chrome absorption, which improves the exhaustion of the chrome bath.

Storage of tanned leathers

Damp storage

Upon completion of the tanning process the leather is intermediately stored on trestles or pallets for at least 24 hours. This is necessary in particular for leathers tanned by means of inorganic mineral salts in order to achieve further binding and fixation of the tanning agents to the skin fibres. The shrinking temperature is increased and insufficient resistance to boiling can be further improved by this intermediate storage. Unbound tanning agents are removed from the skin by draining.

Vegetably tanned leathers are washed or preferably soaked upon completion of the tanning process in order to remove the considerable excess of unbound tanning agents, mainly from the grain layer.

Possible defects

Folds	With storage on trestles or pallets the leathers should be piled smoothly and without folds to avoid pressure marks which are fixed by tanning and difficult to remove.
Drying	During prolonged storage a drying of the edges should be avoided, particularly in warm climatic zones. Such dry sections of the leather are very difficult to resoak.
Mould	Formation of mould during prolonged storage at warm temperatures should be avoided. The mould causes stains on the leather which are difficult to remove.
Efflorescence of salt	Salt crystallization may occur when working with large quantities of neutral salt in the pickle and in the tan liquor. In this case a washing bath should be carried out after tanning.
Heat zones	Extreme stacking heights on pallets should be avoided during prolonged storage because this promotes the development of heat zones in the centre of the stacks which result in staining due to the change of basicity.

Mechanical processes after tannage**Processing of area measured leathers**

Samming The content of water existing in the leather as a result of tanning, even after intermediate storing, is too high for a subsequent treatment of thickness by shaving, chrome splitting or setting out and should be reduced. This is done by treating the leathers on samming machines.

Formerly hydraulic samming presses were used. These had the disadvantage of producing inverted pleats and an uneven draining effect. The modern rotating samming machines consist of a striking out roller for prevention of inverted pleats and two feed rollers, each having a loosely fitted milled felt sleeve. As a result of increasing rationalization efforts, through-feed samming machines have been in use for some years.

Setting out Is mostly performed at the end of wet processing before drying. The set-up is similar to that of the samming machine, however hard rubber rollers of different Shore hardness instead of felt rollers and a striking out roller of special design are used. This ensures good setting out.

Shaving Serves to determine the final thickness of the leather. Formerly this was done manually by means of a shaving knife, today it is performed mechanically on a shaving machine. The leather is fed to a sharp-edged blade-cylinder by means of a pressure roller and shaved to the set thickness. In contrast to splitting, the firmness of the leather is not substantially reduced. The machines have web widths of 300 - 800 mm. The modern broad shaving machines can accommodate widths of up to 3200 mm such that whole hides can be shaved over their entire width in a single operation.

Splitting Band knife splitting machines are used for splitting thick hides over their entire surface into upper split (grain split) and lower split (flesh split). Thereby the

firmness of the leather is reduced, however area is gained by the second split. Compared to the splitting of limed pelts, the splitting of chrome-tanned leathers shows the following advantages and disadvantages:

Advantages:

Saving of manpower
Exact thickness of split
Faster through-feed
Continuous work process without change of drum.

Disadvantages:

More strongly wrinkled grain
Stronger neck folds
Slight loss of area
Higher consumption of material since the lower split is tanned as well.

Processing of vegetably tanned, heavy leathers

Setting out Is used to obtain a smooth surface of leather and gain area. Formerly done manually by means of the setting slicker or electric hand setting machines. Today carried out by means of table or drum setting out machines which achieve a higher pressure and higher output. A striking out roller with V-shaped blunt blades of bronze or brass leading outwards in spiral form is driven along the leather surface under pressure. The leathers are fixed by means of a clamping device.

Blanching This refers to the smoothening, cleaning and removal of flat cuts on the back (flesh side) of vegetably tanned leathers in order to obtain a very smooth surface. A treatment of the grain side is called buffing and serves to eliminate grain defects.

Formerly done manually by means of a doling knife, today mostly by means of a buffing machine. Its design is similar to that of a shaving machine with the difference that the blade head has spiral-type blades arranged very close to each other. This serves to achieve a fine cut and a very smooth surface. Excessive rotating speeds should be avoided as they might cause burns on the leather.

Detannage

The aim and purpose of detanning is to eliminate interfering constituents and thus create uniform initial conditions. This is important for subsequent processing stages, especially dyeing, fatliquoring and retanning of vegetably/synthetically tanned leathers. It is mainly carried out on so-called East Indian skins or kips = vegetably tanned dried skins of small animals or zebu hides, and also on vegetably tanned sheep and lamb skins from Mazamet-Graulhet/France. Recently it has also been applied to chromosa leathers = dried, chrome-tanned skins of small animals topped with light-coloured syntans. The cow-hide crust leather produced in many countries also requires preliminary treatment in most cases.

Measures and elimination of disturbing factors

1. Unbound, bleaching tannin particles.
2. Filling and loading agents.
3. Deposited fatty substances (of grain oils or still existing natural fats).
4. Adjustment of a uniform pH value.
5. Correction of an excessively varying thickness of leather by shaving, dry shaving or dry splitting.

Detannaging procedure

- Wet back:** Is done at 35 - 40 °C by adding a wetting agent for quicker wetting back of the leathers.
- Degreasing:** In the case of large amounts of disturbing fat special degreasing agents are added or short-float degreasing is carried out in a separate bath.
- Detanning:** Adding proportions of alkaline agents such as sodium bicarbonate, soda, sodium hydrogen-sulphite, sodium sulphite, less often borax, applied alone or combined. It is important that a constant pH value be maintained during detanning. Often followed by subsequent bleaching in order to remove iron stains or disturbing pigment stains.

Deacidification (neutralization)

After tannage chrome leathers (also other mineral salt tanned leathers) separate acid as a result of oxidation during intermediate storage before further processing. It is absolutely necessary to remove this free acid as it disturbs the subsequent processes. Colour stains and overloading of grain are caused by dyes and tanning agents existing on the surface, and smudging and fat stains result from precipitation of the fat emulsions. Further consequences are defects in the leather or also in the end products.

The softer the leather and the more even the expected results of dyeing, the more thorough and complete must the deacidification process be.

If the first step consists of a cationic retanning process, deacidification is not necessary. In this case it has to be carried out before dyeing, retanning and fatliquoring.

Controls of deacidification

Operational: Cut off a small piece of leather, if possible from a section of dense texture. Then let an 0.1 % indicator solution of bromocresol green (dissolved in 50 % alcohol) drip onto the cross-section. The change of colour indicates the progressive depth of penetration of the neutralizing agent and the pH value on the leather.

Transition interval of bromocresol green:

yellow	= pH 3.4 and below
yellow-green	= pH 4.0
green	= pH 4.5
blue-green	= pH 5.0
blue	= pH 5.4 and above

The following indicators can be used for ranges below and above the mentioned values:

Bromophenol blue	= pH 3.0 - 4.6 (yellow-blue)
Bromocresol purple	= pH 5.2 - 6.8 (yellow-purple-red)
Bromothymol blue	= pH 6.0 - 7.6 (yellow-blue)

The most important neutralizing agents

Strong products

Sodium carbonate (soda),
borax: Products of this category are seldom used, possibly in combination with mild products. Used in small quantities their neutralizing action is only superficial. Larger amounts result in good penetration, however with overneutralization of the grain zone and a simultaneous detanning effect.

Mild products

Sodium hydrogen carbonate: One of the most frequently used products. It is important that a float and dissolving temperature of $< 38\text{ }^{\circ}\text{C}$ be observed in order to avoid soda formation. Overneutralization is possible if large amounts are used.

Ammonium bicarbonate: Rapidly penetrating product. Very suitable for leathers of dense texture (pig leather, reptiles).

Sodium formate: Mild neutralizing effect with low pH value. Overneutralization is not possible. Mostly used in conjunction with sodium hydrogen carbonate.

Calcium formate: Mild neutralizing effect with no risk of overneutralization. Formation of calcium sulphate can cause trouble and may produce stains.

Sodium acetate: Mild neutralizing effect with low pH value and bleaching of the chrome tanning colour towards blue. Overneutralization is not possible.
Very suitable for pale leathers and aluminium-tanned leathers.

Sodium sulphite: Mild neutralizing effect with uniform penetrative power, without overneutralization. Due to formation of sulphite complexes the chrome tanning colour is intensified towards green.

Sodium thiosulphate: Large amounts are required. Bleaching of the tanning colour is obtained by deposition of colloidal sulphur. Is therefore used for white and pale leathers.

Sodium aluminium silicate:	Besides a mild neutralizing action this has the added effect of aluminium silicate retanning, which improves fullness and firmness of grain.
Polyphosphates:	Mild, penetrative neutralizing agent without risk of overneutralization. Often used in combination with sodium bicarbonate.
Ammonia/ ammonium salt buffer mixtures:	This combination results in a uniform, mild neutralizing effect. However, ammonia should not be used in excessive amounts in order to prevent overneutralization of the grain zone.
Safety neutralizing agents	Special mixtures produced by the chemical industry for the purpose of obtaining an even, penetrative neutralization without risk of overneutralization.

Neutralizing products with tanning effect

Neutralizing tanning agents:	Products on the basis of mild, non-astringent tanning agents and highly buffering salts. They permit deacidification without overneutralization and with a slight lightfast retanning effect. If higher final pH values are required a combination with sodium hydrogen carbonate is used.
Dispersing tanning agents:	These are neutralized alkali salts with small particles of aromatic tanning sulpho acids, mostly in combination with sodium hydrogen carbonate. Besides their neutralizing and retanning action they have a bleaching effect without overloading the grain.
Acid auxiliary tanning agents:	Neutralization is not possible by means of these products. The strong sulphuric acid is replaced by weak organic acids. Mostly used in conjunction with sodium formate. Particularly good for leathers with a sensitive grain because a tight grain is obtained. Serves as a base for compact retanning of corrected grain side leather.

Parameters of deacidification

- Float length:** With float coefficients of 0.5 - 2 depending on type of leather, thickness and type of vessel. A washing or rinsing bath should take place after deacidification in order to remove the salts that have formed.
- Temperature:** Carried out in a range of 30 - 40 °C. < 38 °C if sodium hydrogen carbonate is used.
- Intensity:** Depends on the type of leather to be produced. Neutralization of the entire cross section is required for soft leathers, mostly in the upper pH range of 5.0 - 6.0. For firm upper leathers the pH range is between 4.2 - 5.0. The outer zones are neutralized in the higher pH range, the inner zones are only slightly neutralized. Leathers which tend to develop a loose grain should always be treated in the lower pH range.
- Duration:** About 30 minutes to 2 hours depending on the thickness of leather and texture, type of neutralizing agent and type of leather to be produced.

Possible defects

- Inadequate deacidification:** If the middle zone of the cross-section remains unneutralized problems may arise in subsequent processing.
1. Astringent retanning agents diffuse only with difficulty into this zone.
 2. Fat emulsions crack in this zone and cause smudging and fat stains.
 3. In the leather the free acid migrates into the outer zone, causing corrosion at metal parts of final products. Fatty spew may also occur to a greater extent.
- Overneutralization:** Results in detanning of the grain zone and thus in loose grain, strawy, brittle grain or in unfavourable cases even crackiness of the grain. Furthermore, may lead to uneven, pale and thin dyeings.

Fatliquoring

After the beamhouse works and tanning, fatliquoring is the next important process in leather production. Except for some types of sole leather all other sorts of leather are fatliquored to a greater or lesser degree. Fatliquoring has the following purposes:

1. Deposit of fatty substances in the interfibrillar spaces in order to give the leather the desired softness and handle properties.
2. Correction and control of the physical properties like tensile and split tear strength, extensibility, wetting properties or water-repelling capacity, water-proofness, permeability to air and water vapour, water absorption and moisture storage capacity, thermal and electrical thermal conductivity.

Fatliquoring methods for leather

1. *Methods without float*

Oiling off

Mainly for vegetably tanned heavy leathers, on the grain side of sammed or set out leathers with neutral oils such as clear fish oil, also mixed with mineral oils, and special bleaching oils. Is performed by means of oiling machines or manually.

The purpose of oiling off is to prevent unbound tanning agents from diffusing out towards the grain surface. This keeps the grain elastic and avoids saddening of the tanning colour, staining and crackiness of the grain.

Cold stuffing:

Now seldom used. Is performed manually, by table-greasing the set out, moist leather from the flesh side with fatty mixtures such as fish oils, tallow, degreas, lanolin and mineral oil. In this process the loosely structured sections of the skin are treated less and the densely structured zones more intensely. A homogeneous composition of the stuffing is important in order to avoid spew.

**Hot air
fatliquoring:**

This method is more efficient than table-stuffing, and is also mostly used for vegetably tanned leathers. The sammed leathers which have been brought to an even content of moisture by stacking are placed in a hot air drum and dressed with consistent fatty mixtures, similar to cold stuffing, under a stream of hot air. The viscosity of the fatty mixture is reduced by the hot air, evaporation of the water is accelerated and quicker penetration is possible. Temperatures exceeding 50 °C should be avoided as otherwise damage by burning might occur. Exact controls are necessary.

Hot stuffing:

Now rarely used for special leathers such as chrome-tanned sole leathers and technical leathers. The dried leathers to be treated are soaked in melted solid fatty substances such as paraffin, stearin, tallow, waxes or resins in heatable hot stuffing boilers until the air in the leather has been displaced by the fatty substances. This procedure can be considered equivalent to impregnation.

2. *Fatliquoring in the float***Fatliquoring:**

The most common method in leather production. It is a treatment with fatty substances emulsifiable in water which are introduced into the interfibrillar spaces in an aqueous float. A distinction is made between main fatliquoring, preliminary, intermediate and top fatliquoring. All of these fatliquoring processes can be applied to one kind of leather at the same time, depending on the type of leather and type and amount of fatliquoring agents used. Furthermore, fatliquoring can be done in a warm or cold float, by dry fatliquoring and also oiling by brush.

Principal basic fatliquoring substances

Marine animal oils:

Train oil, fish and liver oils

The degree of purity of the oils should be observed. Filtered or refined products are suitable. Heavy impurities cause odour problems. Products of high iodine value (except for chamois tannage) have a tendency to effect intensive yellowing of the leather and quick oxidation.

Land animal oils:

Neatsfoot oil, lard oil, olein

When using neatsfoot oil, cold-resistant products should be chosen. Lard oil should not have solid constituents either as otherwise there is a risk of fatty spew.

Animal fats:

Beef tallow, lard, bone fat

All products have an increased content of stearic fatty acid and thus a very strong tendency to form fatty spew. The use of raw materials which have been stored for some time should be avoided because of the rancid smell.

Vegetable fats:

Coconut fat, palm kernel fat

Only refined products should be used as this category of products is prone to rancidity which may cause disagreeable smells.

Vegetable oils:

Palm oil, rape oil, soya bean oil, sunflower oil, cotton seed oil

Only semi-drying and non-drying oils are suitable for fatliquoring of leathers. Some products have a tendency to oxidation and thus to develop strong, disagreeable smells.

Waxes:

Carnauba wax, montan wax, lanolin

Wool grease (lanolin) should be used in purified form because products of inferior quality have a disagreeable smell. Products based on wool grease reduce the wetting properties of the leather.

Synthetic fats:

Paraffin oils, olefines, mineral oils, fatty acid esters, fatty alcohols, alkyl benzenes, processed hydrocarbons

Paraffin oils only have an adequate fatliquoring effect from a medium chain length of C₂₀.

Mineral oils should be light-coloured, odourless, and the viscosity should not be too low. Furthermore they should have only a low content of aromatic hydrocarbons as otherwise increased yellowing may occur.

Fatliquoring products used

Sulphited oils, fats or fatty alcohols	Anionic products with a high stability to electrolytes. Good penetrative fatliquoring is possible. If larger quantities are used there is a tendency to loose grain.
Sulphated oils, fats or fatty alcohols	Anionic products with a stronger surface fatliquoring effect. Low stability to electrolytes and resistance to storage.
Sulpho chlorinated paraffin oils or fats and oils	Anionic products with a very low tendency to yellowing on heat. Their fatliquoring effect is dryer than that of sulphited natural oil fatliquors.
Hydroxyethylated esters	Anionic and soft; good penetration. Low loading of the grain and low wettability.
Emulsified oils (anionic, cationic, non-ionic, amphoteric).	Mostly used for preliminary and top fatliquoring. Different effects are obtained, depending on the charge. They mostly have a low tendency to bond with the fibre.
Unsaturated oxidized or chlorinated oils	Water-insoluble products which are added to the fatliquor for special effects.
Combination formulas of the above products	Extremely diverse fatliquoring preparations produced by the chemical industry, having particular properties.

Testing the fatliquoring agents

Operational	Visual inspection for separation of layers, creaming or oiling of the fatliquor in the container. For safety reasons thorough mixing by stirring is recommended before each use.
Analytical	1. Random sampling to check the content of volatile substances and mineral substances and thus to verify the pure fat content. 2. If trouble occurs during fatliquoring, the following more detailed analyses are recommended: - Stability to electrolytes, determination of free fatty acids, degree of sulphonation, emulsified and emulsifying components, yellowing on heat or lightfastness.

Parameters of fatliquoring

Time of application

Main fatliquoring: For chrome-tanned leathers usually following deacidification, often together with dyeing and retanning. In the case of sulphated fatliquors it is done in a separate bath.

Preliminary fatliquoring: Already performed during pickling or chrome tanning. It provides greater softness and improved breaking strength compared to main fatliquoring on its own.

Top fatliquoring: Mostly following acidified dyeing, fatliquoring and retanning in a separate bath. It provides special superficial fatliquoring effects and two-way nap and seasoning effects on suède and nubuk leathers.

Float length

Floats of 50 - 200 % are used, depending on the thickness and type of leather. To reduce loading of the waste water short float methods are increasingly preferred. However, in the case of dry fatliquoring, almost without float, attention should be paid to the prevention of pebbled grain, chafe marks and excessive content of salt in the leather. Processing in short floats is nevertheless preferable as it saves time by ensuring better exhaustion of the bath and improved fat absorption.

Temperature

Fatliquoring temperatures of up to 60 °C for chrome-tanned leathers and up to 45 °C for vegetably tanned leathers. For economical reasons (saving of energy) lower temperatures are often preferred. Even cold fatliquoring is used. In this case the fatliquoring agents must be emulsifiable and stable in order to prevent smudging.

pH value

If anionic fatliquors are used on chrome-tanned leather higher pH values > 4.5 improve penetration of the fatliquor, however exhaustion of the bath is reduced.. Lower pH values < 4.0 improve surface fatliquoring and exhaustion of the bath. This applies only to slightly unstable fatliquoring agents. The opposite fatliquoring effect occurs in the case of anionic vegetably tanned leathers.

Electrolyte content	A high content of electrolytes, in particular common salt and sodium sulphate, but also a high content of retanning agents or dyestuffs which are heavily diluted with salts disturb the fatliquoring process if unstable fatliquors are used. This applies especially to sulphated fatliquors. These products should be used in a separate fatliquoring bath.
Emulsifiers	The fatliquoring effect and process are considerably influenced not only by the fatliquoring agents and how they were produced, but also by the structure and different charges of the emulsifiers they contain. In view of the great number of surface-active agents available today, the unstable soaps formerly used as emulsifiers are now only employed for special fatliquoring processes.
Duration	Depends on the type of leather, thickness of the leather and the desired fatliquoring effect as well as on the degree of exhaustion. It generally takes about 30 - 60 minutes.
Binding	This is important for the washing properties and dry cleaning of leather. It is even more important for preventing fat migration in subsequent processes, i.e. drying, finishing and storage (fatty stains and fatty spew).
Distribution	The distribution surface is basically determined by the loosely and densely structured sections of the hide. Vertical distribution depends on the degree of neutralization, the charge conditions in the leather, type of fatliquoring agent and on how the fatliquoring process is conducted.

Controls of fatliquoring

Operational:	Visual inspection to determine exhaustion of the fatliquor and smudging and precipitations caused by the fatliquors used.
Analytical:	In the case of relevant waste water problems an analysis of the residual fat content of the fatliquor is recommended.

Errors in application

Precipitation of the fat emulsion

Effect: Strong smudging of the leathers and inside walls of vessels, inadequate fatliquoring effect and formation of fatty stains.

Causes: High content of electrolytes in the float, use of unstable fatliquors, high content of neutral oil in the fatliquor, excessive cationic charge of the leathers or pH value of the float too low.

Remedy: Extension of the liquor by means of water at about 60 - 70 °C and addition of ammonium and nonionic wetting agents. If unsuccessful, discard the float and repeat the operation in a new bath with subsequent corrective fatliquoring.

Premature breaking of the fatliquor

Breaking at the inner zone is often desired for firm leathers, however not for soft leathers.

Effects: Slightly greasy handle of the leather surface and a hard, tinny condition of the dried leather.

Causes: Inadequate penetration of neutralizing agent or incomplete penetration of tanning agent as well as lime components still existing in the inner zone. Fatliquors which are near the stability limit may break in the inner zone and prevent penetration of the fatliquor.

Remedy: Avoid the causes. Furthermore, use highly hydroxyethylated wetting agents or penetrative fatliquoring auxiliaries and increase the pH value of the float.

Reduced absorption and exhaustion

Apparent from the mostly turbid, milky state of the residual fatliquor.

Remedy: In the case of anionic fatliquoring by: reducing the float, lowering the pH in the float, addition of unsulphated oils or fats, proportionate use of cationic fatliquoring agents, reducing the amount of anionic vegetable and synthetic retanning agents and avoidance of highly stable fatliquoring agents having a high content of emulsifiers.

Excessive surface fatliquoring

Effect: Grain surface too fatty and in extreme cases uneven distribution of the fatliquor and formation of fatty stains.

Cause: Using an excessive amount of superficially acting fatliquors or neutral oils, excessive cationic charge of the grain surface, pH of the leather and of the liquor too low or use of auxiliaries and tanning agents which react with the fat.

Remedy: Avoid the causes.

Formation of soap

Effect: Poorly soluble, greasy to tough stains of different size and uneven distribution on the outside of the leather.

Cause: Unstable fats, neutral oils or content of natural fats which react with free metal salts such as chromium, aluminium, zirconium or lime components.

Remedy: Avoid the causes.

Possible defects in the leather**Resin spew**

Effect: Sticky resin-type exudations on the grain side, mostly of vegetably tanned leathers, in the shape of round flat drops.

Cause: Use of excessive amounts of highly oxidative train oils. Is intensified during storage due to the action of ultraviolet radiation, moisture, heat, high contents of mineral substances or substances that can be removed by washing, and also as a result of high pH values.

Remedy: Use mineral or chlorinated paraffin oils. Existing exudations can be wiped off with a cloth soaked in fat-dissolving agents or mineral oil.

Formation of factice

Effect: Rubber-like stinky exudations or deposits.

Cause: Is the reaction product of unsaturated fatty substances with free sulphur deposits (sulphur tannage, thiosulphate deacidification). Sometimes improves the firmness of the leather.

Fatty spew

Effect: White to white-grey foggy coating all over the leather surface or irregular patches. Occurs mainly in leathers tanned with mineral tanning agents, less in vegetably tanned leathers. The spew is of fine, crystalline consistency and is largely made up of free fatty acids of palmitic acid and stearic acid. Fatty spew as opposed to efflorescence of salt is identified by touching it with a naked flame which makes the fatty spew melt and disappear.

Cause: High content of natural fat in the leather due to inadequate degreasing or introduction of fatty substances having large amounts of free saturated and unsaturated fatty acids. Fatty spew is promoted by storage under alternating temperature conditions (cold/warm), high humidity and by microbial action.

Remedy: Avoid the causes. An existing spew can be wiped off with a cloth soaked in mineral oil or chlorinated paraffin oils. However, this cannot be prevented for certain.

Fatty stains

Effect: Dark, oily, fatty stains which may occur in all sections of the leather. In cattle hides they occur mainly in the region of the kidneys, in sheep skins mainly near the neck, back and butt edge. Pig skins and goat skins may also exhibit fatty stains.

Cause: Inadequate distribution and saponification of the natural fat in beamhouse processing, inadequate degreasing and/or use of unstable fatliquoring agents or large quantities of untreated neutral oils.

Remedy: Avoid the causes. If stains exist on the leather, additional degreasing in the aqueous phase or by means of organic fat-dissolving agents is required.

Fat oxidation and polymerization

Effect: Resin spew, formation of fatty specks, increased smell, rancidity.

Cause: Changes caused by oxidation or polymerization may occur due to the large, distributed surface of the fatty substances in the leather. This applies especially to fatty substances having a high content of unsaturated compounds. Besides train oil and fish oil, vegetable oils such as soybean lecithin, coffee oil, rice oil and nut oils are also sensitive products.

Remedy: Avoid using such fatty substances, especially for garment and upholstery leathers as they tend to produce a penetrating smell which is difficult or impossible to remove.

Fat wrinkles

Cause: High content of natural fat near the back, mainly occurring in fine-wooled sheep skins.

Remedy: Intensive degreasing (qv).

Fat soaps

Effect: Whitish uneven stains on the leather surface.

Cause: High content of natural fat or unstable fatliquoring agents which react with metallic tanning salts to form soap.

Remedy: Avoid the causes.

Fat splitting

Effect: Whitish, crystalline fatty spew due to the formation of free fatty acids. Furthermore, corrosion occurring on metal parts of the final leather products.

Cause: Hydrolytic splitting of natural fats or fatliquoring agents having a high content of free saturated or unsaturated fatty acids, in particular palmitic or stearic acid.

Remedy: See fatty spew.

Fat spots

Effect: Hardened, pinhead-like, dark raised spots on the grain surface.

Cause: Oxidative change of fatty substances, particularly train oils, similar to resin spew.

Remedy: See resin spew.

Fat migration	<i>Effect:</i> Dark fatty stains on the leather surface, mainly at the edges or in loose sections. <i>Cause:</i> Inadequate binding or fixation of the fatliquoring agents used, or use of excessive quantities of untreated neutral oils. <i>Remedy:</i> Avoid the causes.
Free fatty acids	<i>Effect:</i> Formation of fatty spew and metallic soaps, corrosion on metal parts of the final leather products. <i>Cause:</i> Are caused by hydrolytic splitting or fermentative action of fatty acid esters of the natural fats and fatliquoring agents. <i>Remedy:</i> See fatty spew.
Smell, rancidity	<i>Effect:</i> Intensive, penetrating off-odour can develop during prolonged storage of leather. <i>Cause:</i> Oxidation, hydrolytic splitting or chemical decomposition of the triglycerides contained in the leather. Is promoted by the action of atmospheric oxygen on the extremely large distributed surface of the fatty substances. <i>Remedy:</i> Avoid using train oil or fish oils having a high iodine value and high degree of impurity as well as oils and fats with a high content of unsaturated compounds, mainly of vegetable origin.
Lightfastness	Is determined by many factors such as tanning agents, dyestuffs, auxiliary agents, but also fatliquoring agents. Many fatliquoring agents have a more or less pronounced inherent colour which often intensifies or shifts the colour of the leather. However, upon exposure to ultraviolet light a bleaching effect instead of a yellowing effect is always caused by fatliquoring agents. If yellowed leather is bleached by exposure to ultraviolet light, this can be due to fatliquoring agents or dyestuff which is not resistant to light. Phenolic tanning agents become intensely yellow or dark on exposure to light.

Hardening of the leather

Effect: After storage the original condition of dried leathers has often changed from soft to hard and tinny.

Cause: Mainly due to the use of fatliquoring agents having a higher content of drying oils or fats. These are mostly products on a vegetable base.

Remedy: Change the fatliquoring agents in the fatliquor.

Over-fatliquoring

Effect: Loose, flabby condition of the leather and formation of large flank sections with excessively greasy handle of the grain surface. Poor glazing properties of finishes. There is a risk of fat migration and inadequate adherence of the pigment finish.

Cause: Use of excessive quantities of fat, in particular of solid fatty substances in the fatliquor of vegetably tanned leathers.

Remedy: Avoid the causes. Otherwise additional degreasing or an ammoniacal washing bath with addition of wetting agents should be carried out in order to emulsify the excessive fatty substances.

Yellowing due to heat

Effect: Yellowing of the entire surface of the leather can be caused by heat during storage. This is particularly disturbing on pastel-coloured and white leathers.

Cause: Mostly caused by fatliquoring agents having a high content of unsaturated compounds, mainly in marine animal oils and vegetable oils and fats. Phenolic tanning agents may also cause yellowing.

Remedy: Avoid using such fatliquoring agents or tanning agents, in particular in the production of light-coloured leathers.

The tendency to yellowing of fatliquoring agents can be tested by soaking a filter paper in a 10 % emulsion of the fatliquoring agent to be tested, allowing it to air-dry and storing it for 24^h in a heating cabinet at 100 °C.

Adhesive capacity, vulcanizing properties of greased leathers

Consequence, cause: A high content of fat and excessive stuffing of the grain surface or an uneven distribution of the fat can reduce the glueing and vulcanizing properties of the leather. Problems arise if the content of fat exceeds 12 - 15 %. Best results are achieved with mixed adhesives. Furthermore, the quality of adhesion or vulcanization can be improved by roughening the leather surface. However, solvent-based adhesive systems may further reduce the effect due to fat migration to the surface.

High water absorption of greased leathers

Effect: Excessive wettability of the leathers and formation of water stains or water marks on the final leather products during use.

Cause: Use of highly sulphated or sulpho-chlorinated fatliquoring agents. Excessive content of emulsifying wetting substances in the fatliquoring products ²⁷ or caused by preceding beamhouse operations.

Remedy: Avoid the causes. Addition of neutral oils in order to reduce the wettability of the leathers. Cationic top fatliquoring, fatliquors based on wool grease or also a partial water-repellent treatment will reduce the wettability.

Water-repellent treatment

For many types of leather which come into frequent contact with water during use there is a growing demand for a reduction or, if possible, prevention of absorption and penetration of water. This is achieved by the deposition of substances in the interfibrillar spaces of the leather. These increase the interfacial tension between the leather fibres and water and thus have a water-repellent effect. Some substances have an oil and dirt-repellent, or "oleophobic" effect at the same time.

Methods of water-repellent treatment

1. *Fill impregnation*

Dipping treatment, used only in special cases, with melted filler mixtures such as solid fatty substances, paraffins, waxes, stearins, synthetic or natural resins, polymers, polyisobutylenes, rubber derivatives.

The air is completely displaced from the interfibrillar spaces by the fillers to make the leather completely impermeable to air. Is therefore used only for firm, loosely structured sole leathers to improve abrasion and water-tightness and for gas-meter leather, diaphragm leather, packing or hose leather.

2. *Surface water-repellent treatment*

Is applied by spraying, pouring, brushing or plush-wheeling on the dried leather, on the final piece of leather or on leather products such as shoes or garments. In a strict sense this treatment is already part of the finishing process.

The products used are silicones, alkyl succinic acid derivatives, metallic soaps, fluororganic compounds²⁸, chromium stearato complexes, alkyl phosphoric esters.

For fancy leathers a waterproof surface layer is obtained by application of a hard nitrocellulose finishing. However, an additional thorough water-repellent treatment of the fibres should be carried out on highly absorbing vegetable leathers.

3. *Water-repellent treatment in the solvent phase*

For ecological, economical and health reasons this method is gradually being used less often.

It is applied with many products which are also used for surface impregnation.

The organic solvents used are alcohols, aromatic and aliphatic hydrocarbons, esters, ordinary ether and hydroaromatic hydrocarbon compounds. For health reasons chlorinated hydrocarbons are now only seldom used.

4. *Water-repellent treatment in the aqueous phase*

Today the most commonly used method for water-repellent treatment of leather. In many cases the water-repellent products also have a fatliquoring effect so that additional fatliquoring is not necessary. Systems which do not use emulsifiers and solvents are advantageous for an optimum economical and ecological water-repellent treatment.

The advantage of this treatment is that only small quantities of water-repellent substances are deposited in the interfibrillar spaces and the air and vapour permeability and thus breathability of the leathers is therefore preserved.

The products used are nitrogen-containing fatty acid condensation products in the form of free monocarboxylic or dicarboxylic acids. These are fixed by means of cationic metal salts such as chrome and aluminium tanning agents or calcium and magnesium chloride. Other products include special silicone oils or polysiloxanes and polymer products^{29 30} which have a fatliquoring effect such that fixation is not necessary in many cases.³¹

The water-soluble or emulsifiable products employed for surface water-repellent treatment are naturally also used in the aqueous float method.

Some water-repellents are also applied in combined form as a preliminary, intermediate or subsequent treatment in order to achieve maximum penetrometer or Maeser values³².

In future such methods will gain greater significance compared to fatliquoring, as the properties and service value of the leathers in terms of resistance to defects caused by water or dirt will increase.

Disturbing factors and possible mistakes in carrying out water-repellent treatment in the aqueous phase

Raw skin	Loosely structured, spongy skin material results in an inadequately dense deposition of water-repellent substances in the interfibrillar spaces. Increased water absorption or quicker water penetration may occur in some sections.
Water quality	When diluted some water-repellents are sensitive to an increased hardness of the water, especially if calcium and magnesium ions are present. In this case it is recommended that they be added undiluted or diluted with soft water.
Beamhouse process	Excessive opening up of the skin in the lime and in the bate should be avoided as skin structures that are too loose have an adverse effect on the water-repellent treatment. The use of surface-active agents should be limited to a minimum, but it is better not to use them at all.
Deacidification	Penetrative deacidification is absolutely necessary as otherwise the water-repellent substances are not deposited evenly all over the cross-section of the skin. A pH value of > 5 is favourable. The use of salts having divalent cations such as calcium formate should be avoided. Neutralization salts that are formed should be removed as far as possible by rinsing because a high salt content in the leather has a negative effect.
Fatliquoring agents	The water-repellent effect is reduced by fatliquoring agents having a high content of emulsifiers or by highly sulphated and highly sulphochlorinated fatliquors. Corrective fatliquoring as a separate preliminary treatment with the lowest possible quantity should be carried out before application of water-repellents.

**Mineral
tanning agents**

Leathers tanned by means of mineral tanning agents, in particular wet blue products of ill-defined composition, should not contain unbound tanning components. Such components prevent an even penetration due to premature reaction with the water-repellent. Therefore highly cationic products such as chromium salts, aluminium salts, zirconium salts, cationic resin salts, magnesium or calcium salts should not be applied immediately before or during a treatment with water-repellents.

**Anionic
retanning
agents and
auxiliary
substances**

Highly sulphited vegetable tanning agents, synthetic tanning agents and auxiliary substances with a high salt content or wetting character reduce the water-repellent effect.

Retanning and treatment with auxiliary substances should preferably be carried out in a separate bath before the water-repellent treatment.

Dyestuffs

If used in larger quantities basic dyestuffs and metal complex dyes may have a negative influence on water absorption and water penetration³³. The wetting properties of the leather are reduced with increasing number of sulpho groups in the dye molecule³⁴.

Owing to their low salt content, liquid dyes are particularly suitable for leathers that are to be made water-repellent.

**Water-
repellent
agents**

It is of utmost importance that the water-repellent be deposited evenly and completely over the entire cross-section of the skin. The thicker the skin material, the longer the treatment should be. In general, 1 - 3 hours are sufficient, however an overnight treatment is also possible. The use of short floats promotes penetration.

In most cases water-repellents should be added in diluted form.

Fixing substances	Should always be added after extensive exhaustion of the water-repellent. In order to avoid strong shifts of shade of the tanning colour, vegetably tanned leathers which have been made water-repellent should not be fixed by means of aluminium salts. Calcium salts or magnesium salts should be used instead.
Finishing	Since they are produced on an industrial scale some finishing agents, in particular polymer binding agents, have a higher content of water-repellent, wetting substances. These constituents may have a negative effect on the water-repellent result. In this case special finishing products from specialized manufacturers should be used.
Storage	Many leathers which have received a correct water-repellent finishing only achieve optimum water-repellent properties after several days or weeks of storage. Therefore, analyses of test values should not be made prematurely.

Controls of the water-repellent treatment

Exhaustion of the bath	In the case of water-repellents that are to be fixed, several millilitres of a 10 % aluminium chloride solution are added to a sample of the residual water-repellent liquor to be tested. A milky appearance or whitish precipitate of the sample indicates that the content of unabsorbed water-repellents is still too high. In such a case the time of reaction should be extended.
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Dyeing³⁵

Dyeing with soluble, organic dyes gives the substrate leather any desired or fashionable shade.

The following dyeing processes are possible, depending on the requirements:

1. Surface dyeing for levelling and correcting defects on the grain side.
2. Deep dyeing to reduce the conspicuousness of patches damaged by impacts or scratches during use.
3. Penetration dyeing of the entire cross-section of the leather in order to avoid bright edges on the goods.

Classification of the dyes (according to application)**1. Anionic dyes**

The most commonly used dyes for dyeing chrome leathers or vegetably-synthetically tanned leathers which have been submitted to a preliminary cationic treatment. The depth of penetration of the dyestuff can be controlled by means of the pH value of the leather and of the dyebath. When the desired depth of penetration has been reached, binding of the dye to the fibre is achieved by reducing the pH to < 4.0 , mostly by means of formic acid. The affinity of dyes in respect of absorption capacity or levelling can be widely influenced by appropriate dyeing auxiliaries.

a. Simple acid dyes

Mainly low-molecular dyes. Their advantage consists in their low price and good dyeing and penetrating capacity, and in most cases they give clear, brilliant shades. Their disadvantages are inadequate lightfastness, and insufficient fastness to wetting, perspiration and washing.

b. Substantive (direct) dyes

Used for chrome leathers, mostly as surface dyes with good coating properties and corrective power for defects. On intermediately dried suède leathers they also enable a good dyeing effect with complete penetration and intensive colouring of fibres. Due to benzidine or benzidine derivatives contained in the dye complex they have been removed from the manufacturers' range of products.

c. *Special leather dyes*

Dyes developed for leathers with particular fastness properties, which are easily combined and have good levelling properties.

Mainly available in powder form. However, a growing number of liquid dyes have been put on the market during the last few years. These evolve no dust, are easy to proportion and, above all, they have a very low salt content.

In general, they are divided into two groups:

- **1:1 Metal complex dyes**

In these dyes a dyestuff molecule is bound as ligand to a metallic central atom such as chromium, iron, copper or cobalt. They possess good lightfastness and washing properties and have good levelling capacity. However, rich deep shades are not obtained by means of these dyes. Their main field of application is dyeing of garment and glove leathers and of pastel shades. For perfect dyeing results the applied temperatures should not be too high and the $\text{pH} < 5$. Furthermore, combination with other classes of dye or complexing substances should be avoided because demetallization in the dye complex might occur, resulting in a shift of shade or loss of fastness.

- **1:2 Metal complex dyes**

In these dyes two dyestuff molecules are bound as ligands to a metallic central atom. The dyes of this group are also very fast to light, wetting and perspiration. They are also good for dyeing vegetably-synthetically retanned chrome leathers. However, their levelling and penetration capacity is considerably reduced. This group is further divided into dyes which are free of sulpho groups and dyes which contain sulpho groups. If the solubilizing group is not present in the molecule, these products are only soluble in organic solvents and particularly suitable for spray-dyeing. However, they then have the disadvantage of being less fast to migration on flexible PVC or crêpe material. With increasing content of these groups the dyes become increasingly soluble in water. When dyeing is performed in a dyebath they are used as covering dyeing component in a separate bath, mostly after penetration dyeing with acid dyestuff.

2. Cationic (basic) dyes

Leather will only be dyed by means of these dyes if there is a sufficiently high content of negatively charged groups, i.e. vegetably-synthetically tanned or retanned leathers. They have the advantage of high covering power and provide brilliant shades. Their disadvantages are low lightfastness, inadequate dry and wet rub fastness, insufficient fastness to migration and accentuation of existing grain defects by more intense dyeing. Excessive amounts may result in undesired bronzing. Therefore, they are mostly used as separate intermediate dyes in the so-called sandwich method.

3. Oxidation dyes

Exclusively used for dyeing wool and hair of fur skins. These dyes are mainly aromatic oxiamines, oxidiamines and aminophenols which oxidize on the substrate or develop into dye.

4. Reactive dyes

Dyes with reactive groups such as vinyl sulphone, dichlorotriazine, trichloropyrimidine, dichloroquinoxaline, which link up with the reactive substrate by a direct primary valency bond. A high degree of fastness to washing, dry-cleaning, migration and light is achieved on wool, cotton and polyamide fibres. They have not yet gained importance for dyeing leather.

5. Dispersing dyes

Originally developed for dyeing artificial silk, nowadays they are also used for dyeing synthetic fibres. In leather dyeing they are sometimes used to dye wool of fur skins in light and medium shades.

6. Sulphur dyes

Are used to dye chamois leather. They have to be dissolved by means of alkali sulphides. They give high fastness, but flat shades. Some dyes now available have already been solubilized for special applications. These are used as low-price penetration dyes for chrome leather.

7. *Natural (mordant) dyes*

These vegetable wood dye extracts have gradually lost importance and are used only in special cases. Together with metal salts such as potassium alum, cuprous sulphate, ferric sulphate, titanium salts or ferrous lactates they produce different, coloured complex compounds in the form of colour lakes. They dye grain side and flesh side evenly without accentuating the defects of the leather.

8. *Fat and oil-soluble dyes*

Free dye bases such as nigrosine bases or also some azo dyes which do not contain water-solubilizing groups dye neutral fats, oils and waxes. They are used for colouring shoe polishes, wax finishes, special fat mixtures or organic solvents.

Dyeing methods**1. *Float dyeing in closed vessels*****Drum**

The most commonly used vessels are wooden drums as they can be manufactured at low costs and ensure a constant temperature in the dyebath. Stainless steel drums are meanwhile being used in some cases. Their advantage consists in the inert state of the material with regard to chemicals, which means that dyeing of all shades is possible in the same vessel without soiling. However, these drums are expensive to buy and as they do not maintain the temperature well an additional heater has to be installed.

Flawless dyeing in these vessels depends on the material to be dyed being rapidly mixed at a higher speed and the provision of drums which are not too large, as well as boards and pegs in order to prevent rolling up of the leather at the bottom of the drum. Extremely high loading weights are not advisable.

- Sector tanning machines** These are new types of dyeing vessels made of stainless steel. They have the advantage of providing automatic process control such as temperature control, continuous pH measurement, different directions of rotation and speed settings, a float recirculation system for quick mixing and discharge of liquor and automatic time-controlled proportioning of the chemicals. Their low space requirement, low energy requirement and careful treatment of the material to be dyed are further advantages.
- Tanning mixer** Oblong, inclined vessels of the cement mixer type which are specially manufactured for leather production. Their main advantage is that they are quick and easy to load and unload and can be installed in low rooms. However, they are seldom used for dyeing.

2. Float dyeing in open vessels

- Paddle** Mainly for dyeing sensitive skin material in order to avoid felting of the wool of fur skins, tangling and tearing of thin skivers and garment or reptile leathers.
- Tray dyeing** Now a seldom used dip-dyeing method in troughs in order to obtain a light reverse side of the leathers. Such leathers, placed back to back, are racked with the sleaker and drawn through the dyebath by hand for several minutes.

3. Continuous dyeing methods

- Through-feed dyeing machine** Originally developed by Messrs. Staub in Maennedorf/Switzerland as the so-called "Multima" dyeing machine of which many copies are in use. Leathers that have been intermediately dried (crust leathers) are dyed as they pass through a trough filled with a heated dye solution and are subsequently squeezed through a roller of rubber or stainless steel. Absorption of the dyeing liquor by the leather can

be influenced by regulation of the belt speed and by variation of the pressure and rotational speed of the squeezing rollers. This continuous dyeing method achieves almost the same degree of fastness as drum dyeing. Favourable factors are the detection of defects when sorting the crusts and the possibility of handling short-term orders quickly.

Spraying machine

The dye solution is applied by means of a pneumatic atomizer or even better by means of the airless spraying method at high pressure. High-quality dyes should be used in order to obtain an adequate level of fastness. Besides variation of the belt speed and of the amount of dye applied, the depth of penetration is influenced by addition of organic solvents or penetrating agents.

Curtain coater

Used only seldom purely for aniline dyeing. It is mainly employed for application of grain impregnations and finishes containing binding agents.

Roll coater

Up to now used mainly for application of bottom coats and finishes and for achieving fashionable finishing effects. It is the most advanced and most economical coating method by means of roll coating. However, the leather should be of uniform thickness in all sections in order to obtain even, flawless prints. Very soft, elastic leathers are also difficult to coat by means of this method.

4. Special dyeing methods

Brush dyeing

Has mostly been replaced by the more efficient spraying method.

Screen printing

Should be classified as a finishing since an effect print is obtained by the manual application of pigment preparations containing binding agents using a doctor blade and a fine-meshed negative stencil like that used in textile printing.

Requirements to be met by leather dyes

Alkali-fastness	The dissolved dye should be fast to diluted alkalies such as soda or ammonia and should not show any change of colour.
Build-up properties	Dyeing is determined by the chemical composition of the dyestuff and by the properties of the leather to be dyed. The build-up properties of a dye are established by dyeing in different concentrations and defined in a build-up graph. The saturation limit of the dye has been reached if the intensity of colour does not increase. Excessive dye remains in the liquor, becomes loosely deposited in the substrate or penetrates deeper into the inner zone. The build-up graphs will then show that dyeing beyond the saturation limit is uneconomic ³⁶ . At the moment there is no standardized official method for determining the build-up properties for chrome leathers or retanned leathers. ³⁷
Absorption properties	The absorption properties of a dye are determined by dyeings, and characterize how much dye (%) is absorbed by the leather substrate in a time unit (min.). Besides the chemical structure of the dye the rate of absorption is considerably influenced by the type of tannage, by the type and amount of retanning agents used, by the pH value and by the dyeing temperature. The absorption properties provide information about compatibility with other dyes.
Homogeneity of dyes	According to the recommendations of the German Fastness Commission up to 5% of a shading dye can be added to industrial products, which may contain only one main dyeing component, in order to still classify them as homogeneous. The homogeneity of a dye can be quickly tested by means of the blow-up test or the so-called capillary method.

Intensity of dye

This is an important quality factor for the practitioner and is determined by different methods. A reference analysis of the dye solution is performed without dyeing on leather by a dip test using filter paper or by a comparative measurement in a colorimeter. Another method taken over from the textile branch is dyeing according to penetration standards. They are divided into several stages such as 1/25, 1/12, 1/6, 1/3, 1/1 and 2/1, the weakest concentration being 1/25 and the strongest concentration 2/1. Different amounts of dye are required for a specific penetration standard depending on the type of dye and on the tannage and retannage method.³⁸

Stability to hard water

The dissolved dye should not show flocculation when diluted with hard water. Dyes that are not resistant to hardness of water often result in increased staining of the flesh side, unevenness and shifts of shade. Therefore such dyes have been removed from the range of products of most suppliers.

Solubility

Solubility of a dye is important for dyeing at low temperatures, dyeing by the powder method and dyeing without liquor. Poorly soluble dyes can produce staining in some sections of the leather and smudging on the grain side and on the flesh side. Combinations of dyes may result in shifts of shade. Due to their hydrophilicity dyes which are extremely soluble may result in poor exhaustion of the bath and over-dyeing of the surface after acidification. Solubility is tested by dissolving the dye in distilled water at 20 °C and at 60 °C. The amount of dye which remains dissolved after dissolution by bringing to the boil and cooling to the specified temperatures is then determined. The amount is indicated in grams per litre.

Complex stability	Some metal complex dyes, in particular iron complexes, can be displaced from their bonds by highly complexing metals such as copper and thus cause shifts of shade. Therefore the leather to be dyed should not be brought into contact with metals, e.g. copper nails, copper covers or copper pipes.
Metamerism behaviour	Metamerism is the behaviour of dyes which, after dyeing in dye mixtures, show different shades in daylight or under artificial light sources such as a light bulb, neon light or also twilight. In the latter case the term dusk colour is also used. In order to avoid complaints about the shade, the luminance factor of the dyes to be used should be measured and adjusted such that it is identical with the original colour or very near to it.
Content of extenders in dyes	As the manufacture of dyes comprises many chemical processes and the most different processing steps, each batch should be adjusted to a constant colour intensity for the user. In the case of powder dyes this is done by adding inorganic salts such as common salt, sodium sulphate or organic substances such as dextrine, dyeing auxiliaries which are called extenders. Liquid dyes have the advantage of being free of extenders.
Stability to acids	The dissolved dye should be resistant to diluted acids such as formic acid or sulphuric acid solutions and must not flocculate.
Fastness to acids	The dissolved dye must not result in a change of colour on contact with diluted acids.

Requirements to be met by leather dyeing³⁹**Levelness**

Every dyer endeavours to obtain uniform, level dyeing results on the grain and flesh side in order to conceal defects of the grain as far as possible and to achieve every required fastness. Many factors have to be taken into account to meet these requirements in practice. Besides the condition of the raw hide, correct preliminary operations in the beamhouse and uniform tanning and deacidification processes, all parameters of the dyeing process itself have to be considered, which requires every experience of the practical specialist. There are no official methods for testing the levelness of dyes. Many dye manufacturers test it by means of reference colourings on standard test leather and judge the levelness by a visual inspection.

Lightfastness

Lightfastness is important for high-quality leathers such as garment and furniture leather and for the unfinished suède and nubuk leathers. The dyed leather samples are tested using official methods in daylight or by means of the xenon lamp and the blue scale (fadiometer) and judged in grades of lightfastness of 1 - 8, where 1 is the worst grade and 8 the best. A lightfastness of 4 is adequate for most leathers. In particular, the dyeing substrate itself determines the degree of lightfastness. If it is low, it cannot be improved even by means of dyes which are extremely lightfast. In order to achieve colouring results which are fast to light, lightfast dyes should be selected from the sample cards of the manufacturers, and fading tanning and retanning agents, dyeing auxiliaries or yellowing fatliquoring agents should not be used.

Fatliquor fastness	This provides information on the bonding strength between the dyes and the leather substrate. It is tested on standard chrome leather by means of standard fatliquoring and subsequent wet storage between filter paper. The intensity of dyeing of the filter paper is evaluated.
Solvent fastness	Any solvent of interest can be used for the test. Sections of dyed leather are immersed in the solvent, and after a certain time bleeding of the dye into the solvent is evaluated.
Fastness to migration into crêpe and PVC	The diffusion of the dye from leather into PVC foil or green rubber crêpe is tested and the dyeing of these materials is subsequently evaluated. Good fastness depends on the selected dye. Dyes having a low content or no content of free sulpho groups such as cationic dyes, 1:2 metal complex dyes and some liquid dyes are unfavourable. Spray and pressure dyeing, a high amount of dyestuff and dyes having a high covering power result in increased migration.
Fastness to cleaning	Many garment and glove leathers are dry-cleaned. The dyeing of these leathers must be fast both to the solvents used, such as perchloroethylene or the milder trifluorotrichloro-ethane, and to the cleaning intensifiers and should dissolve out only small amounts of dye. This means that solvent-resisting dyes should be used in these cases.
Fastness to buffing	After buffing or roughening, the dyeings of suède and also nubuk leathers should show little change of shade or brilliance. This is extremely difficult to achieve because the outer zones always bind more dye than the cross-section. The choice of suitable dyes and uniform through-dyeing are absolutely necessary.

Fastness to perspiration

This is of importance for all types of leather which are in contact with human perspiration during use, i.e. unlined upper leathers, furniture and car upholstery leathers, garment and glove leathers. Leathers of inadequate fastness to perspiration may produce changes of colour on textiles and ugly, dark stains on upholstered products. This is caused by bacterial decomposition of perspiration in the transition from a weakly acid to a slightly alkaline reaction. For perspiration-resistant colourations it is therefore important that tannage be performed using mineral tanning agents which are fast to perspiration and have a high content of acids. Secondary treatment with glutaraldehyde, cationic fixing agents and a mild deacidification are also favourable. Furthermore, dyes which are fast to perspiration should be chosen from the suppliers' sample cards.

Fastness to perspiration is tested according to a standardized method. A multi-fibre accompanying fabric is soaked in an artificial perspiration solution and placed for some time on the section of leather to be tested under load at 37 °C. After drying the change of colour of the section of leather and the dyeing of the accompanying fabric are evaluated.

Fastness to dry and wet rubbing

The leather is tested by rubbing it several times by hand with a dry or wet cotton cloth or in a rub fastness tester using dry or wet felt. This test is applied especially in the case of uncovered sorts of leather such as suède and nubuk leathers and indicates the fastness of the dyes bonded to the fibre. In many cases buffing dust is the cause of inadequate fastness to rubbing. In order to remove the dust it is necessary to wash the leather again with water. Intensive fatliquoring of the surface and a high content of neutral oils also reduce fastness to rubbing.

**Fastness to
overspraying**

Often, many coating finishes still have a high content of solvents which, when applied, dissolve the dyes which are not fast to solvents or migration and cause migration to the surface. This applies especially to aniline spray dyeing or aniline dyeing by means of the multima, roll coater or curtain coater as there is an increased concentration of dye on the grain surface compared to drum-dyeing. For good fastness to overspraying it is therefore absolutely necessary to use dyes containing sulpho groups.

**Fastness to
washing**

This is required for garment leathers which are worn directly on the skin such as shirt or glove leathers. It is not only a matter of using dyes that are fast to washing, but of using an appropriate procedure because it is also necessary to ensure softness and stability of shape. The test is performed by washing with a lauryl sulphate solution and accompanying fabric, followed by evaluating the change of colour of the section of leather and the dyeing of the accompanying fabric.

**Fastness to
water**

The behaviour of leather under the action of moisture is tested. The test is identical to that for fastness to perspiration, but distilled water is used instead of the artificial perspiration solution. Changes of colour and dyeing of the accompanying fabric are evaluated.

**Fastness to
water spotting**

The surface behaviour of the leather is tested by application of water drops. The test is particularly important for aniline leathers, suède and nubuk leathers. Whereas there are no problems in the case of drum dyeing if carried out correctly, increased spotting with formation of edge marks occurs if the dyeing is of inadequate fastness. Metal complex dyes have much more favourable properties than simple penetrating acid dyestuffs.

Factors which influence leather dyeing**Choice of dyestuff**

The choice of dyestuff depends primarily on the demanded fastness for the type of leather to be produced, on the desired shade and on the respective main tanning method or the retanning agents used. Perfect combinability of the dyes is a further criterion. This depends on the build-up properties, on the absorption rate and chemical structure of the dyes. In principle, the dyer should adjust the desired shade by means of the smallest possible number of shading dyestuffs in order to restrict the possibility of introducing additional defects. Price is a further factor which influences the choice of dyestuff. However, when using low-price dyestuffs their fastness and intensity should be examined thoroughly. Often they have a high content of extenders or extremely different mixed dyes. At any rate the specifications of the suppliers' sample cards should be considered when choosing dyes according to fastness.

Solubility of dyes

Anionic, readily soluble dyes are dissolved in water at 70 - 80 °C in a ratio of 1:10 to 1:20. Poorly soluble dyes should be brought to the boil briefly and if they are intended for high-quality aniline leathers filtered through a fine-meshed cloth to be on the safe side.

Cationic dyes are made into a paste by means of acetic acid with about half the weight of the dye, especially if hard water is used, and dissolved in water at 80 - 90 °C. Boiling should be avoided. Anionic and cationic dyes should not be dissolved together as otherwise precipitation or colour lake may occur.

Liquid dyes have the advantage of being dust-free and better to handle because they are easily diluted.

Quantity of dyes	In the case of wet leathers the quantity is calculated in relation to the shaved weight of the leathers, in the case of intermediately dried leathers according to the dry weight. However, it would be more favourable to relate the calculation to the leather surface because the thinner a leather, the greater is its surface per kilogram. In this case better constancy of shade without significant variations is achieved for the subsequent lots.
Addition of dye	For high-quality aniline leathers the addition of dyes in dissolved form and in several portions is always advantageous for an even and levelled absorption. Liquid dyes should therefore also be added in diluted form. Powder dyes in short float processes mostly result in reduced depth and brilliance of colour. With this form of application it is absolutely necessary to ensure that all dye components are evenly and readily soluble.
Float ratio	A large quantity of dye-liquor promotes the distribution of the dyes and auxiliary agents used. Furthermore, it prevents an excessive rate of absorption on the surface or reverse side. This should be considered especially when dyeing pastel shades which should therefore be dyed in larger quantities of dye-liquor. The quantities of dye-liquor commonly used are 100 - 250 %, and up to 400 % for pastel shades. The "dyeing without float" or "short-float dyeing methods" with floats of 0 - 30 % have to be performed at low temperatures in order to avoid unlevelled dyeing. Short floats should not be used for very thin leathers to avoid tearing or tangling of the leather material. These processes should be performed more gently in the automatic chamber or sector machine.

Dyeing temperature

The most commonly used dyeing method is dyeing in a hot float. The temperature of application is 50 - 70 °C for chrome leathers and 35 - 45 °C for vegetable/synthetically tanned leathers. In the short float dyeing methods penetration dyeing is done at a temperature of 20 - 25 °C and then the temperature is increased to 60 - 70 °C for fixation of the dyes. It is a general rule that high dyeing temperatures enhance the depth of shade due to increased affinity and faster rate of absorption while low temperatures reduce the fullness of shade due to quicker penetration of the dyes and even distribution over the entire cross-section.

Mechanical movement

Increased mechanical movement in the drum promotes the distribution and penetration of the dyes, thus reducing the duration of the dyeing process. Conventional rotating speeds are between 10 - 15 rpm. In order to avoid tearing of thin leathers dyeing should always be performed at low speed and with an increased amount of liquor or in the automatic chamber or sector machine.

Affinity of the leather to be dyed

Purely chrome-tanned leathers have a highly positive charge which is more or less reduced by vegetable/synthetic retanning or by a treatment with resin tanning agents, glutaraldehyde or other organic aftertreatment agents. Thus it is possible to control the different affinity of dyes. On the other hand, leathers retanned by means of vegetable/synthetic agents have a negative charge. When dyeing with acid dyes the charge should first be reversed by means of cationic agents in order to achieve fixation of the dyes.

Duration of dyeing	For most types of leather a dyeing time of 45 - 60 minutes is adequate. It depends on mechanical movement, on the size of the load and for penetration dyeing on the thickness of the leather.
Exhaustion of dyebath	Every dyeing process should aim at maximum exhaustion of the dyebath. However, excessive deposition of dyes on the surface of the leather should be avoided. Such depositions may result in bleeding due to migration into the finish layer or in the case of suède and nubuk leathers inadequate buffing properties or unsatisfactory fastness to wet and dry rubbing. Besides the correct choice of dyes, exhaustion may be influenced by several factors such as temperature, pH value, retanning agents, dyeing auxiliaries, float length and mechanical movement.
pH value	Chrome leather has an isoelectric point of about 6.5 or 4.5 depending on whether tannage is cationic or anionic (masking) whereas vegetably tanned leathers have an IP of 4 - 3.2. The IP is increased or reduced by retanning, depending on the type and intensity of the process. If the pH of the dye liquor exceeds the isoelectric point the charge of the material to be dyed is largely negative and if the pH is below the IP the charge is mainly positive. This shows that by changing the pH during the dyeing process the absorption behaviour, penetration and fixation of the dyes can be influenced. In practice this is done by means of diluted organic acid or ammonia solutions. Inorganic acids such as sulphuric or hydrochloric acid should not be used as they are non-volatile during drying and cause high differential values in the leather.

- Deacidification** Correct neutralization is essential for dyeing. An even deacidification over the entire cross-section is very important in order to avoid acid zones. Neutralization has a decisive influence on levelness, depth of shade, dyeing and penetration of dyes. (See also Deacidification).
- Retanning** Due to the wide number of retanning agents available on the market and their varying chemical compositions there are many possibilities of influencing the dyeing process with regard to depth of shade, absorption behaviour and fixation. To compare the influence of retanning agents on the dyeing process a standard chrome-tanned leather is chosen and dyed with a dye content of 1 %. The achieved depth of shade is defined as 100 %. The retanned dyed leather is then compared against the standard leather and checked for depth of shade, change of colour, exhaustion of dye, fixation, brilliance, levelness, dyeing of grain defects and fastness properties.
- Dyeing auxiliaries** These auxiliary agents are used to control the dyeing process, depending on their chemical composition and type of charge, in order to achieve very special effects on the substrate leather or also in the dye or the dyeing process. The auxiliaries are conveniently classified as anionic, cationic, nonionic, amphoteric or special products.
- Anionic products:** These are mainly neutral salt mixtures of aromatic sulphonic acids. In most cases they are used for their levelling effect on anionic dyes. They have a fixing effect on cationic dyes.
- Cationic products:** These are mostly condensation products of urea with formaldehyde or dicyandiamide, ethoxylized fatty amino derivatives or conversion products of polyurethanes or protein hydrolizates.

They have a fixing effect and increase the depth of shade of anionic dyes, and a levelling effect on cationic dyes. If used in anionic dyeing excessive amounts should be avoided at all costs because this could cause stripping of the dye instead of a deepening or fixation of the shade. These cationic auxiliaries should be added only to a completely exhausted dye-bath in order to avoid precipitation with the dye. For safety reasons it is recommendable to use a separate intermediate bath and keep the pH value constantly below 4.0.

Nonionic products: These products are mainly ethoxylizing products on the basis of fatty alcohols or nonyl phenols. They promote penetration and levelness of dyes. They should not be used in larger quantities because of their surface-active properties which would give the leather excessive hydrophilicity or wettability.

Amphoteric products: These products have both anionic and cationic groups in the molecule. The cationic group is active with low pH values, the anionic group is active with high pH values. Thus it is possible to influence depth of shade, absorption rate, penetration, levelness and exhaustion of the bath by regulation of the pH value.

Special dyeing auxiliaries: These products include penetrators used for spray staining, foam-inhibiting agents, resisting agents for drum or effect dyeing on one side, thickening agents for dyeing by curtain coater, tray staining or brush staining as well as polyamides to improve lightfastness and fastness to migration of metal complex dyes.

- Fatliquoring** In view of the large number of available fatliquoring agents and their widely varying compositions the dyeing result can be influenced considerably. This is the case especially if large amounts of fatliquors are used in the dye-bath. The levelness of dye can be impaired as a consequence of an uneven deposition of fatliquors and dyes, caused by unstable mixtures of fatliquors or excessive amounts of neutral oils. An excessive content of emulsifying components in the fat liquor may result in shifts of shade, reduced absorption properties, poor fixation of dye and thus reduced fastness properties. Overfatliquoring should always be avoided. If large amounts of fatliquors are used the mixture of fatliquors should be added in several portions as preliminary, main and subsequent fatliquoring.
- Surface dyeing** High-molecular dyes should be chosen from the range of available products for pure surface dyeing. Simple acid dyes are less suitable for surface dyeing. Liquid dyes on the basis of metal complexes are very suitable. Deacidification should not exceed a pH value of 4.5. Light, cationic preliminary or intermediate treatments increase the depth of shade. The use of wetting agents and higher sulphited or higher sulphochlorinated fatliquors as well as highly sulphited retanning agents should be avoided.
- Penetration dyeing** Products that are particularly suitable for penetration dyeing are indicated in the suppliers' sample cards. These penetrative dyeing agents should be chosen to avoid tedious additional processing. In general, simple acid dyes have a good dyeing capacity, however they are not recommended for high-quality leathers because of their low fastness properties.

The following influencing factors should be taken into consideration to achieve good penetration dyeing: Neutralization should be carried out intensively and without the formation of zones, if possible at the isoelectric point of the material to be dyed. Furthermore, attention should be paid to good mechanical movement, sufficient duration (depending on the thickness of leather) and adequate amount of dyestuff. The addition of dyeing auxiliaries having an affinity for dyes and dyeing with short floats are favourable for penetration dyeing. In particularly difficult cases penetration dyeing is achieved by means of intermediate drying.

Pigment dyeing⁴⁰

In order to increase the percentage of aniline leathers in leather production fine-particle pigments are being increasingly used for drum dyeing. Good covering of defects in damaged sections of leather is achieved. Since it is necessary to match the shades a smooth dyeing of the surface and thus improved quality is obtained. Perfect dyeing results depend on the chemical composition of the pigments, the particle size, the dispersing agents and auxiliaries, on the charge of the leather and the adjustment of exactly identical shades of the aniline and pigment dyeing.

Shading

It is in the adjustment of shades according to samples or in the subsequent shading of large lots where the "good" practical dyer proves his capabilities. A trained eye and an exact knowledge of the dyes to be used are prerequisites for quick and successful dyeing. A detailed knowledge of the shade-intensifying or shade-weakening effect of the auxiliary agents, fatliquors and retanning agents used is also very important. It is always advisable to achieve the desired shade with the smallest possible number of dyes.

The dyes used should be fairly similar in terms of rate of absorption, build-up and fastness properties. Dyeing series, chromatic triangles and the sample cards of the dye suppliers can be used for reference. In larger leather factories increasing attempts have been made in recent years to calculate shade adjustments by computer.⁴¹ However, due to the many influencing parameters in the leather dyeing process the results obtained are often still incorrect.

Leather defects due to incorrect dyeing

1. Drum dyeing

Cloud-like unevenness of the grain side

Causes: Overbasification in chrome tanning, excessive quantity of strong neutralizing agents, insufficient mechanical movement of the material to be dyed, inadequate mixing of the dyeing float, uneven deposition of retanning agents, addition of dyes in excessive concentrations, addition of cationic auxiliaries into a dye-bath that has not been exhausted, combination of dyes possessing too different absorption properties.

In the case of vegetably tanned leathers inadequate removal of unfixed tanning agents.

Remedy: Check and avoid the above-mentioned causes.

Dark, dot-like specks

Causes: Residual dyestuff not dissolved completely, sedimentation in liquid dyeing agents or excessive dyeing temperatures when dyeing in short floats using powder dying agents.

Remedy: Observe the solubility charts of the dye manufacturers, choose an adequate dilution factor and adequate dissolving temperature. In the case of sensitive shades filtering of the dye solution is recommended, especially if cationic dyes are used.

Light, dot-like specks	<i>Causes:</i> Use of saw-dust containing resin or tannin when sprinkling the leathers for shaving, poorly soluble particles in neutralizing or masking agents when adding powder. <i>Remedy:</i> Sprinkling with talcum or, better, dissolving of the auxiliary agents.
Blue-black specks	<i>Causes:</i> Iron chips from shaving, sleeking or splitting. <i>Remedy:</i> Reduce by treatment with oxalic acid or complexing agents.
Dark, uneven stains	<i>Causes:</i> Fat stains due to accumulation of natural fat or uneven absorption or precipitation of unstable fatliquors or a very high content of neutral oils, brief contact with hot water in beamhouse processing, overbasification of individual sections in chrome tanning, uneven deposition of cationic auxiliaries or retanning agents, soiling due to contact with the floor or greasy machine parts. <i>Remedy:</i> Check and avoid the above-mentioned causes.
Light stains	<i>Causes:</i> Sections not dyed because of lime blasts or resisting caused by soiling with machine oil. <i>Remedy:</i> Avoid the causes.
Empty, pale dyeing	<i>Causes:</i> Excessive deposition of anionic retanning agents and auxiliaries on the grain surface, excessive amounts of masking agents used in chrome tanning or in deacidification, excessive pH value in deacidification or in the dye-bath. <i>Remedy:</i> Reduce the amounts used and the pH value, perform dyeing in steps or intermediate cationic treatments. Combined application of aniline dyes with pigments.

**Bluish-grey
blunt dyeing**

Causes: Use of iron-containing water, chemicals and auxiliary agents, occurring particularly in vegetably tanned leathers or leathers that have been retanned mainly by means of vegetable retanning agents.

Remedy: Remove soiling by iron by means of complexing agents.

**Strongly
accentuated
grooves on the
shoulder**

Causes: Uneven deposition of tanning and retanning agents, uneven deposition of cationic dyeing auxiliaries, unsuitable combination of dyes, inadequate washing after deacidification, use of unstable fatliquors.

Remedy: Check and avoid the above-mentioned causes.

**Paler shade on
the grain side
and
darker shade
on the flesh
side**

Causes: Use of dyestuff combinations with different absorption behaviour, excessive amounts of cationic dyeing auxiliaries or fatliquors used in a pH range above 4.0, use of unstable fatliquor mixtures, use of extremely basified chrome retanning agents or aluminium tanning agents in a very long float, inadequate neutralization, excessive content of electrolytes in the dyeing float.

Remedy: Check and avoid the above-mentioned causes.

**Visible crease
marks caused
by lying
Change in
shade during
dyeing**

Causes: Prolonged standstill of drum during the dyeing process.

Remedy: Ensure continuous drum movement.

Causes: The presence of stronger complexing agents causes demetalling of 1:2 metal complex dyeing agents, in particular the more unstable iron complexes.

Remedy: Select a different dye or do not add complexing agents to the dye-bath.

**Difference in
shade from lot
to lot**

Causes: Variation of the float length, different moisture content of the lots and thus different weight in relation to the existing area of leather,

temperature fluctuations, different running time during fixation with formic acid, incorrect weighing of the dyes.

Remedy: Avoid the above-mentioned causes.

Bronzing of the dyeing

Causes: Excessive amounts of cationic dyes.

Remedy: Reduce the amount of dyes used and/or treat with cationic levelling agents.

Torn off pieces, tangling during dyeing

Causes: Inadequate float length, excessive loading weight and drum speed.

Remedy: Avoid the causes or perform dyeing in the sector-type dyeing machine.

2. Spray staining

Inadequate penetration of the spray dye

Causes: Spray dyes too dry or inadequate absorbing capacity of the leather due to excessive water-repellent fatliquoring of the surface.

Remedy: Apply full spray coats and increase the addition of wetting agents, penetrators or water-miscible solvents.

Unlevelled, cloudy spray staining

Causes: Uneven spraying with spray stripes too far apart; spray jet too narrow and round or evaporation of the spray dye too quick.

Remedy: Change the causes.

Splattering effects

Causes: Spraying pressure too low, nozzle opening of the spraygun too large or excessive viscosity of the spraying float.

Remedy: Avoid the causes.

Dot-like specks

Causes: Undissolved particles of dyestuff, oil droplets in the compressed air.

Remedy: Dissolve the dyestuff more thoroughly, filter the spray dyestuff, check the oil separator of the compressor.

Visible unevenness

Causes: Leathers wavy or creased on the spraying grid or band.

Remedy: Place the leathers carefully and smoothly.

3. *Brush staining*

**Streaky,
uneven dyeing**

Causes: Inadequate brush coats with dye solutions of excessive concentration, inadequate wetting before first coating. In the case of glove leathers inadequate wet-back.

Remedy: Avoid the causes.

**Cloudy
dyeing**

Causes: Insufficient fixation and thus uneven migration of the dye into the inner zone.

Remedy: Increase the acid concentration or apply additional fixation.

Light stains

Causes: Insufficient wetting, inadequate wet-back, natural fat stains due to inadequate degreasing.

Remedy: Avoid the causes.

**Empty, pale
dyeing**

Causes: Use of unsuitable, very penetrative dyes.

Remedy: Use high-molecular dyes and intermediate fixation layers.

**Bleeding of the
dye**

Causes: Excessively wetting leathers.

Remedy: Change fatliquor, perform wet-back by means of cationic agents, increase the viscosity of the brush staining liquor by means of thickening agents.

4. *Through-feed dyeing machine*

**Uneven
dyeing and
staining**

Causes: Increased content of natural fat, larger deposits of insoluble substances in the leather, excessive superficial, water-repellent fatliquoring.

Remedy: Avoid the above-mentioned causes and add more water-miscible dissolvents, anionic surfactants or penetrators.

**Dye specks,
streaky
dye stains**

Causes: Use of residual dyeing floats which have been stored for some time and which contain precipitations of dye.

Remedy: Avoid overstorage, filter the residual floats, use liquid dyes of higher stability.

Inadequate fastness to water drops

Causes: Very high content of electrolytes in the dyeing float due to an excessive content of extenders in powder dyes.

Remedy: Use salt-free, selected liquid dyes and organic acids in the dyeing float.

Inadequate dyeing

Causes: Low concentration of dyes in the float, insufficient time of immersion in the float or excessive dyeing temperature.

Remedy: Avoid the causes.

Darker shade in the middle zone

Causes: Delayed drying due to high-boiling dissolvents.

Remedy: Do not use dissolvents that evaporate slowly, avoid places of contact during drying of the dyed leather.

5. Sector-type dyeing vessels**Irregular staining**

Causes: Inadequate quantity of dye liquor, excessive loading weight. As the leathers are hanging too close to each other the auxiliary agents and the dyes do not reach all sections of the skin evenly.

Remedy: Change the quantity of dye liquor and the loading weight.

Mottled dyeing

Causes: Precipitations in the chemical feeding pipes.

Remedy: Rinse the feeding pipe briefly when changing the dye product.

Stripping of incorrect dyeings

Even if processing is carried out with utmost care, some of the dyed leather lots will not be uniform, will exhibit stains or fail to achieve the desired shade. Lots which have already been dyed may have to be redyed to achieve a different shade.

Redyeing to a black or intensive dark shade involves no problems. However, if light or medium colour shades are desired it is necessary to remove the faulty dyeing by means of stripping or decolouration before dyeing in the new shade can be carried out.

The following decolouration methods are possible:

1. Treatment with oxidizing agents

The products used are sodium chlorite, potassium permanganate/sodium bisulphite or in some cases hydrogen peroxide. When treating chrome-tanned leathers or leathers retanned with chrome retanning agents the formation of chromium VI compounds can be expected. Reducing substances should be used in such cases.

2. Treatment with reducing agents

The products used are sodium dithionite (hydrosulphite), stabilized sodium dithionite compounds or the sodium salt of hydroxomethane sulphinic acid.

3. Treatment with bleaching or brightening products

The products used are synthetic bleaching or tawing agents, neutral salts of synthetic tawing agents or sodium thiosulphate with addition of acid.

4. Combined methods ⁴²

- a. Pretreatment of syntan neutral salts with sulphophthalic acid, tartaric acid or citric acid.
- b. Pretreatment with an acidic, synthetic bleaching tanning agent and addition of oxalic acid.

Drying of leather

After termination of all stages of wet processing the leathers are dried and prepared for the subsequent finishing process. As drying is mostly performed under the action of heat for efficiency reasons the drying conditions should be adjusted to the respective tanning method. The maximum temperatures should not exceed 30 - 35 °C for vegetably/synthetically tanned leathers and 60 °C for chrome-tanned leathers in order to avoid changes of the leather properties.

Drying methods

Hang-drying

1. *Air drying without supply of energy:*

(Drying lofts, covered drying areas)

Low-price drying method, however dependent on weather conditions and therefore only economical in regions of suitable climate. This method has a gentle drying effect.

2. *Air drying with supply of energy:*

(drying room, tower or rack drying method with supply of hot air, drying in channels or tunnels by a through-feed or rotary system, without or with separate temperature zone sectors).

Quick drying methods whereby a uniform residual moisture content is kept in the leather, especially in the case of sector drying.

3. *Cold-air drying by air dehumidification:* ⁴³

This method consists of drying of batches at room temperature in a tightly closed drying chamber. The recirculated air is cooled by means of a cooling cell and the water contained in the air condenses as dew. On reheating this air, which has a highly reduced content of water, it has a quick-drying effect on the leather (principle of the heat pump). It is a very gentle, softening drying method.

Stenter frame drying

Mainly used for subsequent drying of the moisture contained in the leather after staking. Some leathers, in particular furniture and upholstery leathers, are directly stentered on frames while wet. A good area yield is achieved and wrinkleness is reduced. The leathers were formerly nailed on wooden gratings by means of special nails. Today they are fixed to corrosion-resistant, perforated metal plates by means of special clamps for chamber or through-feed drying. Fully automatic stenter frame driers are also in use.

Pasting process**1. *Paste drying:***

Mainly used for firm upper leathers with corrected grain. The wet halves of leather are flattened by means of a sleaker onto both sides of glass panels to which adhesive has been applied and dried in a hot air stream at 50 - 60 °C by the chamber through-feed method. The advantage of this method compared to hang-drying is a considerable gain of area. The composition of the adhesive is important. The adhesive should remain on the glass panel when the leathers are pulled off and should be easy to remove.

2. *Secotherm drying:*

This method is a less expensive initial investment compared to paste drying. It is performed in double-walled boxes of glass, stainless sheet steel or enamel panels whose inside walls are heated by means of hot water, hot oil or also electrically. The advantage of this method is the reduced drying time, but it is less favourable for the operators who have to flatten the leathers onto the continuously heated panels.

**Vacuum
drying*****Method with one and several tables:***

This drying method is based on the property of water to boil at low temperatures under reduced air pressure and thus to evaporate more quickly. The wet leathers are flattened by means of a sleaker onto a heatable metal plate without creases and then hermetically covered by means of an air-tight bell. The inside air pressure is reduced by evacuation and the leather is dried in about 4 - 10 minutes depending on the preset vacuum, the heating temperature of the metal plate, and on the thickness and moisture content of the leather. The area yield, thickness and softness of the leathers can be influenced by changing the vacuum, the counterpressure and the temperature. Vacuum through-feed method.⁴⁴

**Drying
by radiation*****1. Infrared drying:***

Drying is performed by means of heat radiation from inside the leathers. Suitable for chrome-tanned leathers and leathers tanned by combined tanning agents and especially for thin leathers. Less suitable for purely vegetably-tanned leathers because signs of charring occur, especially at the end of the drying process.

2. High-frequency drying:

This drying method is carried out by means of electromagnetic waves having a very high oscillation frequency and is mainly performed in a through-feed process⁴⁵. The advantage of this method consists in the exact regulation of the residual moisture content in the leather. It is less economic for complete drying of wet leathers, but a very suitable redrying method. Small sections of leather can be dried very quickly in microwave devices to achieve adjustment of shade without producing serious colour differences with regard to the entire lot.

Drying defects**Area loss
of the leather**

Causes: All leathers which are dried by free-hanging methods show a shrinking of area of between 5 - 15 % depending on the type of tannage. Elevated drying temperatures, especially towards the end of the drying process, have more influence on area reduction than high temperatures at the beginning of the process. The area loss is reduced to some extent in the mechanical finishing processes, mainly by staking and stretching, but it cannot be entirely made up.

Remedy: Choose mild drying temperatures and include conditioning zones in the final stage of the drying process. For firm leathers a switch to modern drying methods is strongly recommended in order to achieve area gains.

**Hardening of
the leathers**

Causes: Excessive drying temperatures, over-drying of the leathers or a tanning method which is not temperature-resistant.

Remedy: Avoid the causes. Moderate preliminary fatliquoring during tanning reduces hardening.

**Saddening
of the surface**

Causes: Use of vegetable retanning agents which are not heat-resistant or highly unsaturated fatty substances which have a yellowing tendency.

Remedy: Check the retanning agents and fatliquoring agents.

**Dark
edge zones**

Causes: Occur in hang-drying due to migration of the dyeing float containing unfixed matters into the outer zones of the leather.

Remedy: Achieve good exhaustion of the dye-bath by means of adequate acidification and fixation. If necessary, apply a short rinsing bath after dyeing.

Large areas of unlevelness	<i>Causes:</i> Staining through contact of leathers which were stuck together during hang-drying, delaying the drying process as a result. <i>Remedy:</i> Ensure an adequate spacing of the leathers.
Dark stains	<i>Causes:</i> Migration of fat or precipitation due to the use of unstable fatliquors, excessive amounts of unsulphited oils or strongly cationic top fatliquoring. <i>Remedy:</i> Check the fatty substances, reduce the amount of neutral oils.
Stains caused by air bubbles	<i>Causes:</i> Air bubbles produced because the leathers were not horsed up smoothly or because they were not flattened onto the vacuum plate smoothly and with care. <i>Remedy:</i> Avoid the causes.
Drop stains	<i>Causes:</i> Drips of condensed water from the felt panel of the vacuum bell because the felt lining is very soiled and no longer absorptive. <i>Remedy:</i> Clean or exchange the felt lining.
Greasy spew	<i>Causes:</i> Precipitation and migration of fatty substances or very strong superficial fatliquoring with excessive amounts of fats and oils which are not bondable. <i>Remedy:</i> Change the combination of fatliquors.
Visible pressure marks of gratings	<i>Causes:</i> Mostly caused by contact of the leather with the supporting surfaces of the drying devices, especially in the case of vacuum drying. <i>Remedy:</i> Avoid excessive contact, reduce the contact pressure during vacuum drying.
Longish strips visible on the leather	<i>Causes:</i> Caused by the poles during hang-drying, especially on very wet leathers. The rate of evaporation is reduced in these sections. <i>Remedy:</i> More thorough samming of the leathers or change to free-hang drying.

Bleaching of shade of the entire leather

Causes: The presence of large amounts of bleaching agents, mainly sodium sulphite, sodium bisulphite or oxalic acid, results in a bleaching of the shade. This is particularly unattractive on suède and nubuk leathers.

Remedy: Reduce the use of bleaching agents or do not use them at all and change to more stable dyes.

Difference in colour on the plate and vacuum side of the leather

Causes: Migration of dyes due to the use of poorly fixed dyes.

Remedy: Use dyes with better fastness properties and ensure adequate fixation of the dyes at the end of the dyeing process.

Pale marginal zones on the leather

Causes: Drying of the edge zones of leathers by storing for too long on trestles before drying, especially in warm rooms and in countries with hotter climates.

Remedy: Cover the leathers to be stored on trestles with plastic sheets.

Excessive residual adhesive on the grain side

Causes: Especially disturbing for leathers which have been produced for aniline finishes. Mostly caused by leathers with excessive wettability or due to the use of adhesive mixtures having excessive adhesive power.

Remedy: Change adhesive formula, reduce the amount of highly emulsifying fatliquoring products in the mixture of fatliquors or perform cationic top fatliquoring.

Mechanical processes after drying

After drying the leathers are intermediately stored. This has the purpose of compensating overdried or overwet sections in the leather and also of providing an adequate work-in-process capacity in order to ensure a continuous course of production for the subsequent process stage.

The mechanical processes after drying serve to further treat the leathers to achieve the desired softness or firmness and the desired size of area, to treat the grain and flesh side and in the case of suède and nubuk leathers to process the fibres.

Mechanical processes ⁴⁶

Conditioning For the respective subsequent processes it is necessary to add a small amount of moisture to the leathers that have hardened and dried to a different extent. A suitable water content is 20 - 28 %. A higher moisture content may make the fibres stick together during subsequent drying. The traditional moistening method, mostly used in smaller factories, is sawdusting of the leathers with moistened sawdust of hard wood. Sawdust of soft wood is not suitable because it has a higher resin content and is prone to splitting. The sawdusted, stacked leathers remain in this condition for some hours or over night, depending on the type of leather. The formerly used dipping or brushing methods are seldom applied nowadays because they do not allow accurate proportioning. Leathers are now conditioned more efficiently using through-feed moistening systems (spraying, moistened conveying belts, water vapour) and stacked. However, direct further processing is also possible.

Staking	Treatment method for softening, working out the edge zones and slating of creases after conditioning of the dried leathers. Formerly, the leathers were drawn over a stake to which a blunt iron disk had been fixed or crutched by means of an arm breaking iron. Today staking is accomplished with the jaw-type staking machine, universal staking machine (Schödel type), roll staking machine (Mercier type) or by means of the through-feed vibration staking machine (Mollisa type).
Milling	Softening of the conditioned leathers by moving them in a rotating drum at about 12 - 16 r.p.m. Mainly used for suède and split leathers, for soft upholstery, garment and rustic upper leathers. Besides the softening effect a special grain marking is achieved. The leathers should not be milled in an extremely dry state in order to obtain an evenly cracked grain.
Stretching	After staking the softened wet leathers are stretched on wooden or metal frames for drying. However, the most important criteria are achievement of a maximum possible area yield as well as smoothness of area, firmness and dimensional stability.
Trimming of edge zones	This process serves to eliminate marks caused by clamps, holes due to nails, hardened edge zones, protruding corners or fringes and to correct torn edges. The leather will then lie more smoothly on the conveying belts of the finishing and further processing machines. Furthermore, it saves on finishing floats for these unusable sections of leather.

**Dry splitting
or
dry shaving**

Both processes are used for exact adjustment of the final thickness, in particular for very thin garment nappa and garment suéde leathers made from the skins of small animals. With a thicker starting material the advantage of dry splitting consists in obtaining a usable upper and lower split. Additional softening of the leathers is achieved by dry shaving due to the racking and stretching effect of the blade cylinder. The shaving blades should be arranged very close together on the blade cylinder in order to achieve a uniform and smooth cut on the leather.

Buffing

Buffing has the following functions:

1. Cleaning the flesh side from irregular fibres and residues of connective tissue in order to create uniform pressure conditions for mechanical finishing processes (plate and glaze finishing) and furthermore to give the leathers an attractive appearance for sale.
2. Giving suéde and nubuk leathers the desired even nap length (velveteen, short nap, longer two-way nap).
3. Fine buffing of grain for grain correction or for production of corrected grain side leathers.

Buffing is performed by means of cylinder-type buffing machines or cylinder-type through-feed buffing machines. Wet buffing on rotating oval pumice stones or dry or wet buffing on buffing wheels sprinkled with carborundum powder are methods used for special sorts of leathers, especially for loosely structured skins of small animals.

The cylinder-type machines work with abrasive papers of different grain size sprinkled with

carborundum powder. The following sizes of grain are distinguished:

- 24 - 120 = for coarse buffing,
- 120 - 300 = for medium buffing,
- 320 - 700 = for fine buffing,
- 800 - 1200 = for superfine buffing.

For the production of suède leather buffing is first carried out with a coarse paper followed by a paper of finer grain. Apart from the size of grain the rotational speed of the buffing cylinder also determines the fineness of nap.

In order to roughen the fibres of worn garments made of suède or nubuk leather dry cleaners often treat the surface by means of a sand blaster.

Dedusting

The dust occurring during buffing is removed by means of exhaustors and collected in chambers or wet dust systems. However, fine dust particles remain on the leather and cause impaired adhesion or formation of clots during subsequent finishing. Furthermore, suède and nubuk leathers will lose more colour and cause staining because the dust is also dyed. Therefore, a separate dedusting process is necessary. This is done by means of a brush or air-blast dedusting machine. When using brush dedusting machines increased friction produces an electrostatic charge which makes complete dedusting more difficult. Electrostatic charging is reduced if the relative air humidity of the leather and in the dedusting rooms is more than 70 %. The leathers to be dedusted and the processing rooms should therefore be conditioned by means of corresponding air humidifying plants.

Polishing

Polishing of leathers is performed by means of special polishing machines in order to smooth the grain, correct defects or to achieve special finishing effects, in some cases by applying special polishing ground coats. The set-up of the machines is similar to that of cylinder-type buffing machines with the difference that a stone cylinder with wedge-shaped milled grooves is used instead of the buffing cylinder. These grooves produce a flattening, racking and staking effect. The stone is heated by the contact pressure, which gives the leather a glossy effect. In some cases polishing is done by means of the cylinder-type buffing machine and the smooth reverse side of the abrasive paper.

Rolling

Is performed on vegetably tanned sole leathers, heavy sleek and harness leathers and leathers for endless belts by means of cylinders, rollers or pendulum rollers. This operation has the purpose of giving the leathers a high density of fibres by treatment under high pressure, which is adjustable up to 50000 kg/cm^2 for leather rollers. This makes the leather stiffer and water resistance is improved. The leathers to be treated should have a uniform moisture content of 20 - 24 % because overdry leathers do not achieve a consolidated fibre density. Unevenly moistened leathers give rise to unattractive dark staining. Small amounts of emulsified fatty substances are often added to the moistening water. This serves to achieve an increased surface gloss and at the same time to improve elasticity of the grain and protect the leather against crackiness of grain.

Finishing ⁴⁷

The final stage of leather production is reached with the finishing process. These treatments have the purpose of making the leather usable and suitable for the manufacture of end products. The following properties of the leathers are to be achieved by application of different substances following final mechanical processing, depending on the type of leather:

1. Desired fashionable shades in transparent, covering or effect finishes.
2. High-gloss, semimatt or matt top coats.
3. Dry, waxy, greasy or blunt surface handle.
4. Levelling of stain patches and grain defects.
5. Protection against soiling, moisture and processing chemicals used in the manufacture of end products.
6. Application of a fully covering artificial grain layer to splits and corrected grain leathers.

Structure of finishes (schematic)

The finish consists basically of three coats:

Base coat * Pigment coat * Top coat

All coats are not absolutely necessary - their application depends on the type of leather to be produced. It is possible to choose intermediate stages or to apply the top coat on its own. Basically, softer products are chosen for the bottom layers and harder and more resistant products for the final coat.

Aniline leather	Semianiline leather	Grain leather, covered	Corrected grain leather	Split leather
	Top coat	Top coat	Top coat	Top coat or film
Top coat	Transparent pigment coat	Pigment coat	Covering pigment coat	Covering pigment coat
Aniline dyeing	Light colour base coat	Covering base coat	Grain impregnation and base coat	Thick, covering base coat

Classification of finishes

In many cases two or more names may exist for the same finish when classified according to finishing techniques, finishing materials and finishing effects:

1. Classification according to the finishing technique:

Glaze finish	Performed by means of a glazing machine and non-thermoplastic binders. Used for high-quality leathers because it accentuates the natural grain marking particularly well. However, plate finishing is also used to seal the finish.
Plate finish	So called because different types of plating machines are used to produce high-gloss and smooth films.
Glaze/plate finish	A combination finish consisting of glazing after the base coat and plate finishing as top coat. It is used for leathers with a sensitive grain in order to avoid overloading with polymer binders and also to improve handle properties.
Corrected grain finish	Is used for leathers which receive grain impregnation by buffing after grain correction and in most cases a covering polymer finish.
Embossed finish	Is used for leathers which receive an artificial or fancy grain by embossing.
Spray finish	This name refers to finishes which are applied exclusively by spraying.

Curtain coating finish These finishes are applied by means of the overflow or slot-type curtain coater. Mostly used for leathers which need a highly covering top coat such as corrected grain leathers or splits.

Roll coating finish In this type of finishing the coat is applied to obtain effect finishes by means of screen rolls or engraved pattern rolls.

2. Classification according to the finishing effect:

Aniline finish This finish is chosen if the leathers receive only a transparent coat. The natural appearance of grain should remain visible.

Semianiline finish This type of finish contains only small amounts of covering pigments, or a covering base coat is applied and then an aniline effect is produced by means of finishing floats containing organic dyes. It is a finish in between an aniline and an opaque finish.

Opaque finish Includes all types of finish which contain covering pigments and binders. It is the most commonly used finishing method.

Easy-care finish Particularly resistant to oil, grease and soiling, wet and dry rubbing, to solvents and detergents. It consists of cross-linking and hardening binders and polyurethane lacquers, also in combination with nitrocellulose products.

Two- or multi-tone finish Is applied in two or more finishing floats of different colour. The effect is achieved by means of oblique spraying, padding or printing.

- Brush-off finish** This is an irregular, streaky two-tone effect method. A dark hard nitrocellulose colour is sprayed onto a leather that has been finished in a pale shade and then rubbed off by using a felt polishing disk.
- Antique finish** An elaborate manual method for achieving irregular two-tone effects. The leathers receive a raised embossed grain and after application of a wax resist are treated with a second, mostly darker graining colour. The recessed parts will then have a darker shade compared to the raised parts.
- Fancy finishes** These include droplet-shaped *splatter effects* produced by reduction of the compressed-air setting during spraying; *crushed grain effects* produced by creasing the leathers unevenly and then spraying them with a high-gloss polyurethane lacquer in a box frame; *kerosene effects* by rubbing bismuth chloride oxide powder over black patent leather; *mother-of-pearl effects* produced by means of special iridescent pigments in the dye coat; *gold beetle effect* produced by spraying a lacquer solution coloured with basic methyl violet which causes bronzing of the surface.
- Invisible finish** A finish which, despite the protective layer, gives the impression of an unfinished surface. Produced on leathers which have been pre-treated by means of a penetrating grain impregnation or a light polishing ground coat. The leathers are then lightly sprayed with a polyamide top coat which contains nitrocellulose matt lacquer for regulation of the gloss effect.

- Craquelé finish** A leather surface to which a light or dark base coat has been applied is sprayed with a hard coat of contrasting colour and embossed after drying. The hard unelastic dye coat is torn open by subsequent dry milling in the drum to produce an unevenly cracked surface.
- Padding finish** Is mostly used for glove leathers. The grain surface is powdered with colourless or dyed talcum powder or it is sprayed with a wax or fatty solution. When pressed against a rotating plush-wheel, heat is produced by friction, which gives the leathers a semimatt finish and a smooth, supple handle.
- Foam finish** ⁴⁸ In this process the finishing floats on the basis of polymer binders contain an additional foam-producing expanding agent. It is mainly used for leathers with highly coating binder finishes, but also for furniture and car upholstery leathers. Improves elasticity and flexing endurance, embossing properties and handle properties of the finish coats.
- Solvent-free or solvent-poor finish** ^{49 50} In response to ecological conditions and the regulation on clean air (TA Luft) increasing efforts have been undertaken during the past years to obtain equivalent fastness properties to those of solvent-based finishing systems by means of water-dilutable finishing systems. The main problems were inadequate fastness to wet rubbing, poorer flow properties, more difficult drying conditions and the production of different handle properties. In order to obtain good results by means of aqueous finishes including aqueous top coats the leather must have been given a particularly uniform absorbing capacity by corresponding retanning, fatliquoring or partial water-repellent treatments.

The following factors should be considered when choosing the finishing and coating systems:

1. Use of pigment preparations which do not contain excessive amounts of hydrophilic dispersing agents.
2. Use of softer acrylate and polyurethane dispersions in the base coat and pigment coat and use of harder top coat formulations.
3. Application of thicker coats than in the case of solvent-based finishes in order to improve the fastness properties by a good flow-out.
4. The addition of cross-linking agents which are "exactly matched" to the amount of binders and thickness of coat is of special importance in order to achieve high fastness to wet rubbing.
5. If matting agents and viscosity regulators are used, constant distribution of these agents should always be ensured by stirring during application.

Film transfer finish

This finishing method is not performed by the application of finishing floats, but by means of transfer films. The transfer films are manufactured in specialized factories by lamination of different coloured aluminium bronzes at high temperatures. They are made in uni-colours or with various patterns. The best known products are gold and silver leathers. These leathers were formerly produced with real gold leaf and silver foils.

Colourless or dyed PVC foils are also sealed onto the surface in order to achieve high gloss effects.

A variant of the film transfer finish is coating with two-component polyurethane mixtures on a coating machine, either by a direct or reversing process.

3. Classification according to the main finishing material used:

Casein finish	Treatment with non-thermoplastic casein products and pigments or organic dyes. Is mainly used for glaze/plate finishes.
Polymer or binder finish	This is the most commonly used type of finish in leather production and is mainly applied as a plate finish. The products used are thermoplastic binders on the basis of polyacrylates, butadiene or vinylidene chloride copolymers. The film-forming properties of these products are adjusted to produce a wide range of effects from soft/stretchy to hard/inelastic, depending on the degree of polymerization.
Nitrocellulose or collodion finish	The film-forming material is nitrated cellulose cotton dissolved in organic solvents, also called collodion cotton. It is applied to binder base coats in a pigmented or transparent thin layer.
Cellulose ester finish free from nitro groups	The film-forming component used is cellulose aceto butyrate dissolved in organic solvents. Compared to collodion the main advantage of these films consists in their resistance to yellowing on exposure to light and heat.
Polyurethane finish	Use of highly polymerized addition compounds on the basis of polyether or polyester polyols. These are binders dissolved in organic solvents, as reactive/non-reactive products and dispersed in water, in cross-linking or non-crosslinking form.
Patent finish	The traditional, very labour-intensive method was a treatment with boiled linseed oil, called "warm lacquer process". Nowadays patent leather is manufactured by the "cold lacquer process". A mostly transparent, thick polyurethane lacquer coat is applied to a pigmented polymer binder base coat. A high-lustre finish is produced.

Basic products for finishing applications

General

There is no uniform process for leather finishing. In each leather factory the finishing floats to be applied have to be prepared from the basic products supplied by the manufacturers. This is done according to the type of leather to be made. The finishing specialist should therefore have a detailed knowledge of the products. Basically, the following requirements need to be taken into account:

1. Achievement of consistent quality and optimum results within the produced lots.
2. Achievement of the desired physical properties of the finish and of the desired surface appearance such as shade, gloss and handle of the leathers.
3. Use of existing machinery for the finishing process.
4. Consideration of the costs for preparing the finishes and compliance with environmental legislation.

1. Leather coating colours (pigment preparations)

Homogenized, finely dispersed pigment pastes are manufactured especially for leather production by the suppliers of the chemicals. A distinction is made between "covering" preparations containing inorganic pigments and "transparent" preparations which contain small-particle organic pigments. Inorganic pigments are mostly resistant to chemical and thermal influences whereas organic pigments give a very high gloss. Both types of pigments are insoluble in water and in organic solvents. In order to save costs for transportation and storage the pigment preparations are highly concentrated. The available ranges of leather coating colours include the entire basic range of the colour scale. The desired final shades are then achieved by mixing and shading these primary colours in the finishing process. For coloured finishing floats they are adjusted to a ready-to-use consistency by means of the necessary additional finishing agents.

The most frequently used pigments are:

Inorganic pigments:

Titanium dioxide	White pigment with high covering power Anatas form = creamish white Rutil form = bluish white
Zinc white	Mixture of zinc oxide and zinc sulphide, white with lower covering power, does not tend to chalk.
Cadmium sulphide	For brilliant lemon yellow and brilliant red shades.
Molybdenum salts	For red and orange shades. Less expensive than cadmium compounds.
Aluminium oxide silicate	For medium blue shades (ultramarine).
Iron oxides	Result in the shades ochre, reddish brown and black, depending on the method of production. They have a high covering power.
Carbon blacks	Used for black shades in many variations.

Organic pigments:

Synthetic, water-insoluble complex dyes

in the colours yellow, orange, red, blue and green. Of these, the phthalocyanines which give high brilliance and good fastness qualities are outstanding.

Natural earth colours:

Rarely used in the leather industry since they mostly give dull, blunt shades.

White	Gypsum, chalk, baryta white, barium carbonate
Yellow	Yellow ochre
Brown	Terra di Siena, Umber
Red	Various sorts of red ochre
Green	Ferric silicate
Grey	Graphite, bauxite, slate

All pigments must be ground with carrier substances or completely embedded in these as otherwise they have no storage stability. Flocculation, strong precipitation or suspensions, encrustation and difference in shade would cause processing problems during finishing.

a. Water-dilutable products

Finishes containing casein

This group of products has been the most common form of application for leather finishes for many decades. The casein used is mainly obtained from skimmed milk. It is insoluble in water and has to be broken down with alkalies such as ammonia, borax soda or amines to make it water-dilutable. It has an excellent protective colloid effect for pigments. Being a protein product it is sensitive to bacteria and decomposes very quickly, especially in hot climates. Therefore preserving agents should be added to these finishes. As casein dries out to a hard, brittle film, it is also necessary to add plasticizers such as castor oil or polyglycols. Furthermore, the finish should be applied in thin coats.

Finishes containing no or little casein

Finishes containing larger amounts of casein are not suitable for leathers with a propensity to loose grain or which must be treated with large amounts of finish. They would cause brittleness or increased loose grain. For this reason leather finishes which contain little casein or no casein at all have been developed. They contain synthetic protective colloids for the pigment pastes which do not overload the leather surface. Therefore the content of casein suitable for the respective type of leather can be determined individually in the leather factory where the finish mixtures are prepared.

Plastic or compact finishes

These finishes already contain all necessary binders and have only to be diluted with water for use. As they allow little variation they are only used occasionally.

Luminous colours

These are organic pigments with very tiny particles which are embedded as microbeads in synthetic resin. The high-gloss surface makes them highly reflecting.

b. Products dilutable with organic solvents**Nitrocellulose finishes**

The binder in this group of products is nitrated cellulose cotton, also called collodion cotton. The solvents used are low to high-boiling esters and ketones, and alcohols or aromatic hydrocarbons are added for dilution. The solvents and diluents must be matched with utmost care in order to achieve correct film formation and an even rate of evaporation and drying. This is important for imparting gloss and for the necessary fastness properties. The dried film is very hard on the surface and therefore possesses excellent resistance to impacts and scratching. Elasticity can be influenced by the addition of plasticizers such as castor oil, rape oil, colza oil, linseed oil or esters of phthalic acid, adipic acid, butylic acid and camphor.

Finishes free from nitro groups

The film-forming product is cellulose aceto butyrate, abbreviated CAB. Unlike nitrocellulose cotton the films are stable to yellowing on exposure to light and heat. Furthermore, they have an excellent fastness to migration. They are also resistant to free amines of polyurethane foams. The solids contained in these finishes present no fire hazard.

c. Finishes dilutable with water and/or organic solvents**Nitrocellulose emulsion finishes**

These are based on specially emulsified NC or CAB cotton. Therefore they are water-soluble, but can also be diluted in solvents or in combination with water. The advantage of these products consists in the fact that they are not inflammable in the aqueous phase and give a pleasing surface handle. But they are sensitive to frost. Emulsifiable, water-free products, which are diluted with water immediately before use, are also available.

2. Organic dyes for finish preparations

a. Soluble in water

Brightening dyes	Selected anionic dyes which are added to the base coating, pigment finishes or top coating mixtures in combination or alone in order to enhance brilliance or the aniline effect. For this application they should be highly compatible with the finishing agents, have good lightfastness properties and good fastness to bleeding and hot plating. Furthermore, only dyes with a low content of extenders such as liquid dyes should be used. The 1:2 metal complex dyes are also very suitable.
Colour lacquers	Now used only seldom. 2 parts anionic dye are mixed with 1 part basic dye in dissolved form at boiling temperature. Such lakes improve covering power while retaining an aniline effect and have good fixation properties.
Polymer dyes	These are dyes which have been polymerized in acrylic acid ester or copolymers. As a result they are well fixed and cannot be dissolved by water or solvents. In some cases it is of disadvantage that excessive amounts of binders have to be applied until the desired effect is achieved.

b. Soluble in organic solvents

Metal complex dyes	These are free from extenders and exhibit varying solubility in organic solvents. The solubility charts of the manufacturers should be consulted. The dyes are mostly used for dyeing transparent nitrocellulose lacquers in order to obtain aniline effects. Only dyes which are free from hydroxyl groups are suitable for use with one or two-component polyurethane lacquers.
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3. Thermoplastic and cross-linking binders

The purpose of all thermoplastic binders is to form a sealing film on the leather surface. The most important binders are polymerisates which have been on the market since around 1930. The starting products of these polymer dispersions are monomers of ethene derivatives. This group includes mainly acrylic acid esters. Due to the reaction conditions of different monomers, including copolymerization, different branched-chain molecules are formed which are dispersed as spherical drops with emulsifiers in water. A great number of such dispersions are available on the market. The monomers as well as the conditions of polymerization determine the properties of the finish film such as film formation, elasticity, stability to acetone, fastness to swelling, adhesion strength, penetration, filling effect, fineness of grain, fastness to hot plating, fastness to wet and dry rubbing.

Since about 1965 aqueous polyurethane dispersions, abbreviated PUR, have been gaining significance. The films have excellent fastness properties, are highly elastic and hardly load the grain. The film is formed by cross-linking.

The most important polymer dispersions

Polyacrylates ⁵¹ The starting products are the esters of acrylic acid. They produce elastic, stretchy films which are fast to light and oxygen. With increasing chain length of the alcohols used for esterification the films become increasingly soft and tacky. However, their resistance to cold and moisture increases. By changing the degree of polymerization and varying the components in copolymerization it is possible to manufacture a great number of products having very different film properties. They account for the largest share of polymers in leather finishes. These products and all other polymer dispersions are sold with a solids concentration of 30 - 60 %.

Polymethacrylate	The starting products are the esters of methacrylic acid. In contrast to acrylates, methacrylates give harder films possessing about the same fastness properties.
Polyacrylonitrile	The starting products are the nitriles of acrylic acid. They give hard films with a high gloss, are very water-resistant and lightfast like acrylates.
Polystyrene	The films are hard, brittle, not tacky and are resistant to swelling. They have a moderate adhesion strength, but good resistance to cold. This product is only used as a copolymer.
Polyvinyl acetate	Gives a harder, clear film of high strength. Due to ester saponification it is sensitive to moisture. Used only as a copolymer.
Polyvinylidene chloride	These films have low elasticity and are slightly sensitive to light. Used as a copolymer with acrylic acid esters.
Polybutadiene	The films are rubber-like and soft, have good filling properties and a high resistance to cold, are not tacky and are resistant to swelling. However, they are sensitive to ageing and exposure to light.
Polyurethane⁵² (PUR)	An increasing variety of aqueous polyurethane dispersions is used in the leather finishing process and their share will no doubt increase in the future. The advantages of these products are good penetration, excellent adhesion of the coats, very low loading of the grain and good fastness properties of the films. Many combinations with polyacrylates, polyesters and other thermoplasts are used in order to achieve very special properties.

4. Non-thermoplastic binders

a. Water-dilutable products

Films of this type of product are less elastic and stretchy. On no account should they be applied in thick coats as this results in brittleness and peeling of the films. High gloss is achieved by exposure to heat, in particular by the frictional pressure during glaze finishing. When added to thermoplastic finishing agents they improve fastness to solvents.

Albumen

Blood: Only oxblood is suitable. When extracted it has to be immediately beaten vigorously in order to prevent coagulation of the blood cells. Addition of preserving agents is required for durability, and storage in a cool place is recommended. When added to black glaze finishes it improves depth of colour and brilliance.

Blood albumen: Blood serum which has been freed from fibrin and blood corpuscles, evaporated and dried. The dissolving temperature should not exceed 40-45 °C as otherwise coagulation will occur.

Egg albumen: Is obtained from the white of hen eggs and available in dried powder form. Suitable for pale glaze finishes to give them a clear, transparent high gloss.

Casein

Is obtained from skimmed milk by precipitation with hydrochloric acid and must not have a high fat content. Correctly dried casein should have a light, whitish yellow colour. Casein dried at excessive temperatures has a brownish colour and can only be redissolved with difficulty. The water-solubility of casein is achieved by dissociation by means of ammonia, borax or sodium bicarbonate. The great number of commercially available products have different viscosities depending on

their application and composition. The basic requirement is that soft casein products be used for the first coats and harder formulations for the top coats. The addition of plasticizers improves only the bending endurance, but not the elasticity. In order to achieve satisfactory water-resistance of casein finishes they should be treated with fixing agents. Nevertheless water drop stains due to swelling of the casein cannot be avoided completely. Such stains can be removed by repolishing with a dry cloth.

Modified casein

The commercially available products have been modified by means of polyamide. This improves flexibility and fastness to moisture. Furthermore fixing agents can be added directly to such solutions without causing precipitation. The benefit of this is that additional intermediate fixation is not necessary.

Gelatine

Additive for glaze finishes. Gives the films a glassy, translucent high-gloss effect. Because of its poor fixation properties it should not be added in excessive amounts. Used especially in glaze finishing of pale snake, lizard and crocodile skins.

Shellac

Derived from lac, the secretion of the Indian lac insect. Improves the gloss effect and handle of casein top coats. Due to its inadequate fixing properties and brittleness it should only be added in small amounts.

b. Solvent-soluble products

Are used as additional agents in solvent-soluble pigment preparations and as top coats. They give matt, semimatt or high-gloss effects and certain fastness or handle properties, depending on the type and formulation of product used.

Nitrocellulose lacquers

The basic product of these lacquers is nitrocellulose. It is manufactured from cellulose or cotton by nitration with a mixture of nitric acid and sulphuric acid. The cellulose nitrate has a nitrogen content of 12-13 %. The degree of nitration and the subsequent treatment determine the future behaviour of the product with respect to viscosity, solubility in organic solvents, filling effect, flexing endurance and elasticity. Highly viscous products give high elasticity and crack stability, but a low filling effect and low gloss. With low-viscosity products the opposite is true. Commercially available NC lacquers contain plasticizers, and possibly resins as well as solvents and diluents, for their intended application. Silicates, calcium, magnesium or zinc soaps are added for matt lacquer effects. The films of nitrocellulose lacquers possess a high fastness to alcohols. They are sensitive to prolonged exposure to light or heat, ultraviolet radiation and amine vapours which result in yellowing, decolouration or embrittlement of the films. This is naturally a particular disadvantage for white and pale leathers, and therefore plating temperatures exceeding 100 °C should be avoided. In order to prevent impaired adhesion of the films, nitrocellulose lacquer systems should be applied only to completely dry base coats and finishes.

- CAB lacquers** The film-forming product is cellulose aceto butyrate. Instead of nitration the cellulose is decomposed by means of acetic acid and butyric acid. Application and the film-forming properties of these products are similar to those of nitrocellulose. However, it is of advantage that they are absolutely stable to light, heat and amine vapours. Therefore they are very suitable as finishes for white leathers and upholstery leathers. Furthermore, the residues of these products are not inflammable. Like the NC lacquers they are available as high-gloss and matt products.
- Polyurethane lacquers** These are highly polymerized polyaddition compounds of polyether or polyester polyols and of aromatic or aliphatic polyisocyanates. Due to the cross-linking reactivity of these products, in particular the isocyanates, there are many possible combinations. Products having the most different film properties are obtained. A distinction is made between reactive and non-reactive polyurethane systems. The reactive systems in turn are subdivided into two-component and one-component systems. In two-component systems polyester or polyether polyols are mixed with precisely measured portions of isocyanate before application. The final reaction to form polyurethane occurs on the leather surface. If a thick coat is applied, a mirror-bright lacquer film is achieved. Films which are particularly resistant to scratching and soiling, often called easy-care finishes, are obtained if the products are sprayed in thin layers and in varied composition. Non-reactive one-component systems which have already been partially cross-linked during production are also used for this

purpose. After spraying them onto the leather they react with the moisture contained in the leather or in the air, or also with the amino groups of the leather substance.

In the case of two-component systems the pot life is an important factor. This means that the prepared solutions have to be processed within 24 hours as otherwise film formation and the properties of the film are impaired due to the final reaction in the product. High air humidity can reduce pot life because the hydroxyl groups of the water also react with the polyaddition compounds. For this reason the solvents used for the preparations should be free of water or not dilutable in water. With non-reactive one-component systems the pot life is increased to several days.

Compared to nitrocellulose lacquers the polyurethane lacquers give a more plastic-like surface handle if applied in thicker coats. They are much more favourable in terms of fastness to rubbing, fastness to ageing, elasticity and flexing endurance, especially in the cold. Lightfastness varies depending on the composition of the products. They have a negative influence on embossing properties, i.e. preserving of an embossed grain in the finish.

Further applications for polyurethane lacquers are coatings by direct or reversal process. With this method the polymer and the hardener solution are kept separate and mixed immediately before application. In another process, polyurethane film transfer finishes are applied to the leather surface by plating using adhesives and drawn off.

c. Products dilutable in water and solvents**Nitrocellulose emulsion lacquers**

They are available as *lacquer-in-water* emulsions and are easy to dilute with water. Compared to nitrocellulose lacquers they give a pleasing handle and have a low fire hazard. The use of expensive organic solvents becomes unnecessary. However, it should be noted that these products are not frost-resistant during transportation and storage. Water-miscible diluents should be used to regulate the rate of evaporation. The use of these lacquers depends on the absorbing and swelling capacity of the respective substrate. In general emulsion lacquers give less gloss than nitrocellulose lacquers. Matted emulsion lacquers or matting agents are used to influence the gloss for individual applications.

Emulsion bases

These exist in the *water-in-lacquer* phase and have not yet been emulsified. Their advantage is unlimited stability in storage and resistance to cold. Due to the very low water content in the base they are inflammable. When diluting with water the water should be added slowly in order to achieve reversal of phases into a *lacquer-in-water* emulsion without excessive formation of lacquer droplets. The films of the emulsion bases result in a very pleasing smooth handle. They can be readily diluted with organic solvents. This gives a higher gloss and improved fastness to wet rubbing than when diluted with water. The choice whether to use water or organic solvents for dilution depends on cost criteria or on the desired leather effect.

5. Grain impregnation agents

These products are employed to compensate the surface properties of leathers which have an excessive absorbing capacity or tend to develop loose grain. Such a treatment is required for buffed grain leathers, and especially for the so-called corrected grain side leathers. However, sensitive leathers are also impregnated. The products to be used for impregnation should penetrate adequately into the top layer of the leather and must not form a sealing film.

Oil ground impregnation

The products used are cationic oil emulsions applied alone or in combination with small-particle polyacrylates. The introduction of fatty substance further reduces the absorbing and swelling capacity of the leather, especially vegetably tanned or intensively retanned leathers. Migration of plasticizers and thus embrittlement of the subsequent finishing coats is largely inhibited. In order to prevent impaired adhesion of the finishes the oil emulsions should not be applied in excessive amounts.

Polymer impregnation

This is now the most common grain impregnation. The products used are small-particle polymer compounds, mainly polyacrylates which are adjusted to the correct depth of penetration by means of exact amounts of penetrators. They are applied either by curtain coater or the airless spraying method. The treated leathers are stored in stacks to promote an even distribution of the impregnating substances.

Polyurethane impregnation

Nowadays this method is used only in special cases. The products are polyurethane prepolymers in the organic solvent phase. They are deeply penetrative and result in an excellent firmness of grain, especially for extremely loose-grained leathers. A great disadvantage is strong hardening of the entire leather structure which in some cases causes problems in shoe production.

6. Base coating agents

Unless the skin has undergone a special pretreatment such as grain impregnation or application of a polishing ground, the base coating provides the base coat for all subsequent finishes and top coats. It serves several purposes:

1. Correction of varying absorbing capacity of the leather surface in the loosely or firmly structured sections of the skin.
2. Levelling fill effect in coarse or fine-pored sections of skin or in any sections of skin defects caused by urine or dung.
3. Adhesion promoter between leather surface and all subsequent finishes.

In general the base coat has softer and more elastic film properties than the subsequent coats (depending on the leathers to be produced).

For casein finishes

Boiled mucilage of seaweeds or vegetable seeds were formerly used. Carboxymethylcellulose was also used. Nowadays the preferred products are mainly film-forming polymer dispersions in combination with low quantities of casein and saponified wax emulsions. In most cases pad or spray coating is followed by a plating or polishing treatment.

For polymer finishes

The products used for these finishes are mainly softer polymer binders. Recently aqueous polyurethane dispersions with excellent adhesion promotion are also in use. Good adhesion of the base coat to the subsequent coats is a prerequisite for the quality of the entire finish. As the application of the base coat is mostly followed by plating or embossing of grain, saponified waxes are added in appropriate amounts to prevent the leather from adhering to the ironing or embossing

plates. More deeply penetrating binders are used for fine-pored leathers such as aniline and semianiline leathers which receive only small amounts of binders during finishing. The polishing grounds of such sorts of leather are often applied in very thin coats. For leathers which require coating finishes it is recommended that base coats with greater filling properties be used. In many cases combinations of polymers or aqueous polyurethane dispersions with casein binders or water-dilutable emulsion lacquers are also chosen as base coats.

The base coats for split leather finishes must have a high filling effect in film formation and at the same time an agglutinating effect for the loose velour fibres. Combinations of polyacrylates with butadiene or acrylonitrile binders and cross-linking polymers are also used.

Solvent finishes

Finishes of solvent-dilutable products from base to top coats are used for special leathers. They give finishes which are particularly resistant to swelling on exposure to increased moisture (tube leathers for camera bags, glove leathers for skiers and motor-cyclists or leathers for bicycle saddles). The base coating agents used for this purpose are soft nitrocellulose lacquers, but also polyamide or solvent-soluble polyurethane lacquers. A treatment with polymer binders or polyurethane dispersions is sufficient for grain leathers which are subject to normal wear and tear and which receive a solvent finish after base coating. It is important that the base coat dries completely as otherwise flow-out and adhesion of the top coat may be impaired by the residual moisture.

7. Top coating agents

Top coats are the final coats applied in the finishing process. They serve several purposes, depending on the type of leather:

1. Protection from soiling, moisture, solvents and abrasives as well as damage caused by impacts and scratching. Furthermore they should be resistant to heat up to 100 °C and cold up to -30 °C, if possible.
2. Imparting of the desired surface handle (dry, smooth, blunt, fatty, waxy or greasy).
3. Imparting of a matt or gloss effect with all possible intermediate stages.

Application of the top coating agents:

The products can be used alone or, if compatible, in combination according to the respective requirements. Except for patent leather the top coats should be sprayed in thin coats. However, they should not be sprayed too dry in order to ensure adequate film formation.

Casein products

The products used are non-thermoplastic binders such as milk casein, modified casein products, and blood and egg albumen. A distinction is made between hard and soft products. In general the harder products should be used for high-gloss top coats. Thorough fixation of casein-based top coats is required to achieve sufficient water-resistance.

Emulsion lacquers and emulsion bases

In most cases these products are applied in the water-diluted phase. Compared to solvent-diluted cellulose products they give the leather a pleasing handle. Dyed products are used for black leathers to avoid gray fog and to achieve a brilliant black shade.

**Nitrocellulose
and
CAB lacquers**

Top coats on the basis of nitrocellulose lacquers are used less frequently. The cellulose aceto butyrate lacquers, which are more expensive but not inflammable and provide better fastness to amines and light, are now increasingly employed. Both groups of products should never be applied as top coats on pure casein finishes because the casein films are not solubilized and adhesion is therefore not sufficient.

**Polyurethane
products**

Besides the solvent-soluble polyurethane lacquers, which are employed for production of mirror-bright patent leather and for easy-care finishes, the water-diluble one-component polyurethane dispersions are becoming more popular. These top coats are water-resistant, fast to ageing and do not require additional fixation. Combined application is possible to improve the handle and fastness properties of the solvent-soluble or water-diluble nitrocellulose lacquers.

**Polyamide
lacquers**

Polyamides are polymerized or polycondensed amino acids (textile raw material for Nylon, Perlon). Copolymers, which are soluble in mixtures of alcohols and hydrocarbons, are obtained by additional condensation with dicarboxylic acids and diamines. In the leather industry they are used alone or with nitrocellulose lacquers. Such top coats increase water-resistance, improve flexing endurance and fastness to rubbing. Furthermore they inhibit migration of brightening dyes, avoid damage to the finish during spraying of plastic soles in shoe production and improve the lightfastness of dyeings.

8. Plasticizers

Varying amounts of plasticizing substances should be added to the finishing floats depending on the flexibility of the leathers, the film hardness of the binders used and the thickness of the finish coats. They are employed to increase the stretchiness and elasticity of the respective binder coats and prevent embrittlement of the entire finish during storage and during use of the final leather products.

Different types of plasticizers are required for aqueous or solvent-soluble finishing agents.

a. Products for water-soluble finishing agents

Sulphated castor oil This is also called Turkey red oil. As it has additional wetting properties excessive amounts should be avoided to prevent impaired fastness properties of the finish.

Higher molecular alcohols The derivatives of polyglycols, glycolether, glycerol or their esters are the mainly used products.

Wax emulsions These give the films additional fullness and elasticity and reduce tackiness during plating. They should not be used in large amounts as otherwise the coats become extremely water-repellent (may result in impaired adhesion).

b. Products for solvent finishes (non gelatinizing)

Vegetable oils The most commonly used product is castor oil, less frequently rape oil. They are only loosely deposited in nitrocellulose films. Therefore it is advisable to apply them in combination with synthetic plasticizers.

c. Products for solvent finishes (gelatinizing)

Synthetic plasticizer oils These are mainly esterification products of the phthalic and adipic acid. They have a solubilizing effect on nitrocellulose and polymers.

Camphor This is a ketone in a crystallized form. Besides having a plasticizing effect it improves the glazing properties of nitrocellulose lacquers.

9. Finishing auxiliaries

Antisticking agents

The leather surface may become tacky as a result of film formation by heat treatment, especially when using soft polymers. This causes sticking of the leathers to the ironing or embossing plates and tackiness during piling on trestles. Apart from the additional work required to remove the leathers from the plates or cylinders or to pull the leathers apart, the finishes may also be damaged. Furthermore there is a risk of soiling by adhesion of dust and fibre particles.

Tackiness can be reduced or eliminated by adding antisticking agents. The products used for this purpose are wax or paraffine emulsions, non-thermoplastic binders, polyurethane dispersions or the addition of emulsion lacquers. Silicone oils also have a high antisticking effect. However, their use is not recommended as adhesion of the subsequent finishes may be impaired.

Defoamers

Strong foaming may develop especially during curtain coating because of the constant recirculation of the finishing floats. As a consequence many air bubbles are trapped in the finish film and make an even film formation impossible. Furthermore, smooth running of the curtain is disturbed which may result in complete tearing of the curtain. Foaming can be prevented by adding alcohol, ethyl glycol, emulsion lacquers or by using stable binding agents. If foaming does not disappear it is recommended that the circulation rate of the feed pump be reduced.

Fixing agents

Finishes on the basis of albumen binders have no adequate water-resistance and therefore require additional fixation. Formaldehyde is still the most commonly used product. It is mostly applied as a 5 - 10 % solution and sprayed onto the slightly dried casein binder coat. With polyamide-modified casein binders the formaldehyde solution may also be added directly to the ground or top coating float without causing flocculation. Additions of acetic acid and/or chromium(III) salts improve the fixing effect, however they are not compatible with the modified casein binders.

In view of ecological requirements and the often unpleasant odour of formaldehyde, modified melamine compounds are also in use. For effective fixation they require a minimum temperature of 175 °C. Glutaraldehyde can also be used, however it is not suitable for white and pale leathers as it results in yellowing.

Filling agents

Mainly employed for splits and buffed grain leathers. Products on the basis of wax emulsion and albumen binders containing fillers such as talcum, caoline, silicic acid derivatives or bentonite are used. Besides their filling effect and the concealing of defects they provide a smooth and well settled surface appearance.

Modifiers

These products give the leather the desired surface handle. A variety of finishes can be achieved such as smooth, blunt, slippery, supple, dry, waxy, greasy or fatty. They are added to the top coats or mostly applied as separate top coats.

Matting agents

Besides the desired matt effect these products provide fullness, settled surface appearance, smooth handle and reduced tackiness of the finish coats. They are available both for aqueous and organically dissolved finishing systems.

Optical brighteners

Are used to improve the white effect in the finish of white leathers. The effect of these products is based on conversion of invisible short-wave light into visible long-wave light. They are applied in aqueous finishes and top coats. They have no effect in organically dissolved finishing agents.

Penetrators

Mainly used for grain impregnations and base coatings to achieve deeper penetration of the finishing agents below the grain layer. These products are water-miscible organic solvents and/or capillary-active substances. The necessary quantity of penetrators should be determined exactly by means of preliminary tests as the penetrative effect is reduced if they are applied in excessive amounts. Furthermore, they may cause undesired swelling of the fibres and excessive sensitivity to moisture because of their extreme wetting effect.

Polishing agents

These are used to achieve fashionable light/dark contrast effects and a smooth, glossy surface, or also as a polishing ground for aniline and pull-up finishes. They contain mainly modified synthetic or natural wax or oil emulsions and often additions of silicone polymer emulsions as well as casein binders or polyurethane dispersions.

- Flow improvers** Many leathers have a closed surface with high interfacial tension due to fatty substances, water-repellent agents, vacuum and paste drying; this can cause wetting problems during finishing. However, it may also occur with sealing base and top coats, especially if applied in spray and curtain coats without mechanical rubbing. Uneven wetting produces dark zones or drops in the affected sections and results in an uneven finish. This can be remedied by adding flow improvers to the finishing agents. These consist of surface-active, foamless wetting agents on the basis of fatty alkyl sulphates, paraffin or alkylarene sulphonates or esters of sulpho succinic acid. The required amount should be determined carefully to avoid impaired fastness properties of the finish.
- Cross-linking agents and hardeners** Polyisocyanates are used to harden polyurethanes. The film is formed by a cross-linking reaction. Products based on polyfunctional aziridine compounds have a cross-linking effect on dispersion binders. When added in small amounts to the finishing floats, they clearly improve the properties of the finish, especially the fastness to wetting. As they are highly reactive, the relevant safety regulations should be observed when using these products.
- Thickeners** Finishing preparations of higher viscosity are required for splits and buffed grain leathers, or for curtain coats or spray coats applied by the airless method in order to prevent excessive absorption into the leather. The products used are binders which can be thickened by means of ammonia or highly viscous polyvinyl ether compounds.

10. Organic solvents and diluents

Products based on nitrocellulose, cellulose aceto butyrate and polyurethanes require the use of organic solvents. In addition, non-dissolving thinners are used as low-price extenders and also to regulate the rate of evaporation. This does not apply to reactive lacquer components as these must be used only with water-free solvents which are free from hydroxyl or amino groups.

Correct adjustment of the rate of evaporation is essential for these solutions. The rate of evaporation must not be too high and not too low because this will impair proper film formation, gloss, adhesion or flow out. The mixture of solvents with diluents should also be carefully matched.

a. Solvents

Esters	Methyl acetate, ethyl acetate, propyl acetate, butyl and isobutyl acetate, methoxypropyl acetate, amyl acetate.
Ketones	Acetone, methyl ethyl ketone, methylisobutyl ketone, butyl ketone, diisobutyl ketone, anone, cyclohexanone, methylanone, 2-ethyl hexanol.
Ether alcohols	Methoxyethanol, ethoxyethanol, butoxyethanol, 2-isopropoxyethanol, ethylene glycol, methyl-digol, butyldigol.
Ether alcohol ester	Methoxyethyl acetate, ethoxyethyl acetate, butoxyethyl acetate.

b. Diluents

Alcohols	Ethanol, propanol, isobutyl alcohol and n-butanol, diacetone alcohol, benzyl alcohol.
Aromatic hydrocarbons	Toluene, xylene, white spirit, decalin, tetralin. In some countries they are no longer permitted because of ecological aspects.

Information about boiling range and rate of evaporation should be taken from the suppliers' charts.

General composition of finishing floats

(To be used only for orientation as most types of leather have to receive a finish which is matched to the individual requirements).

Spray staining	100 - 200 parts metal complex dyestuff-liquid 0 - 200 parts water- miscible solvent (ethoxyethanol, isopropanol) 900 - 600 parts water														
Grain impregnation	250 parts impregnation binder 50 parts penetrator 0 - 100 parts liquid brightening dye 700 - 600 parts water														
Base coat	<table><tr><td><i>Grain leather</i></td><td><i>Corrected grain</i></td></tr><tr><td>30 - 50 parts pigment colours</td><td>50 - 100 parts</td></tr><tr><td>100 - 150 parts polymer binders</td><td>150 - 250 parts</td></tr><tr><td>10 - 30 parts casein binders</td><td>20 - 50 parts</td></tr><tr><td>860 - 770 parts water</td><td>780 - 600 parts</td></tr></table>	<i>Grain leather</i>	<i>Corrected grain</i>	30 - 50 parts pigment colours	50 - 100 parts	100 - 150 parts polymer binders	150 - 250 parts	10 - 30 parts casein binders	20 - 50 parts	860 - 770 parts water	780 - 600 parts				
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Fixation	300 parts formaldehyde (30 %) 650 parts water 0 - 50 parts acetic acid (6 °Bé)														
Top coats	<table><tr><td><i>Casein basis</i> 150 - 300 parts casein binders 5 - 20 parts plasticizers 680 - 850 parts water</td></tr><tr><td><i>Emulsion lacquer</i> 600 - 900 parts emulsion lacquer 100 - 300 parts water 0 - 100 parts formaldehyde 30 %</td></tr><tr><td><i>Nitrocellulose lacquer or CAB-lacquer</i> 0 - 50 parts pigment colours 200 - 300 parts gloss/matt lacquer 10 - 20 parts plasticizer 630 - 790 parts solvent</td></tr><tr><td><i>Polyurethane lacquer for patent leather (after application of a special base coat):</i> 100 parts polyurethane lacquer component 120 - 150 parts water-free organic solvent 30 - 60 parts cross-linking agent</td></tr></table>	<i>Casein basis</i> 150 - 300 parts casein binders 5 - 20 parts plasticizers 680 - 850 parts water	<i>Emulsion lacquer</i> 600 - 900 parts emulsion lacquer 100 - 300 parts water 0 - 100 parts formaldehyde 30 %	<i>Nitrocellulose lacquer or CAB-lacquer</i> 0 - 50 parts pigment colours 200 - 300 parts gloss/matt lacquer 10 - 20 parts plasticizer 630 - 790 parts solvent	<i>Polyurethane lacquer for patent leather (after application of a special base coat):</i> 100 parts polyurethane lacquer component 120 - 150 parts water-free organic solvent 30 - 60 parts cross-linking agent										
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Application of finishes

Padding, brushing, sponging

The chief method for application of base coating floats is manual padding by means of the plush board or mechanical padding by means of the plush belt. Hair brushes or brushing machines are in use for split or coarse-fibred leathers. Fell-covered rollers are mostly employed for grain impregnation. In the case of reptile leathers albumen top coats are applied by sponging to achieve a particularly high gloss.

Spraying

It is the most common method and is applied by means of compressed air. It is suitable for applying aqueous and solvent-containing finishing floats. This is done by means of manual spraying guns in spraying cabins with exhausters or by means of automatic spraying guns on continuous spraying belts. These work either in horizontal to-and-fro movement or by a rotary principle. 2 - 10 spraying guns are interconnected to achieve an even, well settled surface appearance and to increase the through-feed rate of the leathers. The required amount of finishing agent can be regulated by means of the belt speed (8-18 m/min), the spraying pressure (2-5 bar) and the nozzle opening of the spraying guns (1.5-3 mm).

An alternative method is spraying without compressed air, called *airless spraying method*. The finishing liquor is pressed through a very fine nozzle by means of pneumatic pressure (80-120 bar) and sprayed onto the leather without admixture of air. As there is no atomization by air, spraying is much wetter in this method and the loss of colour is reduced compared to spraying by means of compressed air.

Curtain coating The curtain coating float is poured onto the leather being fed through the machine through a slot in the head or by means of an overflow system. The unspent float flows back into the supply tank and is continuously recirculated. To ensure an even flow of the curtain it is important that the float be free from foam bubbles and possess adequate viscosity so that it does not break off abruptly due to air whirls or trapped air. For aqueous floats the average viscosity is 17-25 DIN seconds (measured with the DIN flow cup no. 4). The required quantity of float is regulated by the belt speed (about 30-40 m per minute) and the height of fall (about 20-25 cm). Furthermore, the leathers should be placed onto the belt free of creases to avoid so-called shadows. In view of the increased thickness of coat thorough drying should be ensured. The drying section must not be too short and the drying temperature not too high. As the polyurethane lacquer coats are very thick and need more time for complete drying it should be ensured that drying takes place in an absolutely dust-free environment.

Padding Method to achieve high gloss or a mostly dark contrast colour on raised sections of embossed grain leathers. This is done manually with a sponge, a folded cloth, cleaning wool or cotton wool covered with a permeable cloth. The pad is first dipped into a lacquer or dye solution and then lightly wiped over the raised parts.

This serves to achieve two-colour effects and high-gloss or matt effects.

A former variant consisted in applying wax coats onto the raised parts of embossed grain leathers. The recessed parts were dyed in dark shades by spraying with black dye solutions. After removing the wax coat with a cloth soaked in benzine a reversed two-colour effect had been achieved (was called antique finish).

Printing

Several methods are possible. One method is performed with negative stencils, i.e. the sections to be printed remain free on the stencil. The stencil is placed onto the leather and a finish paste is pressed through the openings by means of a doctor blade. After removing the screen box the pattern is visible on the leather. Multicolour printing is possible by placing several stencils on top of each other. Instead of the finish paste, colourless binders can be applied by means of the doctor blade and then sprinkled with textile flakes. This produces velvety, raised patterns.

A method which has increasingly been used in the last years is screen printing on printing machines by means of calender rolls⁵³. To ensure a perfect printing process the leather should not be too thin and of uniform thickness so that it is fed into the printing machine without creases. There are two printing methods. In the direct method the printing colour is carried in the recessed, engraved printing surface of the print roll and printed onto the leather. In the offset or high-pressure method the colour is carried on the tips of the engravings and then applied.

With the indirect method the colour is transferred from the screen roll to a rubber roll and from there onto the leather. This method is very suitable for uniform printing, that is, for top coats, lacquer emulsions or pigment finishes. The printing method results in a reduced loss of colour compared to spraying.

Laminating

A ready-made finish film which is on a carrier foil is applied to the leather surface. For this purpose an adhesive, mostly a polymer binder, is sprayed onto the foil and this side of the foil is placed smoothly onto the leather. It is then plated at about 80 °C, after which the carrier foil is drawn off. Uni-colour laminating or any effect is possible by this method.

Firm polyvinyl chloride foils can also be applied. As the foil is about 0.2 mm thick this method is classified as coating.

Coating

Two-component polyurethane starting material is applied to split or buffed grain leathers by means of special coating machines. The cross-linking agent and the polymer are mixed together directly before use and applied onto the leather on stencils or foils. The films obtained are highly resistant and very suitable for football leather, for example. The use of expanding agents is also very common. Due to the formation of polyurethane foam they provide particularly good films which have high flexing endurance and bending elasticity. The firmness properties can be improved by inserting fleece or textiles between the polyurethane coat and the leather.

Drying of finishes

It is essential that a proper drying method be selected and employed after application of the finishing floats. The importance of this process is often underestimated and it is not performed correctly for reasons of time. This results in defects in the finishes and also on the leather. Drying is required each time a finish coat has been applied.

Airing off: The leathers are suspended or hanging on bars at ambient temperature or in slightly heated rooms, mostly without movement of air. This is a gentle method without risk of overdrying.

Through-feed hang-drying or horizontal drying:

The drying temperature is 60-80 °C in the middle of the drying section and lower in the feed-in and discharge areas. Adequate air exhaustion should be ensured to remove the air saturated with humidity.

First application of base coats	To achieve an even penetration of the base coating float it is important that the leathers have a uniform residual moisture content all over the surface. Uneven drying results in a different degree of swelling of the fibre surface and thus in loose grain, wrinkled grain or impaired adhesion.
Inadequate drying	Results in abrasion of coats which have previously been applied by padding or brushing, and thus in unlevelness. In subsequent nitrocellulose finishes it causes impaired adhesion and/or greying.
Overdrying at excessive temperature	Results in a top coat that is hardly wettable and causes formation of streaks or droplets and adhesion problems. Residual moisture increases the tackiness of films of thermoplastic binders. Films of albumen binders may become brittle. Furthermore, fatty substances and plasticizers may migrate into the outer finish layers.

Requirements to be met by leather finishes and testing**Abrasion properties of finish coats**

The surface of the final leather products is subject to the most different kinds of stress in everyday use. In order to determine optimum properties of the finish coats with regard to their fastness to erasing abrasion, reference tests are performed with standardized rubber test specimens. The degree of damage of the wet and dry leather and the change of colour of the finish are assessed. This is an additional test of the fastness to dry and wet rubbing besides the fastness test with felt pads.

Resistance to detergents, cleansing agents and shoe polishes

In shoe fabrication the leathers are particularly soiled through mechanical processing or by contact with dust, oil, perspiration or fatty substances. Therefore they have to be cleaned or wiped with a variety of agents. As they have received different types of finishes, it is necessary to determine by means of preliminary testing with test solutions which product is suitable to prevent defects or changes of colour. The test solutions are neutral cleaning agents, weak alkali solutions or benzine. The suitable shoe polish is determined by three basic types of product: products based on oil, emulsions and aqueous products (see also Care of Leather).

Resistance to amines (DABCO)

The finish of furniture leathers upholstered with polyurethane foam, but also of shoe upper leathers manufactured with mould-on polyurethane soles, can be damaged by the escape of gaseous 1,4-diazabicyclo(2,2,2)octane = triethylene diamine (abbreviated as DABCO). This causes cracking of the film, especially with nitrocellulose finishes, and results in yellowing of white and pale leathers.

Polyurethane finishes or films of cellulose acetate butyrate and albumen binders are stable to DABCO vapours.

Resistance to ageing⁵⁴

A change of the finish due to ageing is mainly indicated by embrittlement of the film. This is mostly caused by migration of plasticizers from the pigment coat into the interior of the leathers. In a quick reference test the leather is stored in the drying oven for several days at different temperatures (50 and 80 °C). After conditioning, the leather samples are assessed as regards embrittlement, yellowing, elasticity and flexing endurance of the finish films.

**Fastness to hot ironing,
resistance to hot air**

To process finished leather it is important to know which maximum temperature is admissible for subsequent ironing or lasting without causing damage to the finish. The test is performed by means of a hot iron or ironing machine and with temperatures increasing in increments of 20-25 °C in order to assess smearing, damaging or change of shade of the finish.

The resistance of the top coat to hot air is tested by means of a hot air current. The initial temperature is 210 °C. If changes occur, further tests are performed with temperatures reduced in increments of 20 °C respectively.

Fastness to hot steaming

This test serves to determine the fastness of the top coats to hot steam, to which the leather in shoe production is exposed before lasting. The leather sample is laid into a test chamber saturated with steam for 5 minutes at 65 °C. Swelling of the finish coat or migration of dye is assessed.

**Elasticity
endurance**

If leather is stretched, extended or deformed by bulging the finish should be so elastic that it does not tear or crack off.

A quick reference test is performed by means of a key or a mandrel. These are drawn with pressure along the unfinished side of the leather to cause stretching and bulging of the leather. The finish is assessed for flaking or cracking.

In the lastometer test a sharp mandrel is pressed upwards to determine the "bulging height". In the tensometer test a larger section of leather is stretched over a diaphragm to form a spherical cap. This also serves to test whether the finish flakes or cracks off.

**Adhesion
(dry and wet)**

Correct adhesion of the finish coats to the leather is essential for further processing and the utility value of the materials. It depends on the absorption properties of the leather surface and the degree of penetration of the finishing floats, which is determined by their composition. Adhesion is further influenced by the type of mechanical application and by the drying and processing methods. The adhesion of the finish coat is tested by a quick reference test in which adhesive tape is applied to the leather specimen and stripped off. A quantitative measurement of adhesion is performed in the tensile strength tester. The leather specimens are glued onto a firm supporting surface by means of a two-component adhesive and stripped off after a specified time. To test wet adhesion the leather specimens are only moistened after hardening of the adhesive.

Resistance to cold

Cold may cause crackiness or flaking of finish coats, especially if thermoplastic binders of low cold resistance are used and if the finishes were applied in thick coats. This can also occur during transportation of shoes in cardboard boxes in the cold season.

The test is performed with strips of leather and at temperatures which are reduced in increments of 5°C. The test is started with a temperature of 5 °C and terminated at -20 °C. Each time the respective temperature has been achieved the strip of leather is pressed between two movable rollers and checked for cracks. A correctly applied finish should be resistant to cold at -15 °C.

Resistance to flexing endurance

Especially shoe upper leather is subject to continuous flexing in the walking creases of the vamp. Therefore it is particularly important to use finishes with high flexing endurance to ensure long-time usage.

The test is carried out in the Bally flexometer by continuously flexing the leather specimens over a fixing clamp through an angle of 22.5 degrees. This test is performed on the dry or wet leather until the finish becomes visibly damaged. The leather specimen is examined at intervals of 1000 or 10000, often up to 50000 or 100000 flexings. Cracks, complete breackthrough, peeling, flaking, powdering, greying or change of shade are assessed. Changes of the grain such as loose or pipey grain, loss of an embossed grain pattern or breaking of the entire leather are also assessed.

**Scratch
resistance**

The test is performed by means of the VESLIC rub fastness tester with abrasive paper which is rubbed back and forth along the leather under a specified load. All finishes will exhibit damage in this test. Therefore its reliability is restricted. Basically, polyurethane films are more resistant to scratching than other finishes.

Lightfastness

In general, lightfastness is determined by the leather undersurface. The thickness of coat, the binders and finishing auxiliaries used, top coats and amount of covering pigments are decisive for good lightfastness of the finished leathers. Nitrocellulose films or finishes having a high content of butadiene binders are prone to yellow on exposure to light. Highly covering inorganic pigments and an adequate thickness of coat often improve poor lightfastness properties of the leather. (See also "Requirements to be met by leather dyes".)

**Resistance to
solvents**

During processing the leather is often in contact with organic solvents or adhesives and stiffening caps containing solvents, or it is penetrated by these from the unfinished side. This often results in a softening or solubilizing of the finish films. For the test a specified amount of the respective solvent is dripped onto the unfinished side of the leather. After a short time of exposure the leather specimen is rubbed with a dry or wet felt by means of the SATRA or VESLIC rub fastness tester under a specified load and with an increasing number of rub cycles. The finish coat is assessed for swelling, softening or smearing.

Fastness to migration

Organic brightening dyes, fat-soluble dyes and small-particle organic pigments may cause staining by migration if they are in direct contact with plasticized accompanying substances (upper leather/plastic soles, pale patent leathers/coloured upper or lining leather).

To test the fastness to migration a plasticized, white pigmented PVC foil is laid on the leather surface. This specimen is stored under load in an oven at 50°C for 16 hours. Migration of dye into the foil is assessed by means of the grey scale. (See also "Requirements to be met by leather dyes".)

Polishability

Glazed leathers with a casein-based finish may be particularly affected by matt or blind stains caused by water after drying. The stains should disappear after polishing with a dry cloth or with a shoe polish.

For the test a drop of water is applied to the finished leather surface and allowed to evaporate overnight at room temperature. The formation of edges, swelling stains or matt sections and the intensity of polishability are assessed.

Fastness to rubbing (dry and wet)

The finished leather surface should be largely fast to dry or wet rubbing.

A quick reference test is carried out by rubbing the leather with a white cloth under the pressure of a finger.

Reliable tests are performed with the SATRA or VESLIC rub fastness tester. The abrasion properties are tested by rubbing a dry or wet felt pad or standardized cotton fabric back and forth or by rotation, under a specified load and

with a specified number of movements. The degree of damage or the change of the top coat, the staining of the felt pads and the change in colour of the test specimen are assessed.

Resistance to edge abrasion

Serves to test the resistance of the leather surface to damage caused by blunt edges, especially by metal parts of the leather articles. The abradant consists of a metal bar of hardened steel.

Resistance to swelling by the action of water

Finished leathers should be adequately resistant to the action of water. Drenching by rain or snow water must not cause a swelling of the finish coat, water drops must not result in the formation of warts.

In a quick reference test the leather specimen is immersed in water and subsequently rubbed with a dry cloth. Comparison tests are carried out by means of the VESLIC rub fastness tester. The drenched leather is rubbed back and forth with a dry felt under load. Evaluation as in the dry and wet rub fastness tests.

Yellowing on heat

Yellowing of the finish coat of white or pale leathers can be caused not only by light, but also by storage in the dark under the action of heat. Besides heat, yellowing and brown coloration of nitrocellulose films can also be caused by migration of fatty substances or plasticizers. For the test a leather specimen is stored in the oven at 50 °C for three days. This sample is compared with an untreated leather specimen. Yellowing or change of shade is assessed by means of the grey scale.

Flesh side finishes

These finishes are applied mainly to leathers of which the flesh side is visible in the final product. They serve to protect the leather against mechanical influence and soiling or against the action of moisture. A protective finish is often applied to dyed shoe upper leathers which have no lining to avoid staining of socks or stockings by perspiration. Furthermore, an improved appearance of the flesh side has the purpose of promoting the sales value of the leathers.

Top coats based on:

Binders	The products used are thermoplastic binders containing colourless, coloured or pigmented components. Polyamides are used to increase fastness to perspiration.
Mucilage	Now rarely used since the more elastic thermoplastic binders give better results. The products used are carragheen moss, mucilage of seaweed, tragacanth, linseed, starch, dextrine or methyl cellulose.
Fatty substances or waxes	They are applied as creamy paste and contain neatsfoot oil, bone oil, linseed oil, degreas, talcum, stearin, paraffin, ceresin, beeswax, carnauba wax, montan waxes or synthetic waxes. They are mostly used because of their gloss effect. Employed only seldom these days.
Resins and filling substances	The resins used are colophony, shellac and the filling substances kaolin or talcum. Used mostly as additives.
Proteins	Formerly, large amounts of blood albumin and egg albumin were used. The chief product today is casein which is obtained from skimmed milk. Gelatine and glue are added in appropriate quantities. These top coats give the leathers a glossy finish.

Lustre treatment of suéde and nubuk leathers

Many suéde and nubuk leathers are submitted to a final surface treatment with special top coating agents, the so-called lustres. This treatment serves to increase the utility value of the leathers, to give the leather special handle properties, to improve colour fastness and to level or correct the shade.

The lustres are mainly applied by spraying to ensure a uniform dosage. The products to be applied can be diluted in three different ways:

1. in an aqueous base
2. in a water/solvent mixture
3. in the solvent phase only

These lustres may be classified according to the properties to be achieved.

Levelling or correction of shade

Dyes or shades or also stained patches can be corrected to a large extent by means of pigment dyes having a low content of binders. The binders are necessary to avoid powdering of the pigments. The amounts to be applied for each type of leather should be determined exactly because the fibres mostly stick together if excessive amounts, especially polymer binders, are used. To avoid hardening by an increased content of dry substances of these lustres, plasticizers such as fatty substances, oils or waxes are added. Small amounts of penetrators or cross-linking agents can be added to regulate the depth of penetration of aqueous lustres. Very even lustre finishes, also dye effects, can be achieved by means of printing machines.

**Increase of
brilliance and
depth of shade**

The colouring components used for such lustres are commercially available aniline colours or colour lakes with selected good fastness properties or organic pigment preparations of very fine particles. In many cases colourless lustres also result in a deepening of shade or enhanced brilliance solely because of their content of fat, oil or binder. This effect is caused by a changed refraction of light.

**Improvement of
colour fastness**

All suède and nubuk leathers, especially if they have been rebuffed after dyeing, will cause a greater or lesser amount of staining when rubbed in the dry condition. This is due to the existence of very fine particles of dyestuff dust or residues of dyed fibres which remain on the surface even after thorough dedusting, brushing or dry milling. In such cases a lustre is applied to bind the dust. Its main components are polymer binders of very fine particles which should be as soft as possible. When using these products it is particularly important to ensure that the fibres do not stick together or harden as a result of excessive film formation. In many cases the improvement of colour fastness is insignificant. Better results are often achieved with lustres based on nitrocellulose lacquers in the solvent phase with an addition of linseed oil or castor oil. The use of dust-binding lustres is not recommended for garment leathers so as not to impair the handle properties. Should problems arise with these leathers it is recommended that they be briefly resoaked, washed and redried.

**Improvement
of
surface handle**

Lustres are chosen which improve the surface handle or give a special effect such as a semimatt finish, two-way nap or fatty handle.

The products used are anionic and/or cationic fat mixtures which are exactly matched to each other. Additions of unsulphated fats, oils or also waxes contribute to a variation of the desired effect. In these mixtures of increased fat content it is important to avoid greasiness of the fibre surface.

**Improvement
of water fastness**

These lustres have the function of reducing increased wettability of the leathers. The products used are commercially available water-repellent agents on the basis of chromium stearate, fluorostearate, silicones, polymer products having a fatliquoring effect, paraffin emulsions or modified polyurethane solutions.

Except if used for special effects all lustre treatments should be considered only as final "cosmetic" treatments. Basically, the desired effect should be achieved already during processing in the drum as far as this is possible. In this way a negative change of the handle properties by treating the surface with excessive amounts of lustres is avoided.

Mechanical finishing methods

The described methods are "grain-forming" operations carried out mechanically during finishing. They transform the finish layer into a film, give more or less gloss, smooth the grain, reduce or conceal grain defects and change the grain appearance by the application of an artificial pore grain of the desired kind of animal or of fancy grains which are available on the market in a great variety of designs.

Grain-forming operations

Plating

Plating was formerly done by hand by means of a flat iron weighing 10 - 20 kg. Sometimes this method is still used now, but in general plating is performed by means of:

1. *Spindle plating machines* (Altera type)

The individual leather webs are pressed towards the hot plate by means of rollers.

2. *Hydraulic plating press*

The individual leather webs are pressed towards the plating contact surface in a stationary pressing process.

3. *Cylinder plating machines* (calender type)

Used for continuous through-feed operation by means of conveyor belts.

4. *Running out cylinder plating machines* (Finiflex type)

The cylinder diameter is smaller than on calender machines, however it has a scouring effect and higher temperature range.

On all machines the desired plating effect and film formation are influenced by the temperature and time of contact with the plating surface as well as by the pressure.

Graining

The same machines of group 2 and group 3 as used for plating are used. A steel plate engraved with the desired grain is used instead of the ironing plate.

During the pressing operation it is important that each web constantly follows the preceding one to prevent blanks or double graining. As with plating, the leathers must be placed on the operating table without creases. The durability of the graining on the leather is influenced by the temperature, pressure and time of embossing. Vegetably-synthetically tanned leathers keep the embossed grain much better than chrome-tanned leathers. In these leathers the graining effect may be improved by a more intensive vegetable-synthetic retanning or by wetting the leathers.

Glazing

Carried out on oscillating glazing machines by means of a glass or agate roller which is pushed with frictional pressure over the leather in narrow widths and rapid sequence. Vegetably tanned leathers or leathers which have been finished with a non-thermoplastic top coat are given an intense high gloss which accentuates the natural appearance of grain. The leathers should be of uniform thickness to obtain a perfect appearance of grain. They should not be overfatliquored in the outer zones to avoid blind sections caused by smearing. Glazing is used especially for high-quality chevreaux, calf and box side leathers.

A variation of the described glazing machine is the *plating-glazing machine* (Drees type). This machine has a heatable pointed iron instead of the glass or agate roller. It provides a higher gloss than the plating machines, but not the same gloss effect as glazing machines. The advantage of this machine is that it has a somewhat broader glazing width and gives a more gentle surface handle because compressing of the leather is less severe by this treatment.

Boarding

Unlike plating and glazing, boarding causes a typical cracking of creases in the grain surface. Traditional boarding was a very hard manual work using a boarding board. The leathers were placed on a working table with the grain side on the inside and were squeezed by powerful rolling movements of the boarding board in longitudinal, transverse and diagonal direction. Depending on how often the direction is changed, this method produces a grain with crossing lines up to a pointed grain - the typical characteristic of so-called saffian leathers which are used for fancy leather products. Boarding machines are meanwhile available for this operation. Two contra-rotating cork rollers move the leather over a steel sheet tongue so that it is grained. Besides imparting a characteristic grain, the softness of the leathers is improved at the same time.

Rubbing off polishing

This operation is a variant of normal polishing. A hard brush cylinder or a so-called buffing wheel cylinder (cloth disks arranged close to each other, which are sometimes impregnated with hard wax to achieve the desired effect) is used instead of the stone polishing cylinder. This method is used to give the leathers a two-tone effect, an antique effect or a semimatt waxy gloss.

Finishing defects

Defects of the finishing products

- | | |
|-----------------------------|--|
| Sedimentation | <p><i>Causes:</i> Pigment finishes, lacquer emulsions and mixed finishing products are multi-component systems with different specific weights of the single components. During storage the components having a high specific weight sediment and stick firmly together.</p> <p><i>Remedy:</i> Basically, the products should be thoroughly stirred in the containers before use. Failure to do so results in a greatly varying concentration. This leads to a variable content of solids in the finishing floats and to a more or less significant difference in shade in pigment finishes. In the case of binders, film formation is impaired which reduces the fastness properties.</p> |
| Separation of layers | <p><i>Causes:</i> Mixed products containing components with different charges and emulsified systems can break and result in phase separation into two or more layers.</p> <p><i>Remedy:</i> The products should be stirred well in the containers before use. Absolute homogeneity of the product is important, otherwise it should not be used.</p> |
| Coagulation | <p><i>Causes:</i> Finishing products on an aqueous basis and especially thermoplastic binders are susceptible to the cold. Irreversible coagulation is caused by frost. Damaged products cannot be used any more and should be disposed of.</p> <p><i>Remedy:</i> It is absolutely necessary to protect the products against cold during transportation and storage.</p> |

Foul smell

Causes: Finishing products containing casein are particularly affected by heat and bacterial attack and are subject to decomposition. The products become completely unusable, depending on how long they were exposed. With the beginning of decomposition a disagreeable odour develops and turns into a strong foul smell. In this case the product cannot be used any more.

Remedy: The products should be stored in cool rooms or cooling chambers, especially in hot climates. Short-term storage is recommended for these products.

Change of pH value

Causes: When using nitrocellulose lacquer emulsions, acids may be eliminated by saponification in the presence of ester-based solvents and water. This reduces the pH value in the product and makes the emulsion instable. This results in cracking or the formation of water-insoluble lacquer droplets which produce annoying glossy dots in the film.

Remedy: The fineness of emulsion can be restored by adding some drops of ammonia and thorough mixing. It is recommended that the product be passed through a fine-meshed sieve.

Varying content of solid substances

Causes: The finishing products are supplied in specified concentrations. In certain exceptional cases the products may contain less amounts of solid substances than specified due to different raw materials or fluctuations in production.

Remedy: If the finishing results vary, the content of solid substances should be checked from time to time.

Defects of the finishing floats

- Agglomeration** *Causes:* Inadequately ground pigment colours may agglomerate in the finishing float and thus reduce the intensity of colour and result in dull shades. These agglomerates may also impair film formation and reduce the fastness properties of the finish.
Remedy: Use well dispersed, well-ground pigments from specialized suppliers.
- Flocculation** *Causes:* Flocculation may occur in finishing floats if using brightening colours with a high content of extenders or in binder mixtures which have little resistance to electrolytes.
Remedy: Use liquid dyes which have a low content of neutral salts and binders which are stable to electrolytes.
- Pigment suspensions and separations** *Causes:* If diluted pigment preparations contain inorganic and organic pigments quick separation in the float may occur. In particular very fine carbon-black pigments may rise, whereas heavy pigments separate down to the bottom of the vessel. This results in a change of shade or uneven finishes.
Remedy: Frequent stirring of these floats is absolutely necessary.
- Incrustation** *Causes:* If finishing floats are stored in open vessels for some time, solid incrustations may be produced at the edges by drying. If some of these incrustations fall into the finishing float, they impair film formation and do not provide a smooth finish surface.
Remedy: Avoid storing the floats in open vessels for a longer period, or cover the vessels. Soiled finishing floats should be sieved.

Possible defects of application**Tearing of the finish curtain**

Causes: Caused by insufficient or excessive viscosity of the finishing float, by the use of polymer binders that are not resistant to electrolytes, by foaming and trapped air during recirculation.

Remedy: Adjust correct viscosity by means of stabilizing thickening agents, use binders which are stable to electrolytes or reduce the recirculation speed of the finishing float by diminishing the pump pressure.

Formation of creases during printing

Causes: Uneven feeding of very thin, soft leathers into the print roller results in the formation of creases and thus misprints on the leather.

Remedy: Feed the leathers smoothly and without folds.

Curtain shadow

Causes: Caused by tearing of the finish curtain or by placing the leathers unevenly on the conveyor belt.

Remedy: Stabilize the finish curtain and smooth the leathers by preliminary ironing. Paste leathers, vacuum dried leathers or leathers stretched in the wet state respond well.

Crumbling

Causes: Mostly caused by application methods with intensive rubbing or beating effect (plush or brushing machines) by the presence of unstable polymer dispersions. During rubbing, crumbles form on the coat surface which result in a rough film after drying.

Remedy: Use polymer dispersions which are stable to crumbling for the finishing floats. Preliminary testing of the polymer dispersions for stability to crumbling is possible by rubbing the undiluted binder between the fingers.

Spraying coats too dry

Causes: If spraying is too dry, the finish coats have no closed film. Flow out, covering effect and fastness properties of the finish are impaired.

Remedy: Apply an adequately thick spraying coat. If necessary, reduce the spraying pressure.

Spray noses

Causes: Caused mainly by manual wet spraying of leathers hung up vertically. Especially if using liquors of low viscosity the wet coat begins to run and form raised dye or film grooves, so-called "spraying noses", in these sections after drying.

Remedy: Adjust correct spraying pressure and apply correct amounts of dye. If applying large amounts of liquor the leathers should lie on a horizontal surface and not be hung up vertically or sloping for drying.

Spray specks

Causes: If the spraying pressure is too high and the spraying distance too great, spray drops of higher viscosity may form on the leather surface by quick evaporation of the spray mist. These drops dry on the surface as dots, result in a rough surface handle and reduce the fastness properties of the finish.

Remedy: Avoid the causes.

Spray streaks

Causes: Caused by irregular overlapping of the webs following each other. This results in streaky shadows which are covered to a different extent.

Remedy: Adjust each spray jet exactly to the following web. Adjust the through-feed speed of the leather exactly to the movement of the spray guns and the width of the spray jet.

Formation of streaks during padding

Causes: Cracking of finish coats occurs if they have not dried adequately before the next coat is applied. Uneven padding of the finishing float or the use of worn out plush pads may also result in the formation of streaks and thus in unlevelled coats.

Remedy: Avoid the causes.

Deposition of dust and dirt

Causes: Buffing dust on the leather, particles of dust and dirt in the finishing room or dried residues of finishing float in feed-in lines, spray guns, spray booths and drying sections are deposited in the finish coat and result in a rough surface.

Remedy: Dedust the leathers thoroughly and keep the finishing rooms, drying devices and machines as clean as possible. In patent leather production, work with an overpressure in the spraying and drying room to avoid inclusion of dust particles owing to the high thickness of coat and thus long drying time.

Intermediate fixation too strong

Causes: Excessive intermediate fixation of casein finishes or polymer finishes with a larger content of albumen binders may cause hardening of the grain, brittleness or loss of elasticity and even cracking of the finish.

Remedy: Proportion the amounts of formaldehyde finishes with care. On no account should acetic acid or chromium salts be additionally used for intermediate fixation.

Finishing defects on the leather**Marking off**

Causes: Excessive quantities of brightening dyes or organic pigments, insufficient amounts of binders in the pigment finishes or top coats which have been applied too thin may result in marking off of the finish.

Remedy: Avoid the causes.

Cracking off

Causes: Use of polymer binders which are not cold-resistant, very hard pigment finishes or top coats, inadequate content of plasticizers or impaired adhesion of the individual finish coats.

Remedy: Avoid the causes.

Powdering of surface layers

Causes: Occurs in very hard casein finishes which have been applied in a very thick coat. Boarding treatments in particular cause a fine powdering of the entire finish coat.

Remedy: Reduce the thickness of coat. It is recommended that several thin coats be applied with intermediate drying. Addition of small amounts of polyacrylate dissolved in alcohol to the base coating agent prevents powdering of the finish coat.

Stripping of the finish

Causes: Impaired adhesion of the individual finish layers caused by an insufficient absorption capacity of the leather when applying the base coat and by inadequate reswelling of the preceding finish.

Remedy: If the absorbing capacity is not adequate, use a penetrative pretreatment primer. Reduce the use of sealing, water-resistant binders. If using cross-linking binders continue processing without storing the leathers for a longer period as otherwise the film becomes insoluble by subsequent reactions.

Migration of plasticizers

Causes: Excessive drying temperatures, direct application of nitrocellulose floats to the leather without previous base coating.

Remedy: Control the drying temperatures and if using nitrocellulose finishes apply a barrier layer on the basis of polymer binders.

Chalking

Causes: Caused in finish coats by migration of white pigments based on titanium oxide on exposure to light. Changes the shade of pastel colours. Contact with soft metals may also produce dark streaks.

Remedy: Replace the white titanium oxide pigments by pigments based on zinc white which have a slightly reduced covering effect.

Fissures in the finish coat

Causes: Very high pliability of the leather and inadequate elasticity of the finish coats. Insufficient drying of polymer binders, especially if they contain organic solvents. These binders require a prolonged drying time as the finish films are solubilized and swelled.

Remedy: Use softer, more elastic finishing floats and dry each finish coat thoroughly.

Exudation of plasticizers

Causes: If excessive amounts of non-gelatinizing plasticizers are used such as castor oil or rape oil, they may exude by storing the leathers in cool and warm places alternately or by ironing with excessive temperatures. Visible as a fatty, oily film on the leather surface.

Remedy: Reduce the amounts of non-gelatinizing plasticizers or choose a combination with gelatinizing plasticizers.

Leadened appearance

Causes: Foggy film on the finish surface occurring especially on dark shades. Appears mostly if using highly covering, inorganic pigment colours. This effect may also be produced on matting, colourless top coats of very coarse-pore grain leathers by an unfavourable refraction of light.

Remedy: Use appropriate quantities of organic pigment colours or brightening colours in the pigment or top coats.

Bronzing

Causes: Migration of basic dyes from the pigment coat into the top coat. Migration of organic pigments by the presence of excessive amounts of plasticizers and ironing with excessive temperatures.

Remedy: Reduce or change the application quantities, apply polyamide lacquers as barrier layer or do not use finishing floats containing solvents.

Brittleness or breaking of the film

Causes: Very hard or thick pigment and top coats of glaze finishes. Inadequate addition of plasticizers also causes embrittlement and crackiness of the film. On furniture leathers upholstered with polyurethane foam and in nitrocellulose finishes breaking of the finish coat is mostly caused by exudation of amines. Brittleness is also produced by excessive amounts of hardeners in reactive systems, or cross-linking agents in cross-linking binders. Pigment colours on the basis of copper, cobalt or manganese cause heavy embrittlement by cross-linking with butadiene binders and break-up of the finish films.

Remedy: Avoid the causes. Be careful when using pigment colours in finishes containing butadiene binders.

Fish eyes

Causes: Circular stains in the finish films caused by hardly wettable surfaces of the leathers, base and finish coats. The subsequent finishing float spreads unevenly and forms small, open craters in some sections. With spray coats this effect may also be produced by oil droplets carried along by the compressor, especially in aqueous finishes.

Remedy: Add penetrators or flow-control agents and check the air separator.

Inadequately settled surface appearance

Causes: Uneven and inadequate application of the finishing floats. Different wetting of the leather surface by overfatliquoring or very intensive water-repellent treatment. Very great difference in colour between the aniline dye and the shade to be reached in the finish. Insufficient quantities of pigment colours in the finishing floats. Use of highly penetrative, non-filling binders. Immediate further processing on finish coats which have not dried completely.

Remedy: Avoid the causes. Add appropriate amounts of filling or matting substances to improve the settled surface appearance of the leather.

Greyness

Causes: Caused by uneven refraction of light in leathers with coarse hair pores, especially in dark-coloured glaze finishes or in leathers with very thin finish coats. A very high content of matting agents or chromium salts in the fixation may also cause greyness.

Remedy: Reduce the amount of matting agents or do not use them at all. Increase the filling effect of the finishing floats or apply a polishing ground first. Add brightening colours to colourless top coats.

Greying⁵⁵

Causes: Poor adhesion of the finish coats to each other or to the undersurface by inadequate wetting and swelling. Inadequate flow out or different elasticity of the individual coats. Excessive cross-linking if using cross-linking binders. Use of excessive amounts of fillers or unsuitable fillers, antisticking agents and modifiers. Spray application of the finishing floats too dry. Plating and drying temperatures too high. Inadequate drying may also result in greying. It is absolutely necessary to ensure complete drying of finishes if using finishing floats with polymer binders to which solvent-containing substances have been added. Swelled polymer films are more repellent to organic solvents than to water.

Remedy: Avoid the causes. Use binders with low water resistance. Ensure thorough drying.

Colour change to green

Causes: Foil or metallization effect finishes which contain copper bronze may change to green during storage by a reaction with acids contained in the leather or in the atmosphere.

Remedy: Avoid the use of copper-containing foils or metallized substances containing copper.

Colour change to yellow

Causes: Fixation with glutaraldehyde instead of formaldehyde may produce a yellowish shade which becomes apparent especially on white and pastel finishes.

Other colour changes to yellow (see "Yellowing").

Remedy: Avoid using this product for pale finishes.

**Inadequate
adhesion**

Causes: The adhesion of the finish to the leather itself or of the different finish coats to each other is an important factor for the entire range of fastness properties.

There is a great number of possible influences to be considered: reduced absorbing capacity of the entire leather surface or only incomplete wetting in some sections. Use of excessive amounts of highly coating polymer binders, very hard casein products and the addition of excessive amounts of waxes, plasticizers or fillers. Prolonged times of exposure before application of the next coat when using reactive binder systems. Very strong intermediate fixation and very intensive drying of the individual coats in glaze finish treatments. In nitrocellulose finishes excessive amounts of thinners compared to organic solvents. Drying of thicker curtain or airless finish coats too fast and at elevated temperatures. Adhesion may also be impaired by inadequate dedusting of the leathers.

Remedy: Avoid the causes.

Finish coats applied mechanically by padding or brushing have better adhesion than those applied by spraying. Small-particle, penetrative grain impregnating agents and the addition of corresponding quantities of penetrators or flow-control agents also have a positive effect. Special adhesion promoters on the basis of polyurethane dispersions are very suitable to improve adhesion. They can be used as pretreatment primers or can be added to the base coating floats. In general, thin finish coats which do not contain excessive amounts of solids have better adhesion properties than high-concentration finishing floats. Drying at excessive temperatures should be avoided at all stages of finishing.

Stickiness of the finish film

Causes: All thermoplastic binders on the basis of polymers require a heat treatment by plating or graining for film formation. The softer a binder is formulated, the higher is the stickiness of the film. Sticking of the film to the hot plate disturbs the production cycle and may result in defects in the finish. The use of very high quantities of gelatinizing plasticizers in nitrocellulose finishes also causes stickiness of the finish film.

Remedy: Change the binder composition by adding medium-hard or hard polymers as well as antisticking agents. Dose hardeners and plasticizers carefully.

Inadequate resistance to flexing

Causes: Besides perfect adhesion of the finish coats, elasticity and flexing behaviour are extremely important properties. Finish coats that are too hard and too thick, binders which are not cold-resistant, excessive deposition of pigments or fillers and high-drying reduce the resistance to flexing.

Remedy: Avoid the causes.

Formation of comets

Causes: May occur during glaze finishing. Coarse-grained pigment particles, undissolved dyes in the finishing floats or inclusion of particles of dust and dirt in the finish coats during drying may result in the formation of so-called "comets". When the glazing cylinder glides over the finishing surface colour streaks or scratches are produced by the frictional pressure.

Remedy: Filter the finishing floats and ensure that the environment is free from dust and dirt.

**Inadequate
lightfastness**

Causes: In all cases caused by using products of inadequate lightfastness. They are found in the range of products of all suppliers along with lightfast products, and it is recommended that the information leaflets of the specialized suppliers be read carefully.

In general, pigments have a higher lightfastness than dyes. For example, polyacrylates are lightfast, whereas butadiene binders have little or no lightfastness.

Some nitrocellulose lacquers are more affected by exposure to light than polyurethane lacquers.

Remedy: Check the products to be used for lightfastness or make your choice on the basis of the values indicated by the suppliers.

Loose grain

Causes: In most cases already apparent on the raw hide or is caused by incorrect processing in the beamhouse. The effect may be increased or reduced by the finishing process. It is increased if the base coat does not penetrate adequately into the upper zone of the leather and if the binders used have a very high coating effect.

Remedy: Use small-particle binders for grain impregnation which contain penetrators to achieve maximum depth of penetration. With firm, thicker leathers apply the finish by the airless or curtain coating method to avoid the formation of streaks. With soft leathers grain impregnation by normal spraying is more favourable to avoid callouses of the grain.

Migration

Causes: If leathers which have been finished with simple brightening dyes or organic pigments are in longer contact with PVC material containing plasticizers or with other pale leathers during storage, staining may be caused by migration of these dyestuffs or pigments.

Remedy: Change the product or use less amounts of brightening dyes and pigments. Apply a barrier top coat on the basis of polyamides to prevent migration.

Damage caused by wetness

Causes: Many leather products are exposed to direct wetness during use (rain, snow or dirty water). On glaze finishes or leathers with very thin top coats this may result in complete penetration of the water or swelling of the finish. This gives rise to blind, matt stains after drying or raised sections on the surfaces, called "warts", due to swelling. In extremely severe cases the finish coat may peel off.

Remedy: Reduce the absorbing capacity of the leather by corresponding fatliquoring or water-repellent treatment. If using glaze finishes add waxes to promote polishability, if using polymer finishes add binders of higher water resistance.

Orange peel effect

Causes: Produced by insufficient compactness of the film in splits and corrected grain side leathers. Through bending and stretching of the finished leather the fibres which have not been completely covered by the binders will press through the finish coat and give a slightly rough surface or "orange peel effect".

Remedy: Use highly filling binding agents in the base coating float and apply an adequate amount of substance.

Inadequate rub fastness

Causes: Finishes should have an adequate fastness to dry and wet rubbing. Particularly furniture, car upholstery or garment leathers must meet this requirement to avoid soiling of textiles. Inadequate rub fastness is mainly caused by top coats that are too thin and therefore form no proper film, and also by binders that are too soft and have insufficient water resistance.

Remedy: Avoid the causes. Furthermore, the last top coat should not contain dyestuff or pigments.

Polishability

Causes: Casein glaze finishes in particular are not completely resistant to wetting even after fixation. Wetness, e.g. rain drops, acting on particular sections result in a swelling of the casein coat and leave matt, blind sections after drying.

Remedy: Add saponifiable hard waxes or resins to the top coat which restore the gloss by dry rubbing. Special matt lacquers on the basis of cellulose serve to give a gloss effect on the raised parts of the grain by rubbing or polishing.

Non-polishability

Effect: Furniture and upholstery leathers which have been treated with a matt finish should not become shiny through frequent use and sitting.

Remedy: Use matt lacquers containing small-particle, finely dispersed matting agents which are not, or hardly polishable (observe supplier's information). To preserve the matt effect the rate of evaporation should not be set too low. Avoid large amounts of high boilers.

Efflorescence of salt

Causes: The white, finely crystalline film on the finish surface is produced by wetness and migration of salts from the leather and from the finish coats after drying. This disturbing effect may be caused by a high content of salt in the finishing products, the use of very hard industrial water to dilute the finishing floats or by the thawing salt contained in the water of melting snow.

Remedy: Avoid the causes.

Wrinkled grain

Causes: Wrinkleness means warping, deformation and the forming of fine creases on the finish coat caused by the slightest bending load (not to be confused with loose grain). It is caused by using finishing floats which are too hard or applied in very thick coats, by highly swelled films which have not dried completely or by drying of the finishes at excessive temperatures. Wrinkleness may also be caused by excessive fixation of very thin glaze finishes acting on the grain surface.

Remedy: Avoid the causes.

Formation of specks

Causes: In emulsion lacquers overageing, the action of cold or excessive storage temperatures cause a breaking of the emulsion. This produces fine lacquer particles which, if sprayed onto the leather, form dot-like, very shiny specks on the leather after drying. The same happens if oil droplets carried along from the air separator of the compressor get into the compressed air and thus into the finishing floats to be applied.

Rough specks are produced if droplets of highly viscous binders or lacquers develop because the spraying distance or the spraying pressure is too high.

Remedy: Avoid the causes.

Yellowing

Causes: A distinction is made between yellowing under the influence of heat or on exposure to light. The lightfastness of finishes depends on the dyes, pigments, binders and auxiliary agents used. Yellowing due to heat is caused by products which are affected by oxidation or ageing such as fatty substances, plasticizers or nitrocellulose lacquers. It is particularly disturbing on white and pale leathers.

Remedy: Careful selection of the products to be used.

Disturbance by water in finish coats

Causes: Very large quantities of low boilers contained in the solvent result in an excessive rate of evaporation. In the event of high air humidity the resulting latent heat effects a deposition of water in the film. This causes milky stains and impaired adhesion.

In aqueous finish coats which have not dried completely the moisture may have similar disturbing effects.

Remedy: Pay attention to the composition of solvents. Use appropriate quantities of solvents which form azeotropic mixtures with water such as butanol, ethanol. Ensure thorough drying.

Creases

Causes: Creases appear on leathers which are not smoothly fed into processing machines. Small creases may be produced by squeezing the leather during plating, graining, buffing, dry splitting or dry shaving, and a displacement of grain may be caused by glaze finishing or polishing.

Remedy: Feed the leathers smoothly into the machines and improve the slip of finishing films by adding waxes.

Requirements to be met by leather and tests

The international and national standards on leather testing should be used for analyses.

International standards	ISO	International Organization for Standardization (safety and quality standard)
	IUC	International Leather Chemists' Societies - Chemical leather analysis -
	IUP	- Physical leather testing -
	IUF	- Leather dyes and dyed leather -
National standards	AFNOR NF - G	Association Francaise de Normalisation
	ALCA	American Leather and Chemist Association
	ASTM	American Society for Testing and Materials
	BS	British Standards Institution
	DGF	German standardized methods of the Society for Grease Technology
	DIN	German Institute for Standardization
	EG	European Standardization
	VESLIC	Swiss Material Testing Laboratory
	RAL	Standardization for delivery terms, test, quality and trade marks

For all chemical and physical leather tests exact sampling (size, number of samples), points of sampling (varies depending on type of leather) and preparation of samples (adjustment to uniform climatic conditions, inducement of ageing) have been specified in standards. These standards must be met exactly to obtain test results and findings that are absolutely comparable.

a. Chemical requirements and tests ⁵⁶

Aluminium content

Aluminium tanning salts are used as self-tanning agent in the production of white leathers and fur skins, as combination tanning agent with chromium salts to improve the exhaustion of the chrome bath and the leather properties and also with polymer tanning agents and glutaraldehyde to produce wet white.

To determine the content of aluminium in the leather the sample is ashed and decomposed by a mixture of concentrated perchloric acid and sulphuric acid. With the presence of iron or zirconium they are precipitated with caustic soda as hydroxide and filtered off. Then CDTA solution (cyclo hexandiaminotetra acetic acid) is added and the aluminium complex which has formed is back-titrated by volumetric analysis.

1ml spent CDTA solution corresponds to
 $1.349 \text{ mg aluminium} = 2.549 \text{ mg Al}_2\text{O}_3$

Content of ammonium and hydroxyproline for calculation of nitrogen content and skin substance

Ammonium content: Determination of the ammonium content serves to calculate the skin substance. The sample is acidulated in the Kjeldahl apparatus by sulphuric acid and a mixture of catalysts. Then caustic soda is added and the ammonia that has formed is distilled and determined by titration with sulphuric acid.

Evaluation: The consumption determined is the total nitrogen content in the leather. With the presence of ammonium salts a sample of the total washing-out loss is acidulated in the Kjeldahl apparatus and titrated with sulphuric acid. This then shows the content of ammonium compounds indicated as content of ammonium nitrogen in % nitrogen.

The value obtained from the total nitrogen less

the nitrogen content of the ammonium salts is multiplied by the factor 5.62 and indicates the "skin substance".

Hydroxyproline content: With the presence of other interfering nitrogen-containing substances another method is used to determine the amino acid hydroxyproline. The sample is hydrolyzed with hydrochloric acid, filtered and dried. After treatment with a borate solution and repeated drying, the residue is taken up with boric acid solution, and an oxidizing agent (chloramine T or hydrogen peroxide) is added. A steam distillation follows whereby pyrrole is produced. Reducing tin chloride solution is added to remove excessive oxidizing agent. The addition of paradi-methylamino benzaldehyde results in a highly coloured compound. This is compared to a calibration curve in the photometer and the extinction reading indicates the "hydroxyproline content".

Further values can be determined from these analytical results by calculation:

Bound organic substances in vegetably tanned leathers =

100 % less % moisture content
less % total ash
less % fatty substances
less % organic washing-out loss
less % skin substance

Leather substance =

% skin substance
plus % bound organic substances

Yield value = Indicates the amount of vegetably tanned leather obtained from 100 g skin substance
=

10 000 divided
by % skin substance

Degree of tanning (indicates the amount of vegetable tannin fixed to 100 g of skin substance)

=

% bound organic substances

divided by % skin substance x 100

It should be at least 50 for vegetably tanned leathers, values below 50 indicate that penetration of tannin might be inadequate.

Sole leather = 60 - 95

Upper leather = 50 - 75

Benzidine

Benzidine was a coupling component of dye production and was definitely recognized as a carcinogenic working substance decades ago. Therefore production of benzidine dyes has been discontinued by the most important dye manufacturers since 1970. Different detection reactions and determination methods are in use for benzidine and its salts in dyes and for leathers.⁵⁷

⁵⁸

Chlorinated phenols⁵⁹ (PCP)

Pentachloro phenol (PCP) is a very effective fungicide and was frequently used as preserving agent for leathers to be stored in the wet condition for some time. After a carcinogenic potential had been detected by tests on animals, the use of PCP was restricted in 1989 by an ordinance which limits the use to a maximum of 5 mg/kg dry weight.

Analytical detection is carried out by means of a temperature-programmable capillary gas chromatograph equipped with an Electron Capture Detector (ECD). This method has not yet been standardized.

Chromium content

Several methods are used to determine the content of chromium in the leather:

1. Determination by titration:

In many cases the residue of total ash is employed for this determination method. Different mixtures can be used for the oxidizing melts:

- a. Potassium chlorate/sodium carbonate
- b. Sodium tetraborate/sodium carbonate/potassium carbonate
- c. Potassium chlorate/sodium carbonate/potassium carbonate.

The melt obtained in the melting furnace at 800 °C is dissolved in water and filtered into an Erlenmeyer flask.

a. Iodometric titration

The solution is acidified with hydrochloric acid, and a potassium iodide solution is added. Then an amylum solution is added as indicator and titrated with sodium thiosulphate solution until the colour changes towards light green.

Calculation: % chrome oxide content (Cr_2O_3) =
 spent thiosulphate solution x 0.2534
 divided by g leather weight from
 ash determination

a. Titration with iron(II) sulphate solution

The melt solution is acidified with sulphuric acid, and a ferroin solution is added. Then it is titrated by means of iron(II) sulphate solution until the colour changes from pale blue towards orange brown.

Calculation: % chrome oxide content (Cr_2O_3) =
 spent iron(II) sulphate solution x 0.2534
 divided by g leather weight used in ash
 determination.

2. Photometric determination

The dissolved, filtered melt is acidified with sulphuric acid to pH 1. A reference curve is

tained with graduated quantities of a potassium dichromate standard parent solution in the photometer. Afterwards, the extinction of the measuring solution is determined in a reference curve.

Calculation: % chrome oxide content (Cr_2O_3) =
 $\frac{\text{mg Cr}_2\text{O}_3 \text{ of the measuring solution} \times \text{ml parent solution to be tested}}{\text{g sample weight} \times \text{ml of the withdrawn part of parent solution}} \times 100$.

2. Determination by means of the atomic absorption spectrophotometer (ASS)

Besides chromium this apparatus also serves to determine other cations (metals, semimetals) from the wavelength of arsenic (193.7 nm) up to cesium (852.1 nm). The melt produced for determination by titration as well as other decomposition processes can also be used for this method of determination. This method is not yet officially standardized.

3. Determination by means of X-ray fluorescence analysis (RFA)

This method has not yet been standardized either. It is possible to measure all elements used for tannage (Cr, Al, Si, P, Fe, Zr, Ti).

In purely chrome-tanned leathers the content of chrome oxide should be at least 2.0 %, but in most cases it is clearly higher. If chrome tannage is combined with other tanning methods, the content of chrome oxide may be below this percentage with any possible variations.

Chromium(VI) compounds

Chromium(VI) compounds are no longer used in leather production because they are carcinogenic. However, in leathers tanned with chromium(III) hexavalent chromium compounds may be produced by oxidation. Therefore, a draft standard has been developed for determining the chromium(VI) content in leathers⁶⁰. The pulverized leather is eluted with an aqueous dipotassium

hydrogenphosphate solution and separated from the leather fibres. Then 1,5-diphenylcarbazide solution is added to the acidified solution. With the presence of chromium(VI) compounds the colour changes to red by the formation of 1,5-diphenylcarbazone which is measured by means of a spectrophotometer and compared with a blank reading. The content of chromium(VI) is calculated in relation to the leather dry weight and indicated in mg/kg. The detection limit is 3 mg/kg.

The method might not be applicable in leathers containing highly bleeding substances (such as dyes, tanning agents) due to excessive self-colouration.

Iron content

Unmasked iron compounds (rust, iron-containing water, iron buffing dust of shaving or splitting machines) may cause defects in the leather. In vegetably tanned leathers these are grey/blue-black staining over the entire surface or dot-like patches. Vegetably tanned leathers become brittle by the catalytic oxygen transfer caused by the iron and may be completely destroyed after a longer period of storage. An iron content of the leather in excess of 0.1 % Fe_2O_3 is therefore not acceptable.

Determination: A pulverized leather sample is ashed and dissolved by means of diluted hydrochloric acid. Then hydrogen peroxide and potassium thiocyanato solutions are added. The iron content is determined in the colorimeter and compared with a standard reference solution.

**Substances
extractable by
means of
dichloro-
methane (fatty
substances)**

The amount of fatty substances to be applied to the leather by fatliquoring depends on the type of leather and its intended use. The natural fat existing in different amounts in the raw hides and skins of different provenances is removed to a large extent by the beamhouse processes to prevent impaired adhesion of finishes and fatty spew on the leather. Whereas for example sole leather is fatliquored only moderately with 1-2 %, upper leather with about 4-10 % depending on degree of softness, many furniture or upholstery leathers or russet uppers are treated with 15-25 % of fatliquors. For further processing of the leathers it is essential that the fatty substances be evenly distributed and fixed both over the total leather surface and in the leather cross-section.

Determination: The pulverized, weighed leather sample is put into an extraction thimble and a glass flask dried to constant weight at 100 °C and weighed. The extraction thimble is put into a Soxhlet extractor and the glass flask, filled with about 150 ml dichloromethane, is attached to the extractor. Then the solvent is heated on a hot plate or a hot water bath, and the leather sample is extracted with the solvent rising at least 30 times (3-4 hours). Afterwards, the dichloromethane is distilled. The glass flask is dried in the heating furnace at 100 °C, allowed to cool and weighed. Then the glass flask is dried again for one hour, allowed to cool and weighed. If the difference in weight exceeds 0.01 g, the procedure should be repeated until the weight is constant.

Calculation: % extractable substances =
g flat-bottom flask weight with extract less
g empty weight of flask divided by
g weight of leather = x 100

**Free
fatty acids**

A higher content of free fatty acids may produce fatty spew or, if the leathers are in direct contact with the human skin, cause irritations of the skin. The test is performed on shirt suède leathers or hat and helmet sweat bands and leathers which are likely to be in direct contact with the skin or on leathers which have fatty spew.

Determination: The procedure is the same as that for fat determination, with the difference that petroleum ether is used as solvent instead of dichloromethane. After distillation of the solvent and drying, the extracted fat is dissolved with a neutralized mixture of diethyl ether and ethanol. This solution is titrated by means of 0.1n-potash lye with phenolphthalein as indicator until the colour changes towards red.

Calculation: % free fatty acid =

$$\frac{\text{consumption ml 0.1n-potash lye} \times 282 \times 100}{\text{divided by weight of leather} \times 10\,000}$$

**Non-
extractable
fatty
substances**

This method of determining bound fatty substances is suitable only for chamois leathers as in other kinds of leather the test is disturbed by synthetic fatty substances.

Determination: The leather residue extracted for the determination of fatty substances is transferred into an Erlenmeyer flask and heated with alcoholic potash lye on a water bath. Then the resulting glue-like mass is dissolved in hot water and boiled for 10 minutes after adding concentrated hydrochloric acid. It is then allowed to cool and extracted with ether in the separatory funnel. The obtained ether extracts are washed three times until they are free from hydrochloric acid, and the ether is distilled. The residue is dried to constant weight.

The amount obtained is the content of fat bound in the leather.

Formaldehyde In the leather industry formaldehyde is employed as a preliminary and combination tanning agent, as a preserving agent and as a fixing agent in casein finishes and for fur finishes. In addition, it is used to produce many tanning agents.

Qualitative determination:

- a. A 10 g leather sample is transferred into a distillation flask, covered by pouring 50 ml of 15 % sulphuric acid and set aside for some time. After distillation, 10 ml of the liquid is mixed with the same amount of 30 % caustic soda. Some resorcinol is added and heated. With the presence of formaldehyde the colour changes to red of different intensity.
- b. Or 1 ml of 25 % hydrochloric acid and 1 ml of Große-Bohle reagent is added to 5 ml of the distillate. With the presence of formaldehyde the colour becomes grey blue, changing slowly towards blue violet.

Quantitative determination:

(Highberger and Retsch method) ⁶¹:

A pulverized leather sample of 1-2 g is weighed exactly, transferred into a Kjeldahl flask and 100 ml of 2n-sulphuric acid is added. Then 10 ml of a fresh sodium hydrogensulphite solution (12 g/l) is added and heated. The distillate is collected into an Erlenmeyer flask by means of a Kjeldahl connecting bulb with vertical condenser. The flask is closed by means of a rubber stopper and set aside for 15 minutes. The excessive sodium hydrogensulphite is back-titrated with 0.1n-iodine solution and starch as indicator. To destroy the formaldehyde hydrogensulphite addition compound that has formed, add 10 ml of ethanol and 10 ml of 5 % sodium carbonate solution

and titrate immediately with 0.1n-iodine solution until the iodine colour is achieved.

Calculation: 1 ml 0.1 n iodine solution

corresponds to 1.5 mg formaldehyde

New method of determination⁶².

Content of total ash and water-insoluble ash

Each leather contains different amounts of mineral substances which exist as natural constituents in the skin and are introduced by the products used in the beamhouse processes and in finishing. The content of mineral substances may also be increased by very hard industrial water. Determination of the ash content and mineral substances includes the determination of tanning oxides; these are then deducted from the determined ash content in separate tannin analyses. The total ash content should exceed the content of tanning oxides by max. 2 %. Due to their volatility the ammonium salts must be determined separately and added to the total ash, calculated as ammonium sulphate.

Determination of total ash:

2-5 g of a pulverized leather sample are exactly weighed to within 0.001 g in a porcelain crucible which has been ignited and weighed beforehand. The sample is thoroughly charred at small flame and subsequently moistened with 2n-sulphuric acid. Then it is fumed off at small flame and this residue is ashed in the muffle furnace at 800 °C, fumed off again and afterglowed. Then it is allowed to cool in the desiccator and the residue is weighed.

Calculation: % total ash (sulphated ash) =

g crucible with residue less empty weight of crucible divided by g weight of sample x 100

Determination of water-insoluble ash:

For this test a pulverized leather sample is washed, dried and further treated as for the

determination of total ash.

Calculation: % water-insoluble ash =

g crucible with water-insoluble residue on ignition less empty weight of crucible divided by g weight of sample x 100.

Or determination by calculation only:

% water-insoluble ash = g total ash less washing-out mineral substances.

Total washing-out loss and content of washing-out substances (organic, inorganic)

These tests serve to determine the water-soluble matters contained in the leather, i.e. unbound tanning agents, non-tanning agents and organic, inorganic mineral salts. In vegetably tanned leathers a high washing-out loss is generally an indicator of artificial loading. Leathers which are traded according to weight should therefore be rejected in such cases. This also applies to excessive filling with vegetable tanning agents which causes crackiness of grain and staining and at the same time impairs the fastness properties and reduces elasticity. The simulated fullness of such leathers is lost by elution on exposure to wetness during use.

Determination of total washing-out loss:

This method involves the determination of the total residue, from which the dry residue and the total washing-out loss are determined by calculation. The samples are degreased by dichloromethane after determining their water content. After evaporation of dichloromethane the pulverized sample is transferred into a wide-neck bottle, distilled water is added and the liquid is shaken for two hours. The entire content of the bottle is filtered through a pleated filter. 50 ml of the filtrate are pipetted into an evaporation pan which has been weighed beforehand and evaporated on the hot water bath.

This is followed by drying at 102 °C for two hours and the residue is allowed to cool in the desiccator. Then the pan with the residue representing the total residue is weighed to constant weight.

Calculation: g total residue less

g empty pan = g dry residue

% total washing-out loss =

g dry residue x 10 divided by

g weight of leather x 100

Determination of the washing-out mineral substances:

The dry residue is used and is moistened with 2N-sulphuric acid. After fuming off of the sulphuric acid, it is ignited in the muffle furnace at 800 °C for 15 minutes. The residue is allowed to cool and then weighed in the desiccator.

Calculation: g mineral substance residue less

g empty pan

= g mineral substance residue

% washing-out mineral substances =

g mineral substance residue x 10 divided by

g weight of sample x 100

Besides the determination of loading salts the washing-out mineral substances are also an important determinant for crust and chrome-tanned leathers.

Harmful substances in the leather

These tests determine hexavalent chromium compounds, chlorinated phenols, free fatty acids, free formaldehyde, free sulphur compounds and benzidine, and whether the pH value (qv) is too high or low.

These substances should be tested especially if the leathers are in direct contact with the human skin for a longer time. Allergic reactions or skin irritations cannot be ruled out if the user is very sensitive to these substances.

**Leather smell
(typical)**

Caused by bark tannage, formerly the main tanning method, i.e. tannage by vegetable tanning agents such as extracts of oak, chestnut, pine, quebracho, mimosa, myrobalans or gambir. As they were mostly used in combinations, the leather smell was a more or less strong mixture of one or other of the tanning agents used. A further odour was introduced by the additional use of natural fatliquoring agents such as train oil, degrass, moellon, neatsfoot oil or tallow. Chrome tannage as well as synthetic fatliquoring agents and retanning agents have been used to a greater extent over the past decades, especially for furniture and upholstery leathers. As a result many fastness properties of the leathers were improved, but the typical smell of leather was lost.

Many attempts have been made to bring this smell back into the leather without using vegetable tanning agents. A great number of odorous substances of the cosmetic and perfume industry was used, e.g. birch tar oil, pine oil, spruce turpentine, pine-needle oil, wood turpentine, camphor oil, bitter almond oil, cedarwood oil, benzaldehyde and special leather covering perfumes of unknown composition.

The most favourable method of treatment is spraying odorous substances onto the grain and flesh side of the leather prepared for finishing. Addition to top coats is also possible. Application in wet processes (fatliquoring, retanning, dyeing) has not proven useful as the volatility of the odorous substances is increased by subsequent hot air drying. The amount to be used depends on the desired intensity of smell. All odorous substances

have in common that they possess a more or less pronounced vapour tension, meaning that they are always volatile. It may take some days or at best some weeks until the smell has disappeared completely, depending on the adsorbing properties. Since a lasting effect has not yet been observed, there are natural limits to the use of odorous substances.

Phosporus

Phosphate compounds are used as pretanning agents, pickling salts, masking and neutralizing agents or as complexing agents in different processes of leather production.

Determination of phosphates:

A leather sample is weighed in a crucible, ashed, acidulated with 5 ml perchloric acid and 10 ml concentrated sulphuric acid, and the entire quantity is transferred into a 250 ml measuring flask. Of this, 50 ml is transferred into an Erlenmeyer flask and the chromium that is present is reduced by adding 1 g sodium sulphite and boiling for 15 minutes. This solution is transferred into a 100 ml measuring flask. Of this, take 10/20 ml, add 6n-sulphuric acid, 0.25 % ammonium vanadate and 5 % ammonium molybdate solution and perform colorimetry with a blank test. The indicated absorbency is the content of phosphate.

**pH value and
difference
value**

Many beamhouse processes are carried out in a particular acid, neutral or slightly alkaline range. The exact adjustment for these operations is done by pH measurements. The pH value is the negative, decimal logarithm of the hydrogen-ion concentration of a solution. The measuring range is from pH 1 = highly acid, pH 7 = neutral up to pH 14 = highly alkaline. The pH value is determined with an electrometric pH meter by means of a hydrogen or glass electrode. Another method is colorimetry with liquid indicators or special indicator paper.

For analytical leather tests, the pH and, if necessary, the difference value are important quantities to be measured. Leathers in a pH range of 3.5 - 9.0 are still acceptable. Exceptions are special leathers such as hat leathers and helmet sweat bands which are in permanent contact with the skin (> 4.0) or leathers for optical equipment and membrane leathers for musical instruments which must not cause corrosion (> 4.5). For reasons of safety a pH value of < 8.0 is required for chamois leathers used in orthopaedics.

If a pH value of < 3.5 or > 9.0 is measured, strong free acids or strong free alkalies possibly exist in the leather. These may cause crackiness of grain, damage to the fibres and loss of fastness properties in the leather, especially in vegetably tanned leathers. Permanent contact with the skin may produce irritations or redness of the skin. Therefore it is necessary to determine the difference value. If this value is greater than 0.70, harmful acids or alkalies exist in the leather, and the leather should be rejected.

Determination of pH value:

A pulverized leather sample of 5 g is weighed with an accuracy of 0.1 g, and 100 ml of conductivity water is added in a 250 ml polyethylene bottle, followed by shaking in the shaking machine for 16-24 hours. The unfiltered extract is electrometrically measured at 20 ± 2 °C with an accuracy of 0.05 pH scale divisions.

(The double distilled conductivity water is freshly prepared in quartz vessels and should have a pH value between 6.0 - 7.0 and a specific conductivity of $2 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$).

Determination of the difference value:

Of the aqueous extract for the pH measurement 10 ml are pipetted into a 100 ml measuring flask and filled up to 100 ml with conductivity water. Measurement is then performed as for pH determination.

Calculation: Difference value =

original pH value less pH value of the 1:10 dilution.

The different pH value of the 1:10 dilution is caused by dissociation of acid or alkali. Strong products change the pH value by the factor 1 whereas a weak acid or alkali shows only an increase by the factor 0.5.

Sulphur content

Free sulphur may be deposited in the leather by sodium thiosulphate used in chromium reduction liquors, in neutralization or sulphur tannage. This may cause whitish-yellowish blooms, decolouration or matting of contacting metals by the formation of sulphide, or light redness or irritations of the skin if the leather is in contact with the skin for a longer time. The behaviour of sulphur blooms is similar to that of fatty spew (they disappear when touched by a flame).

Qualitative determination of sulphur:

Leather samples degreased with petroleum ether are moistened with water, placed on a bright silver pan and allowed to dry. With the presence of sulphur, black brown stains of silver sulphide occur in the places where the leather was lying.

Quantitative determination of sulphur:

The leather sample is degreased with sulphur carbon instead of dichloromethane. The sulphur carbon eluates the existing sulphur completely. Fuming nitric acid is poured over the distillation residue, dried to constant weight and set aside on the water bath for 24 hours. To expulse the nitric acid it is allowed to evaporate to dryness on the water bath. To eliminate undestroyed fatty substances which may still exist, a soda potash mixture is added and the content of the pan is melted, allowed to cool and taken up with hot water, heated with a little bromine water and transferred into a beaker by filtration. After acidification with hydrochloric acid the sulphuric acid produced by the sulphur is precipitated with barium chloride in the boiling heat, and the obtained barium sulphate is filtered, dried and weighed.

Calculation: % sulphur content of the leather =
$$\frac{\text{g barium sulphate} \times 0.137}{\text{g sample weight of fat determination}} \times 100.$$

Water content

Determination of the moisture content of leather is essential for chemical analyses. To be able to compare the results of analyses the different values obtained are converted to a uniform water content of 0 %.

The water content of the leather depends on the climatic conditions, ambient humidity, type of

tannage, fatliquoring and on the deposited unbound organic or mineral substances. If stored under identical conditions chrome-tanned leather has a higher content of moisture than vegetably tanned leathers. Extremely dry leathers reduce the leather yield and are more susceptible to embrittlement and crackiness of grain. Excessive moisture may cause increasing flabbiness and formation of mould. Variations of the moisture content may also result in a considerable change of area or volume.

Determination of the water content:

There are two tests. A sample is taken from the unprocessed leather as delivered. It is not pulverized, but immediately weighed with an accuracy of 0.001 g (weight m_3). This sample is placed on a glass tray which has been dried at 102 ± 2 °C, cooled down to room temperature and weighed, and dried at 102 ± 2 °C for five hours (weight m_4).

3 g of a pulverized sample is transferred into a weighing bottle with lid, which has been dried at 102 ± 2 °C and cooled down to room temperature, and weighed with an accuracy of 0.001 g (weight m_1). The open weighing bottle is dried at 102 ± 2 °C in a heating furnace for five hours. For removal from the furnace the weighing bottle is closed with the lid, allowed to cool in the desiccator and weighed, dried once again for one hour and weighed once more. If the weight has decreased by less than 0.1 % of the initial weight by subsequent drying, the test is finished. Otherwise repeat drying for one hour respectively up to a total time of max. eight hours until this value is obtained (weight m_2).

Calculation:

- a. % water content of the sample analysed =
weight m_1 less weight m_2 divided
by weight m_1 .
- b. % water content of the sample analysed,
as delivered =
weight m_3 less weight m_4 divided
by weight m_3 .

Determination of the conversion factor for a particular water content:

factor = 100 less required water content
divided by
100 less water content determined

Water-soluble magnesium compounds

This test serves to determine the soluble compounds, especially magnesium sulphate ($\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$), also called "bitter salt". It is mainly used in sole leather production as a hygroscopic moisturizer to prevent excessive drying of the leathers or as an artificial loading agent to increase the yield. Since the salt is soluble in water excessive amounts in the leather cause migration into the upper leather of shoes if these are exposed to wetness during use. Whitish salt efflorescence is produced in the zones of contact.

Determination of magnesium with absence of interfering phosphate and calcium ions:

First a 0.01 molar EDTA solution (ethylenediamine tetraacetate) is prepared for all test methods to determine the titre factor. Solutions which have already been adjusted are available under the name Komplexon III or Titriplex III.

The obtained mineral substances which are removable by washing are mixed with 2n-hydrochloric acid and dissolved by heating. Then the solution is transferred into an Erlenmeyer flask by adding some more hydrochloric acid and neutralized with 2n-caustic soda or ammonia

solution against methyl orange, brought to the boil and diluted with 150 ml of water. After adding a buffer solution and solid Eriochrome black T indicator until the colour changes towards red it is titrated with EDTA solution until the colour changes towards blue.

Calculation: % magnesium sulphate =

ml washing water x ml 0.01-m consumption of
EDTA solution x factor EDTA solution
x 2.465 divided by ml extracted amount of
washing-out mineral substances x g initial
weight x 1000 x 100.

Determination of magnesium with the presence of interfering phosphate ions:

If a qualitative test shows a positive reaction to phosphate ions these should be removed. This is done by adding ammonium chloride solution, some drops of nitric acid and iron (III) chloride solution. After filtration and washing the filtrate with water it is titrated with EDTA solution.

Determination of magnesium with the presence of interfering calcium ions:

The filtrate obtained in the elimination of phosphate ions is used for this test. It is mixed with ammonium chloride solution, ammonia solution and 5 % ammonium oxalate solution, filtered and titrated with EDTA solution.

All results obtained from the respective tests must be converted into water-free leather substance. In double measurements the results must not differ significantly from each other. If they are greater than 0.2 % magnesium sulphate related to the initial weight, the tests should be repeated.

However, it is also possible to determine the magnesium compounds by means of the non-standardized methods of atomic absorption

**Zirconium
content in
chrome-tanned
leather**

spectrometry (ASS) or X-ray fluorescence analysis (RFA).

In many cases zirconium tanning agents are used to retan chrome-tanned or chrome/aluminium-tanned leathers. Therefore the tests comprise a determination of all tanning oxides and an additional separate determination of zirconium.

Determination of zirconium and tanning oxides:

The pulverized leather is accurately weighed in a platinum crucible and ashed as usual. Potassium disulphate and some drops of concentrated sulphuric acid are added. The content is then melted. The melt is transferred into a beaker into which 50 ml water and 25 ml concentrated sulphuric acid have been transferred, dissolved by heating and boiled until a clear solution is obtained. This is filtered into a 250 ml measuring flask and filled with water up to the mark. The mineral tanning agents then exist in the form of sulphates.

From this measuring flask, 50 ml are pipetted into a beaker, mixed with 5 g ammonium chloride and a little methyl red and heated. Then the metals are precipitated by addition of ammonia. After boiling the precipitate is allowed to settle down, filtered, washed with ammonium chloride solution, ignited in the muffle furnace at 1000 °C and weighed = g total of tanning oxides.

a. *Titration of zirconium:*

50 ml are pipetted from the 250 ml measuring flask into an Erlenmeyer flask, boiled and allowed to cool. Then 250 ml water are added and the existing sulphuric acid is neutralized with 2N-caustic soda. Some drops of xylenol orange are added as indicator. The solution is titrated in the

boiling heat with 0.02 molar Komplexon III solution until the colour changes from raspberry red towards orange. Then 7n-ammonia solution is immediately added in the boiling heat, whereby the colour changes to red again, and titration is continued until the colour changes to a yellow shade.

Calculation: 1 ml consumption of 0.02 molar Komplexon III solution corresponds to 2.4644 mg zirconium oxide.

b. *Gravimetric determination of zirconium:*

This method of determination does not correspond to the standardized method. 50-100 ml are pipetted from the 250 ml measuring flask into a 400 ml beaker, 15 ml concentrated sulphuric acid are added and diluted to 200 ml. Under heating at 50 °C, 25 ml of a 10 % diammonium phosphate solution are stirred in and the resulting precipitate is allowed to settle down on the water bath for 2 hours, then filtered and washed with ammonium nitrate solution until the sulphate reaction disappears. This filtrate is filtered into a platinum crucible and ignited in the muffle furnace and weighed.

Calculation: g residue on ignition x 0.4647
= g zirconium dioxide

The content of chromium oxide is calculated by the usual chromium determination method.

Calculation of aluminium oxide content:

% aluminium oxide = total of oxides less
content of chromium oxide and zirconium
oxide.

The described chemical tests are outlined in an abbreviated form. When performing the tests the respective standards must be observed.

b. Physical requirements and tests⁶³**Abrasion
resistance
of leather**

These tests are performed in particular on sole leathers, mainly by dry abrasion, less frequently by wet abrasion. The test is carried out on special testers with rotating cylinders lined with abrasive paper of a specified grain. The loss of volume of the leather is determined in mm³.

The abrasion properties are influenced by the leather structure and the type of tannage and depend on which zone of the leather is abraded. Compact butt sections have a better abrasion resistance than loosely structured sections, purely vegetably tanned leathers a lower abrasion resistance than chrome-tanned leathers, and the outer layers of the leather a lower abrasion resistance than the central layers.

Testing by means of a rotary abrasion tester is used for soft leathers which are subject to greater wear during use (protective gloves, technical leathers).

**Wettability
of leather**

The time of penetration of a drop of water into the grain surface of a leather sample until it disappears completely is assessed. Before the test the leathers have to be conditioned. The time of penetration is indicated in seconds. It provides information about the penetrative capacity of finishing floats and the absorbing capacity of leathers which have not been finished (suède, nubuk).

The "wetting time", i.e. the time from when the drop of water touches the leather until it begins to penetrate, is also tested on leathers which have received a partial water-repellent treatment.

Bursting strength	The test is performed by means of a bursting tester. A circular piece of leather of 100 cm ² which has been fixed by clamping is exposed to a constantly increasing pressure of 1 bar until it bursts. The pressure determined at the moment of bursting is indicated in bar, related to the thickness of leather. The bulging height is determined at the same time.
Flexibility	This test is carried out on firm, tough leathers to determine which visible defects or damage are caused to the grain by flexing. A special mandrel bending tester (in an angle of up to 180 °) with exchangeable mandrels of different diameters is used.
Resistance to bending	Different types of bending resistance testers are in use. These tests have the disadvantage that highly varying values are obtained because of the great differences in structure found over the entire skin surface.
Elongation at break	Determined in the strength tester when testing the tensile strength (qv) and measured only in one direction on the leather, i.e. parallel to the backbone line. It refers to the change in length of the punched sample at the moment of breaking compared to the initial length of the sample, in mm, and is indicated in %. Elongation at break is only relevant for leathers which are exposed to very high loads (e.g. leather for drive belts).
Resistance to chemicals	These tests are carried out on leathers which are used in the fields of protection and safety. <i>Determination of the resistance to calcium chloride:</i> Performed on upper leathers used for safety shoes and safety articles in the mining industry.

The test is carried out on a conditioned leather sample of which the finish coat has been removed to the first fibres by means of abrasive paper. The sample is compressed with a 10 % calcium chloride solution, to which 1 % nonionic wetting agent is added, for about 60 minutes, dabbed with filter paper and dried in the drying oven at 30 °C for 24 hours. This treatment is repeated twice. The change in area or hardening is assessed.

Determination of resistance to acids:

This test is performed by painting the leather with 37 % hydrochloric acid and measuring the shrinkage (also called crimping test).

Determination of resistance to lye:

Performed by the dropwise application of hot 10 molar caustic soda (100 °C). After rinsing and drying, the sample is tested for surface changes in these sections.

**Extension
of leather
under load**

Tested in the strength tester with a load of 100 N/cm². The values obtained provide more information than the test for elongation at break. In most cases diagrams on the extension behaviour during the entire course of the test are prepared.

Low extension values are required for traditional shoe upper leathers and lining leather (3-8 %) to ensure stability of shape. Glove leathers and chamois-dressed wash leathers have the highest extension values (15-35 %). Garment leathers are in between (10-20 %) because these leathers must also maintain dimensional stability. Technical leathers require the lowest extension values (2-6 %). (See also Tensile Strength and Extension.)

Determination of thickness

Determination of the thickness of hides and leathers is necessary in many areas of leather production, especially for precise adjustment of the splitting and shaving machines. The final thickness of the leathers is important for the leather trade. In the physical tests it is required for evaluation of the test results.

In all cases pressure detectors are used. The micrometer gauges fixed to these indicate the thickness of the test specimens directly. Depending on the softness of the leathers, either flat detectors of different diameters which rest on the leather are used, or also spherical detectors for hard leathers. A reading accuracy of 0.1 mm is sufficient for leather production. For testing purposes, the accuracy is 0.01 mm and the pressure should be 5 N/cm².

Resistance to through-cuts and slashing

Leathers employed in the fields of protection and safety must possess adequate resistance to the action of sharp-edged objects. The test is performed on the tensile strength tester by means of a knife with a specified pressure and rate of penetration. For testing sole leathers a steel pin of specified thickness and rate of penetration is used.

Elasticity of leather

All leathers should be highly flexible to a more or less extent without being damaged. Sole leather may exhibit a slight brittleness of grain under strong bending, however a higher degree of brittleness is not acceptable. Every shoe upper leather or all types of leather which are exposed to bending during use should be capable of resisting a minimum of 20000 flexions without damage. This also applies to the finish coats. (See Flexibility, Resistance to Bending.)

Strength properties of leather

The strength properties of leather are influenced by many factors.

Rawstock: The three-dimensional fibre texture of the animal skin is the main carrier of strength properties. Not only do the various types of raw hides and skins show considerable differences in strength, but even the hides and skins of the same species. The structure is influenced by provenance, age, sex, climate, nutrition and living conditions.

Manufacturing processes: The strength properties of leather decrease with increasing opening up of the skin and the deposition of large quantities of tanning and filling agents.

Mechanical processing: The strength of leather is reduced each time the fibre texture is cut; it is reduced more by splitting than by a shaving or blanching treatment.

Extension of area

Testing the extension of area of leathers provides important information on the properties of leather in shoe production and during use and also for the assessment of upholstery leathers.

Determination of the extension properties under tension by means of the bulging test in a tensometer:

At least three conditioned, circular leather samples of diameter 68 mm are mounted onto a rubber membrane in the tensometer, with the grain side showing upwards. Then the air pressure is increased by 10 bar in 30 seconds. The resulting bulge is examined precisely for changes, formation of fissures and cracking. A diagram is recorded and indicates the bulging values directly. The extension of area and the linear extension are determined in % by placing a template on the leather sample.

Determination of permanent extension of area by means of the plastometer:

Conditioned, circular leather samples (diameter 89 mm) are glued onto a brass ring and clamped into the plastometer. A micrometer is placed on the sample, and the piston pressed upwards by the micrometer screw until it is touching the leather. The condition of extension is maintained for some time, the pressure released and the procedure repeated at specified intervals. If a bulge remains on the leather, the permanent extension can be calculated.

Area weight

The area weight of a leather is indicated in g/m². To determine the area weight, leather samples measuring 100 x 100 mm are conditioned and weighed to constant weight.

The determined area weight provides important information on the heaviness of a leather and also on the yield. Light-weight material is required especially for garment leathers and is regarded as a quality feature.

Resistance to the action of flame

Methods of testing inflammability and burning behaviour of leather have gained importance in the past decades. They are employed especially to test leathers used for motor-car trims, in the aircraft, upholstery and garment industry and for protection and safety applications. The test is performed in a special combustion box with exposure to an open gas flame, and the rate of burning of the leather sample is calculated.

Rate of burning in mm/min = burning length in mm divided by time of burning length in seconds x 60.

A further test consists in exposing the edges and the surface to a flame. The results are assessed

and allocated to different burning classes.

Another method is testing with a glowing cigarette and with a burning match on a wire netting frame tester.

Factors which influence the burning behaviour:

1. Vegetably tanned leathers have a higher resistance to burning than chrome-tanned leathers.
2. Large amounts of fatliquoring agents impair the resistance to burning. Synthetic, chlorinated fatliquors are better than fatliquors containing animal fats or mineral oil.
3. Highly coating finishes, especially nitrocellulose finishes, impair the resistance to burning.
4. The addition of flameproofing agents to the liquor or spraying coats improves the burning behaviour effectively.

Fogging reaction

"Fogging" refers to the condensation of evaporated, volatile components of motor-car trim materials on the window panes, especially on the wind shield. The test consists of two different methods and is carried out with a special fogging tester. This tester simulates the processes taking place in the interior of a motor-vehicle.⁶⁴

1. Reflectometric test:

A car upholstery leather specimen of specified size is placed on the bottom of a glass beaker which is immersed to a certain depth into a heated bath (100 °C) regulated by thermostat. Cooling plates maintaining a temperature of 21 °C are then placed on top of the glass beaker, which is closed by a cleaned glass plate and seal. Cooling causes the substances evaporating from

the leather to condensate on the glass plate. The quantity of fogging condensation on the glass plate is recorded by measuring the 60° angle of reflection of the same glass plate (blind value) without condensation.

Calculation: Fogging value in % = quotient of the 60° reflectometer value of a glass plate with fogging condensation and of the same glass plate without condensation.

2. *Gravimetric test:*

Instead of the glass plate used in the reflectometer test, a light aluminium sheet is used in this test and the specimens are treated for 16 hours instead of 3 hours at 100 °C.

The condensate is weighed and indicated in mg. (Both test methods prescribe that the specimens be dried for 7 days in a desiccator using phosphorous pentoxide.)

This test is applied not only specifically to leather, but to all parts of automobile trim material.

To obtain good fogging values for car upholstery leathers the following factors should be taken into consideration in leather production:

- a. Remove high contents of natural fat by degreasing. The use of glutaraldehyde promotes an even distribution of fatliquors.
- b. Avoid using products which contain ammonium as these sublime easily.
- c. Keep the amount of fatliquors as low as possible and compensate with softening tanning agents. Good results are obtained with sulphited marine oils as they have a high content of double bonds. The use of fatliquors containing paraffin should be avoided because they are highly volatile.
- d. Ensure thorough fixation of retanning agents, dyes and fatliquors.

- e. Upon termination of the wet works thorough washing is necessary to remove all unbound substances.
- f. The use of large amounts of emulsifiers, wetting agents or finishing agents containing plasticizers should also be limited to a minimum because of increased volatility.
- g. Perform drying after the individual processes at maximum possible temperatures. Additional afterdrying of the finished car upholstery leathers at 80 °C has proven useful.

**Resistance to
compression**

This test serves to determine the firmness of sole leathers. It is performed by means of a tester having a metal cylinder having a diameter of 4 mm. The depth of compression is determined on a leather specimen with diameter of 7 cm by applying a load of 70 kg for 120 seconds.

**Air
permeability**

This test determines the breathability of leathers which is a measure of porosity. It mostly provides the same results as those obtained in the water vapour permeability test and has therefore lost importance.

The test is performed with an apparatus in which a circular leather sample clamped by means of a flange is exposed to an even air flow of constant pressure in a specified unit of time. The volume of air which has passed through the test specimen is measured and the air permeability coefficient calculated:

Calculation: Air permeability coefficient $K = \frac{\text{volume of air passed, in cm}^3 \times 100}{\text{gas pressure in cm mercury column} \times \text{flow of transmission in min} \times \text{free area tested in cm}^2}$.

The measured values (K) are between 20 (very low) and 400 (high) depending on the type of leather.

Distension of grain

Ball burst test to measure the distension and strength of grain by means of the lastometer:

This is a test method by which bursting of the grain or the finish is achieved by bulging.

A circular leather sample is clamped into the lastometer so that there is a free area to be tested of 25 mm. A steel ball (diameter 6.25 mm) is pressed from below towards the sample by manually turning a spindle until the grain bursts. The pressure is read off by means of a connected manometer and the bulge height is measured. The pressure attained is indicated in N and the bulge height in mm.

Repellency to oil and fat

The behaviour of leather when exposed to fatty and oily substances is tested. This method determines the oil-repellent effect and the soiling of leathers and thus the intensity of impregnations. *Test of repellency to oil* (according to AATCC 118):

Test substances of increasing surface tension are applied dropwise to conditioned, flat leather samples. If there is no wetting or penetration after 30 seconds of exposure, the next test liquid of reduced surface tension is applied until clear wetting is achieved. The value obtained is the oil repellency value.

1 = paraffin oil, 2 = 65 parts paraffin oil/
35 parts n-hexadecane, 3 = n-hexadecane,
4 = n-tetradecane, 5 = n-dodecane,
6 = n-decane, 7 = n-octane, 8 = n-heptane.

Stability to cleaning*Determination of stability to cleaning:*

Like testing the fastness to washing, the test is performed in the Wacker tester with similar conditions. Conditioned leather samples of size 150 x 150 mm are cut out. Two measuring sections of 100 x 100 mm are measured accurately in the middle of the leather, and 3 mm crosswise cuts are performed in the corners. The specified solvent is transferred to the Wacker vessel in a ratio of 1:20 (related to the dry weight) and heated to a temperature of 30 ± 2 °C. Then the leather samples are added, with or without accompanying fabric and with opposite corners tied together. After 30 minutes the samples are blotted superficially between filter papers and dried in the hood at room temperature.

The stability to cleaning promoters or refatliquoring agents should be tested on separate samples.

After conditioning the dried test specimens, the shrinkage of area is determined by exactly measuring the measuring points.

Calculation: % shrinkage of area =

area before cleaning less area after cleaning,
divided by area before cleaning x 100.

Raw density

The raw density is determined from the weight of the test specimen in g, divided by the volume of the test specimen in cm^3 . It is the weight of the leather including the hollow spaces between the fibres. The former name "apparent density" is not used nowadays for reasons of standardization.

The raw density of dried raw hides/skins or pelts is 1.1 g/cm^3 to 1.4 g/cm^3 . Dry leathers have a raw density of 0.4 g/cm^3 to 0.8 g/cm^3 .

The value may be increased to 1.1g/cm^3 by mechanical compacting, e.g. milling, hydraulic plating, glaze finishing, or also by deposits of unfixed substances. The "real density" (only leather fibres) is $1.3 - 1.5\text{ g/m}^3$ irrespective of the provenance of the skin, type of tannage and type of finish.

Degree of shrinkage of leather

The change of area is tested by exposing the leather to boiling water. A so-called "boiling test" is performed at the end of tannage for wet chrome-tanned leathers. Dry leathers are first soaked in water at $20 \pm 2\text{ }^\circ\text{C}$ for one hour.

Determination of the degree of shrinkage:

Leather samples of exactly $10 \times 10\text{ cm}$ are prepared and the outlines drawn on paper or preferably on graph paper. Then the leather sample is immersed in boiling water for exactly 1 minute and after short draining placed onto the paper with the previously drawn outlines. The loss of area compared to the original sample is determined by planimetry. It is indicated as % degree of shrinkage.

Shrinking temperatures of leather

This test determines the temperatures at which leather begins to shrink under the action of damp heat.

Shrinking temperatures and type of tannage:
Chrome leather $90-100\text{ }^\circ\text{C}$
Vegetably/synthetically tanned leather $70-85\text{ }^\circ\text{C}$
Aluminium/iron leather $70-80\text{ }^\circ\text{C}$
Aldehyde leather $75-85\text{ }^\circ\text{C}$
Chamois leather $65-70\text{ }^\circ\text{C}$
Alum/Glaze leather $70-75\text{ }^\circ\text{C}$

The resistance of leather to higher temperatures varies considerably depending on the type of tannage. Damage caused by shrinkage is irreversible in most cases.

In vegetably tanned leathers, temperatures exceeding 45 °C may darken the tanning colour and impair distension of grain up to crackiness even before shrinkage.

Determination of the shrinking temperature:

A strip of length 50 mm is cut out of the leather to be tested. If the leather is max. 3 mm thick the strip is 3 mm wide, if the thickness exceeds 3 mm the strip is 2 mm wide. Two small holes are punched into the ends of the strip for the fixing hooks. 350 ± 10 ml of warm, distilled water are filled into a 500 ml glass vessel (inside diameter 70 ± 2 mm), and the vessel is placed on a heater (80-100 watt output) which heats the water slowly by 2 °C per minute. The vessel has a vertical thermometer with a measuring range of 50 - 105 °C (maximum deviation 0.5 °C), a circular dial with pointer and a rigid pulley over which a thread is led. To tighten the thread a 3 g weight is fixed to the outer end and the strip of leather to the other end. A magnetic stirrer is connected to heat the water evenly. When the leather clearly starts to get warped or to shorten, the temperature is read off and indicated as "shrinking temperature".

Electrical conductivity of leather⁶⁵

Measurements of the volume resistance of leather provide information about existing electrostatic charge. It is measured by means of a digital multimeter. Low conductivity becomes apparent if buffing dust or fibre particles are difficult to remove. The regulations for safety shoes specify that the volume resistance should not exceed 10⁸ ohm.

Action of perspiration on leather

The tests are performed mainly on vegetably tanned leathers (insole leather, shoe lining leather). The shrinkage of area and length is measured under the action of synthetic perspiration solutions.

Synthetic perspiration solutions

<i>according to Graßmann:</i>	<i>for colour fastness:</i>
10 g sodium chloride	5.0 g sodium chloride
6 g ammonium carbonate	5.0 g tris (hydroxymethyl) amino methane
2 g potassium diphosphate	0.5 g urea
per litre / adjusted to a pH of 9.0 by means of ammonia	0.5 g nitrilo-triacetic acid
	per litre / adjusted to a pH of 8.0 $\pm$ 0.1 by means of hydrochloric acid

Method of determining the action of perspiration:

Conditioned leather samples having an edge length of 100 mm x 100 mm are marked with division marks every 10 mm, and the exact area is calculated by means of a sliding caliper. Then the sample is laid in a dish containing 150 ml perspiration solution (Graßmann method) and completely immersed at 35 °C for 24 hours. Afterwards it is briefly washed and dried, and then dried at 40 °C for 24 hours. For comparison, a leather sample is treated with distilled water. The treatment is repeated five times on all samples, measures being taken and recorded in an area diagram each time. The shrinkage of area is determined by comparison with the untreated original leather and is indicated in percent. The shrinkage of the leather sample caused by distilled water is deducted from the total shrinkage in %. Changes which have occurred such as hardening, crackiness or change of tanning colour are also indicated.

Strip test: This is a further test to determine mineral efflorescence, hardening or discolouration and is used especially for upper leathers, insole leathers and welting leather.

A 20 x 100 mm strip of filter paper is fixed to leather samples of a size measuring 20 x 40 mm on the side to be tested such that it projects 15 mm. Combinations of leather are also possible (to test upper leathers the filter paper is fixed to the reverse side, to test insole and lining leathers it is fixed on the grain side). The leather with the strip of filter paper is placed between two glass plates, pressed together by means of clamps, and put vertically into a vessel filled with 10 ml of distilled water. Insole and lining leathers are additionally tested with perspiration solution according to Graßmann. The duration of exposure is two hours for one sample and eight hours for the second sample. The strip of filter paper is then dried at room temperature and tested for changes. If testing light salt efflorescence it is recommended that black filter paper be used to recognize the efflorescence.

Stitch tear strength

The behaviour of leather at stitched seams is determined in this test. It provides information about weak points caused by possible defects of fabrication since the test does not refer to the fibre texture as a whole like the tensile strength test.

The test can be performed in the tensile strength tester by two test methods. One test is carried out by directly perforating the leather sample by means of a flat mandrel, in the other test an oblong slot (10 x 1 mm) is punched out and a mandrel is introduced. The leather sample is stretched with a feed rate of 100 mm per minute until the leather tears. The method applied should

be mentioned in the test report.

Calculation: daN/cm stitch tear strength = daN load x 10 divided by mm thickness of leather

The *stitch tear force* test serves to determine the maximum force which is necessary to tear the mandrel out of the punched hole.

**Temperature
endurance
of dry leathers**

Leathers used to make shoes are exposed to higher temperatures. Different testing methods with international standardization are in use to test their suitability.

1. Determination of the resistance of air-dried *insole leathers* to heat, especially during direct vulcanization (IUP 17).
2. Determination of the resistance of air-dried *lining leathers* to heat, especially during direct vulcanization and in moulding on soles during shoe production (IUP 18).
3. Determination of the resistance of dry *upper leathers* to heat, especially during direct vulcanization and in moulding on soles during shoe production (IUP 19).

The "area shrinkage behaviour" of dry leathers on exposure to high temperatures is described in a standard for protective gloves. At least two samples of 100 x 100 mm are cut out, specified measuring sections are marked and the samples are stored under standardized conditions for 24 hours. Afterwards, the samples are measured by means of a sliding caliper, laid horizontally on a wire netting in the drying oven at 100 ± 3 °C for 3 minutes and reconditioned. Then they are measured again and the area shrinkage is calculated.

Thermal conductivity

Low thermal conductivity of leather effects good heat retention. Shoes or garments having high thermal conductivity immediately make the wearer quickly feel hot in warm weather and cold in cold weather.

Thermal conductivity is influenced by the air trapped in the leather. The more air is trapped, the lower is the thermal conductivity. A high content of deposits (fatliquors, unbound tanning agents, filling agents) or compacting of the leather texture (plating, milling, glazing) reduces thermal conductivity; it is improved by loosening the leather texture (staking, boarding, milling).

The leather sample is measured in a conductometer in which a constant heat gradient is produced between two chromium-plated copper plates. It is indicated as

coefficient of thermal conductivity $\lambda_x = \text{const.} \times$
thickness of sample

$\times$ quotient of the temperature difference of both plates.

The average coefficients of thermal conductivity obtained are

$\lambda = 0.1$ to 0.2 .

Fastness to washing

Testing the fastness to washing:

Two leather samples with edges of exactly 10 x 10 cm are cut out. Two identical leather samples are additionally required for a test with accompanying fabric. The washing liquor consists of 5.0 g lauryl sulphate per litre. The test is performed in the Wacker apparatus at 27 ± 3 revolutions per minute and a temperature of 30 ± 2 °C, controlled by a thermostat. The Wacker vessel should be equipped with a lifter to avoid rolling up of the leather samples. About 30 glass beads are added to the material to be washed.

The opposite sides of the leather samples are tied together or the leather sample is tied to the respective fabric, washing liquor is added in a ratio of 1:20 (related to the dry weight) and washing is done for 30 minutes. Then the sample is briefly rinsed with distilled water, slightly struck out and dried at room temperature.

The leather is tested for stability of shape, hardening, change of area and colour and compared with the untreated original sample, and staining of the accompanying fabric or union fabric and bleeding of the washing liquor are assessed.

Water absorption

This test determines the quantity of water which is absorbed by the leather, if completely immersed in water, after a specified time (Kubelka test). A circular leather sample is laid into a special glass flask which has a 0.1 cm^3 graduation at its neck. It is filled with exactly 75 cm^3 distilled water, and the sample is flooded with the water by turning upside down. After 2 and 24 hours the glass flask is turned again, and after draining for 1 minute the amount of water absorbed by the leather is read off directly at the measuring scale.

Calculation: % water absorption =
absorbed amount of water in cm^3 divided
by weight of sample in g x 100.

Measured values of leathers with high water absorbing capacity = > 75 %, of leathers with low water absorbing capacity = < 15 %.

Water vapour absorption (WDA)

For this test a leather sample of 6.5 cm in diameter is prepared or taken from a shoe to be tested, conditioned, weighed and clamped into a tester which is filled with 50 cm^3 water.

A vapour-tight aluminium or rubber disk is

tightly placed on top. After 8 hours the sample is immediately weighed.

Calculation: WDA in mg/cm^2 and duration in hours = weight of the conditioned sample less weight upon termination of test.

Permeability to water vapour

This test determines the amount of water which penetrates through a leather in the form of vapour if moisture-saturated air is on one side of the leather and completely dry air on the other side. Like air permeability it is a measure of porosity and thus of the hygienic wearing properties of leather. Permeability to water vapour is determined by the older Herfeld test and by the international Mitton test. The difference consists in that for the Herfeld method the leather sample is laid over a glass filled with water and placed into a desiccator filled with silica gel. In the Mitton test the measuring glass, filled with bead-form silica gel, with the leather sample laid on top, is moved in an apparatus, and the permeability is determined by ventilation of humid air. In both cases the increase of weight of the leather sample is determined after exactly 24 hours.

Calculation:

Water vapour permeability value =
mg permeation of water vapour through a test
section of 10 cm^2 in 24 hours

The average measured values are in a range of 50 - 600 mg/cm^2 depending on the type of tannage, processing and type of leather.

Permeability to water

Since the utility properties of hydrophobed leathers have clearly improved, their sales have constantly increased in the past years compared to leathers which are processed by traditional fatliquoring. The test methods have therefore also gained importance.

Former static tests (Stather-Herfeld test, Otto test) use a constantly increasing water pressure until water permeates, and this is then calculated as the water permeability coefficient.

Today dynamic test methods are in use which provide values of higher reliability for practice because of the flexing movement. Upper leathers are tested by means of the Bally penetrometer or the Maeser tester. The Bally permeometer is used to test sole leathers.

Determination by means of the penetrometer:

Three conditioned leather samples of 75 x 60 mm are punched out for the test and roughened on the grain side by means of abrasive paper, if necessary, or left as they are. The force to be applied for flexing, expressed in N, is determined by means of a special device.

> 100 N	= 5 % flexing
50 N - 100 N	= 7.5 % flexing
20 N - 50 N	= 10 % flexing
< 20 N	= 15 % flexing

The leathers are clamped into the tester and are then in a crucible filled with distilled water, the depth of immersion being 20 mm.

Determination of the water penetration time:

Brass chips are placed into the hollow space formed by the leathers clamped in the tester. If water penetrates and the chips get in contact with the water, a visual or acoustic signal is triggered.

The penetration of water is determined by visual inspection and the time and number of flexions is noted.

Evaluation: Time of penetration =
time of flexion in minutes up to penetration
of water and number of flexions applied.

Determination of the water absorption:

After specified periods of time the leather samples are removed, superficially blotted with filter paper and weighed, and the test is repeated at the next specified time.

Evaluation: % absorption of water =
$$\frac{\text{g leather sample after treatment} - \text{g leather sample before treatment}}{\text{g leather sample before treatment}} \times 100.$$

Determination of the quantity of penetrated water:

A roll of absorptive terry fabric, 40 mm long, which has been weighed beforehand is used instead of brass chips. Weighing is repeated after specified periods of time or after water has penetrated.

Evaluation: g quantity of penetrated water =
g roll of terry fabric after treatment
less
g roll of terry fabric before treatment.

Determination by means of the Maeser appliance

Leather samples of size 100 x 120 mm are clamped and flexed by eccentric movements of 10000/hour in the water bath until water penetrates. This method also determines water penetration in minutes, water absorption in percent and amount of penetrated water in g. The results differ from those obtained by the penetrometer since a different type of flexing is used.

Determination by means of the permeometer for sole leather:

Three sole leather samples measuring 100 x 40 mm, which have been taken from along the back line, conditioned and emeried on the grain side, are weighed and their thickness is measured. The leather sample is fixed to a metal plate and continuously flexed by the back and forward rolling movement of a cylinder. Water is applied by means of a cotton strip which is constantly kept moist and which lies on the emeried grain side. A weighed strip of absorbent chemical pulp is on the bottom side and absorbs the permeating water. The test is carried out for a specified period of time or ends after water has permeated.

The water permeation time, water absorption and quantity of permeated water are determined.

Evaluation:

Permeation time = indicated in minutes.

% water absorption = $\frac{\text{g of the sample after treatment} - \text{g of the sample before treatment}}{\text{g of the sample before treatment}} \times 100$.

g quantity of permeated water = $\frac{\text{g of chemical pulp after water absorption} - \text{g chemical pulp before water absorption}}{15}$

Action of water on leather

Different wetting properties are required for the various types of leather. While upper leathers, sole leathers, garment and upholstery leathers, fancy and pocket book leathers should possess poor wetting properties, high or maximum wetting values are demanded for lining leathers, hat and sweat band leathers, insole leathers, wash and filter leathers or orthopaedic leathers. Furthermore, a distinction must be made between superficial or penetrative wetting.

These different requirements should be taken into consideration by selecting a suitable raw material, by adjusting the production process and by using specific products.

**Swelling
caused by
water**

Swelling warts or raised streaks develop especially on vegetably/synthetically tanned leathers or intensively retanned leathers under the action of water.

Testing the swelling behaviour:

Leather strips of size 20 x 100 mm are hung in about 5 mm of water or synthetic perspiration solution. The liquid is allowed to rise 15 - 50 mm into the leather strip. The time of immersion is 15 minutes or more depending on the wetting properties. Then the leather is hang-dried at room temperature and assessed for swelling, or the degree of swelling is determined by measuring the thickness.

**Split tear
strength**

The split tear strength test determines the force which is opposed by a leather fibre texture to tearing after having been cut vertically or after a slot has been punched. It provides important information about opening up of the skin, intensity of bating and changes caused by tannage. However, the results should be compared with the values obtained in the tensile strength test.

There are two test methods:

- a. trouser tear test
(the leather is slit)
- b. split tear test
(a slot is punched into the leather)

Determination of the trouser tear strength:

The two leather ends produced by cutting are clamped into the tensile strength tester. Pulling is then carried out at a pulling speed of 100 mm per minute until the leather strip tears completely.

At least three leather samples should be tested and a mean value then calculated.

Tearing force = first peak value of beginning tearing at the leather cut

Split tear force = mean value of the force required until the sample tears completely

Evaluation: daN/cm split tear strength =
daN split tear force divided by
mm thickness of the leather sample x 10.

Determination of the split tear strength:

The values determined for the tearing force, the split tear force and the split tear strength should be divided by two in the calculations.

**Tensile
strength
and elongation**

Determination of the tensile strength and elongation of leathers provides information about the quality of the leather texture after processing. Each process in leather production and the difference in quality of the rawstock influence the tensile strength and elongation values. However, the values obtained for split tear strength and stitch tear strength should be included in the test report to enable a comprehensive and detailed assessment.

Determination of tensile strength and elongation:

At least five leather samples should be tested. The thickness of the conditioned leather samples is measured and the samples are punched out. Three specimens of different size are tested, depending on the type of leather. The samples are fixed to the clamping devices of the tensile strength tester. The test is performed with a tensile speed of 100 mm per minute.

The following values are determined by means of this test method:

Breaking load = maximum force measured in the tensile test at the moment of tearing, indicated in N as mean value of five tests

Tensile strength = quotient of breaking load and initial cross-section of the sample in N/cm^2 .

Elongation at break = measured change of length of the test specimen at the time of tearing in relation to the original length in %.

Diagram force/change of length = record showing the entire course of the tensile test, the force applied and the change of length.

Evaluation: N/cm^2 tensile strength =
breaking load in N divided by
initial cross-section in $\text{cm}^2 \times 100$.

% elongation at break =
mm measuring length at break less
mm original measuring length
divided by the original measuring
length.

Ecological factors and requirements

a. In the production processes

Raw hide magazine Sodium chloride (common salt) which is used to preserve the raw hides accounts for as much as 30-40 % (related to the green weight) of the waste volume, and increases the salt content of the effluent considerably. Efforts to switch to other efficient long-term preserving agents have not been successful yet. Short-term preservation without salt, or processing of fresh hides is only of local importance.

Remedy: Remove the salt from the raw skins by intensive sweeping and dispose of separately.

Soaking floats Soaking floats make up about 10-15 % of the total effluent. The floats may contain common salts, soil by blood and dung, natural fatty substances, small amounts of soluble skin proteins and sometimes preserving agents, wetting or enzymic soaking auxiliaries, depending on the type of preservation of the rawstock.

Remedy: In most cases the effluent is not highly loaded by the waste matters. Excessive quantities of liquor should be avoided in the soaking process.

Liming floats Of all waste water produced in leather making the effluent of the liming processes has the highest load values in the waste water treatment plant because of the high chemical oxygen demand. The main substances contained in the effluent are sulphides, skin decomposition products, in particular large amounts of keratin from the hairs or the wool, and different amounts of emulsified natural fatty substances depending on the rawstock used. In the past years many methods have been developed to reduce the content of

harmful substances of lime liquors and some of them have been put into practice in cases where relevant problems with waste water arose.

Remedies:

- a. Reduce the quantities of sodium sulphide, sodium sulphhydrate, reduce the amount of effluent, use the Darmstadt through-feed method.
- b. Use liming systems which do not contain sulphides or contain only small amounts of sulphides (organic sulphides, enzyme treatments).
- c. Recycle the lime liquors. If the quality diminishes (after about 10 cycles) recycling should be interrupted and restarted with a new, spent lime liquor.
- d. Collect the lime liquors separately in gas-tight vessels and add acid to recover the sulphides by formation of hydrogen sulphide with subsequent caustic soda neutralization.
- e. Immunization procedure and removal of hairs by pumping and filtration.
- f. Preliminary fleshing of the raw hides/skins in the utilisation of skins or after soaking (fatty substances).

Rinsing floats

To avoid large amounts of waste water, two washing cycles with closed drum lid are recommended instead of rinsing under running water.

Deliming floats

The most commonly used deliming products are still ammonium sulphate, ammonium chloride and less frequently ammonium salts of organic acids. Since they have a high content of nitrogen all these products load the waste water of the treatment plant by nitrification and have a high chemical oxygen demand.

Remedies:

- a. Reduce the amounts of deliming agents containing nitrogen or do not use them at all.

- b. Use mainly nitrogen-free deliming mixtures. It is also possible to use magnesium sulphate or magnesium chloride in careful combination with hydrochloric acid or cyclic esters, sodium bisulphite, boric acid, and to use gaseous carbon dioxide for thin or split cattle hides.

Bating liquors

The effluent of pure, enzymatic bating liquors has an insignificant amount of loading substances. However, as bating is mostly combined with deliming in the same bath, it is necessary to consider the products used for deliming.

Degreasing floats

Due to its strong environmental impact, wet degreasing with large quantities of organic grease solvents has lost importance. Nowadays wet degreasing is done with emulsifying agents. Thus the waste water load is reduced to natural fat and surfactants. The content of common salt in the rinsing floats can be reduced considerably by the simultaneous use of modified glutaraldehyde or special stabilizing pretanning agents. If the degreasing floats contain large quantities of emulsified fatty substances they should be collected separately and disposed of by decanting or sedimenting, or should be employed in fat processing.

Pickling floats

The necessary addition of salt to the pickle bath loads the waste water.

Remedies:

- a. Reduce the amount of salt by using non-swelling pickling acids.
- b. Use β -naphthalenesulphonic acid as acid component in the pickle.
- c. Perform pickling with short floats thereby reducing the load of the waste water.

Chrome tannage, residual liquors and floats drained from the machines

Many procedures have been developed to reduce the discharge of chromium (III) salts from chrome-tannage into the waste water. The liquors which are drained from chrome-tanned hides and skins stored on trestles or in stacks, and from samming and scouring machines, also produce large amounts of waste water.

Remedies:

- a. Collect all residual floats separately. Add soda, calcium hydroxide or magnesium oxide to precipitate insoluble chrome hydroxide. The sludge obtained is dissolved with sulphuric acid, basified accordingly with soda and recycled as tanning liquor.
- b. If using a short float tanning method, the residual liquor may be directly recycled and used as pretanning liquor, also in the pickle.
- c. Employ chrome tannage to obtain a high degree of exhaustion of the residual floats. The products used are chrome tanning agents with self-basifying effect, additions of magnesium oxide, wetting, masking multi-basic carboxylic acids, modified glutaraldehyde products or additions of aluminium tanning agents.

Vegetable tan liquors

Vegetable tanning agents do not load the waste water directly since they are of natural origin. However, since they contain very fine colloids they have a high chemical oxygen demand. The intense brown colour of the waste water is also disturbing.

Remedy: If problems arise, precipitate the tanning liquors by flocculating agents.

Neutralizing and retanning floats	Neutralizing floats of chrome-tanned leathers are loaded by chromium(III) salts which have been removed from the leather. Like the washing baths they should therefore be discharged in the chrome tannage effluent. The procedure for retanning floats is the same as for vegetable tan liquors.
Dyeing floats	Elimination is very difficult because of the very fine particles. Aim at good penetration of the dyes into the leather substrate.
Fatliquoring floats	From the point of view of ecology and economy a maximum possible exhaustion of the fatliquoring bath should be achieved.
Residual finishing floats	Contain inorganic pigments, organic dyes and pigments, casein and polymer binders, different finishing auxiliaries and solvent-containing lacquers. In all cases they should be disposed of separately.
Organic solvents and air pollution	Organic solvents used in the leather industry are volatile and mostly inflammable substances. Their vapours should not be inhaled over a longer period of time as they may cause headache, fatigue, dizziness or nausea. For this reason maximum concentrations ("MAK" values = Maximale Arbeitsplatzkonzentration) have been specified. They refer to the amounts which can be tolerated by humans, animals and plants without damage and are indicated in ppm or mg/m³. <i>Remedies:</i> - Good aeration and ventilation should be ensured if working in closed rooms. - When using water-miscible solvents, unpleasant odours can be effectively avoided by passing the exhaust air into water baths. However, the saturated baths must not be disposed of in the waste water.

- c. Application of leather finishes by pneumatic atomization, which is still the most common method of finishing, is gradually being replaced by printing machines. With the latter method atomizing agents are not sprayed into the air. Moreover, smaller amounts of solvents are used, and since there is almost no loss of material the consumption of products is limited to a minimum
- d. For reasons of air pollution and health risks, and also for economical reasons, finishes which are free from solvents or have a low content of solvents are being increasingly used

⁶⁶

MEK (minimum emission) ratings for assessing air pollution are laid down in the German Federal Immission Protection Act/ Regulation on Clean Air (TA Luft). The four classes refer to carcinogenic substances, dustlike inorganic substances, vaporous or gaseous inorganic substances and organic substances.

b. Waste water

In many countries directives have been issued concerning the quality of waste water to be discharged directly into a main drain or indirectly into a central treatment plant. For small and medium sized enterprises an independent treatment plant is uneconomic and a system of discharge into central treatment plants is preferable. The minimum requirements for the substances to be discharged differ considerably from one country to another. The average values indicated below refer to Germany.

Settling substances	<i>Max. 0.5 mg per litre.</i> A distinction is made between biodegradable and non-biodegradable solids. Measures for reduction: Mechanical separation (sieves, coarse filters). Add highly polymerized sedimentation agents or flocculating agents such as iron sulphate, iron chloride, aluminium sulphate or aluminium chloride.
Aluminium	<i>Max. 3 mg per litre.</i> Thought to inhibit growth in plants and to be one of the factors causing Alzheimer disease, however this has not yet been proven. Measures for reduction: Flocculation of the residual liquors, washing and rinsing floats by adding alkalies.
Ammonia nitrogen	<i>Max. 10 mg per litre.</i> Is produced through the use of nitrogen-containing products and disturbs biological degradation in the waste water treatment plant by nitrification and high chemical oxygen demand. Measures for reduction: Use nitrogen-free products, especially in the deliming process.

AOX	<i>Max. 5 mg per litre.</i> AOX = refers to substances containing adsorbable, organically bound halogen. They exist particularly in chlorinated fatliquoring agents. Measures for reduction: Use AOX-free products.
Chloride (Salt)	<i>A limit value does not yet exist.</i> Very high concentrations may promote destructive attack of cement building material or inhibit biological degradation. Measures for reduction: Do not introduce the very large amounts of curing salt into the production process. Reduce the amounts employed in pickling by using non-swelling acids.
Chromium(III) compounds	<i>Max. 1 mg per litre.</i> Measures for reduction: Use tannage methods with a high degree of exhaustion, short-float methods, recirculation of residual floats, separate collection of residual and washing floats and recycling by precipitation and redissolution, good fixation of chromium salts in the leather.^{67 68}
Chromium(VI) compounds	<i>Discharge not allowed.</i> Do not use oxidizing agents if processing chrome-tanned leathers in the beamhouse.
COD and BOD₅ values	COD = chemical oxygen demand. Max. 160 mg/O² per litre. BOD₅ = biological oxygen demand in 5 days. Max. 25 mg/O² per litre. Measures for reduction: Do not use oxygen-demanding products, cut down oxygen demand by flocculation, sedimentation and biological degradation.
Iron content	<i>Max. 3 mg per litre.</i>

Substances extractable with petroleum ether (fatty substances)	<i>Max. 20 mg per litre.</i> Natural and synthetic fatty substances are not biodegradable. Measures for reduction: Remove adherent fatty substances to a large extent by preliminary fleshing before processing, dispose of fatty connective tissue from fleshing (furrier's waste) separately after liming, collect degreasing floats separately, allow them to settle down and remove suspended fat by decanting. Remove fat and oils discharged into the collecting or settling basin by means of a separator.
Halogen organic solvents	<i>Discharge not allowed.</i> If their use is necessary in degreasing systems they should be recycled by redistillation.
Hydroxy-ethylated phenols (APEO)	<i>In Germany no longer produced owing to voluntary renunciation on the part of the manufacturers.</i> APEO surfactants are hardly biodegradable and their metabolites are toxic to fish. Can be replaced by fatty alcohol polyether hydroxylates without problems.
Phosphorus (total)	<i>Max. 2 mg per litre.</i> Phosphate ions can cause eutrophication of the waters if they exist in large amounts. In most cases limit values are insignificant when the phosphate is discharged indirectly because larger waste water treatment plants are equipped with phosphate precipitators. Mainly contained in detergents and cleaning agents and in some synthetic fatliquoring agents on the basis of phosphoric esters.
Free phenols	<i>Max. 10 mg per litre.</i> The products may contain different amounts of free phenols depending on the manufacturing processes of synthetic tanning agents based on phenols. In the past years industry has succeeded in producing tanning agents containing small amounts of free phenols or not containing free phenols at all.

pH value	<i>A pH value of 6.0 - 9.0 is demanded.</i> The limit values can be met in most cases by mixing acid and alkaline waste water floats. If the pH value is below or above these limits, acid or alkali should be added for neutralization.
Sulphates	<i>Max. 200 mg per litre.</i> If present in high concentrations, cement building material may be attacked and destroyed. Measures for reduction: Use products having a low sulphate content for beamhouse processes and replace sulphuric acid by other inorganic or organic acids.
Sulphides	<i>Max. 1 mg per litre.</i> Waste water containing sulphides should be collected separately in a collection basin as a split stream. Discharging it directly in treatment plants causes the formation of dangerous hydrogen sulphides by the presence of acid waste water floats. Measures for removal of sulphides: - Catalytic further oxidation by ventilation and addition of manganese sulphate or manganese chloride (180-200 g per m³). - Treatment by introducing flue gas. To dispose of large quantities of sulphide-containing floats, or if the amounts of flue gas are insufficient, sulphuric dioxide should be additionally introduced. - Precipitation of sulphide by adding iron(II) sulphate. The iron(II) sulphide which is formed is deep black. It can be converted into brown iron(III) hydroxide by intensive ventilation. The disadvantage of this method is that very large amounts of sludge are produced.
Sulphite	<i>Max. 1 mg per litre.</i> Measures for reduction: Reduce the use of products containing sulphite.

Temperature *Max. discharge temperature 35 °C.*

Toxic substances *Discharge not allowed.*
Biological degradation in treatment plants is disturbed by the presence of toxic, organic compounds and may be inhibited completely. The waste water is tested by the fish test. A dilution ratio of 1:5 must not be toxic.

Water-polluting substances According to the German Water Conservation Law water-pollutants are solid, liquid or gaseous substances which are capable of changing the physical, chemical and biological properties of water unfavourably.

The water-polluting substances have been classified in four classes of pollutants (WGK) and listed in a catalogue:

WGK 3 = highly water-polluting substances

WGK 2 = water-polluting substances

WGK 1 = slightly water-polluting substances

WGK 0 = substances which in general have no water-polluting effect.

The assessment of water-polluting potential is based on specific properties of the substances:

acute toxicity for mammals,

aquatic toxicity for fish, dolphins,

algae and bacteria,

biological degradability,

abiotic degradability (hydrolysis, photolysis, oxidation)

soil mobility,

ability to accumulate biologically,

carcinogenic effect,

mutagenic effect,

teratogenic effect.

c. Waste

Raw skin trimming waste	<i>Waste produced:</i> By trimming and edge staking when preparing the batches in the raw hide magazine; by preliminary fleshing after soaking. All components which disturb mechanical processing or cause tangling in the vessels are removed, for example parts of the head, genitals, longer parts of the tail or fringes and tail-ends. <i>Utilization:</i> Production of glue, gelatine⁶⁹, high-quality collagen products.
Limed hide waste	<i>Waste produced:</i> By trimming, edge staking or by pieces torn off after defleshing. <i>Utilization:</i> Production of glue, gelatine, high-quality collagen products⁷⁰.
Wool	<i>Waste produced:</i> On the living animal by "sheep shearing". In the leather factory by painting of the flesh side, less frequently by enzyme treatments. Spilling of the lime paint on the wool side must be avoided as the quality is considerably reduced by the action of keratin. Immediate washing with subsequent quick drying is necessary to remove adhering alkali and sulphide residues. <i>Utilization:</i> Textile production.
Hair	<i>Waste produced:</i> Only economical for very long-haired hides or goat skins. Produced by flesh side painting or hair-preserving liming procedures. <i>Utilization:</i> Manufacture of felts and use in spinning, carpet and fibrous web production.
Bristles	<i>Waste produced:</i> On the flayed pig skin by shearing with electrical shearing machines. <i>Utilization:</i> Manufacture of brushes and paint brushes.

Machine offal for glue

Waste produced: By defleshing after liming. Considerable quantities amounting to 8-15 % of the green weight are produced, which is still more than the production of hair and wool.

Utilization: Production of glue and feedstuffs, and use as fertilizers. If more offal for glue than can be sold is produced, it may be disposed of on waste dumps (if the water content is reduced) or in incinerators (with excess of carbonaceous material).

Split offal for glue

Waste produced: By trimming upper and lower splits after splitting.

Utilization: Production of gelatine, wraps of sausages, protein powder and high-quality collagen products such as medical and surgical foil and fabric substrates.

Fatty substances

Produced: Produced directly by degreasing pig skins and by fleshing freshly flayed or presoaked hides. Furthermore in degreasing floats or by oil separation of effluent collectors. The major part of the fatty substances comes from processing to obtain protein.

Fatty substances are obtained by three possible methods:

1. Rising of the fat after thermal or chemical conditioning.
2. Mechanical pressing of the fatty substances by thermal processes and mechanical treatments.
3. Extraction with organic fat solvents.

Utilization: Soap production, chemical industry, production of cosmetics.

Horns, hoofs, shanks

Utilization: Horn processing industry for the production of buttons, combs, trimmings.

**Shavings,
whitenings**

Waste produced: The whitenings of vegetable tanned leathers can be further processed or disposed of without problems. Shavings of chrome-tanned leathers are produced in larger quantities and account for about 95 % of the total produced.

Utilization: Production of leatherboard materials. After dechroming, production of fertilizers, feedstuffs or chemical auxiliaries. To dispose the shavings of chrome-tanned leather on waste dumps they must be mixed with hydrated lime or limed offal for glue to comply with the requirements imposed by the authorities.

Buffing dust

Waste produced: By dry shaving machines and all buffing machines. The dust collector should be connected to a central dust collecting plant. As there is a risk of fire or explosion if using conventional dry dedusting systems with fibrous filters it is recommended that the safer wet dedusting systems be used. For convenient transportation and disposal on waste dumps wet sludge can be pressed through a screw press extruder to reduce the moisture to a residual content of less than 70 %.

Utilization: Disposal on waste dumps.

**Waste of
tanned leathers
(moist and dry)**

Waste produced: Trimming waste before and after shaving, after splitting of chrome-tanned leathers, pieces torn off by staking, edge staking after removal of the leathers from the stakes, during sorting in the leather magazine.

Utilization: Cutting, rasping and grinding for the production of leatherboard material.

Sewage sludge

Waste produced: Produced at all stages of waste water treatment plants, from preclarification after mechanical treatment, clarification after chemical treatment and in the afterclarification basin following biological treatment. A distinction is made between primary sludge from mechanical treatment, and secondary sludge from chemical

and biological treatment.

The volume of primary sludge, i.e. coarse and fine sludge, amounts to about 3-5 m³ per ton of raw skin weight processed with about 5 % of dry substance. The secondary sludge is a fine sludge with about 1-2 % of dry substance.

Utilization: There are different possibilities for sludge disposal. The sludge must first be dewatered by one of the following methods:

- a. Thickening by sedimentation, and removal of the water.
- b. Mechanical dewatering by chamber presses, vacuum or gravel filters, centrifuges or microfiltration and microflotation⁷¹.
- c. Drying by heating in a rotary dryer.
- d. Digestion under anaerobic conditions in digestion towers. Duration about 20-30 days at 33 °C. Organic components are largely decomposed with formation of methane gas.

Disposal is then possible by:

- a. Disposal on waste dumps. Permitted only for compact waste which is harmless from a hygienic point of view. The substances must not be inflammable, must not cause dust or foul odours and must not contain components that are soluble in rain water.
- b. Incineration at high temperatures on condition that the exhaust gas is pure.
- c. Composting, provided that the sludge is free from harmful substances, is a favourable solution to preserve the balance of nature .

Production of leatherboard

In German called LEFA production (LEFA is an abbreviation of the German term „Lederfaserwerkstoffe“ which means leatherboard material).

Leatherboard is made from the basic components leather fibres and binders. Corresponding quantities of felting substances such as synthetic or cotton fibres are sometimes used to obtain special properties. The leather fibres consist of shavings of chrome-tanned leather, vegetable whitenings and leather waste from trimming. Thus the function of leatherboard production is to dispose of the waste produced in the leather industry. The main application of leatherboard material is the shoe industry where it is used to make frames, counters, insoles, middle soles and outsoles for slippers. Further applications are the bag industry, e.g. suitcase frames, school bags, partitions for briefcases or portfolios, and technical products, packings, cup leathers, etc.

Requirements for leatherboard materials

Shoe industry	Bag industry	Technical products
water absorption -low	handle properties: -soft or hard (depending on the need)	resistance to heat
release of water - rapid		-high.
dimensional stability: swelling, growing, shrinking, must be low in all tests	-	-
resistance to deformation: stability of shape, lasting, glueing, must be resistant.	-	-
structural strength: tensile strength, extension, stitch tear strength, abrasion must be high in all tests.	tensile strength -high stitch tear strength -high, split tear strength -high	tensile strength -high, extension -low

Processes of manufacture

There are two manufacturing procedures:

1. Wire box - discontinuous (antiquated, now only used occasionally).
2. Fourdrinier machine - continuous (principle of paper machines).

Both procedures use the same method to make the fibrous pulp. They differ only in mechanical processing. The composition of the fibres, binders, additives and fatliquoring agents varies depending on the intended use.

Coarse leather waste is first reduced in size in knife mills and then defibrated in disk mills or also in beaters by adding water. This pulping procedure is continued until there is no more clots or lumps. Shavings of chrome-tanned and vegetably tanned leathers are only treated in disk mills. The fibrous pulp obtained from different types of waste is transferred into separate storage vessels (content of solids of 5-8 %).

The fibrous pulps are then mixed in a mixing vessel, often a beater, in specified quantities depending on the intended use, and adjusted to a stock density of 1.5-3 %. Since the pH is in the acid range (due to the predominance of chrome fibres), a corresponding amount of diluted fatliquoring agent (5-15 %) is added. The amount of fatliquoring agent depends on the desired softness or firmness and on the fat already contained in the fibrous pulp.

After thorough mixing the pH value of the float is adjusted to 5-7 by weak alkalies.

If dyeing of the leatherboard material is required, simple acid dyes, less frequently inorganic pigments are added subsequently.

After adequate homogenization and complete absorption of the fatliquoring agents and the dyes, if used, the binder which has been diluted to 5-10 % is slowly added while stirring. The quantity used depends on the desired final product and is between 10-40 % (calculated in relation to the content of solids).

If the binder has completely dispersed, the entire fibrous pulp is precipitated with precipitating agents. The end of precipitation is reached if a sample taken from the fibrous pulp and poured onto a filter or a very fine-meshed screen gives a clear filtrate.

The fibrous pulp obtained is further dewatered and compacted by screen exhaustion and in presses. The process can be accelerated by applying a vacuum.

The fibrous leatherboards are then dried by hot air. After a recovery time of 24 hours the leatherboards can be further compacted by means of a hydraulic press or by calender rollers. They are manufactured in thicknesses of 0.15-7 mm and with a specific weight of 0.6-1.0 mm.

With modern continuous processing on the fourdrinier machine (working widths of 160-300 cm) it is possible to manufacture leatherboard webs by rolling them up at the end of the machine. To obtain a high specific weight of the webs a hydraulic press for intermittent processing is connected to such machines. To achieve quick through-feed rates dewatering is an especially important factor.

Properties of the substances used

Fibres

The main substance used are chromiferous fibres. They give a high tensile strength, extension and temperature resistance, whereas dewatering and dimensional stability are low. Vegetably tanned fibres have reversed properties. Therefore the fibres are applied in mixtures depending on the requirements.

Fibrous additives

Added in corresponding quantities depending on the requirements.

Cellulose fibres (pulp) increase dimensional stability.

Synthetic fibres and cotton fibres improve the tensile strength properties.

Binders	Natural rubber latex is the chiefly used product. Its main advantages are that it is inexpensive and gives high flexibility. Disadvantages are low tensile strength, stitch tear strength, rub fastness, and hardness. However, they are sufficient to make many leatherboard materials. To achieve special properties, synthetic polymers such as polyacrylic esters, polyvinyl acetates, polyurethanes or butadiene are added in different quantities.
Fatliquoring agents	The products used are low-price fatliquoring agents which are readily precipitable, on the basis of sulphonated oils, or also soap liquors. It is important that these fatliquoring agents do not retard the dewatering process on fourdrinier machines. The organically bound SO ₂ contained in the sulphonated oils is also decisive for this process.
Neutralizing agents	The products used are sodium silicate, polyphosphate, sodium formate, and sodium bicarbonate in small quantities. Ammonia should not be used as it delays dewatering by the formation of aluminium hydroxide.
Precipitating agents	Aluminium sulphate is applied as 3-5 % solution. Synthetic flocculants (polyelectrolytes) are also used to avoid a high salt content in the leatherboard material or to achieve quicker precipitation. Retanning of the fibrous pulp with vegetable tanning agents also promotes uniform precipitation. The addition of neutral salts on the basis of phenol condensation accelerates the precipitation process.
Stock deaerators	To prevent foaming or the formation of bubbles in the fibrous pulp it is recommended that small amounts of antifoaming agents or stock deaerators be added.

Types of leather

Flowchart of leather production for chrome leather:

Operations	Waste
↓	↓
raw material (assembling of batches)	
soaking (if necessary, preflashing)	residues of flesh and fat
if necessary, painting: depilation, dewooling	wool, hair
depilation, opening up the skin	
fleshing	offal for glue
splitting	splittings
deliming, bating, degreasing	fat
pickling	
chrome tannage, basification	
storage (pallets, trestle, pile)	
samming	
if necessary, chrome splitting, shaving	shavings
sorting (assembling of batches)	trimming waste
neutralization, dyeing, retanning, fatliquoring or water-repellent treatment	
samming, setting out	
drying: (hang-drying, drying on stenter frames, pasting)	
conditioning	
staking, toggling, buffing or milling and trimming	trimming waste
finish applications base, pigment, top coating	
plating or embossing	
sorting, measuring	trimming waste
leather magazine and shipping of leather	

Flowchart of leather production for sole leather:

Operations	Waste
↓	↓
raw material	
soaking	
liming	
fleshing	offal for glue
deliming	
pretannage (colour pit or drum)	
vegetable final tanning (handler, layer and/or drum)	
filling	
bleaching	
soaking	
setting out	
blanching	whitenings
oiling	
drying	
moistening, oiling	
rolling	
trimming	trimming waste
sorting, weighing	
leather magazine	
shipping	

1. Leather for shoe upper construction

Upper leathers are all leathers which are used in shoe production mainly for the shoe upper construction. They have the largest share in the total leather production, i.e. >50 %, whereby upper leathers made from cattle hides account for the major part, followed by calf and goat skins and in descending order sheep skins, pig skins, horse hides, and to a small extent buffalo hides, kangaroo skins and reptile or fish skins.

The most important quality requirements of shoe upper leather:

Tests	Requirements	
flexing endurance in the cold (- 20 °C)	50000 dry, 10000 wet min. 30 000 flexings	
adhesion of finish	3.0 N dry, 2.0 N wet	
rub fastness	min. 50 rub cycles	
fastness to hot plating	min. 80 °C	
distension of grain	bulge height min. 7.0	
split tear force	min. 18 N (with lining) min. 25 N (without lining)	
tensile strength	min. 150 N	
elongation at break	not less than 40 %	
lightfastness	not less than rating 3 (blue scale)	
fastness to migration	max. rating 3 (blue scale)	
pH value (aqueous extract)	not less than 3.5	
mineral substances removable by washing	not exceeding 1.5 %	
water vapour permeability	1.0 mg/h · cm ²	
water vapour absorption	10.0 mg/cm ² (after 8 hours)	
waterproofing	penetration of H ₂ O min. 60 min	absorption of H ₂ O max. 35 %
water spotting test	drying without staining	
substances extractable with dichloromethane	depending on adhesive: one-component: up to 9 % two-component.: up to 14 % PU special adhesive: above 14 %	

a. Grain leather**Side upper leather**

Term: Collective term for leathers of cattle hides which are manufactured by means of chrome tannage with a wide variety of retanning processes in all degrees of softness and the most different types of finish.

Rawstock: Cattle hides of all weight classes and provenances.

Requirements of production: Leather thicknesses of 1.2-1.8 mm, and > 2 mm for hard-wearing and unlined footwear.

Due to the many variations in the production of side upper leather a great variety of requirements exists. In general, side upper leathers should have good fullness and no loose grain. This should be aimed at especially in the sections of poor substance (sides, flanks) for a good yield of area.

Box sides

Term: Purely chrome-tanned side upper leather with reduced fatliquoring to obtain the traditional "bouncy handle". In the last few decades they have been manufactured in a somewhat softer quality. Finishing consists of a casein glaze finish or a glaze/plate finish while preserving the natural appearance of grain.

Rawstock: Mainly cattle hides in weight classes of 15-25 kg.

Requirements of production: Depending on use, in thicknesses of 1.4-1.8 mm for fine walking footwear, 1.8-2.2 mm for boots and hard-wearing shoes. The leathers should have a full handle with firm structure for good stability of shape. Bending the leather inwards must not result in loose grain or flabbiness.

Corrected grain leather

Term: Side upper leather in which disturbing grain defects are removed by correcting buffing of the grain. The quality grade is improved by the increased usable area for shoe production. These leathers receive an "artificial grain layer" by grain impregnation and thicker, filling finish coats.

Rawstock: Cattle hides of all weight classes and provenances which exhibit a high percentage of grain defects.

Requirements of production: Manufactured in leather thicknesses of 1.2-2.0 mm for tough footwear. A more intensive vegetable/synthetic tanning or an additional resin tanning is necessary to improve the properties for buffing, upholstering and embossing. During finishing they receive pigment coats and a pore grain embossing. Top coats dyed with aniline dyes are often applied to accentuate a semianiline character.

Waterproof

Term: Chrome-tanned or also chrome-vegetably tanned side upper leather which has been intensively fatliquored and which possesses good impermeability to water as smooth or grained leather. Advancements in water-repellent technology have meanwhile led to products with maximum impermeability to water and a lower fat content.

Rawstock: Cattle hides of good substance in medium weight classes.

Requirements of production: Used for sports shoes, ski boots and heavy, hard-wearing footwear in thicknesses between 1.8 and 2.4 mm. A full, slightly rubber-like handle with tight and smooth grain is demanded.

Russet upper leather

Term: Natural-coloured, vegetably tanned side upper leather which has been intensively fatliquored. Formerly produced in large amounts, nowadays of little importance. It can be used in shoe production both with the grain side or the flesh side on the outside.

Rawstock: Mainly cattle hides, also kipses, in weight classes of 15 kg and more.

Requirements of production: Produced in thicknesses of 1.8-2.8 mm for heavy footwear such as hiking and mountaineering boots, army boots and industrial shoes. Besides softness, fullness and pliability russet upper leather should have sufficient firmness. Little washing-out loss, good tensile strength and good air permeability in addition to impermeability to water are demanded.

Russian leather

Term: Originally a calf or side upper leather which was only produced in Russia and mainly tanned with willow bark. The Russian leather which is now commercially available is a combined vegetably tanned and chrome-tanned leather. To achieve the characteristic smell of Russian leather it is impregnated with birch-tar oil.

Rawstock: Light cattle hides and calf skins.

Requirements of production: Used as shoe and boot upper leather, sometimes also as harness leather and fancy leather, in thicknesses of 1.4-2.6 mm.

Polishing leather

Term: Soft, chrome-tanned side upper leathers which have been lightly vegetably/synthetically retanned and have received a polishing finish.

Rawstock: Cattle hides of all weight classes.

Requirements of production: Used in thicknesses of 1.2-1.8 mm, similar to aniline, with a light/dark contrast when the grain is extended.

Sandal leather

Term: Vegetably tanned cow-hide leather, manufactured similarly to russet upper, but with reduced fatliquoring.

Rawstock: Cattle hides of all weight classes.

Requirements of production: Manufactured in thicknesses of 1.6-3.0 mm. As they are mostly used unlined, the flesh side is processed with short fibres by dry shaving or buffing.

Boxcalf

Term: Chrome-tanned calf upper leather having a very fine appearance of grain and with a "bouncy handle" like that of box side leather, manufactured with a glaze or a glaze/plate finish. As these leathers have an elegant appearance they are used for fine footwear in smooth, boarded, high-gloss or matt design.

Rawstock: Manufactured from calf skins of all weight classes, from milk calf skins, and grasser skins up to veal skins. Clean-grained skins of good substance and free of cuts should be used.

Requirements of production: Manufactured in thicknesses of 0.8-1.4 mm depending on their use. A full, supple handle with good firmness and good tensile strength is required. Furthermore a fine, firm grain without loose grain sections and flabbiness, and a non-coating finish are desired.

Calf upper leather

Term: Formerly made by vegetable tanning in natural brown, calf leathers have meanwhile lost importance. Today this term refers to all calf leathers which have been chrome/vegetably tanned in all variations of handle and finishes.

Rawstock: Calf skins of all weight classes.

Requirements of production: Manufactured in thicknesses of 0.8-1.8 mm.

Glazed kid leather

Term: Upper leathers of kid skins and small goat skins, formerly manufactured by two-bath chrome tanning, today by the one-bath chrome tanning method, with a smooth glaze finish. One of the highest-quality and most elegant leathers, used mainly for ladies' footwear. The characteristic fine goat skin grain and good strength are outstanding properties.

Rawstock: Kid skins and light goat skins of good substance up to a maximum size of 40-45 dm² (4 sqf). Special provenances in India, Pakistan, China, Indonesia, Spain and North Africa are preferred.

Requirements of production: Manufactured in thicknesses of 0.6-0.9 mm. A firm grain, no poor substance and no elasticity in the sides and flanks and a high-gloss, non-coating finish are demanded.

Goat skin upper leather

Term: Includes all upper leathers of goat skins in all degrees of softness and all variations of finish.

Rawstock: Goat skins of all breeds and sizes.

Requirements of production: Leather thicknesses of 0.6-1.4 mm.

Chevrettes (imitation of glazed kid leather)

Term: Upper leathers of smaller lamb and sheep skins, manufactured in a tanning and finishing procedure similar to that of glazed kid leather. They have lower strength properties and a different appearance of grain.

Rawstock: Lamb and sheep skins of good substance from special rawstock. They must not exhibit a veiny appearance, ribbiness or double skin.

Requirements of production: Manufactured in thicknesses of 0.6-1.0 mm. To fill the loose structure they mostly receive a stronger vegetable retannage.

Horse and foal upper leather

Term: A specialty in the production of horse and foal leathers is that the hide is divided into the horse shoulder and the horse butt of denser texture (see types of raw skins). The appearance of grain of the horse shoulder is similar to that of goat skin. Therefore glazed horse upper leather is also called "horse glazed kid" or "horse side leather".

Rawstock: Horse hides in weight classes of 12 kg and more, and foal hides of 7-12 kg salt weight.

Requirements of production: Manufactured in thicknesses of 1.0-1.6 mm. The horse butt requires a more intensive opening up of the skin by stronger liming.

Pig upper leather

Term: Pig skins are processed to produce upper leathers mainly in the Eastern-bloc states and China and only to a very small extent in Western countries.

Rawstock: Butts in the weight class 2-4 kg, less frequently entire pig skins (with flanks).

Requirements of production: Manufactured in thicknesses of 0.8-1.4 mm. As the bristle holes go through the entire cross-section of the leather, water-repellent treatments have been increasingly applied in the last few years to achieve good waterproofing. To hide defects or weaken an undesired appearance of grain of pig skins the grain is corrected by a buffing procedure, similar to that used for corrected grain side leather.

Kangaroo upper leather

Term: Kangaroo skins possess maximum strength properties and are therefore used especially for hard-wearing footwear.

Rawstock: Selected clean-grain kangaroo skins.

Requirements of production: Manufactured in thicknesses of 0.8-1.2 mm.

Patent leather

Term: These are leathers with a mirror-bright gloss and with a relatively thick finish coat. Manufactured mainly in cold lacquering processes with polyurethane lacquers, less frequently by lamination.

Rawstock: Cattle hides, calf or goat skins and occasionally also cow-hide lower splits.

Requirements of production: Manufactured in thicknesses of 1.0-2.0 mm. Good adhesion values and a lasting resistance to cracking of the finish coat should be ensured.

Shrunk leather

Term: These are leathers in which a grain shrinking effect is produced on the grain side by highly astringent synthetic tanning agents or a line shrinking effect by means of glutaraldehyde. These effects are very firmly fixed by a subsequent chrome tannage and are more resistant during use compared to artificial grains.

Rawstock: Cattle hides, calf and goat skins, less frequently buffalo and zebu hides.

Requirements of production: Manufactured in thicknesses of 1.0-2.2 mm. The stronger and firmer the skin and skin texture, the deeper, more prominent and more even is the effect produced. The shrinking effect is also influenced by the degree of dewatering of the pelt, by the float length and by the duration of treatment.

Leather of reptiles

Term: Are only processed to a small extent for highly fashionable shoes and for trimmings.

Rawstock: Smaller types of crocodiles, lizards, snakes.

Requirements of production: Manufactured in thicknesses of 0.3-1.2 mm. Particularly attractive pigment patterns are achieved by alum tanning, otherwise they are dyed and finished with colourless glaze top coats.

Leather of fish skins

Term: Only of minor importance for upper leather production as the strength properties are insufficient in most types of fish skins.

Rawstock: Some types of shark, seal and dolphin. Several types of cod, pollack and eel are suitable for trimming leathers.

Requirements of production: To avoid excessive decomposition of albumen substance in sensitive types of fish skins, the temperatures for soaking and liming should not exceed 20 °C. Moreover opening up of the skin should not be carried out during liming or be reduced to a minimum for some types.

Upper leather of cow-hide lower splits

Term: When processing cow hides vast quantities of lower splits are produced, especially in the higher weight classes. Due to the advancements in finishing technology over the last decades and the manufacture of highly flexible polymer binders and foils it is possible to make hard-wearing upper leathers from lower splits.

Rawstock: Flesh side lower splits of firm texture made from cow hides.

Requirements of production: Manufactured preferably as half or entire butts in thicknesses of 0.8-2.2 mm. To achieve smoothness with a short-fibre nap the splits receive a more intensive vegetable/synthetic retannage. The use of reactive butadiene binders with the addition of cross-linking agents is advantageous for achieving maximum bending endurance and good filling of the finish coat. For best adhesion values the first base coats should be applied by brushing or roll coating using contrarotating rollers.

b. Suède and nubuk leather**Suède leather**

Term: This designation refers to all leathers which have been given an even, rough or velvety fibre quality on the back (flesh or split side) by repeated buffing. This velvet is kept short-fibred or long-fibred depending on the requirements of fashion. Cow-hide suède leather with grain side is also called hunting-suède, suède calf leather with grain side is known as velvet calf. The common German term "Wildleder" is not correct as a general name for all suède leathers because it strictly refers only to suède leathers obtained from the skins of red deer, chamois, elks, reindeer, buffalos, antelopes, gazelles or kangaroos.

Rawstock: Cow hides, horse hides, pig skins, calf skins, goat skins and less frequently sheep skins (for upper leathers).

Requirements of production: Suède leathers are mainly manufactured by chrome tanning. They receive special retannages, always depending on the requirements, to improve buffing properties, fullness, handle and to achieve even dyeing properties. The products used are chrome and aluminium tanning agents, zirconium tanning agents, glutaraldehyde, resin tanning agents or synthetic condensation products. The conventional method of production includes retanning and light fatliquoring with intermediate drying.

After buffing the leather is wetted back, dyed and the remaining amount of fatliquor is added. To save labour and time suède leathers are nowadays mostly manufactured by direct processing. The low brilliance as a result of buffing after dyeing is corrected by a lustre finish.

Split suède leather

Term: The suède nap is carried out on the split side of the lower split.

Rawstock: Lower splits (flesh splits) of firm texture made from half or whole cow-hide butts in higher weight classes.

Requirements of production: Manufactured from grain splits like suède leathers.

Nubuk leather

Term: Designation for all leathers which are buffed and left coarse on the grain side. A very fine, velvety plush character is achieved by the very dense fibre texture of the grain layer.

Rawstock: Clean-grain cattle hides, horse hides and pig skins or calf skins which are free from defects.

Requirements of production: Nubuk leathers are mainly manufactured with an intermediate drying stage. They receive a water-repellent finish to improve resistance to wetness and to counteract greasiness during use. Apart from that, the process of manufacture is similar to that of suède leathers.

2. Leather for shoe inside construction

This group includes lining leathers. Besides stabilisation of the shoe upper their main function is to compensate the absorption and release of wet transpiration of the foot during use. The leathers used are light types of leather from sheep and goat skins, skivers and split leathers as well as cow-hide grain splits, calf skins and pig skins. The tanning methods are vegetable tanning, a combination of chrome and vegetable tanning and pure chrome tanning. In general, leathers of medium to low quality are used as lining leathers. They should meet the criteria for good softness, pleasing handle, high fastness to perspiration, water vapour permeability and absorbing capacity and should contain only small amounts of substances that are removable by washing.

The most important quality requirements for shoe lining leather:

Tests	Requirements		
	rub cycles	aniline leather	finished
rub fastness			
leather, dry/test fabric, dry	100	> rating 4	> rating 4
leather, dry/test fabric, wet	50	> rating 3	> rating 4
leather, wet/test fabric, dry	20	> rating 3	> rating 4
leather, dry/test fabric with perspiration solution pH 9.0	20	> rating 3	> rating 4
leather, dry/test fabric with benzine	20	no	staining
fastness to water (stripe test after 2h and 8h)	no staining of the zone of diffusion above rating 3 (grey scale)		
water vapour permeability	min. 1.0 mg/cm ² · h		
elongation at break (min. leather thickness > 0.4 mm)			
sheep skivers, unlaminated	min. 25 %		
sheep skivers, laminated	min. 30 %		
other leathers	min. 30 %		
split tear strength	only for lining leather as reinforcement: min. 15 N		
mineral substances removable by washing	not above 1.5 %		
pH value	not below pH 3.5		
substances extractable with dichloro methane	not more than 10 %		

**Lining leather,
vegetably tanned**

Term: Vegetably tanned light types of leather of all provenances.

Requirements of production: To reduce the substances removable by washing, good fixation of the tanning agent and intensive washing or soaking are necessary. If the leathers have been pretanned adequate detanning is required. Since vegetably tanned leathers have only a reduced fastness to perspiration, this should be improved by aftertreatments with glutaraldehyde, resin or aluminium tanning agents. To ensure a good absorbing capacity of the leathers, strong fatliquoring of the surface should be avoided.

**Lining leather,
combination
tanned**

Term: Light types of leather of all provenances manufactured by the chrome/vegetable or vegetable/chrome tanning method.

Requirements of production: Excessive fat content and large amounts of soluble substances should be avoided.

**Lining leather,
chrome-tanned**

Term: Only seldom used as pure chrome-tanned lining leathers.

Requirements of production: Chrome salts that are easily removable by washing, deposits of sulphur and, above all, hexavalent chromium compounds should be avoided.

All lining leathers can be processed on the natural grain side, smooth or roughened, and also on the velvet side. Depending on the requirements of fashion they are also dyed or finished. When dyeing lining leathers it is absolutely necessary to use dyes which are fast to perspiration and bleeding as well as to dry and wet rubbing. Highly coating or sealing top coats should not be used for leathers to be finished in order not to impair absorbing capacity and water vapour permeability.

3. Leather for shoe underside construction

This group comprises the vegetably tanned sole leathers and factory sole leathers. Sole leathers are hard and less pliable, factory sole leathers are more flexible. Chrome-tanned sole leathers are of little importance today.

The most important quality requirements for sole leather:

Tests	Requirements		
	sole leather, old pit tannage	sole leather, modern tannage	insole leather
ash content	0 %	max. 3.0 %	max. 2.5 %
fat content	max. 0.7 %	max. 3.0 %	max. 4.0 %
loss by washing, total	max. 6.0 %	max. 16 %	max. 10 %
“ , organic	max. 6.0 %	max. 14 %	max. 8 %
“ , inorganic	0 %	max. 2 %	max. 2 %
degree of tannage	60-95	60-95	60-95
pH value	aqueous extract not below pH 3.5		
difference value	at pH < 4.0 not over 0.70		
tensile strength, daN/cm ²	min. 200	min. 200	min. 200
elongation at break	max. 35 %	max. 30 %	max. 35 %
stitch tear strength (daN/cm)	min. 130	min. 100	min. 100
air permeability (cm/min. per cm Hg)	min. 20	min. 20	min. 20
water vapour permeability (mg/cm ²)	min. 200	min. 200	min. 200
water absorption (Kubelka) after 2 h	max. 40	max. 40	min. 25
after 24 h	max. 50	max. 50	
permeometer	after 30 minutes max. 30 % not less than 20 minutes		-
water absorption			.-
water penetration			.-
specific weight	1.15 g/cm ³	1.15 g/cm ³	1.05 g/cm ³
abrasion coefficient	max. 2.0 %	max. 3.0 %	-

**Sole leather,
tanned according
to an
old tanning
method**

Term: Thick, relatively hard, firm and less pliable leather which has been produced by purely vegetable tanning. Used for long soles, half soles and heels of heavy footwear.

Rawstock: Heavy cattle hides of good substance with firm, dense fibre texture and greater raw hide thicknesses. Weight classes of over 30 kg, often butted, are mainly used. The flanks of slightly poorer substance are often manufactured separately with a more flexible tannage.

Requirements of production: Only moderate opening up of the skin by short liming, only superficial deliming and no enzymatic bate. Tanning is carried out in pits only (colour pit, lay-away pit, tan-pit) for a period of 4-8 months. Besides firmness and fullness this sole leather should exhibit good impermeability to water with low absorbing capacity and above all high fastness to abrasion.

**Sole leather,
old pit-tanned**

Term: Sole leather of special fullness and fastness to abrasion produced with weak tanning liquors (mostly oak bark) in pits and with long duration of tannage.

Rawstock: See sole leathers manufactured according to an old tanning method.

Requirements of production: Concentration of tanning liquor not exceeding 4.5 °Bé. Pretannage in the colour pit, final tanning in the lay-away pit or tan-pit with a duration of at least 12 months for leather thicknesses of more than 3.5 mm. $\frac{2}{3}$ of the tanning agents should consist of bark tannin (mostly oak and pine).

**Sole leather,
tanned according
to
modern tanning
processes**

Term: This group comprises the sole leathers which are manufactured in a shorter process by special pretanning methods, by increasing the concentration of tanning liquors and by final tanning in tanning vessels. The accelerated tanning methods take 1-4 months, the rapid tanning methods 3-4 days up to 3 weeks.

Rawstock: Cattle hides of good substance and dense texture in weight classes above 25 kg, butted.

Requirements of production: To obtain a good yield, short liming without too intensive opening up of the skin is performed as for the old tanning methods, mostly by superficial deliming without enzymatic bating. However for rapid tanning methods more intensive deliming is necessary in order to accelerate penetration of the tanning agents. Tanning is carried out with higher-percentage tanning agents and extracts such as quebracho, mimosa, chestnut, valonia or replacement syntans. Owing to the use of higher concentrations of tannin a stricter control of the tanning process is absolutely necessary to avoid case-hardening.

**Factory sole
leather**

Term: All sole leathers of higher flexibility are called factory sole leathers. Depending on the process of manufacture or their future use they are subdivided into:

repair leather = stronger sole leather
manufactured with a medium duration of
tannage,

light sole leather for pegging on = stiffer, firm
sole leather,

stitched sole leather = more pliable sole leather,

flexible sole leather = an even softer sole
leather, especially suitable for glueing.

These factory sole leathers are used in shoe production as long and half soles for lightweight footwear.

Rawstock: Cow hides and light cattle hides in weight classes of 15-30 kg as domestic and wild hides, but also grasser veals and heavy calf skins.

Requirements of production: The method of processing and the tanning agents used are the same as for sole leather production. Besides a more intensive deliming process moderate enzymatic bating is performed. To achieve softness and suppleness of the leathers more soft-tanning vegetable and synthetic tanning agents are used in appropriate quantities and with higher contents of fatliquoring agents, depending on the intended use.

Insole leather

Term: Insole leathers are manufactured by the tanning process used for factory sole leathers. The only difference is that the leather is less thick and the texture is less firm and dense.

Rawstock: Shoulder and flanks of cattle hides of all weight classes and larger calf and grasser skins.

Requirements of production: Unlike sole leather, insole leather has to be capable of absorbing transpiration of the foot and thus certain amounts of moisture. Moreover it must be fast to perspiration and thus resistant to a resulting shrinking of area or embrittlement. Furthermore insole leather must not have a high content of substances soluble in moisture. Intensive washing and good fixation of the tanning agents are required. Glutaraldehyde or condensation products should be used in appropriate quantities for fastness to perspiration.

Welting leather

Term: Vegetably tanned, softer factory sole leathers of dense texture which are punched in strips up to 20 mm wide and are mostly given fashionable embossed patterns. In an even thickness of split they serve as outer, closing joint between the upper leather shaft and the shoe underside structure. The welting leather is applied by stitching, in natural colour or dyed in a matching colour to that of the upper leather.

Requirements of production: Besides good flexibility the welting leathers should have high stitch tear strength.

Chrome sole leather

Term: Manufacture of this product has greatly decreased due to the improvement of synthetic sole materials over the past decades. These leathers are produced by pure chrome tannage from heavy cattle and buffalo hides and very strong lower splits. Nowadays they are only used for footwear which has no contact with wetness as they change their shape under the action of moisture and become very slippery. As opposed to vegetably tanned leathers they have an increased fastness to abrasion.

Requirements of production: In order to achieve firmness and toughness of the sole it is high-dried in the wet-stentered state. The stability of shape in wetness can be improved by a special water-repellent treatment.

Sole leather, combination tanned

Term: Sole leathers which receive a chrome retannage after vegetable tanning or which have been pretreated with a mineral tannage. This combination tanning improves fastness to abrasion and perspiration.

Rawstock: Same as for the production of vegetable sole and factory sole leathers.

4. Furniture and upholstery leathers

These leathers are almost exclusively manufactured from entire large-area hides. While upholstery leathers as covers for plastic foam are manufactured very soft and also elastic, furniture leathers for covering armchairs, chairs and three-piece suites are somewhat firmer.

The most important quality requirements for upholstery leather:

Tests	Requirements	
	grain leather	suède and nubuk leather
rub fastness ♦ test felt, dry ♦ test felt, wet ♦ with perspiration solution staining of the felt - grey scale	rub cycles 500 80 50 not below rating 4	rub cycles 50 20 20 not below rating 3
flexing endurance	no visible changes after 20000 flexings	no test
adhesion of finish	mean value min. 2.0 N/cm	no test
dyeing	deep dyeing in the leather cross-section	penetration dyeing if possible
lightfastness	min. rating 3	
split tear force	min. 20 N/mm	
tensile strength	up to 2mm min. 100 daN/cm above 2mm min. 250 daN/cm	
pH value, aqueous extract	min. 3.8	
ash content	max. 2.0 % (after deduction of tanning oxides)	
test not required, but to be carried out if necessary	stability to amines fastness to migration stability to ultraviolet light	

**Vachettes
leather**

Term: Vachettes are soft, large-area cow-hide leathers manufactured by vegetable tanning. Buffalo hides are also processed to a small extent. However, during the last decades vegetably tanned leathers have been replaced in terms of volume by chrome-tanned and lightly vegetably/synthetically tanned leathers. They are manufactured in thicknesses of 1.0-1.5 mm and classified as vachettes for furniture, upholstery, cars, carriages, aniline vachettes, case and border vachettes, split suède, nubuk vachettes, vachettes for camera cases, fancy or saddlery vachettes.

Rawstock: Bull hides of large area and also cow hides in weight classes above 30 kg.

Requirements of production: The most important requirements for furniture and upholstery vachettes are uniform softness and suppleness without loose grain over the entire leather area. This is achieved by opening up in an intense liming process and by splitting the limed pelts. Often the hides are limed in a pure lime pit. Good colour fastness, high lightfastness, fastness to migration and amines, good adhesive strength and high resistance to scratching and abrasion of leather finishes are further important properties. Aniline vachettes in particular should be protected against staining by means of an oleophobic treatment.

**Furniture
leather
for
chairs**

Term: Vegetably tanned or chrome-tanned leathers and more intensively vegetably/-synthetically retanned leathers in thicknesses of 2.5-4.0 mm.

Rawstock: Bull and buffalo hides of heavier weight classes.

Requirements of production: As the edges are visible penetration dyeing is necessary. To ensure good stability of shape these leathers should possess only moderate elasticity.

Upholstery leather for cushion covers

Term: Very soft chrome-tanned cow-hide leathers with only a light synthetic/vegetable retannage treatment in thicknesses of 1.0-1.4 mm are used. Polyurethane foam is the main filling material.

Requirements of production: Besides very good softness of the leathers particular attention should be paid to fastness of the finish to amines.

Car upholstery leather

Term: All large automobile manufacturers demand a very high quality for these leathers by setting their own standards which vary from company to company. Cow-hide leathers in thicknesses of 1.1-1.4 mm are processed.

Requirements of production: The values demanded are often above the limit values requested for normal upholstery leathers. Important properties of the finish are high adhesion, enhanced rub fastness, enhanced resistance to cracking, very good fastness to scratches and a high temperature range for resistance to cold and heat. Moreover, these leathers should have low fogging values.

Upholstery leathers for aircrafts

Term: Similar manufacturing methods, leather properties and quality requirements as for car upholstery leathers.

Requirements of production: An additional flameproof finish is required for this application. Furthermore, area weights of the leather per m² are prescribed (sometimes also demanded for car upholstery leathers).

Corrected grain upholstery leather

Term: Upholstery leathers with heavier grain defects are lightly buffed with fine abrasive paper on the grain side to remove these defects. Then they receive a filling, elastic preliminary base coating and often a fine pore embossing treatment followed by a normal finish for upholstery leathers or also a foam finish. Processing of these assortments enables the manufacture of upholstery furniture at low prices.

**Nubuk
upholstery
leather**

Term: After intermediate drying a velvety plush is produced on the grain side by repeated buffing with fine abrasive paper.

Rawstock: Large-area cattle hides of good substance which are free from defects.

Requirements of production: Dyestuffs which are combinable and have very high lightfastness and fastness to migration should be used for dyeing. Good fixation of the dyes is absolutely necessary. The dyed, dried leathers should be resoaked to completely remove the dye powder and to prevent possible staining on textiles during use. As nubuk leathers have an open fibre texture a final oleophobic treatment is recommended for adequate protection against staining.

**Suède
upholstery
leather**

Term: After intermediate drying of cattle grain splits, mainly however cattle lower splits of dense texture, a plush of short or long fibres is produced on the split side by repeated buffing.

Requirements of production: The requirements are the same as for nubuk upholstery leathers. When processing suède leathers from lower splits attention should be paid to adequate strength properties.

5. Garment, glove and hat leathers

Leathers of this category are manufactured from almost all types of rawstock, but mostly from sheep, lamb, goats and kid skins, followed by cattle and horse grain splits, calf skins, pig skins and skins of red deer.

The most important quality requirements for garment leather:

Tests	Requirements	
	finished grain leather	aniline, nubuk and suède leather
rub fastness ♦ test felt, dry ♦ test felt, wet ♦ with perspiration solution staining of the felt -grey scale	rub cycles 50 20 20 not below rating 3	rub cycles 20 10 10 not below rating 3
lightfastness	min. rating 4	min. rating 3
flexing endurance	min. 50000	-
adhesion of finish	min. 2.0 N/cm	-
split tear strength	min. 200 N/cm	min. 150 N/cm
tensile strength	1200 N/cm ²	1200 N/cm ²
stitch tear strength	min. 25 daN/cm	min. 25 daN/cm
elongation at break	max. 60 %	max. 60 %
wettability	15 minutes	10 minutes
resistance to dry cleaning	No stripping of the finish and no change of handle after cleaning and fatliquoring. Change of colour < rating 3-4; area <± 3%	No change of handle after cleaning and fatliquoring. Change of colour < rating 3-4; change of area <± 3%
washability	No change of leather handle after washing, drying and light staking; change of colour < rating 3 of the grey scale (rating 4 is recommended); change of area < ± 3%.	
PH value	min. pH 3.5 of the extract	
ash content	max. 2 % (after deduction of tanning oxides)	
chrome oxide content	min. 2.5 % Cr ₂ O ₃	
fat content	4-10 % fatty substances	

**Garment
nappa leather**

Term: The term "nappa" is a collective name for all types of soft, elastic grain leather. The original nappa leather was manufactured from alum tanned glove leather by retanning with gambier extract and chrome alum, but later by modern, efficient tanning methods. The thicknesses of leather are 0.6-1.0 mm depending on use.

Rawstock: Small skins of all provenances, cattle and horse hides, pig skins, calf skins and red deer skins, which are processed from rawstock, wet blue or crust. Grain skivers of sheep and lamb skins are also used for garment leathers. However due to their low strength properties they have to be glued with stretch materials. Manufacture of the formerly widely used East Indian skins, i.e. vegetably tanned goat, hair sheep and lamb skins, has decreased to a minimum.

Requirements of production: Today's garment grain leathers are mainly chrome-tanned and retanned with lightfast retanning agents, where possible. Chamois tannage is preferred for wild skins (deer, roe, chamois, elk). It is important that good softness and a low area weight of the leathers be achieved to get as close as possible to the soft quality of textiles. Only thin finishes, which are fast to rubbing, should be applied if an elegant appearance is desired. The leather is often dry shaved to increase softness and homogeneous strength. As garment leathers are thin they must have an adequate firmness of texture.

**Protective
clothes for
motorcyclists**

Term: Special cow-hide grain leathers, to a small extent also leathers from kangaroo skins and stronger goat skins of dense texture, in thicknesses of 1.3-1.5 mm for added safety and protection against grazes or fractures in the case of an accident.

Requirements of production: The finishes of these leathers should exhibit increased adhesion and fastness to abrasion. Improved fastness to cleaning is also important for removal of adhering dead insects. Furthermore, the leathers should possess good breathability to allow good dissipation of transpiration through these high-necked suits. Finishing is mainly performed in very bright shades which are easily visible.

**Garment
suède leather**

Term: A short-fibre or long-fibre plush character is achieved on the flesh side by repeated buffing. Depending on the fatliquoring method it is possible to obtain a dry, velvety velour or also a semimatt velour with all intermediate stages.

Rawstock: Same as that used for the production of grain leathers. Besides lamb skins, goat and calf skins are preferred on account of their denser fibre texture and good strength properties.

Requirements of production: Besides softness it is important that the dyeing of these leathers be fast to dry and wet rubbing. Garment leathers must never be buffed after dyeing, but after intermediate drying to remove residues of dye powder. Moreover the dyeing should be very lightfast and fast to cleaning. To avoid increased wettability the leathers should receive a final water-repellent finish.

Suède leather for shirts and blouses

Term: Special thin fabric-soft suède leathers, in thicknesses of 0.4-0.5 mm. Mostly manufactured from hair sheep skins or smaller goat skins of dense texture.

Requirements of production: In many cases the grain is split and the split side of the lower split is buffed. This is done to achieve a very fine, velvety velour plush of special density. As this type of leather is often in direct contact with the skin of the wearer, the leathers must be free from soluble, harmful substances. They should also be washable.

Leather for Tirol style trousers

Term: The leather for original Tirol style trousers, also trimming leather for breeches, is manufactured by old or new chamois tannage. They are processed with both the grain side and the suède side on the outside.

Rawstock: Deer, roedeer, elk, reindeer and chamois skins.

Requirements of production: Soft and lightly elastic quality, full handle with short, dense fibre texture. Dyed leathers should have good lightfastness and fastness to washing. They must not contain free acids or alkalies nor harmful substances.

Suède leather for trousers

Term: Leather trousers are also manufactured in less expensive variants from cow-hide grain splits and lower splits of dense texture by means of chrome tannage and moderate retannage.

Requirements of production: The leathers are buffed after intermediate drying. Dyeing is performed as penetration dyeing or as spray dyeing, less frequently as brush dyeing, the reverse side mostly having a yellowish shade similar to that of chamois leather.

The most important quality requirements for glove leather:

Tests	Requirements - glove leather		
	chrome-tanned	aluminium-tanned	chamois-tanned
tanning oxides	min. 2.5 %	min. 2.0 %	-
ash content (after deduction of tanning oxides)	max. 2.0 %	max. 8.0 %	max. 6.0 %
fatty substances (extracted with dichloro methane)	4-10 %	max. 10 %	(with diethyl ether) max. 10 %
tensile strength ♦ goat skin ♦ sheep skin	min. 200 daN/cm ² 100 daN/cm ²	min. 200 daN/cm ² 100 daN/cm ²	min. 200 daN/cm ² 100 daN/cm ²
extension at 20 daN/cm	min. 20	min. 20	min. 30
split tear strength	min. 25 %	min. 25 %	min. 25 %
stitch tear strength (daN/cm)	min. 60	min. 40	min. 40
elongation at break	min. 50 %	min. 50 %	min. 50 %
rub fastness 20 rub cycles-dry 20 rub cycles-wet 20 rub cycles with perspiration solution	min. rating 3 of the grey scale		
adhesion of finished leathers	in finished leathers min. 2.0 N/cm		
washability	The maximum washing temperature is 30 ± 2 °C		
fastness to perspiration	no staining below rating 3 of the grey scale		
pH value	aqueous extract (1:20) not below 3.5	aqueous extract (1:20) not exceeding 8.5	
difference value	not exceeding 0.70		

**Glove leather,
chrome-tanned**

Term: The most common type of glove leather manufactured in the past decades. Besides a high degree of softness the leather should have good elasticity with adequate tensile strength and stitch tear strength. It is produced in thicknesses of 0.6-1.2 mm depending on use requirements.

Rawstock: Mainly kid and lamb skins and in descending order goat and sheep skins, deer skins, peccari or carpincho skins.

Requirements of production: Good opening up of the skin in liming, good penetration deliming, strong bating and intense penetrative neutralization. Dyeing is performed with metal complex dyes which are lightfast and fast to bleeding. High-quality glove leathers are only sprinkled with talcum powder and subsequently pushed to make aniline glove leathers. Very soft, elastic binder finishes with an emulsion lacquer coat are applied for tougher use requirements or for lower-grade assortments. Glove leathers should be free from harmful substances and should be washable without undergoing serious changes.

**Glove leather,
aluminium-
tanned**

Term: Leathers tanned with aluminium salts are used to manufacture white gloves because of their light tanning colour. Glove leathers having a white reverse side are obtained by brush dyeing on one side.

Rawstock: As for chrome-tanned glove leathers.

Requirements of production: Combinations with fatty alkyl sulphates or with sulphonyl chlorides are common to achieve a high degree of softness and elasticity. Reducing bleaching agents, sometimes containing optical brighteners, are used to enhance the whiteness of the tanning colour.

**Glove leather,
chamois-tanned**

Term: Very soft and stretchy leathers, manufactured by means of old or new chamois tannage. They have excellent washing properties.

Rawstock: Predominantly the skins of roe deer, deer, chamois and reindeer and small animal skins of lambs, sheep, kids or goats.

Requirements of production: New chamois tanning is now carried out more often using soft-tanning glutaraldehyde for pretanning instead of the conventional formaldehyde. Paraffin sulpho chloride is often used in corresponding amounts for final tanning to accelerate grain oxidation. Dyeing is performed as brush dyeing on one side or as penetration drum-dyeing for which pretanning with chrome is required.

Kid glove leather

Term: Manufactured only seldom today. These are very soft, stretchy thin leathers in a white tanning colour. Nowadays they are made by aluminium tannage and special fatliquoring methods.

Rawstock: Selected small lamb, kid and goat skins.

Requirements of production: Tanning is performed with a mixture of alum, common salt, flour and egg yolk. After drying, the skins are stored in the crust condition for some time to allow them to cure, then wetted back and hand-staked and dyed by brush dyeing on one side. For drum-dyeing kid glove leathers require a preliminary tanning with chrome.

**Nappa glove
leather**

Term: Originally kid glove leathers which were retanned with gambier extract. If an aftertreatment with basic chrome salts is applied, they are usually called "chrome nappa leather". Otherwise the designation "nappa leather" refers to all soft leathers which are similar to the original nappa leather. Today manufactured by chrome tannage with vegetable/syn-

thetic retanning.

Rawstock: Mostly somewhat larger and thicker lamb, kid or goat skins.

**Glove leather
for skiers**

Term: Stronger types of leather manufactured by chrome tanning with a particularly strong water-repellent finish and very high fastness to abrasion.

Rawstock: Full goat skins or lamb skins of dense texture.

Requirements of production: A thorough water-repellent treatment is important. Separate pretreatment primers should be applied in the finishing to improve adhesion.

Gloving leather

Term: Kid or lamb skins buffed on the flesh side, which have minor defects on the grain side and can therefore not be used for grain glove leather. They are also called "Danish leather" or "Swedish leather". Formerly manufactured by alum/formaldehyde tanning, today by aluminium tanning.

Requirements of production: The buffed fibre should be kept short so that it does not result in a visible two-way nap or gloss when coated. This is achieved only by wet buffing with abrasive papers of fine grain, by wet fluffing with a rotating pumice or wet buffing stone.

Mocha leather

Term: These are leathers buffed on the grain side, formerly manufactured by glacé tanning, today by aluminium tanning and retanning with chrome.

Rawstock: Lamb skins, especially skins of hair sheep and gazelles, and also kid skins.

Requirements of production: After intermediate drying they are wetted back and wet buffed before dyeing, which imparts a velvety, very short-fibred plush quality.

Quality requirements for hat and helmet sweat leather:

Tests	Requirements
	hat sweat/ helmet sweat leather
ash content	max. 2.0 % (after deduction of tanning oxides)
fat content	3-8 %
pH value (extract)	not below 3.5 and not over 7.0
difference value	not over 0.70
loss by washing	max. 4.0 %
degree of tannage	min. 50
tensile strength	min. 100 daN/cm ²
elongation at break	max. 50 %
water absorption	
◆ after 5 minutes	min. 100 %
◆ after 2 hours	min. 130 %

Hat and helmet sweat leather

Term: Leathers preferably manufactured by vegetable tanning, less frequently by combined chrome/vegetable tanning.

Rawstock: Mainly sheep, lamb and goat skins.

Requirements of production: The leathers should contain only small amounts of soluble substances removable by washing out. They should be free from harmful, skin-irritant substances and from strong free acids. Good absorption of perspiration and water is important for helmet sweat leathers. Therefore they are used without top coat finish and undyed. By contrast, hat sweat leathers have the function of keeping transpiration of the scalp away from the hat felt or cap fabrics and preventing fabric penetration of perspiration. Therefore they receive a nitrocellulose pigment coat finish in most cases.

6. Leather for sports equipment

Besides the mentioned types of leather this group also comprises upholstery leathers for gymnastics apparatus, leather for sports gloves, upper leather for a wide variety of sports shoes (shoes for football, handball and tennis, running shoes, walking shoes, ice hockey boots, mountaineering boots). Nowadays sports equipment is often made from synthetic material instead of leather.

Leather for the cover of balls

Term: The leathers used are mainly chrome-tanned leathers that have not been retanned or only lightly retanned, in thicknesses of 2.5-3.0 mm.

Rawstock: Compact cattle hides of dense texture and good substance.

Requirements of production: The leathers should be non-elastic to a large extent. This is achieved by wet stretching and high-drying of the leathers which have been thoroughly struck out. Furthermore high resistance to water is required which is achieved by a water-repellent treatment. The finish should exhibit high fastness to abrasion and is therefore applied on the basis of polyurethane. In many cases footballs undergo a final dip-treatment with polyurethane lacquer solutions.

Leathers for the handles of tennis rackets and golf clubs

Term: The leathers used are grain leathers of almost all types of raw hides which should have a slightly tacky, non-slippery surface handle. In the fabrication of rackets they are glued around the grip of the racket in thin-split tapes.

Requirements of production: The effect is achieved by spraying or plush-padding soft, slightly tacky acrylate compounds which are applied in the solvent phase as final treatment to finished or natural leathers.

7. Saddlery leathers and leathers for bags

The leathers of this group have to meet the most different requirements as they are used for different purposes. Fancy leathers are used for briefcases, camera cases, bags or handbags, larger cases or knapsacks, the more hard-wearing saddlery leathers are used for riding saddles, harnesses, stable halters or car trim leathers.

Tests	Requirements	
	leather for belts and seats, vegetably tanned	leather for belts and seats, chrome-tanned
fat content (with dichloro methane)	5-11 %	5-11 %
mineral substances	max. 2.5 %	-
tanning oxides	-	min. 2.5 %
substances removable by washing	max. 8 %	max. 2.0 % (mineral)
pH value	min. pH 3.5	
tensile strength	min. 2250 N/cm ²	min. 2500 N/cm ²
elongation at break	max. 50 %	max. 75 %
split tear strength	min. 400 N/cm	min. 500 N/cm
thorn bending test	with double thickness of leather no cracks up to a bending angle of 180°	
rub fastness ♦ 50 cycles, dry ♦ 20 cycles, wet ♦ 20 cycles, with perspiration solution	min. rating 3	

Leather for belts and seats, vegetably tanned

Term: Vegetably/synthetically tanned leather which has been moderately fatliquored and has received a smooth or embossed finish, in thicknesses of 2-4 mm.

Rawstock: Cattle hides of medium weight classes.

Requirements of production: Thorough penetrative deliming, uniform penetrative tannage, good elasticity and firmness with tidy processing of the reverse side.

Leather for belts and seats, chrome-tanned *Term:* Manufactured by chrome tanning, mostly with vegetable/synthetic retanning, similar to vegetably/synthetically tanned harness leather. These leathers have a higher elasticity and better strength properties.

Tests	Requirements		
	harness leather		stable halter
	vegetable	chrome	chrome
fat content (with dichloro methane)	10-25 %	10-25 %	10-18 %
ash content	max. 2.0 %	max. 2.0 %	max. 2.0 %
tanning oxides	-	min. 2.5 %	min. 3.5 %
pH value	not below pH 3.5		
tensile strength	min. 2500 N/cm ²	min. 3000 N/cm ²	min. 3000 N/cm ²
elongation at break	max. 60 %	max. 75 %	max. 75 %
split tear strength	min. 400 N/cm	min. 600 N/cm	min. 600 N/cm

Harness leather *Term:* Similar to the vegetably tanned harness leather, however with stronger fatliquoring, mostly performed in a hot air or light hot stuffing process. Besides good softness the more intensive fatliquoring treatment makes the leathers very fast to alkaline manure and animal excreta.

Stable halter leather *Term:* Leather manufactured mainly by chrome tannage and more intensive fatliquoring. The leathers should be highly elastic and pliable and should exhibit no crackiness of grain. Chrome tannage also improves the strength of the leathers.

Rawstock: Cattle hides of all weight classes.

8. Fancy and fine leathers

The leather types of this group are manufactured mainly from small animal skins and calf skins, to a lesser extent also from cattle hides, often from the thinner flanks, from pig skins and a wide range of wild skins and exotic skins. The latter are especially interesting for fashionable leathers because of their special grain patterns. Almost all types of tannage are used for making these leathers, however vegetable/synthetic tanning and retanning are the most common processes. Likewise, most of the finishes are applied as smooth or embossed finishes and many special effect finishes.

Tests	Requirements - fancy leather		
	vegetably tanned	chrome-tanned	combination tanned
fat content	5-11 %		
ash content	max. 2.5 %	max. 2.0 % (above content of tanning oxides)	
substances removable by washing	max. 8.0 %	max. 2.0 %	max. 7.0 %
tanning oxides	-	min. 2.0 %	min. 0.6 %
degree of tannage	min. 50	-	-
pH value (extract)	min. pH 3.5		
tensile strength (N/cm ²)	up to 1.25 mm min. 1000; above min. 1500	min. 1500	
elongation at break	max. 50 %	max. 75 %	
thorn bending test	up to a bending angle of 180° no cracking of the leather or grain.		
flexing endurance	min. 10000 flexings without cracks		
adhesion fastness	min. 2.50 N/cm		
rub fastness ♦ 50 cycles, dry ♦ 20 cycles, wet 20 cycles, with perspiration solution	min. rating 3		

- Portfolio leather** *Term:* This denotes all pocket book and wallet leathers used for wallets, purses, cases, ladies' belts less than 1 mm thick, smaller handbags or bags, protective covers, etc.
Requirements of production: The somewhat firmer leathers should have good stability of shape and low elasticity. To avoid corrosion by metal parts thorough neutralization of chrome-tanned leathers is very important. The finish should exhibit good adhesion and fastness to scratches. When processing skivers into upper material, linings are required for a good tensile strength.
- Morocco leather** *Term:* Real Morocco leathers are always vegetably tanned goat skins which have a characteristic raised bead grain produced by boarding in 16-32 ways. Imitation Morocco leathers are also manufactured from pretanned sheep or lamb skins and differ by their less firm grain.
Requirements of production: A further characteristic of Morocco leather is its so-called squeak effect which is achieved by detanning with acid auxiliary tanning agents and the use of dry fatliquors.
- Bookbinding leather** *Term:* Thin types of leather made from goat and sheep skins, sheep grain splits (skivers), calf skins or pig skins, by vegetable/synthetic tanning. Parchment leathers are also processed in special cases.
Requirements of production: Lightfast tanning agents which are low in acids and stable to oxidation (sumac, readily buffering synthetic products) should preferably be used for tanning to ensure durability of the book bindings.

Gold and silver leather

Term: Smaller vegetably tanned lamb or kid skins are coated with real gold or silver foils for high-quality de luxe articles. These days they are manufactured by applying metallized transfer foils by means of plating, also on the larger skins of small animals, calf skins and cow-hide grain splits. A soft thermoplastic polymer binder is used as contact adhesive for the base coating. Bronze powder is employed for special metal effects, mostly in top coats.

Skivers

Term: Thin sheep grain splits made by vegetably/synthetic or chrome/synthetic tanning. Used for pocket book leathers and for feedstuff. Lined with stretchy fabrics they are also used to produce soft bags.

Reptile leather

Term: This group refers to all leathers which are made from the skins of reptiles. These include a great variety of different species of crocodiles, alligators and caymans, lizards, snakes, turtles and bullfrogs. Owing to their extremely attractive surface patterns, scaling, keratinization and grain quality they are in great demand for fashionable, elegant leather goods. Following the Washington Agreement on Preservation of Species they are increasingly bred on large farms.

Requirements of production:

Crocodiles, caymans, alligators⁷² : The tanning methods for these types of skins are vegetable/synthetic, chrome/vegetable/synthetic or purely alum tanning with synthetic white-tanning agents. In the liming process thorough removal of the scales has to be ensured. For larger hides a deossification pickle with hydrochloric acid and/or organic acids is

applied for several days prior to liming to achieve a higher degree of softness. Oxidation bleaching with sodium chlorite or potassium permanganate/sodium sulphite is required to make leather in white, uni-colour or pastel shades. The leathers receive chiefly a casein glaze finish.

Turtle flanks, lizards and bullfrogs: In principle the same procedure as for crocodiles. A deossification pickle is not necessary.

Snakes: In order to avoid knotting and tangling during the processes of tanning, bleaching and dyeing, snake skins should be basted or tied together by their head and tail ends and processed in large quantities of liquor. Alum tanning with synthetic alum tanning agents is performed to accentuate the often very beautiful natural grain pattern.

Fish leather

Term: Leathers of fish skins have been manufactured for many decades. The chiefly processed materials are the skins of sharks, different species of dolphins, rays, sturgeons and eels. More recently the skins of various scaly fishes have also been used to make leather, e.g. salmon, perch, codfish, cod, haddock and also carp. The great variety of surface structures gives diverse leathers of interesting appearance. While the larger fish skins can be used to make certain leathers for briefcases and also for shoes, the smaller skins are employed to make pocket book leathers and trimming leathers as they often exhibit an inadequate tensile strength. Altogether the worldwide production of fish leather is insignificant compared to the yield of raw skins.

Requirements of production: In processing fish skins several peculiarities should be taken into consideration. The collagen of many types of fish skins is extremely sensitive to heat and stronger alkalies, especially lime. For the sensitive types the beamhouse processes including tanning should be performed in a temperature range up to 20 °C and soda should be used instead of lime hydrate in the sodium sulphide lime. Thorough removal of the scales is necessary after liming. Many types of shark skins require desilification with high concentrations of acids and salts. In principle all tanning methods are suitable for tanning fish leather.

Ostrich leather

Term: The most characteristic feature of this type of leather are the prominent burls to which the feathers of the living bird were attached and which give the leather a very special appearance. Raw skins from breeding farms are used for leather making.

Leather of the second stomach and the first stomach⁷³

Term: Despite the large yield of raw skins the parts of the second stomach and first stomach of cattle which can be utilized by the tanner are processed only to a small extent. The leathers made from the second stomach have a surface structure similar to honeycomb, the leathers made from the first stomach have an appearance similar to terry towelling owing to the so-called intestinal villi. For connoisseurs they make interesting bags and pocket books, and also leathers for garment trimmings.

Requirements of production: The products used are sodium sulphide/sulphydrate/lime. Very positive results are also achieved with oxidation limes on the basis of sodium chlorite. The first stomach, which is rich in fat, should be degreased before liming. Chrome tannage with vegetable/synthetic retanning should be chosen as the tanning method.

9. Orthopaedic leathers

Orthopaedic leather is a collective name for all types of leathers which are employed for orthopaedic purposes. They are made from the most different groups of leathers. As these leathers are constantly in contact with the human skin and therefore require lasting durability, special quality guidelines have been set up and should be strictly observed by the manufacturer.

The most important quality requirements for orthopaedic leather:

Tests	Requirements - orthopaedic leather		
	harness leather	russet upper	pebbled leather
fat content (with dichloro methane)	5-11 %	18-26 %	2.5 % max.
total ash content	max. 2.5 %	max. 1.5 %	max. 2.5 %
loss by washing	max. 7.0 %	max. 7.0 %	max. 10.0 %
pH value (extract)	min. pH 3.5		
apparent density	-	-	max. 1.15 g/cm ³
tensile strength	min. 2250 N/cm	min. 2500 N/cm	min. 2000 N/cm
elongation at break	max. 55 %	max. 70 %	max. 40 %
stitch tear strength	min. 1000 N/cm		-
split tear strength	min. 350 N/cm	min. 400 N/cm	-
thorn bending test	180 degree	-	-
water absorption			
♦ after 2 hours	-	max. 35 %	max. 90 %
♦ after 24 hours	-	max. 45 %	max. 100 %
water vapour permeability	-	min. 180	min. 250
flexing endurance	-	-	min. 20000 flexings
harmful substances	none	none	none

Harness leather *Use:* For leather edgings, straps and buckles, bandages, leather insoles, leather soles, seatbelts, leather covers and coatings of artificial limbs and accessories.

Russet upper *Use:* Instead of harness leather for softer products.

Pebbled leather *Term:* Similar to harness leather with the exception that pebbled leather has an untanned middle zone. After wetting and milling on completion these formed pieces possess an extremely firm and high stability of shape.

Rawstock: Cattle hides of the heavier weight classes.

Requirements of production: Application of a white relime pit to achieve elasticity and avoidance of vegetable penetrative tanning.

Use: Coating material for artificial limbs and supporting elements, in thicknesses of 2-3 mm or 3-4 mm.

Tests	Requirements - orthopaedic leather	
glove leather	sheep skin nappa	goat skin nappa
fat content (with dichloro methane)	5-15 %	5-15 %
chrome oxide content	min. 2.5 % Cr ₂ O ₃	min. 2.5 % Cr ₂ O ₃
total ash content (sulphated)	2 % max. (after deduction of tanning oxides)	max. 2 % (after deduction of tanning oxides)
pH value (extract)	min. 3.5	min. 3.5
tensile strength	min. 1200 N/cm ²	min. 2000 N/cm ²
elongation at break	min. 40 %	min. 50 %
stitch tear force	min. 500 N/cm	min. 600 N/cm
split tear strength	min. 200 N/cm	min. 250 N/cm
fastness to perspiration	good fastness	
colour fastness	adequate colour fastness, no bleeding	
harmful substances	must not be contained	

Glove leathers

Use: Sheep nappa leather for the glove covers of artificial arms and hands, goat skin nappa leather to make hard-wearing work glove covers.

Colouration follows the RAL standard in a specified dark brown and a slate grey shade.

Tests	Requirements - orthopaedic leather	
	vegetably tanned	chrome-tanned
leather for drive belts		
fat content (with dichloro methane)	5-12 %	5-12 %
total ash content (sulphated)	max. 2.5 %	max. 2.5 % (after deduction of tanning oxide)
loss by washing (total)	max. 7.0 %	-
chrome oxide content	-	min. 2.5 %
pH value (extract)	not less than pH 3.5	
tensile strength		
◆ thickness up to 2.5 mm	min. 2000 N/cm ²	min. 2750 N/cm
◆ exceeding 2.5 mm	min. 2500 N/cm ²	min. 2750 N/cm ²
elongation at break	max. 50 %	max. 75 %
stitch tear strength	min. 1000 N/cm	min. 1100 N/cm
split tear strength	min. 400 N/cm	min. 500 N/cm
thorn bending test (double thickness of leather)	no fissures or cracks up to 180 °	no fissures or cracks up to 180 °
fastness to perspiration	good fastness	good fastness
colour fastness	colour-fast, no bleeding	colour-fast, no bleeding
harmful substances	none	none

Leather for drive belts

Use: For straps, buckles and shoe-laces in thicknesses of 1.5-4.5 mm. High tensile strength, pliability, good colour fastness and fastness to perspiration are demanded.

Tests	Requirements - orthopaedic leather
	chamois leather
fat content (with dichloro methane)	max. 20 %
total ash content	max. 6 %
pH value (extract)	4.0-8.0
tensile strength	min. 1000 N/cm ²
elongation at break	min. 50 %
split tear strength	min. 150 N/cm
water absorption ♦ after 2 minutes ♦ after 1 hour	min. 150 % min. 175 %
harmful substances	must not contain harmful substances

Chamois leather *Use:* For lining parts of artificial limbs and support straps. High softness and absorbing capacity of the leathers is required. For new chamois tannage a pretanning with glutaraldehyde is more favourable than pretanning with formaldehyde because of the better binding.

Tests	Requirements - orthopaedic leather	
	transparent leather	parchment leather
total ash content (sulphated)	max. 1.5 %	max. 10 %
pH value (extract)	3.5-7.0	3.5-7.0
tensile strength	5000 N/cm ²	min. 5000 N/cm ²
elongation at break	max. 30 %	max. 30 %
split tear strength	min. 600 N/cm	min. 600 N/cm
thorn bending test	min. 180° without fissures and cracks	min. 180° without fissures and cracks

Raw skin leather *Use:* The main cover material for wooden artificial limbs. High stability of shape, very high resistance to loading and shattering are achieved.

10. Leather for safety and work protection

All leathers of this group are designated as workers' protective leathers (in German: ASA leathers). Protection and safety leathers have to meet very high requirements depending on their use, e.g. compact, firm texture, high fastness to abrasion, good softness, high distension, good stability under radiant heat, high resistance to naked flames or glow heat and to the action of chemicals. Special DIN standards exist for these leather sorts with distinctions made according to use in dry or wet areas, light or heavy mechanical loading and use in the industrial sectors mining, construction, non-metallic mineral industry.

The most important quality requirements for safety leathers for footwear:

Tests	Requirements		
	shaft upper material	insole leather	lining/tongue
thickness:	min.	min.	min.
for dry areas	-	2.0 mm	0.8 mm
all other areas	-	2.5 mm	0.8 mm
ladies' footwear	1.5 mm	-	-
men's shoes	1.8 mm	-	-
men's boots	2.4 mm	-	-
abrasion	-	max. 5 %	-
distension of grain	min. 7.0 mm	-	-
split tear force	min. 100 N	-	min. 18 N
water vapour permeability	min. $0.85 \text{ mg} \times \text{h}^{-1} \times \text{cm}^{-2}$	-	$2.0 \text{ mg} \times \text{h}^{-1} \times \text{cm}^{-2}$
water absorption	-	after 8 ^h min. 35 %	-
release of water	-	after 16 ^h min. 40 %	-
waterproofing (depending on type of shoe)	min. 60/90 min	-	-

	shaft upper material	insole leather	lining tongue
water penetration	< 2.0 g	-	-
water vapour value	min. 20 mg/cm ²	-	-
volume resistance	-	not exceeding 5x10 ⁶ Ohm	-
fastness to calcium chloride	-	< 6 % area loss	-

Leather for safety shoes

Requirements of the leather: Only grain leather may be used to make safety footwear. A light correcting buffing of grain is permitted. Leathers used for insoles, linings and tongues must not be purely chrome-tanned.

The most important quality requirements for work gloves

Tests	Requirements
	work gloves
mineral content	max. 2 % above tanning oxides
chrome oxide content	min. 3.5 % Cr ₂ O ₃
fat content	4-12 %
removable substances	not more than 2 %
tensile strength	2500 N/cm ²
elongation at break	min. 70 %
stitch tear strength	min. 1250 N/cm
split tear strength	min. 600 N/cm
heat conductivity	not more than 0.12
area shrinkage after storage under heat	max. 4 % (at 100 °C/ after 15 min)

Protective gloves

Requirements of the leather: The thickness of leather, firmness and softness varies considerably depending on the field of application. Proper fit, safe handle, good fastness to cleaning are fixed in the standard and should be observed.

Safety clothing

Term: This group includes leathers which protect large parts of the body such as safety suits, leather aprons, lap leathers, protective leathers for the head or face, chest protections and in a wider sense also the protective suits for motor-cyclists made of special garment leathers.

Requirements of the leather: The leathers used are grain and split leathers in greater thicknesses, chiefly made by pure chrome tanning with moderate fatliquoring. They should receive a water-repellent treatment for use in wet areas. Special surface finishes, for instance containing reflective aluminium powder, are applied to protect against high temperatures from radiant heat. Hygienic wearing properties should also be taken into consideration when making leathers for safety clothing. It is important that they have a high capacity for absorbing and releasing transpiration under the effect of high temperatures.

11. Technical leathers

Many types of leather of this group have to meet the most stringent requirements with regard to their physical properties. In industry most of the belt drives have been replaced by shift transmissions.

The most important quality requirements for technical leather:

Tests	Requirements - leather for drive belts	
	vegetably tanned	chrome-tanned
fat content (with dichloro methane)	cold-stuffed 12 % hot-stuffed max. 17 % burnt-in max. 25 %	
loss by washing (total)	max. 6.0 %	-
chrome oxide content	-	min. 2.5 % Cr ₂ O ₃
degree of tannage	50-75	-
pH value (extract)	not less than pH 3.5 or above pH 7.0	
tensile strength	min. 2500 N/cm ²	min. 3000 N/cm ²
elongation at break	max. 50 %	max. 75 %
stitch tear strength	min. 1000 N/cm	min. 1200 N/cm
split tear strength	min. 400 N/cm	min. 500 N/cm
thorn bending test	with 5 times the leather thickness no fissures or cracks up to 180°	with double the leather thickness no fissures or cracks up to 180°

Leather for drive belts, vegetably tanned

Rawstock: Cattle hides of dense texture and good substance, medium weight classes, without cutting or grain defects and without fibre damage.

Requirements of production: The leathers should be thoroughly wet stentered to reduce extensibility to a minimum. Cold-stuffed or warm-stuffed leathers are used for high-speed belt drives, burning-in processing is employed for leathers used in wet areas.

**Leather for
drive belts,
chrome-tanned**

Rawstock: As for vegetably tanned leather.

Requirements of production: One-bath chrome tannage with burning-in process. Should not contain free acids due to the risk of corrosion.

Tests	Requirements	
	Helvetia leather	picker band leath.
fat content (with dichloro methane)	max. 35 %	max. 35 %
loss by washing (total)	-	max. 6.0 %
chrome oxide content	min. 1.0 % Cr ₂ O ₃ (chrome fat-tanned leather)	min. 1.0 % Cr ₂ O ₃ (chrome leather)
pH value (extract)	not below pH 3.5 or above pH 7.0	
tensile strength	min. 3500 N/cm ²	min. 3500 N/cm ²
elongation at break	max. 90 %	max. 40-90 %
stitch tear strength	min. 1500 N/cm	min. 1500 N/cm
split tear strength	min. 600 N/cm	min. 600 N/cm
thorn bending test	with double the thickness of leather no fissures or cracks up to 180°	

**Helvetia
leather**

Term: Highly fatliquored leathers which receive only a very weak tannage with alum, formaldehyde or chrome tanning agents. The weak preliminary tanning and fat impregnation produces leathers of high toughness and pliability. Drying is carried out by wet toggling to restrict extensibility.

Rawstock: Light cattle hides of poor substance, all provenances.

Use: Laces, belt laces and whip thongs.

**Picker band
leather**

Term: These are leathers made from heavy cattle or buffalo hides for textile looms which have to withstand continuous jerky battening.

Requirements of production: Combined vegetable tanning or chrome tanning with sulphur tannage and high fatliquoring, mostly up to 35 % fish-oil and manufactured with or without hair. Besides good softness and elasticity they should exhibit high toughness and firmness.

Roller leather

Term: Cover leather for rollers in spinning mills. These are calf leathers made by chrome or vegetable tanning having an even thickness of 0.5-0.8 mm and no variation of thickness.

Cover leather

Term: Cover leather for the rollers of textile combing machines. The leathers used are chrome-tanned, vegetably or combination tanned cattle hides in thicknesses of 3 mm.

Packing leather and hose leather for pumps

Term: These are leathers produced in many variations for valves, hydraulic presses, pumps, brakes etc. with a very broad range of thicknesses, tanning methods, types of fatliquoring and impregnation.

Rawstock: Cattle hides, calf, sheep and goat skins.

Leathers for musical instrument

Term: Different types of leather for membranes in organ building, bellows, valves, keys and hammers of pianos, etc. Manufactured in very different degrees of softness.

Rawstock: Mainly sheep or goat skins and also skivers.

Requirements of production: The leathers are vegetably, chamois or combination tanned, depending on their use. They should not contain strong free acids and free fatty acids to avoid corrosion. The pH value should not be below 4.5. In addition, it is absolutely necessary to ensure a very low content of substances removable by washing out.

Gas meter-leather

Term: Soft, firm and dimensionally stable leathers which are buffed on both sides and are available in thicknesses of 0.6-0.8 mm. They are used as meter membranes in gas meters to determine the flow rate and should therefore be gastight. This is achieved by impregnating the pieces which have been cut to size with special soft, liquid paraffins before they are fitted.

Rawstock: The skins used are vegetably pretanned Indian hair sheep skins which have a particularly dense fibre texture.

Requirements of production: The leathers are detanned and receive a chrome tannage with 2.5-3.5 % chrome oxide (related to dry substance).

Tests	Requirements
	wash and filter leathers
ash content	max. 5.0 %
fat content	max. 10.0 %
pH value	max. pH 8.0
shrinking temperature	min. 65 °C
tensile strength	min. 100 daN/cm ²
stitch tear strength	min. 40 daN/cm
split tear strength	min. 15 daN/cm
elongation at break	min. 50 %

Wash and filter leathers

Term: Soft, cloth-like, supple and elastic leathers which receive a train-oil tannage by the old or new chamois tanning method.

Rawstock: Sheep, goat, deer skins.

Requirements of production: Good loosening of the fibre texture in the beamhouse. The leathers should be resistant to tearing and besides good resistance to hot water and washing exhibit a good absorbing and filtering capacity.

12. Raw skin products

Tests	Requirements
	raw skin and transparent leather
ash content	max. 1.5 %
pH value	4.0-8.5
tensile strength	min. 600 daN/cm ²
elongation at break	max. 35-60 %

Raw hide leather *Term:* Briefly limed, depilated, lightly delimed and washed skins to which a disinfecting solution has been applied on both sides and which are dried as quickly as possible at room temperature in the wet toggled condition or cut to shape. Pieces manufactured for use in wet areas receive a protective nitrocellulose lacquer coat.

Rawstock: Mostly heavy bulls or buffalo hides.

Use: To produce special technical products such as gears, pinion gears or pickers in weaving mills. The advantage of these parts made from raw hide leather consists in smooth and silent operation at high running speeds. Today they have been partly replaced by special plastics, but are not entirely obsolete.

Transparent leather

Term: Manufactured like raw hide leathers with the exception that these products receive a penetrative deliming treatment, and glycerol or polyglycols are rubbed onto both sides during drying in the toggled condition. The required amount depends on the desired degree of reinforcement.

Rawstock: Cattle hides in medium to heavy weight classes, also calf skins or pig skins.

**Parchment
leather**

Requirements of production: To achieve high transparency the skins should be strongly stretched so that the skin fibres glue together without voids.

Use: Used as laces and belt laces, to reinforce leather goods, as covers for kettle drums and drums, as lampshades or as covering material for orthopaedic products.

Term: Parchment leather manufactured in thicknesses of 0.6-1.0 mm has a whitish to yellowish colour and should be opaque.

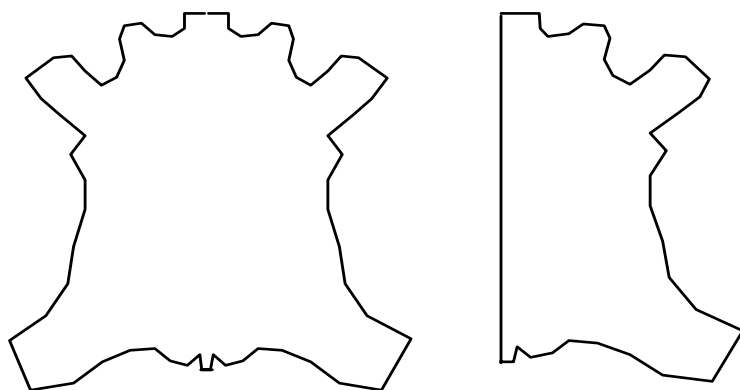
Requirements of production: The production method is similar to that for transparent leather with the difference that the fibres must not glue together during drying. This is achieved by less intensive toggling and a slower drying process. A weak treatment with aldehyde after deliming, and rubbing with prepared chalk on both sides during drying promotes the parchment quality.

Dog-bones

Term: These products are made in the same way as raw hide leathers. After deliming and washing the hides, skins or split offal are cut into strips and plaited in the shape of a dog-bone. This is followed by a quick hot air drying process to achieve high strength of the material. Sometimes aromatics and flavouring matters are applied by dipping, spraying or brushing before drying.

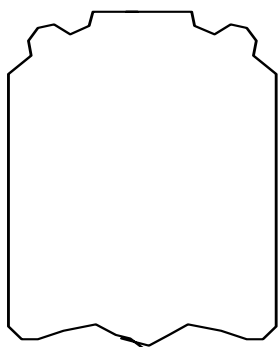
Sorting and storage of leather

Customary forms of cattle hide leather:

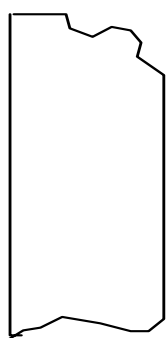


Whole hide

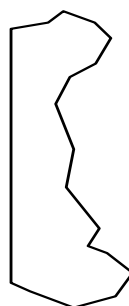
Side (half hide)



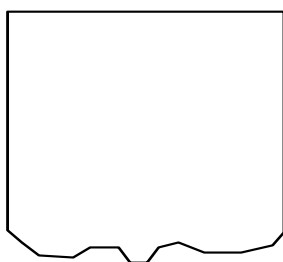
Back



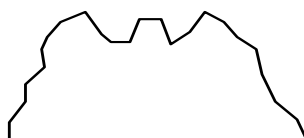
Half back



Belly (shanks)



Butt (bend)



Shoulder

Sorting:

In area measured leathers the usable area related to the whole area determines the assortment and thus the market price. Measuring of size is done by pinned roller measuring machines or electronic measuring machines. The official unit of measure is square metres (m²) or square decimetres (dm²). In some countries square feet (sqf) are still in use, with figures given to within ¼ sqf. Sole leathers are marketed by weight.

Leather defects and defects of fabrication are assessed:

Leather defects	Defects of fabrication
Loose substance in the shanks, strong appearance of veins, grain defects, natural creases, fat creases, growth marks or ingrown creases in the shoulder region, holes caused by insects or beetles, cracked, blind or open grain.	Thin sections due to cuts or gouges, uneven dyeing, cloudy or inadequate coating of the finish, very loose grain, drawn or wrinkled grain, crackiness of grain, defects caused by buffing, shaving or splitting.

General classification of area measured leathers:

- size I = min. useful area 80 %
- size II = min. useful area 65 %
- size III = min. useful area 50 %
- size IV = min. useful area 25 %
- size V = rejects

Storage of leather

To avoid damage leathers should be stored in air-conditioned rooms (temperature 10-25 °C, relative air humidity 50-75 %). Storage on radiators or in direct sun light also has a negative effect. To avoid self-heating or the formation of pressure folds the leathers should be stacked in low piles if they are stored flat, in rolls or on trestles. If stored for longer periods it is recommended that the leathers be rearranged on the stacks.

Properties of leather compared to synthetic substitute materials

Repeated attempts have been made to replace leather, with its special properties, exclusively by synthetic substitute materials. With some exceptions such as the technical or some garment leathers, bag leathers and leathers for the shoe underside construction, the largest consumer market, i.e. for shoe upper leathers, has not succeeded in finding an adequate substitute despite all efforts.

In general, the following factors determine the outstanding properties of the "natural product leather" compared to synthetic substitute materials:

1. The enormous number of fibres and bundles of fibre in the animal skin, which are irregularly interlaced with each other in three dimensions, give the material maximum strength properties. Tensile and tear strength, extensibility and elasticity are not changed significantly, even under the action of moisture or fluctuating temperatures.
2. Due to the large inner surface of the skin the leather exhibits excellent breathability. Its porosity ensures good permeability to air and water vapour, excellent water sorption, storage of water and thermal insulation.
3. With regard to wearing properties leather has the advantage of being highly adaptable to changes of the foot during everyday use. This ensures stability of shape and makes the shoes comfortable to wear.

Care of leathers

The leather manufacturer endeavours to make a durable final product from the waste product "raw hide and skin". Different types of tannage stabilize the putrescible proteins, a water-repellent treatment protects the leather against excessive wetting and the final finish protects it against mechanical and climatic influences. Although the so-called "easy-care finish", a type of finish which is hardly affected by impacts and scratches, has been propagated and applied for the last few years, all leather articles of everyday use require permanent care. In most cases this comprises purely superficial treatments which should be chosen individually for each type of leather. The method of care basically depends on the finish and surface condition of the leather in question.

Leather care products

Polishes, sprays and liquids

On grain leathers these products have the function of cleaning the surface of the leather, imparting gloss and providing a protective film against water, dust, dirt, snow or salt. Such film-forming substances must not be used for suède and nubuk leathers.

The products are divided into:

Oil products: Pure oil products, colour-less or coloured, consist of waxes, paraffins and heavy benzine or small quantities of terpentine oil as solvent. These products are very suitable for the care of shoes. There is a risk of staining on leathers which have porous finishing coats.

Emulsions: There are *water-in-oil emulsions* and *oil-in-water emulsions*. The first have a similar field of application as the pure oil products, without the risk of increased staining.

If applied carefully oil-in-water emulsions can also be used for aniline leathers.

Aqueous products: Products of this category are free from organic solvents. They are available as colourless or milky liquids, filled in bottles or aerosol cans. They are used to treat leather garments, upholstery leathers and also fine leather articles.

Mild detergents	In dissolved form these can be used to clean superficial dirt from finished leathers by rubbing lightly. The surfactants contained in these detergents help to dissolve the dirt.
Neutral soap	Non-alkaline soap solutions. Made from palm oil or olive oil (Marseilles soap). Used for suède leather with a light fatliquoring effect.
Leather oils, leather greases	These consist of mixtures of neutral fats, synthetic fats or oils, mineral oils and waxes. They serve the purpose of preserving pliability, mostly of vegetably tanned leathers.
Water-repellent agents	Many water-repellent substances are used (see water-repellent treatment). Application by means of aerosol can is recommended to achieve a thin, uniform protective coat.

Recommendations for the care of different leathers

For perfect leather care the surface of the leather must be clean from residual dirt particles. Furthermore the leathers should not be wet through or moist in parts. This would impair adhesion of the products and cause uneven gloss and hardening of the material. It is always recommended that the selected product be tried out on unexposed sections. Aniline leather should be protected from direct sunlight.

	Unfinished grain leathers (aniline leathers)	Finished grain leathers (with thin or thick coat)	Suède and nubuk leathers
Shoes and boots	A preliminary treatment with water-repellent agents is recommended to protect the articles against water. The care substances are emulsions or aqueous products.	The care of these leathers accounts for the majority of all articles. After dirt has been removed the shoes are treated with oil shoe cream and subsequently polished.	Good brushing of the leather surface with a foam sponge or soft brush. Treat regularly with colour sprays or water-repellent sprays.
Furniture and upholstery leathers	After removing dust wipe off the dirt in large sections with a cloth soaked in neutral soap solution.	Wipe with a moist cloth. After drying treat with a special leather milk or mousse. Do not treat deep fatty stains.	Wipe off stains at once if possible. Be very careful when treating deeper stains.
Garments	Smooth leathers should be lightly wiped with the foam of a mild detergent and carefully rubbed with neutral oils. Afterwards, special oils are dabbed on with cotton-wool. To clean suède and nubuk leathers brush the fibres. Dry cleaning is recommended for heavily soiled garments.		
Gloves	Wipe gloves with a mild detergent while wearing them and dry very gently. Put the gloves on once again towards the end of drying to maintain their shape.		
Bags, fancy articles	Clean the surface from dirt. Gently wipe stains on aniline leathers or leathers which have received an aqueous finish with the corresponding care products. After drying, treat the leather with colourless polish or polishes of the corresponding colour and buff with a cloth or a very soft brush. With Nubuk or suède leathers simply brush up the fibres with a sponge or brush.		
Saddlery leathers and leathers for drive belts	These vegetably tanned leathers are often subject to high loads. Rub them with leather oil or leather grease from time to time and allow the grease to penetrate. Heat the products slightly if necessary.		
Work shoes	Clean the surface, rub with leather oils or leather grease and allow to sink in. The treatment should be repeated from time to time, depending on how often the shoes are worn. It serves to preserve softness and pliability of the upper leather. Avoid using excessive amounts of oil or grease.		
Shoe soles	Hard-worn shoe soles can be regularly rubbed with linseed oil or special grease/water-repellent pastes.		

Some stains and how to treat them

Blood	Fresh blood stains are easier to remove. Wet them lightly with water and rub them with a cloth that has been moistened with citric acid or neutral soap solution. Stubborn stains should be treated by applying a solution of mild detergent on the basis of enzymes and left for some time.
Stains of roast meat and gravy	Remove the stains immediately if possible. Rub them gently with a cloth moistened with benzine or grease solvent and blot by means of filter paper.
Fats, oils	If the stains have penetrated rub them lightly with benzine or grease solvent and blot by means of filter paper. Repeat these procedures alternately.
Resins, oil-based paints, varnish	Dab the stains repeatedly with cyclohexanol, turpentine oil, acetone, white spirit or neutral soap solution and allow to dissolve. Afterwards, rub with a mild detergent using chlorine bleaching liquor at the same time and wipe several times with a solution of neutral soap.
Grasses, leaves	Result in greenish staining due to chlorophyll. Wipe them lightly with a cloth soaked in neutral soap solution. If necessary, repeat the treatment with alternating application of spirit solution.
Coffee, cocoa	Dab the stains with glycerine or glycol. Then wipe several times with neutral soap solution using spirit and some ammonia at the same time.
Nail varnish	Carefully dissolve by means of acetone and wipe lightly with a cloth moistened with spirit.
Fruit, wine, coloured fruit juices	Sprinkle fresh stains which are still wet with generous amounts of common salt and brush it off after some time. Then wipe by carefully dabbing with a solution of mild detergent to which bleaching agents have been added. Otherwise soften with a solution of citric acid and wipe off.

Rust	Dab the stains with diluted solution of hydrochloric acid or oxalic acid. Afterwards treat them with solutions of complexing agents, bisulphite or bleaching agents. Then remove these substances by repeatedly rubbing with a solution of mild detergent or neutral soap.
Stearin, paraffin	Leathers which have received a top coat finish should be rubbed carefully with a cloth moistened with white spirit, benzine, tetraline or light petroleum. Stains on aniline, suède or nubuk leathers are removed by blotting with filter paper using a heated flat iron (50-60 °C). Repeat this procedure with fresh sections of the filter paper until the stains have disappeared completely.
Ink, ballpoint pen, indelible pencil	Ink stains are often very difficult to remove due to the different composition of the inks, indelible pencils and refills of ballpoint pens, e.g. iron/gallic compounds, anionic or cationic aniline dyes or finely dispersed pigments. Light-coloured stains or finish defects may be caused, depending on the degree of penetration and the condition of the leather surface. Try to remove them by rubbing with solutions of citric acid or tartaric acid, spirit, complexing agents and oxidative or reductive bleaching agents.

Care treatments and products should always be applied with utmost care, especially on leather materials. Very stubborn stains should be removed by specialized firms to avoid damage to the leather.

Cleaning of leather

The manufacture and use of leather garments such as coats, jackets, skirts or suède shirts has steadily increased over the past decades. As the materials go through a lot of wear and tear in use they require cleaning or freshening up just like textiles. Considering that leather garments are manufactured in the most different types of leather which have been treated with a great variety of tanning agents, dyes, fatliquoring or finishing agents, the cleaning of leather is much more difficult and labour-intensive than the cleaning of textiles. Moreover the garments include materials which are not fast to cleaning, such as buttons of synthetic resin, non-woven fabrics and adhesives which are sensitive to solvents. In addition, there are many different types of possible soiling and wear marks such as staining by different items of daily use, stains caused by rain drops, discolouration, greasiness of suède or nubuk fibres, perspiration marks, stripping of finishes or change of handle. As this requires broad specialist knowledge, special dry cleaning factories for leathers have developed.

Cleaning procedure

Sorting

Sorting of the leather garments is essential for an individual treatment. The leathers are sorted according to suède and nubuk leathers, finished and unfinished grain leathers and leather/textile combinations. The nature and extent of soiling also has to be taken into consideration. Moreover the leathers are sorted according to colours. Similar shades should be cleaned together, if possible. Pale pastel shades must not be mixed with dark shades because additional staining may be caused by migration of dyes.

- Pretreatments** Sections of garments which are heavily soiled should be precleaned by hand with detergents, solvents, if necessary by adding cleaning intensifiers (special surfactants) if the stains are water-soluble. If finishes of nappa leathers are damaged or shabby it is necessary to remove the old finish coat by washing with solvents or also by sandblasting. Appliqués which are not fast to cleaning should be removed before the actual cleaning treatment.
- Surface treatment** Surface cleaning is carried out on sensitive materials or materials which are only lightly soiled. This includes either sawdusting or also light sandblasting. Sawdusting consists of dry milling in the drum by means of hardwood sawdust which has been moistened with grease solvents. Sandblasting is done with a spray gun whereby very fine corundum particles are sprayed onto the surface through the spray nozzle by means of compressed air. The soiled surface layer is removed by the friction produced in this way. Deep soiling is not removed with either of these methods, and for health reasons they should only be employed in exceptional cases.
- Washing** Wet cleaning is only possible if the leather material is labelled as washable. This is not the case with most leather garments. For this method the garments are washed in washing machines with a maximum water temperature of 35 °C and the use of detergents or neutral soaps. Drying should be very gentle because otherwise hardening of the leather, shrinking or considerable changes of shape may be caused. Therefore this method should only be applied with utmost care.

Dry cleaning

This method is the most frequently employed and is performed in closed cleaning machines. The detergents used are perchloroethylene, fluorocarbon 113 and 11. The use of heavy benzine, which has a very gentle cleaning effect, is now prohibited in Germany and some other European countries because of the fire and explosion hazard. The ratio of liquor - material to be cleaned to solvent - should be at least 1:20 to avoid maltreatment of the material and scuff marks. The addition of small amounts of water (not more than 0.5 % in relation to the solvent) and of 0.1-0.2 % cleaning intensifier improves the cleaning effect, especially if water-soluble soil substances are present. The time of application should not exceed 30 minutes to protect the leather material. In most cases 10-15 minutes are sufficient. A bath temperature in excess of 40 °C should be avoided because of the greater risk of shrinking. As the solvent withdraws fatty substances from the leather to a greater or lesser extent, hardening of the leather is inevitable. This disadvantage is compensated by subsequent fatliquoring. Either small amounts of unsulphited neatsfoot oil are added directly to the cleaning bath or a separate bath with about 8-10 % of weakly sulphited neatsfoot oil or triolein (related to the dry weight of the material to be cleaned) is applied after cleaning, especially when treating suède leather jackets. The fatliquoring substances can also be applied by spraying onto the dried garments.

Drying

Drying of the cleaned leather garments should be as gentle as possible, if possible on hangers or wire netting frames.

	Otherwise there is an increased risk of shrinkage and deformation. Only short spin-drying is recommended to drain the cleaning float before drying.
Subsequent treatment	If the garments are highly water-absorbing they can be subsequently treated with water-repellent agents. This can be carried out directly after cleaning in a separate, aqueous bath (or a combined water-repellent and refatliquoring treatment is possible). This treatment can also be applied by spraying after drying. Should the colour of suède or nubuk garments fade out or change shade a secondary spray treatment with aniline dyes is applied. These consist of 1:2 metal complex dyes dissolved in water/solvent. If necessary, small amounts of binders are added. They result in good fastness to wet and dry rubbing. If the finish of nappa leathers is damaged and a removal of the old finish is necessary by washing or sandblasting, a new finish is applied by spraying an aqueous mixture of pigments and binders and applying a subsequent lacquer top coat.
Final treatment	To restore the attractive appearance of the cleaned garments final mechanical treatments are carried out such as brushing or milling of the velour fibres and subsequent ironing on special heatable presses for the purpose of reshaping.

As chemical cleaning of leather is a very complex process, it should be carried out by specialized firms only!

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