Günter Reich, Michael Meyer



Ecological aspects of important tanning processes

A comparative view of chrome tanning and chrome-free tanning

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Tel +49 69 97843141, Fax +49 69 78800009
E-Mail info@vdl-web.de
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Author:
Dr. Michael Meyer
FILK Freiberg Institute gGmbH
Meißner Ring 1-5, 09599 Freiberg, Germany
E-Mail mailbox@filkfreiberg.de

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Sibylle Weiß, GrafischesBüro, Frankfurt am Main, Germany
E-Mail weiss@grafischesbuero.de

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Foreword

The aim of this publication is to provide leather processors, consumers, authorities, associations, journalists and other interested parties with information on the ecological aspects of leather and its production. This seems all the more necessary as there are many misunderstandings, misinformation and lack of knowledge in this field. For example, chrome-free leather and tanning processes (described using terms such as "heavy metal-free", "eco" and "organic leather") are often assumed to be the preferred option without any discussion or basis in the media and by consumer organisations. The term "leather" is not uniformly protected in Europe. In Germany, standards and the law against unfair competition help to protect the term leather (RAL 060 A 2 / DIN EN 15987:2015). However, there is an increase in the manufacture of imitations based on synthetic polymers with marketing-promoting additives (e.g. apple, cactus) or made from completely different raw materials, such as mushroom mycelium or cellulose, such that the materials bear no relation to leather, i.e. tanned animal skin. Discussions relating to this are not always objective.

Extensive investigations were conducted in a project funded by the German Federal Ministry of Economics via the German Federation of Industrial Research Associations „Otto von Guericke" e.V. (AiF) to compare the various tanning processes in terms of their overall ecological impact. The project was carried out in collaboration between the Research Institute for Leather and Imitation Leather Technology (FILK), now FILK Freiberg Institute gGmbH, and the former Leather Institute Tanning School (LGR). The results of this project provided the impetus for publishing this brochure for the first time. The focus was on the ecological and technological assessment of the most important current tanning processes - mineral chrome tanning, wet white tanning with synthetic-organic tanning agents and tanning with vegetable tanning agents within the scope of a Technology and Ecology Assessment. The basic statements arising from the results obtained for the example of upholstery leather production can be transferred to leather production in general.

For the first and second editions, the internationally renowned tanning scientist and author Prof. Günter Reich kindly took on the difficult task of summarising the results achieved within the framework of the project and the diverse international findings in a clear presentation that was also accessible to laypersons.
Prof. Reich (*1928) studied chemistry at the TU Dresden, was awarded his doctorate and habilitation based on research in the field of tanning chemistry. After working in industry for several years, he joined the German Leather Institute, today's FILK, in Freiberg as its director from 1967 until his retirement in 1993. He played a decisive role in the further development of tanning science, and ensures scientific accuracy is combined with general comprehensibility, thus promoting the aims of this publication. For the third revised edition, Dr Michael Meyer, the current Scientific Director at FILK in Freiberg, checked the literature for topicality and re-evaluated some of it.

This presentation on the „Ecological Aspects of Important Tanning Processes" is intended to contribute towards the factual assessment of environmental protection issues in connection with modern state-of-the-art leather production. In this way we hope to gain further supporters of leather.

Forschungsgemeinschaft Leder e.V.

Andreas Meyer

Frankfurt am Main, July 2021

Preface to the 3rd edition

It is with pleasure that I have taken note of the fact that my book „Ecological Aspects of Important Tanning Processes“, which was published in two editions, has been updated in an impressive manner after so many years by Dr rer. nat. et Ing. habil. Michael Meyer, Scientific Director at the FILK Freiberg Institute.

In the long period between the 2nd and 3rd editions, the state of knowledge on the science and practices of leather production has expanded significantly. However, the conclusion reached in the past that the production and use of chrome leather was harmless is confirmed in the new edition, and no superiority is demonstrated for chrome-free leathers.

I hope the Forschungsgemeinschaft Leder, as the editor, finds attentive readers in all circles concerned with leather, true to my often-expressed conviction:

“Leather, an old material with a future”.

Prof. Dr. rer. nat. habil. Günter Reich

Glossary of terms used in the text

Term	Dimension	Explanation
AOX	mg/l (as chloride)	Sum of all adsorbable organic halides on activated carbon
BOD_5	mg O_2/l in 5 days	Biochemical oxygen demand: O_2 required by microorganisms to oxidatively decompose organic matter
COD	mg O_2/l	Chemical oxygen demand: compounds that are oxidised by dichromate, predominantly, organic substances in water
DOC	mg C/l	Dissolved organic carbon, carbon content of dissolved organic compounds remaining after filtration
EC	mg/l	Effective concentration, required for triggering a defined effect
G_L value (G_{L20}/G_{L50})	dimensionless (sometimes also used for the limiting concentration in mg/l)	Dilution level (factor) in the luminescent bacteria test at which light emission is reduced by < 20 (< 50)%, based on the blind test
LC_{50}	µg-mg/l	Lethal concentration; lethal to 50% of the test organisms
LD_{50}	µg-g/kg body weight	Lethal dose; dose lethal to 50% of the test organisms
MWC	mg/m^3 (ppm)	Maximum workplace concentration: exposure over 40 hours/week or 8 hours/day without adverse effects
Phenol index	mg/l	Content of phenol-like ("couplable") substances
WHC	1 = weak to 3 = strong hazard	Water hazard class

Introduction

Since ancient times, humankind has satisfied its needs for protection, comfort and adornment with leather or furs made from the hides and skins of hunted or slaughtered animals. Leather production has evolved into the current modern industry over thousands of years, guided by scientific knowledge. A vivid example of this is upholstery leather, the properties of which are subject to the highest demands, with its production requiring sophisticated high-tech methods.

Despite this long tradition and the current high level of leather production, increased environmental awareness, a sharp eye for ecological deficits and improved analytical methods have led to critical questioning of the ecological aspects of leather production. Chrome tanning, in particular, has occasionally been criticised, as trivalent (III) and hexavalent (VI) chromium were not correctly distinguished: oxidation states that result in the relevant chromium compounds having fundamental differences in relation to their effects on living nature and their physiological role.

The task of this paper is to objectively describe the most important current leather production processes, both economically and in terms of volume, on the basis of the latest scientific findings and practical experience. Since the processes upstream and downstream of the actual tanning process are largely independent of this, a focus on the comparative ecological assessment of the most important current tanning processes is justified, i.e. chrome tanning with chromium(III) compounds, chrome-free tanning using glutaraldehyde and vegetable and/or synthetic organic tanning agents (wet white process), and classical tanning with vegetable agents (vegetable tanning). Stather (Stather, 1957) and Heidemann (Heidemann, 1993), but also more recent compendia (Covington, 2009), describe further tanning processes that are also marketed today. These include tanning based on masked isocyanates (Traeubel, 2005) or triazine compounds (Gamarino and Trimarco, 2010), tanning with aluminium, which is made available as zeolite tanning and, last but not least, cross-linking with extracts from olive leaves or privet, which are presumably based on the principle of glutaraldehyde tanning (Antunes et al., 2008; Schroepfer and Meyer, 2016). These tanning processes have by no means yet achieved the market penetration of the dominant tanning processes based on chromiumIII salts and glutaraldehyde. The available data on wastewater pollution and mass balances has not been published adequately, and will therefore, not be the focus of considerations here.

The comparison presented here is based on a careful evaluation of the international literature, the information in the product manufacturers´ safety data sheets and, above all, on the experimental data from a research project carried out from 1st February 1996 to 28th February 1998 at the Research Institute for Leather and Plastic Sheeting Freiberg (FILK) and at the Leather Institute Tanning School Reutlingen (LGR) on the topic of comparison of the various forms of tanning with regard to their overall ecological impact, using the example of upholstery leather production (Trommer and Kellert, 1999). The data collected in this research project is still valid.

The aim was to also make this publication accessible to non-specialists, without sacrificing scientific accuracy, and to hereby contribute towards factual information and to provide interested parties with well-founded information material.

1. The economic importance of the leather industry

The harvesting of hides and skins, mainly from cattle, sheep and goats, and regionally (e.g. China) also from pigs, is connected to meat, milk and wool production, and therefore directly linked to supplying the world's growing population (Fig. 1). Hides and skins are thus secured renewable raw materials that are increasing in availability, which undergo a high level of refinement through conversion into leather.

Depending on the type of raw material and the choice of technology, the part of the hides and skins that can be exploited with leather engineering methods, the corium (Fig. 3), can be used to produce different types of leather, such as firm sole leather, sturdy upper leather for shoes or soft glove leather. Leather can therefore be used to make shoes and clothing, bags, upholstery for furniture and car seats, and many other consumer goods.

Leather's physiological advantages for clothing, namely its ability to store moisture up to 30% of its own weight while maintaining a dry feel and to allow water vapour to pass through thanks to its porosity (breathability), its high mechanical resilience and its aesthetic surface and grip design, justify a utility value that has not been achieved by any synthetic or other natural material to date, despite intensive research into substitutes (Meyer et al., 2021).

Thanks to these characteristics of leather and the consistently high availability of raw materials, world leather production remains at a high level (Table 1). Hides and skins are increasingly being processed at the place of origin, which has led to significant processing capacities in developing countries (FAO, 2016).

This development has also had a lasting impact on the German leather industry. Although its volume decreased in the past, it has largely stabilised in recent years (Table 2; Fig. 2). On the one hand, this is due to the high quality of German leather, the origin of which lies in the quality of the German raw material. On the other hand, the orientation towards the demanding growth markets for upholstery leather, especially the automotive sector, was achieved at the right time. The German leather industry is thus still of considerable importance and the third largest leather producer in the EU after Italy and Spain.

Figure 1:
The hides and skins of our farm animals are valuable raw materials and form the basis for leather production

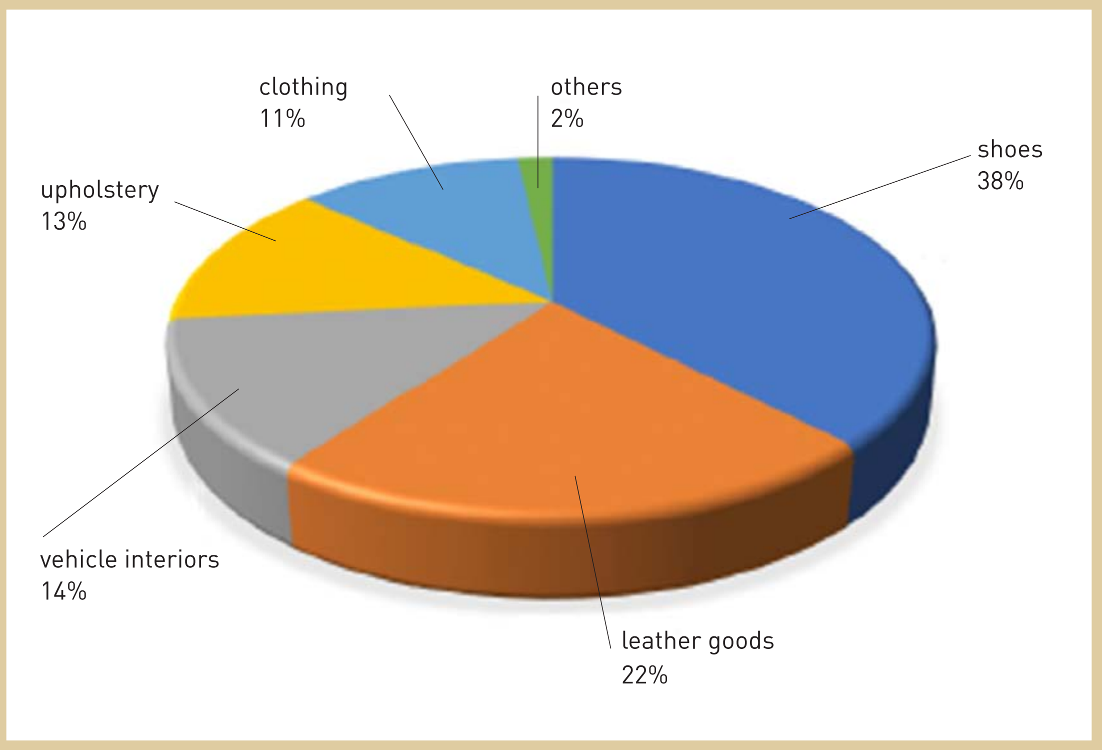
Table 1:
Selected data on the global economic importance of the leather industry
(based on the "World Statistical Compendium for Raw Hides and Skins", (FAO, 2016)

	Cattle	Sheep
Livestock	1,659.6 m animals	1,163.7 m animals
Raw material	6,531.1 thousand tonnes	414,2 thousand tonnes
Leather production	14,298.7 m sq ft or	5,335.2 m sq ft or
	1,328.4 m sq m	495.7 m sq m
Out of this, shoes with leather upper	4,483.6 m pairs	
Heavy leather	558.4 thousand tonnes	

Table 2:
Economic and structural data on the German leather industry. Status 2020
(based on data from the German Federal Statistical Office)

Data on the German leather industry	number of companies with > 50 employees	13
	number of employees	2,038
Hide and skin production	cattle hides (1,000 pieces)	2,976
	calf skins (1,000 pieces)	315

Figure 2:
Use of leather in the EU by application
(based on the Social & Environmental Report 2020, COTANCE)



2. The technology of leather production

Hides and skins consist of the epidermis with hair, the corium (cutis) and the subcutis. The corium is processed into leather, the epidermis with hair / wool and the corium into furs (Fig. 3).

The main component of the corium that is processed into leather and determines its properties is collagen, a fibrous connective tissue protein with a unique chemical and structural composition (Reich, 1966; Bailey and Paul, 1998; Reich, 1999, 2007). Approximately 1,000 amino acids are linked to form a long, spirally twisted peptide chain, a helix. Three such helices form the collagen molecule, which is approx. 300 nm long and 1.4 nm in diameter; this forms fibrils, which in turn grow into fibril bundles and fibres. This is how the three-dimensional fibre network of the corium is formed, which determines the diverse natural properties of the leather (Table 3). While the structures of the collagen molecule and fibril are now largely elucidated and their properties understood, the remarkably stable mechanical properties at the level of the fibres and the tissues are still the subject of more intensive research (Buehler, 2006; Fratzl, 2008; Basil-Jones et al., 2010; Sizeland et al., 2013; Chang and Buehler, 2014).

During the transformation of collagen into leather, the crucial tanning processes take place in the region of the fibrils (Figs. 4 and 4a).

Table 3:
Relationship between the structural composition of leather and its most important properties

Category	Characteristics	Chemical-structural causes
Clothing physiological properties	breathability, moisture absorption while maintaining a dry feel, thermal insulation	hydrophilicity and porosity of the collagen
Mechanical properties	yielding to small forces (shape adaptation) and resistance to large ones (shape retention), high tensile and bending strength; temperature-independence of the mechanical properties, high resistance to ageing	net-like deformation of the fibre network, elastic behaviour of the fibres and fibrils; low glass transition temperature (< -30°C), bonds in collagen resistant to hydrolysis
Aesthetic properties	variety of surface design (natural or embossed full grain nubuck, velour, gloss and matt effects etc.), grip, drape, (odour)	natural grain pattern (hair pores, mast folds, etc.), diverse surface finishes possible, fleece-like fibre network; (substances used, in particular natural tanning substances)

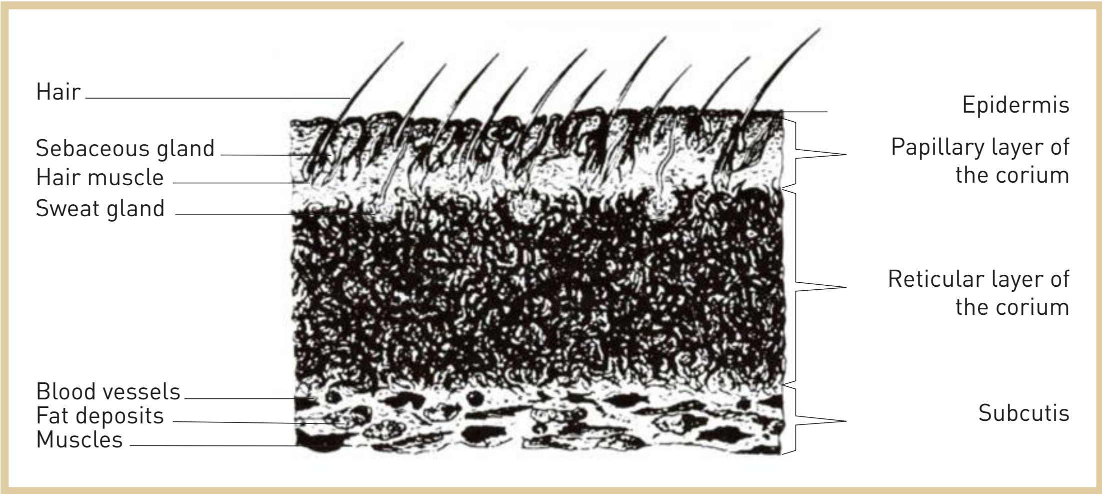
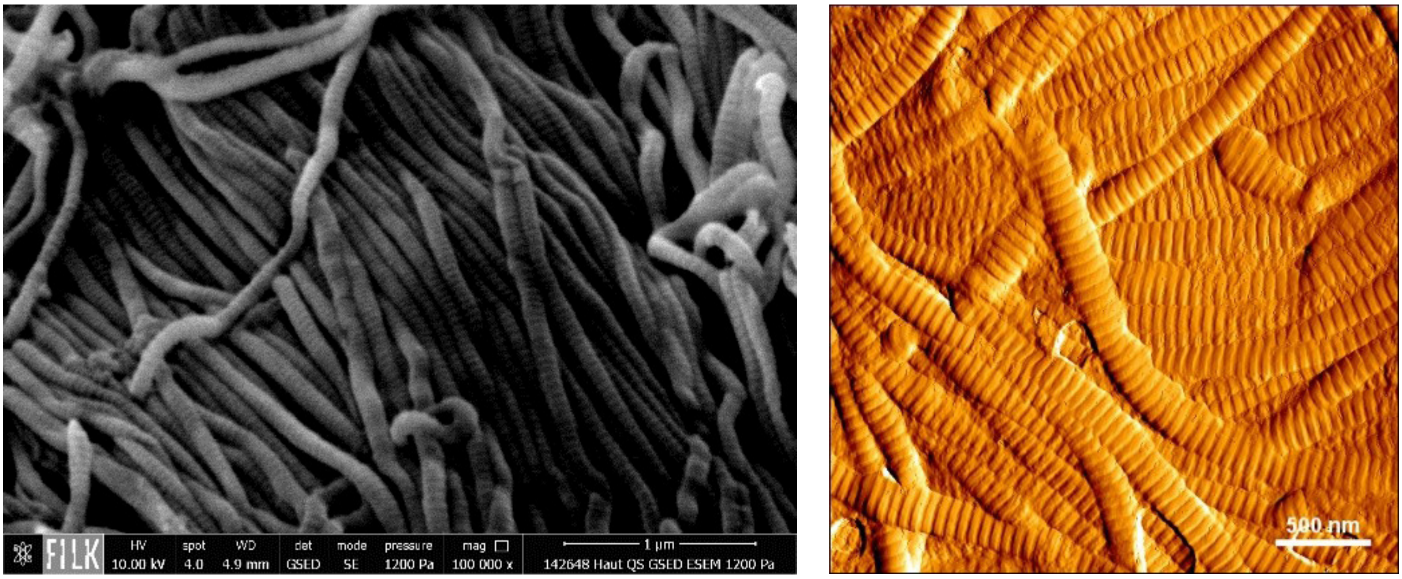


Figure 3:
Histological structure of a cattle hide (Schröer 1993)



Figures 4 and 4a:
Scanning electron microscope and atomic force microscope image of the fibril structure in bovine skin (x20,000, 1.00kV).

Despite the countless technical advances, the basic operations in leather production have remained unchanged over the centuries. They start with the **preservation** of the hides and skins from freshly slaughtered animals. Preservation is predominantly carried out by salting with sodium chloride. Preservatives can be used to support this in tropical areas, if necessary. Drying is now only of minor regional importance.

In Europe, in particular, the initial fresh skin processing of cattle hides (Fig. 5) is now playing an increasingly important role: the raw material is cooled to 4°C immediately after slaughter, plate/ crushed ice or biocide ice is added, it is transported in a chiller and then freshly processed within a few hours. Dispensing with salt preservation has decisive ecological advantages, avoiding salt loads in the wastewater.

The first processing step in the leather factory (Fig. 6) is **soaking**. Dirt, salt used for preservation and soluble skin components are removed in this step and the hides are prepared for the subsequent processes. These are a lime/sodium sulphide treatment for loosening/destruction of the hair and skin break-down (controlling the softness of the leather) in the so-called **liming process**, which is followed by enzymatic treatment in the bating process. Intensive **washing** and **deliming**, as well as mechanical processes such as **fleshing** (removal of the subcutaneous connective tissue) and **splitting** to determine the thickness, produce the ready-to-tan **pelt** in the 'beamhouse' (wet production) area.

Figure 5:
Freshly delivered cattle hides being prepared for tanning

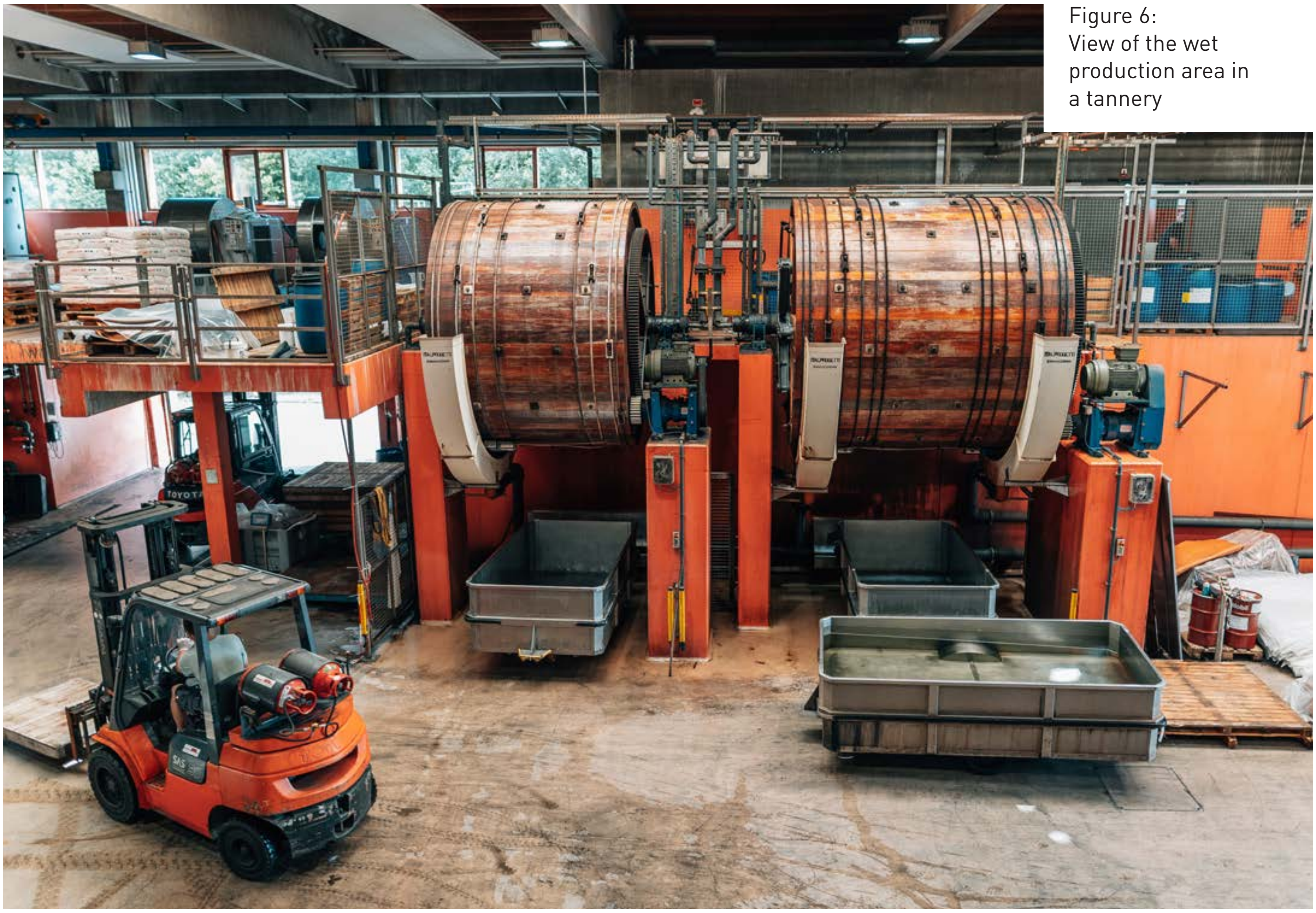


Figure 6:
View of the wet production area in a tannery

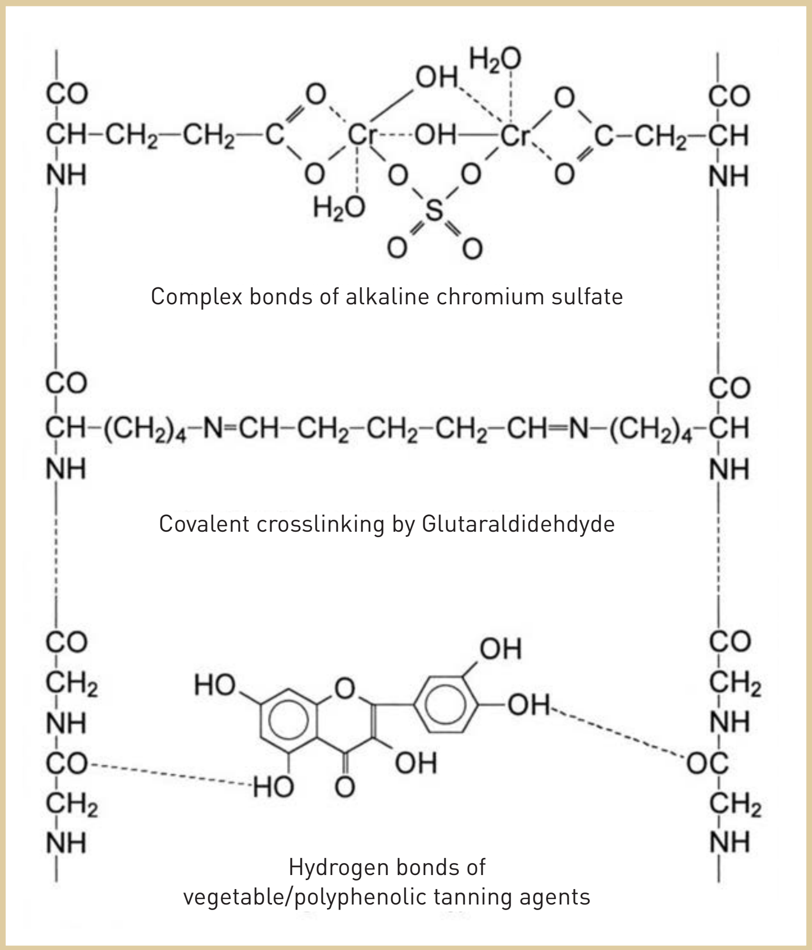


Figure 7:
Cross-linking (tanning) of collagen using alkaline chromium (III) sulfate, glutaraldehyde, and vegetable and synthetic (phenolic) tanning agents.

With regard to an ecological comparison of the tanning processes, these processing steps are irrelevant, insofar as they are independent of the subsequent type of tanning. Their technological management depends rather more on the initial processing of the raw material and the desired properties of the leather. **Tanning** transforms the collagen in the pelt, otherwise perishable when wet and hard and tough when dry, into a largely rot-resistant, soft-drying material, i. e. leather (Reich 1999 b). Tanning agents that bring this about must be able to react with the collagen and have a particle size that permits them to penetrate into the collagen fibrils (Fig. 4), on the one hand, and have a cross-linking effect on the fibrils, on the other. For thousands of years, vegetable tanning agents have been used for this purpose, with extracts of mimosa, quebracho and tara mainly being used today. As polyphenols, they are bound to the peptide groups of the collagen via hydrogen bonds (Schroepfer and Meyer, 2016). The synthetic replacement tanning agents (syntans) are also phenolic in nature, which can be used instead of vegetable tanning agents (Fig. 7). Since the beginning of the 20th century, the salts of trivalent chromium, which are alkaline, predominantly dinuclear chromium (III) sulfates, have steadily increased in importance as tanning agents. The binding of the chromium tanning agents presumably takes place through complex formation with the side chains of the collagen. The chromium salts impart an inherent bluish colour to the initially still moist, semi-finished leather product, which is where the widespread expression **wet blue** for this semi-finished product comes from. A wide range of leather properties are possible with chrome tanning, especially with regard to colouring, desired grip properties and surface design. Unlike any other tanning process, this allows the wet blue semi-finished product to be produced first. The desired properties, which depend on the type of leather and its intended use, can only be imparted in the subse-

Table 4:
Theoretically possible binding and standard tanning agent availability in practice for different tanning types

Tanning agent	Type and number of binding partners in the collagen, theoretically possible binding in %, based on collagen (molar mass 350 000)	Use in praxis on 100 kg pelt mass (surface leather)
Vegetable tanning agents	3,936 Peptide and amino groups/ mol collagen; 281% tanning agent (equivalent weight ≈ 250)	20-35 kg tanning extract, ≈ 17-25 kg pure tanning agent
Chrome tanning agents	476 carboxyl groups/mol collagen; 7% Cr oder 10% Cr_2O_3	6.0-8.0 kg alkaline solid chrome tanning extract ≈ 1.5-2.0 kg Cr_2O_3 or 1.0-1.4% Cr
Glutardialdehyd	105 amino groups/mol collagen; 1.5% $C_5H_8O_2$	1.0-2.0% commercial product liquid, ≈ 0.5-1.0% $C_5H_8O_2$

quent processes. Chrome tanning enables rational, fast and cost-effective process management. Because of its advantages, it is currently used for the production of about 85% of all leathers worldwide.

For about 20 years, tanning with glutaraldehyde has played an increasingly important role in the production of chrome-free leathers. Its tanning effect results from cross-linking with selected amino groups in the collagen. In contrast to the wet blue product, leathers tanned in this way are yellowish white, which is where the term **wet white** comes from. Due to the variable availability of reactive groups in the collagen relative to pelt weight, the different binding mechanisms of the categories of the three tanning agents mentioned above require quite different use of the tanning agent, leading to significant variation in the quantity of bound tanning agent (Table 4).

After tanning and various **mechanical processes**, such as dewatering (**samming**) and thickness regulation (**shaving**), the chrome-tanned or chrome-free leathers are **retanned**. Vegetable tanning agents or syntans are used for this purpose, also called polymer and resin tanning agents since the 1950s. The leathers then need to be **fatliquored and dyed**. All three of these measures, together with intensive washing processes, form part of **wet finishing**. This shows that the process steps of wet finishing, especially retanning, must always be seen in connection with tanning and are therefore essential for the ecological comparison of tanning processes.

Tanning and retanning are decisive in determining the achievable leather properties. The choice of tanning and retanning agents depends on the type of leather that is being produced. The tanning and retanning agents mentioned above differ significantly with regard to their characteristics and effects, e. g. imparting fullness and softness, increasing the shrinkage temperature as a sign of improved hydrothermal stability, as well as correspondingly with reference to their fields of application (Table 5).
Following this, the leather **finishing** is carried out. This involves coating the surface of the leather with colours, either by means of brushing, rolling or spraying, ironing and possibly providing it with a grain pattern that is modified as desired by embossing. These process steps are irrelevant with regard to the ecological assessment of the tanning processes, as they are independent of the tanning process and determined exclusively by the desired characteristics of the leather.
Leather production requires large amounts of water up to the wet finishing stage. Over the course of past decades, however, water consumption has been reduced by well over 50%. Nevertheless, wastewater treatment is still a task of high ecological importance. Not all of the process chemicals that are used are absorbed quantitatively by the leather; they enter into the wastewater.

Ecological assessments must take this into account.

Before tanning, the skin requires separation into the parts that are suitable and unsuitable for tanning. Therefore, not only

Table 5:
The most important tanning and retanning agents, their characteristics and fields of application

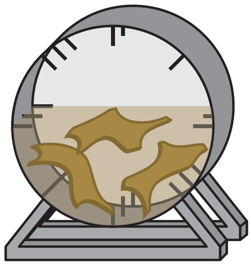
Category	Important representatives	Chemical characteristics	Fields of application, effect
Mineral tanning agents	Chrome tanning agents	Mostly bi- or polynuclear, alkaline chromium(III) sulfates: $[Cr_2(OH)_2(H_2O)_4]SO_4$	Most commonly used main tanning agent, low filling effect, high hydrothermal stability
	Aluminium, Zirconium, and Titanium tanning agents	Various salts, e.g. aluminium formate, zirconium sulfate, titanyl sulfates	Of minor importance as lightfast tanning agents (Zr, Ti) and in fur finishing (Al); dyeing auxiliaries (Al)
Natural organig tanning agents	Vegetable tannins, mimosa, quebracho, chestnut, tara, etc.	Higher molecular weight polyphenols (> 500 Dalton) of catechinic substances or gallic acid type	Formerly dominant main tanning agents, strong filling effect, now mostly retanning agents for chrome leather
	Oil tanning agents	Highly unsaturated fish oils (blubber)	Chamois leather tanning
Synthetic organic tanning agents	Aromatic syntans (auxiliary tanning agents)	Formaldehyde condensate aromatic (e.g. naphthalene) sulphonic acids	Dispersing agents towards vegetable tanning agents, tanning accelerating; dyeing auxiliaries in chrome tanning
	Aromatic syntans (replacement tanning agents)	Formaldehyde condensate of phenols or dihydroxydiphenyl-sulphone with weak degree of sulphonation	Sole tannin instead of, or in combination with, vegetable tanning agents, retanning agent for chrome leather
	Functionalised, bio-based retanning chemicals	Functionalised hydrolysate or hydrolysate mixtures of proteins, amylose or cellulose	Filling retanning agents
	Polymer tanning agents	Modified acrylic polymerisates	Filling retanning agents, possibly also with greasing properties (lubrication tanning agents)
	Resin tanning agents	Formaldehyde condensates of nitrogen bases, e.g. urea, melamine, dicyandiamide	Filling retanning agents
	Reactive tanning agents	Aldehydes, especially glutardialdehyde	Pretanning agents with standalone tanning capacity but very low filling effect
		Aliphatic sulphochlorides (chain length ≈ C_{15})	Replacement product for fish oil in the case of the chamois leather tanning (tanning acceleration)

the subcutaneous connective tissue and the epidermis, including hair, are removed, but also native collagenous sections of the corium. During thickness processing of the tanned semi-finished products, shavings and trimmings are produced. These by-products containing collagen are valuable raw materials for the production of gelatine, sausage casings, protein hydrolysates and condensation products, leather fibre materials, glue and fertiliser. The fat from the glue stock is utilised for the production of chemical raw materials and for energy generation.

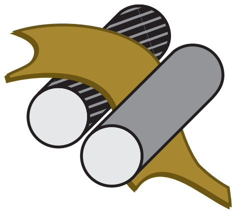
With vegetable tanning, the fact that the pelt available for tannage can be thinner due to the stronger filling properties of the vegetable tanning agents should be mentioned; such that this type of tanning shifts the product balance towards the collagenous by-products that do not need to be tanned.

1

Storage and sorting
Raw hides and skins /materials are stored in refrigerated rooms.



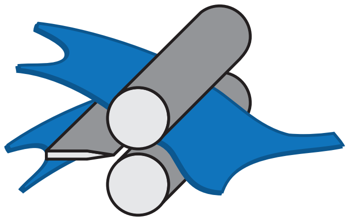
Soaking
Soaking removes dirt and salt used for preservation from the raw material and restores its original water content.



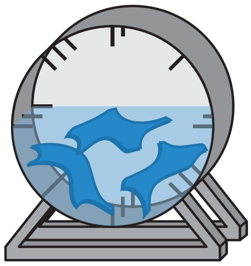
Fleshing
During fleshing, tissue, flesh and fat residues are removed with sharp blades.

2

Liming
The hair is detached from the skin in the lime bath by adding lime and sulphur compounds.

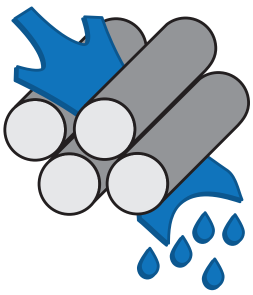


Splitting
The leather is split to obtain a uniform grain of a certain thickness. The resulting split leather can be further processed, including into suede.

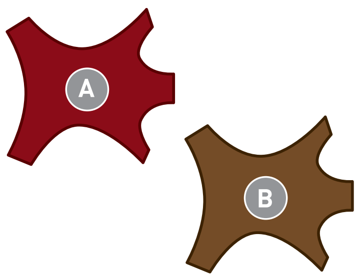


Bating, pickling, tanning
During bating and pickling, the hide is prepared for tanning firstly with enzymes and then with acid and salt. The skin fibres absorb the tanning agents during tanning. This turns the raw hide into leather.

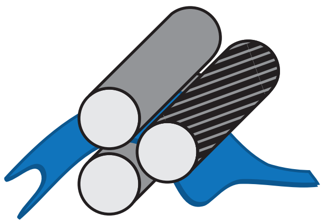
3



Samming
The wet leathers are dewatered by squeezing through felted rollers.

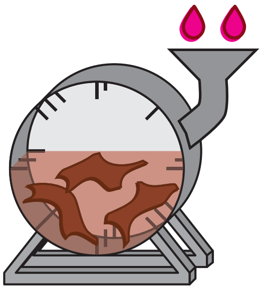


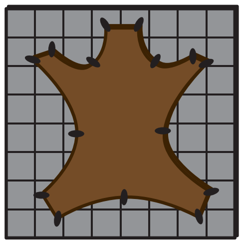
Sorting
The leathers are sorted according to various quality criteria.

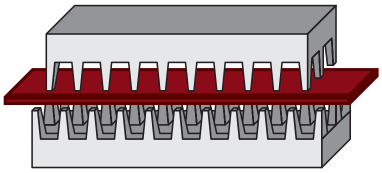


Shaving
The grain leather is adjusted to a uniform thickness by using a sharp bladed cylinder to remove leather fibres (shavings) on the reverse side. The leather is then assembled into batches for dyeing.

4





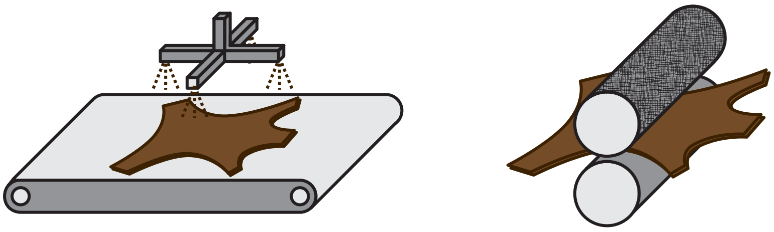


Neutralising, retanning, dyeing, fatliquoring
The acid from the tanning process is first neutralised. Depending on the type of leather, this is followed by re-tanning and dyeing with water-soluble dyes. Finally, the softness required for the finished leather is achieved by adding oils / fatliquors.

Setting, drying
Three methods are typically used to dry the leather following setting (mechanical squeezing out of the water): vacuum drying, in which the moisture is removed with negative pressure, drying by hanging or toggling (using clips called toggles), in which the leathers are dried with a stream of hot air.

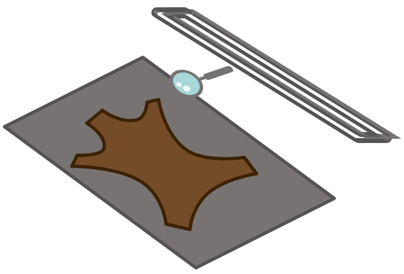
Staking
To soften the leather after drying, it is mechanically pummelled with blunt pins (staked) and prepared for finishing in further process steps.

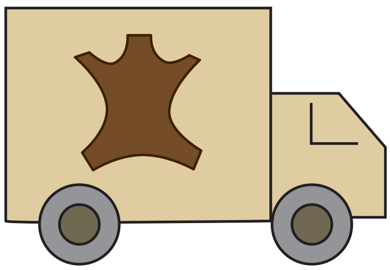
5



Finishing
The leather is given its final appearance in a final surface treatment step. By priming, applying colour, dressing, pressing and ironing, the leather is given a glossy or matt, single or multi-coloured, smooth or grained surface, depending on the fashion requirements. The art of finishing consists of applying wafer-thin layers to the leather without compromising its appearance and valued properties, such as suppleness and breathability.

6





Quality control
The quality is checked repeatedly between all process steps. The final inspection checks whether the individual production batches comply with all specifications for the leather type or sample. The leathers are also sorted according to various quality characteristics.

Shipping
The leathers are measured electronically, packed and sent to the shipping department.

Figure 8: The most important steps in leather production

3. Principles of the ecological comparison

Ecological balance sheets, footprints for water use and pollution, and carbon dioxide or the greenhouse gas potential, are examples of balancing systems that are now also used in many ways in the leather industry, especially to compare sub-processes and sites with each other. The tanning processes, in particular, are responsible for the ecological differences between the most important current leather production processes. The comparative evaluation of the economically most important tanning processes was therefore the main subject of the ecological comparison that was carried out. The entire process was only considered where objectively necessary, for example in the case of wastewater. Methodologically, the principles of a technology assessment and the fundamentals of ecological balance sheets (Technology and Ecology Assessment) were followed. In view of their actual significance, standard recipes for the same end product, upholstery leather, were selected for the ecological comparison of tanning processes in the project mentioned at the beginning. For this purpose, the standard processes of chrome tanning, wet white tanning with glutaraldehyde and organic tanning agents, and vegetable tanning with mimosa were compared. All three processes are only used as alternatives for the production of upholstery leather, thus allowing this comparative procedure.

The tanning and retanning agents that were used, the processes of tanning and wet finishing, as well as the solid and liquid waste products were balanced and evaluated according to quantity and composition, their recycling or disposal. Economic aspects were also briefly considered. The numerical data and analyses of the ecological balance sheets stem from the project and international literature with references. The assessment is also based on the knowledge gained in the project and available internationally (Table 6).

Table 6:
Balanced and assessed fields of tanning and wet finishing (Technology and Ecology Assessment)

Assessment fields	Balanced and evaluated variables
Tanning agents and retanning agents	Origin Physiology, toxicology Handling
Process performance for tanning, wet finishing	Hazard potential at the workplace Material and water consumption Utilisation rates Process parameters (time, temperature)
Process-related waste products	Exhaust air emissions Waste water generation Quantity, composition Cleaning Solid waste generation Recycling Disposal
Leather properties	Physical and chemical Clothing-physiological Aesthetic
Leather products	Utility value Disposal

Terms such as hazard potential, hazard or pollutant classes play a major role in ecological assessments. The following should be noted at this point: statements on hazard potential are only meaningful and assessable if what is threatened, in what form, and by which quantity and/or concentration (dose) is stated. For example, a distinction must be made between the effects on biological (BOD_5) and chemical oxygen demand (COD), on aquatic toxicity and phytotoxicity, and effects on humans and animals, as well as between general toxic, mutagenic, carcinogenic and allergic effects. Specification of the critical dose is always required, because only this "makes the poison", as we have known since Paracelsus. These principles are considered in the elaborations below.

4. Products and processes in tanning and wet finishing

The tanning agents used in the main tanning process are primarily alkaline chromium(III) sulfates, vegetable tanning agents or glutaraldehyde. In wet finishing, the retanning agents that are used depend on the main tanning process and, accordingly, must be covered in detail. The dyes and fats are used largely independently of the selected tanning process, such that an evaluation of the materials can be brief.
In accordance with the importance allocated to the individual tanning processes and depending on the quantities used relative to hide mass, chrome tanning agents predominate, followed by vegetable tanning agents, syntans, polymer and resin tanning agents. Glutaraldehyde and its derivatives play a minor role globally, however, with the proportions increasing in Germany.

4.1 Chrome tanning agents and chrome tanning

When chrome (leather) is mentioned, the danger of „heavy metal contamination" is sometimes feared, as if heavy metal were to be equated with „poisonous" from the outset, which is incorrect. The assessment criteria outlined above must be observed. In the case of chromium, the fact that this is a widespread chemical element is also overlooked, with chromium objects being ubiquitous and chromium(III) compounds being present as a natural component in the air, water and soil, even in the human organism. Chrome tanning agents account for only about 1% of the chromium used in industry (Table 7).

Table 7:
Selected data for chromium occurrence across the globe
(based on Trommer 1996 and Schwedt 1992; communications Lanxess 2021)

Object under consideration	Numerical values
Chrome ore production (chrome ironstone, chromite) $FeOxCr_2O_3$; 46% Cr	20 million t ore/a
Chrome tanning production Tanning extract (25% Cr_2O_3 = 17% Cr)	0.085 million t Cr/a (approx. 1% of chrome production)
Chromium levels in nature	
In the atmosphere	0.005-300 mg/kg
In surface water	0.001-0.01 mg/l
In soils	1-3,500 mg/kg
In marine plankton	2.2-7.5 mg/kg
In land plants	0.03-20 mg/kg
Humans and chromium	
Chromium content in bone	0.1-33 mg/kg
Chromium content in the kidneys	0.05-4.7 mg/kg
Average chromium intake [Cr(III)]	0.05-0.2 mg/d
Essential requirement [Cr(III)] (glucose tolerance factor)	0.05-0.2 mg/d
Chromium content in technical products	
Steel	180-260 g/kg
Chrome leather	14-28 g/kg
Thomas flour	0.8-1.8 g/kg

Chrome tanning agents are currently mainly supplied by the chemical industry in the form of alkaline trivalent chromium sulfates. Their starting products are produced during the decomposition of chrome ore for the metal industry. An additional depletion of resources is therefore not associated with the production of chrome tanning agents. Misunderstandings, and sometimes also superficial information on possible hazards posed by chromium compounds, have occurred time and again. A physiological comparison of both valence states of chromium compounds shows that only hexavalent chromium compounds may present a potential hazard in connection with the production and use of leather, whereas trivalent chromium compounds do not. The incomparably lower toxicity of Cr(III) compounds (alkaline chrome tanning agents) when compared to Cr(VI) compounds has been confirmed in numerous studies (Dartsch et al., 1997; Vincent, 2007; Tegtmeyer and Kleban, 2013; Nair, 2019). It must therefore be emphasised

Table 8:
Physiological comparison of chromium(III) and chromium(VI) compounds
(Sequi et al., 1996; Dartsch et al., 1997; Schwedt, 2018)

Hazard category	Effect	Cr(III) compounds	Cr(VI) compounds
Aquatoxicity	Water hazard class	2	3
	LC_{50} (zebrafish)	10,000 mg/l	
	EC_{50} (activated sludge bacteria)	10,000 mg/l	
	G_{L20}	83 mg/l	16 mg/l
	G_{L50} (luminescent bacteria)	185 mg/l	35 mg/l
Phytotoxicity	Permissible values for fertilizers	1,800 mg/kg (ppm)	< 1 mg/kg (ppm)
	General toxicity	100-1,000x lower than Cr(VI)	
Toxicity to humans and animals	LD_{50} oral (rat)	3,530 mg/kg	
	Toxicity after oral ingestion (human)	< 350 g Cr(III) sulfate for oral ingestion without a toxic effect	Lethal in oral intake of < 1 g potassium dichromate
	Membrane diffusion	Very slow	Rapid
	Teratogenic effect	Not observed	Possible
	Mutagenic effect	Not observed	Proven
	Carcinogenic effect	Not observed	Proven for inhalation
	Allergenic effect	Rare	Very common

that all data relevant to chromium, assessments, regulations and definitions of limits must always be related to the specific valence state: elemental chromium(0), Cr(III) or Cr(VI) (Table 8).

The first question that is essential to an ecological comparison of tanning processes is therefore: "Do Cr(VI) compounds occur in the technical chrome tanning extracts that are used?" According to all available facts, this question can definitely be answered in the negative.

The second question is: "Can the process of leather production lead to the subsequent formation of Cr(VI) compounds?" The answer to this question has only become relevant with the further development of sample preparation and analytical techniques, which now make it possible to reliably and reproducibly detect Cr(VI) compounds at levels greater than 3 ppm, in addition to Cr(III) compounds, in leather and in tanning agents (EN ISO 17075, 2017; ISO 19071, 2016). In fact, up to 50 ppm Cr(VI) has occasionally been found in leather, triggering extensive research. According to the state of the art, chrome-tanned leathers do not contain Cr(VI) compounds. The formation of Cr(VI) compounds in the leather is only possible in the case of unrealistic stress in extreme resilience tests, such as unusually high UV irradiation or heat treatment (Hedberg, 2020). However, various parties have demonstrated that even this secondary formation can be effectively prevented, e.g., through the correct selection of the fatliquors that are used, by adding reducing substances during neutralisation, or by concomitant use of vegetable tanning agents in retanning (Hauber and Germann, 1999; cads, 2018; Klüver et al., 2019). A third question is: "Does Cr(VI) formation occur during the use of chrome leather products?" This question can be answered in the negative as well, also with regard to the possible exposure to sweat (pH between 4 - 7, usually 4.5). Cr(VI) ions only form at non-physiologically high pH values (> 11.2), as has been demonstrated in experiments with test solutions (Schwedt, 1992; Anderi and Schulte, 2011; Meyndt and Germann, 2011).

The extent of binding of the chrome tanning agent used in tanning to the collagen (depletion) depends on tanning agent availability (1.5 - 2% on pelt mass), the type of tanning agent, the pH value and temperature, as well as on the addition of additives that promote depletion. The utilization rate is usually at least 75%. However, this can be increased considerably by modern, so-called high chrome depletion tanning processes. What is not possible with any other tanning agent, namely recovery by alkaline precipitation and acid redissolution, is achieved with chrome tanning agents. Chromium recovery is also practiced in some places, although highly exhaustive tanning processes predominate. A certain amount of chromium(III) sulfate therefore always enters into the wastewater with the residual and washing liquors from chrome tanning.

This raises the question on the formation of Cr(VI) compounds in wastewater containing Cr(III) and in landfill involving sewage sludge containing chromium. This is excluded in this case as well. Cr(VI) compounds can only form from Cr(III) compounds under strong oxidising conditions (higher oxygen contents) and in alkaline solution (pH > 9). Tannery wastewater, however, does not have oxidising potential, but rather reduction potential. This is proven by both the measurement of the redox potential and the determination of the chromate reduction potential (Schwedt, 2018). Precipitated chromium is present in sewage sludge as Cr(III) hydroxide ($Cr(OH)_3$), which exhibits decreasing solubility with ageing. Mobilisation of Cr(III) compounds occurs only under extreme conditions, such as pH < 3 and/or in the presence of complexing organic acids. Cr(III) is thus difficult to mobilise. This is also true for mobilisation from leather in landfill, as shown by model experiments with leachates (Schwedt, 1992). On the basis of the project results, the questions outlined above will be returned to later on.

Figure 9:
First quality control on wet white skins

4.2 Vegetable tanning agents and vegetable tanning

Vegetable tanning agents are predominantly polyphenols, which occur naturally in plants as protective compounds. The dry substance of technical tanning extracts consists of about 75% tannins, which are absorbed and bound by the skin, and 25% non-tannins. Tannin depletion depends on availability, process parameters and tannin type, but is > 90%, relative to the tannin that can be bound. The non-tannins remain in the residual liquor. Due to their organic and phenolic character, they must be considered accordingly during wastewater treatment, as they lead to an increased BOD_5, COD and phenol index, which can, however, be controlled.

Insofar as the advantages of vegetable tanning agents/tanning are occasionally referred to, for example in the sense of "organic" or "eco-leather", the arguments are usually based on the avoidance of the assumed disadvantages or even risks of chrome tanning. The postulated ecological "advantage" is often also derived solely from the fact that vegetable tanning agents are natural products. The effect on the overall process, e.g. with regard to wastewater pollution, is not considered. Conversely, supporters of chrome tanning also sometimes put forward subjective arguments against vegetable tanning, such as the over-exploitation of the rainforests (quebracho). An objective assessment of the situation reveals the following: vegetable tanning agents are either cultivated (mimosa) or their extraction is carried out with legally defined quotas (quebracho). Their current global supply could certainly be increased, since twice the quantity of plant extracts was produced in the 1950s because of the large amount of vegetable tanned leather that was produced at that time (Slabbert, N.P., 1999).

Nevertheless, if chrome tanning were completely dispensed with, the quantity of available vegetable tanning agents would be far from sufficient to produce the same amount of leather, not to mention the limitations on the range of products, especially leather for shoe uppers. The cultivation of renewable plant resources containing tannin, such as knotweed and rhubarb, would not change this situation, since the amount of tannin that can be obtained in this way is rather

Figure 10:
Vegetable tanning carried out in pits

small and its economic extraction is tied to the use of other ingredients (Oertel et al., 1994). In the meantime, intensive efforts have been made to use residual materials from olive production (pomace, water) and also olive leaves for tanning. Tanning based on olive leaf extract has been developed to technological maturity (Zotzel et al., 2011). Despite the large quantities of leaves in plantations, this process has not yet been able to establish itself in the market either. In addition, it should be noted that, from a chemical perspective, the tanning agent obtained from olive leaves is a natural masked glutaraldehyde and tanning is therefore more like wet white tanning.

The production of vegetable tanned (eco) leather as a novelty is incorrect, because tanning with vegetable tanning agents is an ancient tanning process, which was developed to high perfection long before the discovery of chrome tanning and is still used today where it is meaningful due to the required properties of the leather.

4.3 Glutaraldehyde and wet white tanning

Wet white processes are chrome-free (pre) tanning processes using metal salts (aluminium, titanium, zirconium), aldehydes or special syntans (Döppert et al. 1994) and the newer processes (X-Tan, Easy White, zeolite tanning) can also be included (Traeubel, 2005; Gamarino and Reineking, 2011; Tysoe et al., 2011; Blach et al., 2012). When applied as pretanning agents, the aforementioned compounds stabilise the hide structure such that mechanical thickness processing (splitting, shaving) is possible and, as a result, chromium-free leather waste is obtained. This pretanning is followed by filling retanning with vegetable tanning agents, syntans and polymer tanning agents. The more intensive use of wet white processes over the past 15 years is due, not least, to the use of glutaraldehyde or its derivatives. However, the spontaneous formation of higher molecular weight conversion products is possible and is responsible, for example, for the yellowish colour of leathers tanned with glutaraldehyde. A welcome side effect of glutaraldehyde pretanning is its softening effect when combined with vegetable tanning agents. In contrast to formaldehyde, glutaraldehyde is physiologically harmless if the maximum permissible workplace concentration (MWC value) of 0.8 mg/m^3 air is observed. Furthermore, glutaraldehyde is firmly bound in the protein matrix and cannot be released again.

4.4 Aromatic syntans

Aromatic syntans (formaldehyde condensation products of aromatic sulfonic acids or with phenols or dihydroxydiphenyl sulphone), originally only auxiliary tanning agents, now have good intrinsic tanning properties and are frequently used instead of vegetable tanning agents. They are used in the retanning of chrome leather, usually in combination with polymer and resin tanning agents and a certain proportion of vegetable tanning agents. They have no influence on the ecological comparison of chrome leather and wet white leather, since both tanning processes make use of aromatic syntans. Aromatic tanning agents are also used as dispersing, and thus tanning-accelerating additives (auxiliary tanning agents), in pure vegetable tanning.

4.5 Polymer and resin tanning agents

Resin tanning agents are historically older condensation products of urea, melamine or dicyandiamide with formaldehyde. They are mainly used to fill loosely structured parts of the skin (flanks) as they have no intrinsic tanning properties. However, their use is on the decline due to the increasing importance of polymer tanning agents (Reich 1996b). Polymer tanning agents, as polymerisation products, do not have any intrinsic tanning properties either, but have a filling and, more recently, also a softening effect. They are physiologically harmless and their use is on the increase (Reich 1995b). Polymer and resin tanning agents are rarely used in pure vegetable tanning, but they are used in equal measure in chrome and wet white tanning. Their depletion is also > 90%, depending on type and process.

Like polymer tanning agents and resin tanning agents, novel bio-based retanning chemicals have a filling effect, but no tanning effect; fixation and good penetration/distribution in the leather matrix are achieved by functionalisation. The bio-based content in these products can be up to 95%

of the dry content, with the BOD_5 content in the wastewater liquor therefore being much higher than in the synthetic polymer tanning agents. Since these products make up a large proportion of the finished leather in quantitative terms (up to 25% by weight, depending on the article), the use of this chemistry can significantly improve the bio-content and thus the climate neutrality of leather.

4.6 Dyes, fatliquors, preservatives

Irrespective of the tanning process that is selected, the following can be stated in relation to the dyes and fatliquors that are used: lubricating agents are physiologically harmless. However, considerable quantities enter into the wastewater as a result of incomplete depletion, which can lead to corresponding BOD_5 and COD pollution. More recent developments have now led to readily biodegradable products.

A few years ago, there was considerable discussion about dyes. In the meantime, there has been clarification on the use of such azo dyes, which can form carcinogenic amines after reductive cleavage, and they are legally regulated and prohibited. Compliance with this regulation is ensured in Germany and the EU, and has already been in place for a long time in Germany through voluntary renunciation of their use. Results of leather tests occasionally published elsewhere were always traced back to cheap imported leather.

Wet blue leather, as a semi-finished product that is traded worldwide, requires biocidal treatment to prevent microbial infestation during the sometimes-lengthy transport and storage times. Only biocides that are toxicologically largely harmless and approved under the EU Biocide Regulation 528/2012 are now used as preservatives.

Figure 11:
Dyes that are harmless to health are now available for all shades of colour, whether traditional or fashionable

5. Three tanning processes in direct comparison

After this general evaluation of the substances used today in tanning and wet finishing, the process data obtained in the above-mentioned project will be considered in detail.

5.1 Selection and basic technological features of the tanning processes

The selection of the three tanning processes was based on their current significance. The „upholstery leather“ objective was based on the requirement for all the selected tanning processes to be suitable for this purpose. The individual technologies (Table 9) differed as follows:

Technology I: Conventional chrome tanning with alkaline Cr(III)sulfates and organic retanning agents (comparative technology).

Technology II: Wet white tanning with glutaraldehyde and organic retanning agents.

Technology III: Vegetable tanning with mimosa.

All the process steps in the beamhouse, the mechanical treatment processes and the finishing of the leathers were uniformly selected. The process parameters and leather properties relevant to an ecological assessment are discussed below.

It should be noted at this point that, for methodological reasons, the hides had to be split into the same thickness for all types of tanning during these investigations. Due to the better filling properties of vegetable tanning agents, thinner splitting thicknesses are generally used in vegetable tanning, such that the consumption of chemicals and wastewater values are more favourable under these conditions in practice.

Table 9:
Key data for the selected technologies

Cattle hides of the mass class 15-19.5 kg were uniformly and conventionally processed (hair removal) until the beamhouse process steps were complete. In tanning and retanning, the following tanning and retanning agents (quantities in % of pelt mass) were used differently in the three technologies. In wet finishing, lubrication was again uniformly carried out with 15% fatliquor and dyeing with 4% dye. Finishing was also uniform.

Technology I (chrome tanning)	
Main tanning	8% Chromitan FM (25% Cr_2O_3)
Retanning	2% Eskatan GLS 2% Tanigan PAK
Technologie II (wet white tanning)	
Pretanning	1% Relugan GT 50 (50% glutaraldehyde) 2% Relugan RF (35% polymer) 2% Basyntan DLX (65% pure tanning agent, replacement tanning agent)
Retanning	2% Eskatan GLS 2% Tanigan PAK 2% Relugan RF
Technology III (vegetable tanning)	
Main tanning	1% Relugan GT 50 (50% glutaraldehyde) 12% mimosa extract (65% pure tanning agent)
Retanning	2% Eskatan GLS 3% Tannit LSW 10% mimosa extract (65% pure tanning agent)

5.2 Process flow

Since the choice of tanning agents and auxiliaries used already dictates possible ecological consequences, a database was created in the project that gives information on the water hazard class (WHC), toxicity to warm-blooded animals (LD_{50}) and aquatoxicity to fish and plankton (threshold concentration). This revealed no crucial differences in risk for the compounds that were used. The products used in tanning and wet finishing can be handled without any problems in all the technologies that were investigated, provided the instructions given in the safety data sheets are observed. Hazards at the workplace are excluded.

The ZDHC approach (Zero Discharge of Hazardous Chemicals) in industrial leather production now obliges tanneries to exclusively use registered chemical products in compliance with the requirements of MRSL v2.0 (Manufacturing Restricted Substances List) (www.roadmaptozero.com, 2021). The focus is on both the assessment of the compounds with regard to their impact on aquatic systems and on the requirements for wastewater discharge into a body of water after treatment when selecting suitable chemical additives.

The individual technologies employed in the project differed in time requirements, (hot) water consumption, temperature control and thus in energy consumption and other technological parameters. The differences in the process times for tanning and wet finishing of pure chrome leather (54 h) in comparison to wet white (55 h) and vegetable tanning (59 h) are significantly lower. On the other hand, these parameters can be controlled within broad limits in operational practice. In this respect, they will not be further evaluated here. The same applies to the yield of leather (area yield). This was 18 m^2 / 100 kg raw hide weight for chrome leather, 15 m^2 / 100 kg for wet white leather and 13 m^2 / 100 kg for mimosa tanned leather. In terms of process flow, none of the selected tanning processes is clearly superior to any other process.

5.3 Wastewater situation

The residual liquors and washing water from the tanning process, combined into mixed wastewater, exhibit the expected high value for the biological oxygen demand, BOD_5, for vegetable tanning. The other two tanning processes exhibit significantly lower values, with chrome tanning having the lowest value. The same sequence also applies to the chemical oxygen demand, COD, and the dissolved organic carbon, DOC (dissolved organic carbon). The special status of vegetable tanning with regard to the G_L value (ISO 11348-2:2007, 2007) and that of wet white tanning with regard to the aldehyde value is particularly clear. Neither are surprising. The phenol index hardly differs (Table 10).

As expected, wastewater pollution arising from the mixed wastewater from retanning/wet finishing is higher than from the wastewater from tanning for all three technologies that were investigated. In the case of wet white tanning, the high phenol index, aldehyde and G_L value in comparison to chrome tanning are to be emphasised, which is caused by the syntans used in the process. The aldehyde value in the wet tanning of the vegetable tanned leathers can also be attributed to the syntan content. Overall, the retanning of the chrome leathers with high proportions of polymer tanning agents proves to be advantageous. There is no evidence of Cr(VI) compounds in the wastewater. It has already been demonstrated above that their formation is excluded (Table 11).

With the exception of the G_L value, the data given above refer to the litre unit of volume. The overall evaluation must, of course, consider the total amount of wastewater. This therefore refers to the quantity of leather obtained, as this is the actual calculation and benefit variable. The yield is included in such a calculation. However, as already mentioned above, this can vary within broad limits depending on operational factors, including drying conditions. Irrespective of this uncertainty, the project compared the environmental loads for tanning and wet finishing per 100 m^2 of leather in a sunray

Table 10:
Composition of mixed wastewater after tanning

Analysis	Technology I	Technology II	Technology III
COD (g O_2/l)	4.3	7.1	14.9
DOC (g/l)	1.0	1.5	5.6
Phenol index (g/l)	0.3	1.2	1.3
Aldehydes (mg/l)	< 1.0	9.9	0.9
G_{L20} Value	14.0	18.0	340.0

Table 11:
Composition of mixed wastewater after retanning/ wet finishing

Analysis	Technology I	Technology II	Technology III
COD (g O_2/l)	6.2	10.6	16.7
DOC (g/l)	2.6	4.4	6.1
Phenol index (g/l)	0.15	4.25	1.5
Aldehydes (mg/l)	9.7	19.6	16.9
G_{L20} value	≤ 1,400	9,000	≤ 2,200

Table 12:
Comparison of data on biologically treated wastewater

Tanning process	Initial COD values (beamhouse and tanning) (in mg O_2/l)	COD values for wastewater treated biologically (in mg O_2/l)	Degradation rate (in %)
Technology I (chrome tanning)	3,600 (3,000-4,250)	850 (550-1,150)	76
Technology II (wet white tanning)	4,500 (3,800-5,250)	1,150 (700-1,550)	74
Technology III (mimosa tanning)	4,750 (3,900-5,750)	1,000 (750-1,300)	79

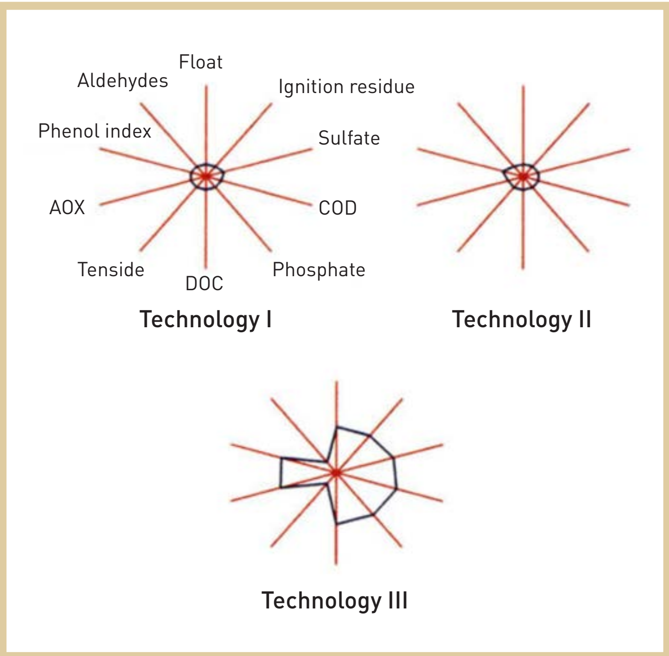


Figure 12: Environmental loads produced by tanning - comparison in the sunray plot

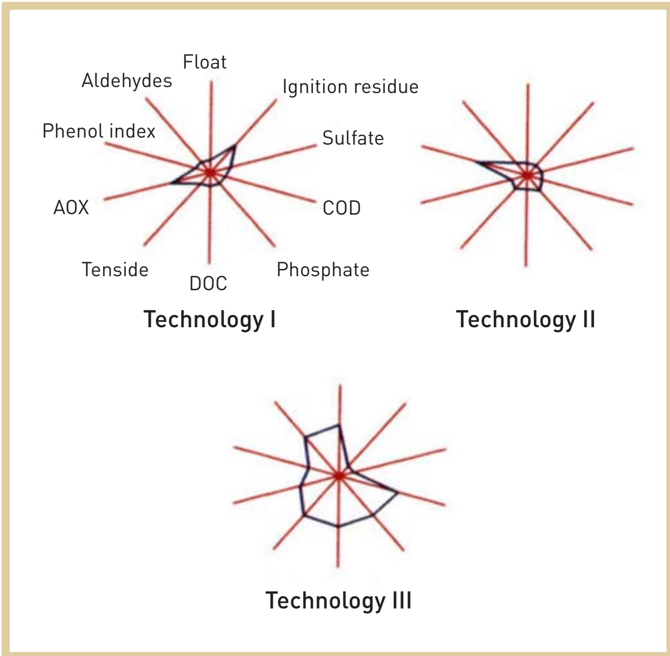


Figure 13: Environmental loads produced by wet finishing - comparison in the sunray plot

plot. The sunray plot allows a rapid comparison of a large number of parameters for multiple objects. In the diagram, a ray is assigned to each parameter, whereby the greater the distance of the tip of the ray from the centre point, the higher its relevance. The larger the area, the higher the environmental impact (Trommer and Kellert, 1999).

The wastewater load was found to be lowest for chrome tanning, only slightly higher for wet white tanning and significantly higher for vegetable tanning (Figs. 12 and 13). In practice in leather production, all wastewater is cleaned mechanically, chemically and biologically. The resulting sewage sludge is separated. Significant differences were no longer found in the COD values after wastewater treatment in laboratory plants. However, when considering the total amount of wastewater and referring to 100 m^2 of leather, the COD load for vegetable tanning is clearly higher than that for wet white and chrome tanning (Table 12).

In chemical and mechanical wastewater treatment by flocculation/precipitation, the sludge from the vegetable tanning proves to be very voluminous and poorly dewaterable. The specific filter cake resistance in pressure filtration was clearly above the values for the other sludges. Auxiliary additives would be required to further increase the sludge volume to address this problem. The resultant sludge was subjected to an eluate test to assess landfillability, which was still permitted in Germany at that time. No Cr(VI) compounds were detected. This is in agreement with findings on industrial wastewater from a chrome leather tannery (Schwedt, 1992). In the tests, the phenol index was very high for wet white tanning, however, experience in industrial practice shows that this does not always have to be the case, but can be influenced technologically. In Germany, sewage sludge from tanneries that contains chromium is usually now subjected to thermal treatment (survey of members of the German Leather Federation (Verband der Deutschen Lederindustrie e.V.), 2021).

5.4 Solid by-products, waste and sewage sludge

As is the case in all industries, the principle of avoidance before recycling, and recycling before disposal, also applies in the leather industry. Given the considerable quantity of non-tannable by-products, this is particularly essential in leather production, also for ecological reasons. However, while there is a certain potential for avoidance in relation to the tanning agents and chemicals used in leather production (high depletion, economy tanning, chrome recovery), this is practically non-existent for the hide substance. The quantity of solid by-products produced during the required recomposition of the skin is determined by the raw material being processed and the desired leather thickness, and varies within broad limits. Vegetable tanning results in an additional increase in thickness due to the high quantities of tanning agent that are used, which must be considered when regulating the thickness before tanning. This raises the question of what the options are for recycling and the influence of the tanning processes on this.

5.4.1 Recycling options

The quantity of solid by-products from leather production is largely independent of the type of tanning. The preferred method of splitting the pelts allows for sensible recycling of the surplus untanned hide collagen. Only the tanned shavings and trimmings are then left over. However, the different tanning processes give rise to clear qualitative differences, which are reflected in their suitability for the primary recycling options that can be exploited. These are mainly the use of shavings for the production of leather fibre materials for book covers, haberdashery goods, insoles and heel counters for shoes,

Figure 14: Wastewater treatment is state-of-the-art for a modern, environmentally friendly leather factory.

heels and frame material, as well as for the production of hydrolysates and derived protein condensation products in the sense of a circular economy.

As far as the recycling of dressed (finished) leather waste is concerned, this is severely restricted by the dressing alone, regardless of the type of tanning. Due to the unavoidable incineration in this case (disposal of biodegradable waste materials in landfill has been prohibited by law in Germany since 2005), the qualitative differences between the different types of tanning must be taken into account. As far as the use for the production of leather fibre materials is concerned, chrome shavings are a product that is easily recycled (Reich, 1990). However, shavings from vegetable-tanned leather are also generally accepted without problems in the dry state. The hydrolysate manufacturers who produce protein condensation products have so far largely used the chrome-tanned waste. Only the chrome tanning agent can be almost completely released from its bond with the collagen and separated from the protein hydrolysate by precipitation. This is a long-established process.

The situation is different with wet white shavings. For a long time, the insufficient accumulation, but also the high microbiological susceptibility and the tendency to dry out during intermediate storage of the shavings were obstacles to the production of leather fibre materials. However, these shavings are now also used for leather fibre production with suitable material flow management. In addition to hydrolysate production (Sagala, 1996), there are other possible uses, such as aggregates in other industries (bricks, wood-processing industry), through to use as tanning and filling agents in the tanning industry.

Insofar as hydrolysates are to be produced for animal feed or fertiliser, the following must be observed: regardless of the type of tanning, the processing of tanned waste into animal feed is prohibited. With reference to its use as fertiliser, a comprehensive Italian study (Watanabe, 1984; Ciavatta and Sequi, 1989; Sequi et al., 1996) demonstrated that a Cr(III) content (extraction with 0.1 m EDTA) of up to 1,800 ppm in fertiliser was acceptable. However, reviewing of this value every 3-5 years is recommended. Reference is also made to the requirement for further research to investigate the Cr cycle in soil and plants in more detail in other climatic zones. The decision taken by the US environmental authorities to lift restrictions on the application of sewage sludge containing Cr(III) on agricultural land is also noteworthy. This occurred based on the correct appreciation of the harmlessness of Cr(III) compounds. Studies on the effect of Cr(III) compounds in sewage sludge on plant growth revealed no evidence of phytotoxic effects. Nevertheless, long-term application on the same agricultural land would lead to accumulation in the soil, such that the Cr_{tot}. value in the current applicable fertiliser and sewage sludge ordinances has been set at 900 mg/kg.

Wet white or vegetable-tanned shavings are essentially also suitable as raw materials for fertilisers after upstream composting. Good compostability has already been demonstrated for wet white leather waste (Püntener and Gschwind, 1995), while the compostability of vegetable-tanned leather, among others, was poorer (Zuriaga-Agustí et al., 2015). Of the numerous other conceivable uses for leather waste, none has attained any significant importance. This is also true regardless of the type of tanning and is unlikely to change.

5.4.2 Disposal in landfill

According to the Landfill Ordinance (implementation of European regulations, in particular the Landfill Directive 1999/31/EC) in the German Closed Cycle and Waste Management Act, which has been in force since 2009, landfill sites are no longer permitted to accept waste with significant proportions of organic matter. This means that waste from tanneries, which is usually organic in nature, cannot be sent to landfill without pre-treatment. If the prescribed parameters are achieved after pre-treatment (such as TOC limits, respiration activity and elutability), sending it to landfill is possible. However, the requirement to recover phosphorus from sewage sludge, which will apply in the Sewage Sludge Ordinance (AbfKlärV) from 2029, will definitively prevent its disposal in landfill. Even sewage sludge incineration ash must undergo phosphorus recovery processes, through which at least 80% of the phosphorus content in the incineration ash or carbonaceous residue is recovered.

5.4.3 Disposal by incineration

As far as the incineration of sewage sludge or leather containing chromium is concerned, the formation of chromates in the ash is to be expected. Incineration tests conducted by IUTA e.V. (2003) have established the correlation between the degree of burnout and the chromate content in the slag, reaching the conclusion that a proportion of up to 5% in a mixture with household waste is possible without endangering slag recycling (Schröer and Knoedler, 2006). However, considerable quantities, up to one third, remain in the form of insoluble Cr(III) oxide. Cr(VI) compounds, that occurred in the combustion gases at up to 0.1% of the total chromium, can be removed upstream from the exhaust air using appropriate filter technology (Schwedt, 1992; Ferreira et al., 1999) and their formation can be almost completely suppressed with suitable combustion control and temperature levels.

In summary, it can be stated that there are hardly any ecological risks posed by waste products containing chromium if they are properly processed. Waste products originating from chrome-free tanning processes are thus not superior to chrome tanning waste products.

5.5 Leather properties

Just as leather for the soles of shoes is typically not be produced using chrome tanning, it is impossible to produce the current variety of shoe uppers, for example, using vegetable tanning. The hydrothermal stability required, for example, to stabilise the shape of shoe uppers (heat setting) can also only be achieved with chrome tanning. All experts therefore agree on the importance of chrome tanning for lasting (Reich, 1993; Covington, 1998, 2008).

Things are somewhat different with upholstery leather for furniture and vehicle interiors. Hydrothermal stability is not an indispensable prerequisite in this case, but rather dimensional stability that needs to be ensured, even at high temperatures and changing humidity, especially in leathers for instrument panel coverings. All desirable leather properties can be achieved with the three tanning processes tested here as examples (Figs. 15 - 17). This is emphasised by the detailed analysis of the chemical and physical leather properties investigated within the scope of this project. As far as the chemical properties are concerned, no Cr(VI) compounds were detectable and also no free formaldehyde. The pH values of the leathers

Figure 15:
Furniture made with soft chrome-tanned nappa leather

are in the desired range, corresponding to the optimum effect of the three tanning processes. The leaching losses correspond to expectations. These increase with the greater use of organic tanning agents, from chrome through wet white to pure vegetable tanning. The lower water content in the vegetable tanned leathers is related to the high proportion of tanning agents and thus lower collagen content in the leather, and is to be regarded as typical for this process.

The physical leather properties initially exhibit clear differences in the achievable shrinkage temperature. This is highest for chrome leather. Due to the high quantities of tanning agent used in vegetable tanning and the associated increase in thickness, thicker leathers are produced, but this can be taken into account when splitting the pelt. The various strength and elongation values are not dependent on the type of tanning, when the range of such values is considered. With regard to light fastness, chrome leather proved to be superior, as was expected.

A number of other parameters relevant to utility value were also tested, including the important water vapour permeability. No significant differences were found between the leathers produced using the three technologies. Finally, a subjective evaluation and grading of the haptic and aesthetic properties, as well as the odour of the three types of leather, was carried out. The assessments were in line with expectations. Vegetable leather, for example, performed better than chrome leather in terms of fullness, while softness reversed the order. No differences were found in odour (Trommer and Kellert, 1999). The results can be considered as representative, although, of course, the subjective leather properties, in particular, can be controlled by technology variants in all three technologies, which may lead to different evaluations.

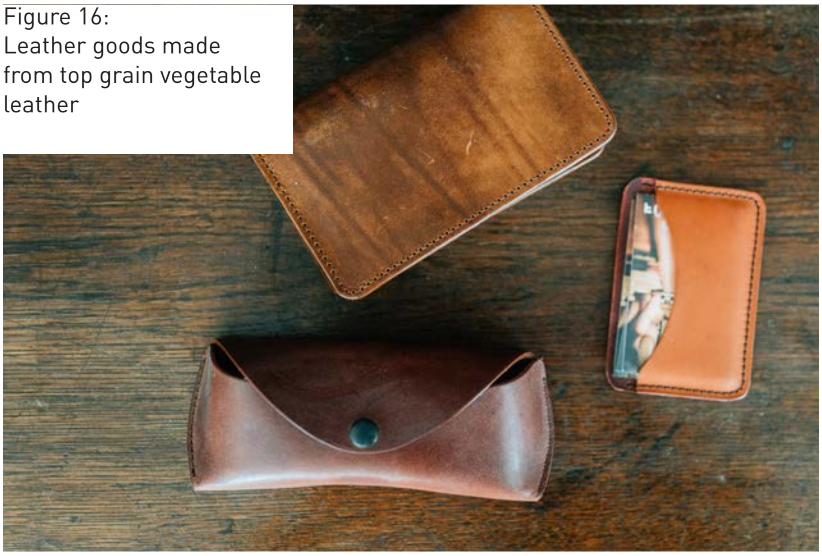


Figure 16:
Leather goods made from top grain vegetable leather

Figure 17:
Leathers for vehicle interiors are high-tech leathers that have to do justice to all comfort-related and climatic influences

6. Conclusions

None of the tanning agents, retanning agents, fats, dyes and other auxiliaries used in any of the three tanning processes pose a risk to the workers handling them, provided they are handled properly at the workplace in accordance with the relevant safety guidelines. There is no unacceptable air pollution due to emissions in the areas of tanning and wet finishing. Wastewater pollution occurs due to the fact that the residual liquors are not completely depleted, which must therefore be considered in detail in the comparative ecological balance sheets. This also applies to the solid waste products, which differ less in quantity but more in composition and thus in the available options for recycling and disposal.

Chrome tanning with harmless Cr(III) salts is possible without posing any ecological risks in relation to the secondary formation of Cr(VI) compounds. Tried and tested technologies are available which, through suitable additives, also exclude Cr(VI) formation under non-typical UV and heat test conditions. No Cr(VI) compounds are formed in wastewater or under landfill conditions. Due to the pH dependence of the oxidation of Cr(III) to Cr(VI), this can be excluded under normal soil conditions. Cr(VI) compounds are naturally produced during incineration. If they are found in the incineration residue, proper reprocessing to Cr(III) compounds is possible without any problems. Cr(VI) components in the flue dust can be removed from the exhaust air using appropriate filters. There is a technical solution to the dechroming of the filters.

The evaluation of the international literature and data obtained experimentally in an ecological comparison of three different tanning processes, including the associated specific retanning and wet finishing processes, chrome tanning and chrome-free wet white and mimosa tanning, clearly demonstrated that there are no factually justified ecological objections against chrome tanning. Accordingly, chrome-free tanning processes are not established as superior. Insofar as differences pertain between these tanning processes with regard to properties of the leather, wastewater pollution, recycling and disposal of waste, these favour chrome tanning, rather than militate against it. In industrial practice, a separate independent assessment of the specific technologies and production conditions is indispensable in all cases. No hazards arise from the product itself during the processing and use of leather, irrespective of the tanning process and wet finishing, so long as the presence of Cr(VI) compounds, amines in the dyes that are of concern toxicologically, and the presence of prohibited preservatives are excluded. In leather processing, exhaust air and wastewater pollution, if any, are process-related, not related to the leather. Substantial quantities of leather trimmings are produced, which cannot be completely put to further direct use (small leather goods, patchwork, etc.), but must be disposed of elsewhere. Insofar as landfill or incineration can be considered as options for disposal, the leathers are to be evaluated differently depending on the type of tanning. In summary, the data evaluation leads to the clear conclusion that there are no objectively justified objections to the use of properly produced chrome leather and its manufacture, or to the recycling or disposal of the resultant by-products. There is no general superiority of chrome-free leathers or their tanning processes. However, chrome-free leathers can also be produced safely using the best available technologies.

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Bibliography

Anderi, I., Schulte, K., 2011. Relationships in the formation of hexavalent chrome [Cr(VI)] (Part 2). World Leather 24, 27–32.

Antunes, A.P.M., Attenburrow, G., Covington, A.D., Ding, J., 2008. Utilisation of oleuropein as a crosslinking agent in collagenic films. J Leather Sci 2, 1–12.

Bailey, A., Paul, R., 1998. Collagen: a not so simple protein. J. Soc. Leather Technol. Chem. 83, 104–10.

Basil-Jones, M.M., Edmonds, R.L., Allsop, T.F., Cooper, S.M., Holmes, G., Norris, G.E., Cookson, D.J., Kirby, N., Haverkamp, R.G., 2010. Leather Structure Determination by Small-Angle X-ray Scattering (SAXS): Cross Sections of Ovine and Bovine Leather. J. Agric. Food Chem. 58, 5286–5291. https://doi.org/10.1021/jf100436c

Blach, R., Reineking, C., Scheider, R., 2012. Sustainability through the leather production chain. World Leather.

Buehler, M.J., 2006. Nature designs tough collagen: explaining the nanostructure of collagen fibrils. Proc. Natl. Acad. Sci. 103, 12285–12290.

cads, 2018. Der Leitfaden für Lederhersteller – Empfehlungen zur Vermeidung der Chrom(VI)-Bildung.

Chang, S.-W., Buehler, M.J., 2014. Molecular biomechanics of collagen molecules. Mater. Today 17, 70–76. https://doi.org/10.1016/j.mattod.2014.01.019

Ciavatta, C., Sequi, P., 1989. Evaluation of chromium release during the decomposition of leather meal fertilizers applied to the soil. Fertil. Res. 19, 7–11. https://doi.org/10.1007/BF01080680

Covington, A.D., 2009. Tanning chemistry: the science of leather. Royal Society of Chemistry, Cambridge, UK.

Covington, A.D., 2008. Quo vadit chromium? The future directions of tanning 103, 17.

Covington, A.D., 1998. 1998 John Arthur Wilson Memorial Lecture: new tannages for the new millennium. J. Am. Leather Chem. Assoc.

Dartsch, P., Lalla, P., Germann, H., Schmahl, F., 1997. Nephrotoxizitat von sechswertigen Chromverbindungen im Vergleich zu einem basischen Chrom (III)-Gerbstoff: Untersuchungen an kultivierten Epithelzellen der Niere. Leder 48, 8–13.

EN ISO 17075, 2017. Leder - Bestimmung des Chrom(VI)-Gehalts in Leder - Teil 1: Kolorimetrisches Verfahren.

FAO, 2016. World statistical compendium for raw hides and skins, leather and leather footwear 1999-2015 133.

Ferreira, M., Almeida, M., Pinto, T., 1999. Influence of temperature and holding time on hexavalent chromium formation during leather combustion. J. Soc. Leather Technol. Chem. 83, 135–8.

Fratzl, P. (Ed.), 2008. Collagen: structure and mechanics. Springer, New York.

Gamarino, R., Reineking, C., 2011. EasyWhite Tan leather: A new tanning evolution. World Leather 5.

Gamarino, R., Trimarco, L., 2010. Tanning process and tanning composition. WO2010/130311A1.

Hauber, V.C., Germann, H.-P., 1999. Untersuchungen zur Entstehung und Vermeidung von Chromat in Leder aus dem Jahre 1999 13.

Hedberg, Y.S., 2020. Chromium and leather: a review on the chemistry of relevance for allergic contact dermatitis to chromium. J. Leather Sci. Eng. 2, 20. https://doi.org/10.1186/s42825-020-00027-y

Heidemann, E., 1993. Fundamentals of leather manufacture. Roether, Darmstadt.

ISO 11348-2:2007, 2007. Wasserbeschaffenheit - Bestimmung der Hemmwirkung von Wasserproben auf die Lichtemission von Vibrio fischeri (Leuchtbakterientest) - Teil 2: Verfahren mit flüssig getrockneten Bakterien.

ISO 19071, 2016. Leder - Chemische Prüfungen - Bestimmung von Chrom(VI) und deren Reduktionspotential für Chrom-Gerbstoffe.

Klüver, E., Morgenstern, U., Schulz, H., Meyer, M., 2019. Erste Untersuchungen zum Einfluss von Fettungsmitteln und Antioxidantien auf die Bildung von Chrom(VI) in gefettetem Wetblue. -Leder 18–19.

Meyer, M., Dietrich, S., Schulz, H., Mondschein, A., 2021. Comparison of the Technical Performance of Leather, Artificial Leather, and Trendy Alternatives. Coatings 11, 226. https://doi.org/10.3390/coatings11020226

Meyndt, R., Germann, H.-P., 2011. Relationships in the formation of hexavalent chrome [Cr(VI)]. World Leather 24, 14–17.

Nair, S., 2019. Metabolic effects of chromium—Potential molecular mechanisms, in: The Nutritional Biochemistry of Chromium (III). Elsevier, pp. 175–191.

Oertel, H., Reich, G., Meyer, L., Lange, E., 1994. Vegetabilische "nach Maß" - ein Beitrag zur Sicherung der Rohstoffgrundlage der Lederindustrie. Leder 9, 7.

Püntener, A., Gschwind, A., 1995. Composting of Wet White-Leather-Waste. JALCA 90, 220–224.

Reich, G., 2007. From collagen to leather-the theoretical background. BASF Service center.

Reich, G., 1999. The structural changes of collagen during the leather making processes. J. Soc. Leather Technol. Chem. 83, 63–79.

Reich, G., 1993. Betrachtungen zur Zukunft der Chromgerbung. Leder Häutemarkt 53–59.

Reich, G., 1990. Verwendungsmöglichkeiten für chromgare Lederabfälle. Leder 41, 217–222.
Reich, G., 1966. Kollagen. Theodor Steinkopff Verlag, Dresden.
Sagala, J., 1996. Herstellung und Verwendung von Eiweisshydrolysaten aus chromfreien Falzspanen-Production and application of hydrolysates from chrome-free shavings. leder 47, 102–107.
Schroepfer, M., Meyer, M., 2016. Investigations Towards the Binding Mechanisms of Vegetable Tanning Agents to Collagen. Res. J. Phytochem. 10, 58–66. https://doi.org/10.3923/rjphyto.2016.58.66
Schröer, T., Knoedler, J., 2006. Die Entsorgung von chromhaltigen Gerbereischlämmen. -Leder 14–17.
Schwedt, G., 2018. Chemische Elemente und ihre Spezies. Springer Berlin Heidelberg, Berlin, Heidelberg. https://doi.org/10.1007/978-3-662-55829-4
Schwedt, G., 1992. Beiträge zur Frage der Umweltverträglichkeit von Chrom aus Leder.
Sequi, P., Tittarelli, S., Canali, F., 1996. Admissible levels for chrome in fertilizers (Final Report No. ETD/95/84083). lnstituto 42 Sperimentale per la Nutrizione della Piante, Roma.
Sizeland, K.H., Basil-Jones, M.M., Edmonds, R.L., Cooper, S.M., Kirby, N., Hawley, A., Haverkamp, R.G., 2013. Collagen Orientation and Leather Strength for Selected Mammals. J. Agric. Food Chem. 61, 887–892. https://doi.org/10.1021/jf3043067
Slabbert, N.P., 1999. The basics of practical tanning systems reconciled with vegetable tanning theories. J. Am. Leather Chem. Assoc. 94, 1–7.
Stather, F., 1957. Gerbereichemie und Gerbereitechnologie.
Tegtmeyer, D., Kleban, M., 2013. Chromium and Leather Research A balanced view of scientific facts and figures - IULTCS; IUR-1.
Traeubel, H., 2005. A new Approach to tanning - an unconventional attempt. JALCA, Advances in polymer science 304–316.
Trommer, B., Kellert, H.-J., 1999. Ökologischer Vergleich verschiedener Gerbarten aus dem Jahre 1999 22.
Tysoe, C., Hombeck, M., Reiners, J., Tegtmeyer, D., 2011. X-Tan-new leather qualities by sustainable organic tanning. World Leather i–iv.
Vincent, J.B. (Ed.), 2007. The nutritional biochemistry of chromium (III). Elsevier, Amsterdam ; Boston.
Watanabe, H., 1984. Accumulation of chromium from fertilizers in cultivated soils. Soil Sci. Plant Nutr. 30, 543–554. https://doi.org/10.1080/00380768.1984.10434722
www.roadmaptozero.com, 2021.
Zotzel, J., Kerscher, M., Kück, M., 2011. Innovatives biotechnologisches Verfahren zur Herstellung eines natürlichen Vernetzungsmittels aus Ernteabfällen der Olivenproduktion zur Modifikation und Stabilisierung von Proteinen und Zuckerderivaten für Lebensmittel- und Kosmetikprodukte (No. AZ 13210). DBU, Darmstadt.
Zuriaga-Agustí, E., Galiana-Aleixandre, M.V., Bes-Piá, A., Mendoza-Roca, J.A., Risueño-Puchades, V., Segarra, V., 2015. Pollution reduction in an eco-friendly chrome-free tanning and evaluation of the biodegradation by composting of the tanned leather wastes. J. Clean. Prod. 87, 874–881. https://doi.org/10.1016/j.jclepro.2014.10.066

Summary

Following a brief description of the economic importance of leather production and its basic technological features, the three important tanning processes (chrome tanning, chrome-free wet white tanning with glutaraldehyde and organic tanning agents, and vegetable tanning with mimosa), the process flow, the resultant wastewater, solid waste and the leather that is obtained are documented quantitatively and qualitatively with regard to their ecological aspects. This is based on the results of a comprehensive project conducted by the Research Institute for Leather and Plastic Sheeting (FILK) and the former Leather Institute Tanning School (LGR), under consideration of the international literature. The evaluation of the data leads to the clear conclusion that there are no factually justified objections to the use of properly produced chrome leather and its manufacture, or to the recycling or disposal of the resultant by-products and waste.

There is no general superiority of chrome-free leathers or their tanning processes. All three leathers can be produced in an ecologically safe fashion using the **Best Available Technology**.