PROCESS OF LEATHER TANNING

Investigation, analysis and evaluation from a Cradle to Cradle® perspective based on the wet-green® OBE tanning agent

EPEA Summary Report

EPEA
The Cradle of Cradle to Cradle

Introduction

The German wet-green GmbH has developed an ecological leather tanning agent based on olive leaves, which accrue as a by-product in olive cultivation. Thus it is possible for the leather industry to tan the material not only in an environmentally friendly manner, but also in the context of a safe post-industrial use for the manufacturer and for the environment.

In 2013 the wet-green GmbH successfully completed the certification of the Cradle to Cradle Certified™ Products Program, version 3.1. The tanning agent wet-green® OBE has been awarded the Cradle to Cradle Certified™ Gold certificate.

The author of this study, EPEA Internationale Umweltforschung GmbH, was founded in 1987 by Prof. Dr. Michael Braungart. As an internationally active scientific research and consulting institute, EPEA cooperates with stakeholders from business, politics and science and supports them with the introduction of circular processes as well as product optimization and product development.

Within the C2C® certification project, it was decided in 2016 to develop a comparative study of selected tanning processes using the Cradle to Cradle® design concept. The following tanning processes are subjects of the evaluation:

- Chromium tanning
- Glutaraldehyde tanning
- Plant extract tanning: General
- Plant extract tanning: wet-green® OBE

Within the framework of a scientific semi-quantitative comparative study, the tanning processes are compared and evaluated with regard to their method, the materials and ingredients used, the use of water and energy as well as their recyclability. The social aspects are examined and evaluated as far as possible in a separate chapter.

The scope of the investigation is limited to the tanning process and the subsequent retanning. The aim of the study is to evaluate the advantages and possible disadvantages of wet-green® OBE tanning as an alternative for plant tanning compared to other tanning processes from a scientific perspective.

Cradle to Cradle®

Cradle to Cradle® is a design concept developed by Prof. Dr. Michael Braungart, William McDonough and EPEA Internationale Umweltforschung in the 1990s. It stands for innovation, quality and good design, and describes the safe and potentially infinite use of materials in material cycles.

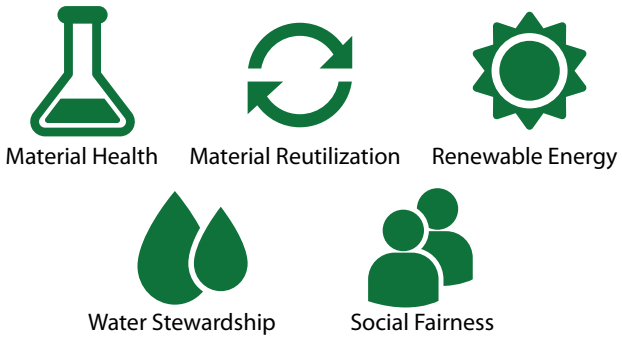
Nature is the role model of this innovative design concept. All products are designed according to the principle of an ideal Circular Economy and can be returned to the biological or technical cycle. This distinguishes Cradle to Cradle® from conventional recycling and the concept of eco-efficiency. It is eco-effective and goes beyond the conventional instruments and approaches, which primarily focus on a negative human impact on the environment. In its fundamentals the Cradle to Cradle® concept thus follows the Triple Top Line and takes economic, ecological and social aspects into account.

An important component of the concept is a positive definition of materials and material flows, which makes it possible to control optimization processes in a targeted and quality-oriented manner. Essential for the development of a Cradle to Cradle® product is the identification of suitable materials based on human- and eco-toxicological criteria.

This means that products and their ingredients, including those such as pigments and additives, are selected or optimized in such a way, that preferably no toxic effects occur during production, utilization or after-use.

Evaluation of leather tanning according to Cradle to Cradle®

The Cradle to Cradle Certified™ Product Standard stipulates that product materials and manufacturing processes are evaluated in five categories: material health, material reutilization, renewable energy, water stewardship and social fairness.



Since the starting material for leather (animal skin) is a natural product, leather products are particularly suited for a use in the biological cycle. In the Cradle to Cradle® design concept, materials are considered to be safe for the biological cycle, which are completely biodegradable or contain excipients, e.g. certain pigments, which are unproblematic in the biological environment.

No negative effects must emerge for humans and the environment. Toxic properties are only relevant when a substance is also in contact with humans (in production, use and after-use). Environmentally toxic substances, when they not enter the environment, could be used in the technical cycle. However, they are not suitable for the biological cycle.

In order to produce an eco-effective leather according to Cradle to Cradle® principles, the product in its optimized state must be free from toxic substances and can be returned to the biological cycle. The consideration of ingredients also plays an important role in the evaluation of the tanning processes. Hazardous leather chemicals can pose a great health risk to workers in the tanning industry. Proper application is therefore of great importance.

The following assessment criteria were used for the evaluation of leather tanning processes, which also cover the already mentioned Cradle to Cradle Certified™ criteria.

The social aspects, which must also be taken into account when looking at the leather tanning process, are evaluated separately. From the point of view of the Cradle to Cradle® design concept, social fairness must ensure that progress is made towards sustainable business activities, that protect all involved along the value chain.

The assessment criteria from the Cradle to Cradle® perspective are transferred into a semi-quantitative evaluation system, which follows a four-step scale, ascending from - / 0 / + / ++.

Criteria for the evaluation of tanning processes	
Hazardous properties of the ingredients used	- Consideration of the materials / chemicals used - Evaluation of problematic chemicals
Material health in tanning process and application	- Assessment of application scenario and the associated risk to humans and the environment - Evaluation of chemicals contained in the final product - Release of problematic substances (risk assessment)
Tanning process (Energy and Water)	- Water management (sewage, sludge, etc.) - Energy management - Amount of raw materials used (and their production)
Recyclability	- Recyclability after the use of the leather (as well as production residues) - Existing & possible traceability of the product or behavior in the biological environment

Chromium Tanning

	Tanning agents used	Auxiliaries used
	Basic sulfate complex of trivalent chromium	Salt, formic acid, sulfuric acid, basifying agents (magnesium oxide, sodium carbonate or sodium bicarbonate), fungicides, masking agents (e.g. formic acid, sodium diphthalate, oxalic acid, sodium sulfite), fatliquors, synthetic tanning agents, resins

The chromium tanning process is a fast and cost-effective tanning process. In addition, chromium-tanned leather has very good reproducible optical and functional properties. Due to its bluish intrinsic color, the chromium-tanned moist leather semi-finished product is called "wet-blue".

Chromium tanning is criticized because of the environmentally and socially incompatible production conditions. According to the European Union (EU) regulation of March 2014 leather products and articles containing leather parts may not be placed on the market if they have a chromium(VI) content of 3 mg/kg or more of the total dry weight of the leather.

The basic problem of chromium tanning is as follows: The chromium(III) salts crosslinked in the protein are bound relatively stable inside the leather. During tanning, however, not all of the chromium used is fixed inside the leather. The chromium(III) salt is added in excess. Already during the tanning process, as well as after the subsequent processing steps, chromium(III) salts, especially unbound ones, can be converted to chromium(VI) compounds by oxidation.

The used chromium(III) is not readily soluble in water and non-toxic. In contrast, the hexavalent chromium(VI) is readily soluble in water and has a high bioavailability and mobility so that it can be absorbed very well by the body. Chromium(VI) compounds are classified as carcinogenic, skin contact can cause severe irritation and allergic reactions.

It should also be noted that chromium(VI) can be present in toxically relevant quantities in the waste water and in the solid waste of the tanneries. The waste water from this industry is often also contaminated with other pollutants because a large number of different chemicals is used for tanning. The mining of chromium ores, which are required for tanning agents, often leads to negative effects for the surrounding ecosystems and the workers in the mines, especially in stripe mining projects.

Assessment chromium tanning	
Hazardous properties	- The basis is chromium ore, from which the basic sulfate complex of trivalent chromium(III), which is inherently nontoxic, is formed via sodium dichromate. - Use of various chemical auxiliaries, some of which can be classified as problematic.
Material health	- In addition to the bound chromium (1-2% in the product), residues of free chromium(III) can also be detected in small amounts in the final leather product (limit value according to RAL-UZ 148: 200 ppm) (RAL 2015). - During production of leather, oxidation, especially in the case of unbound chromium(III) salts, may lead to formation of chromium(VI) compounds, which are highly toxic and carcinogenic. - Chromium(VI) in leather products is prohibited according to the EU regulation of March 2014, but can still be found in leather products to some extent.
Tanning process	- The demand for chromium ores is low compared to the quantity of tanned leather, but the extraction of the non-renewable resource can be problematic (both ecologically and socially). - Less energy and water-intensive compared to other tanning processes. - Required waste water treatment for the specific removal of chromium as a precarious substance is problematic.
Recyclability	- Costly disposal tasks for chromium-containing waste water and solid wastes, natural spreading is prohibited. - During combustion of chrome-containing leather waste highly toxic chromium(VI) can be formed from chromium(III).

Glutardialdehyde tanning

	Tanning agents used	Auxiliaries used
	Glutardialdehyde	Salt, formic acid, sulfuric acid, basifying agents (magnesium oxide, sodium carbonate, sodium bicarbonate), syntans (synthetic tanning agents), fatliquors, fungicides

At the end of the 1970s, in the early 1980s the concept of wet-white pre-tanning was developed, aiming for a reduction in the use of chromium salts and thus a reduction in the chromium content in the waste water but also in solid waste. The solution was the combination of pre-tanning with glutardialdehyde and retanning with aromatic syntans, besides vegetable tanning agents and polymer tanning agents.

By using synthetic tanning agents almost all technological, economical and fashionable leather requirements can be met. Synthetic tanning agents can be prepared chemically from easily accessible fossil raw materials. Usually, synthetic tanning agents are not used isolated in the tanning process, but are used in combination with plant extract or chromium tanning.

Two fairly new wet-white tanning processes are the Clariant Granofin® F-90 and Lanxess's X-Tan®, which are supposed to be a more sustainable alternative to the use of glutardialdehyde in wet-white tanning in the long run.

Glutaraldehyde is inherently toxic and can cause severe irritation of eyes, nose, throat and lungs, furthermore it is particularly strongly aqua-toxic. The commonly employed amounts of glutardialdehyde as well as controlling of the pH value allow for almost complete consumption and reaction of the astringent glutardialdehyde.

Regarding the alternatively used tanning agents, it is, from an ecological point of view, only reasonable up to a point to regard glutardialdehyde as an ecological alternative to chrome tanning, due to the toxicological data.

The waste problem of synthetically tanned leather is generally reduced compared to chromium-tanned leather. On the basis of the available products, the chances for the development of leather, which is equally usable and recyclable, are quite possible.

Assessment glutardialdehyde tanning	
Hazardous properties	- Glutaraldehyde is inherently toxic and has severe health consequences. It is particularly toxic to aquatic organisms. - As in the case of chromium tanning further auxiliaries are used, that can be problematic from a toxicological point of view.
Material health	- The commonly employed amounts of glutardialdehyde as well as the controlling of the pH value, allow for an almost complete consumption and reaction of the astringent glutardialdehyde, which therefore is not found in the final product. - Particular migration behaviors, remaining residual aldehyde etc., intolerances from accordingly tanned leather are not known. - The application requires special regulations, but can be carried out safely in advanced tannery production sites.
Tanning process	- The tanning process is more elaborate compared to chromium tanning; temperature control causes higher energy demand. - Water must be purified in waste water treatment plants, but does not require special treatment, contrary to chromium tanning. - Chemical processing routes in synthetic tanning chemicals, which often involve carcinogenic monomers, can be problematic.
Recyclability	- Leather capable of circulating is possible based on available products. - Glutaraldehyde is not detectable anymore in the end product; compostability of synthetically tanned leather is principally possible.

Plant extract tanning: General

	Tanning agents used	Auxiliaries used
	Polyphenol compounds extracted from plant material (e.g., quebracho, mimosa, oak), partly sulfited	Bleaching agents and fatliquors, formic acid, resins, fungicides, (synthetic) pre-tanning agents

Prior to the development of chromium tanning, tanning with vegetable tanning agents was by far the most important tanning process. Vegetable tanning agents are a broad group of complex compounds also called tannins. These are formed in virtually all plants. Tanners are most interested in the abilities of tannins, which protect plants from rot, mold infestation and wild animals.

Vegetable tanning agents are complex in nature and contain many substances that are not involved in the tanning process, but that can significantly influence it. A consistent quality is hardly achievable. Vegetable tanning agents offer a great advantage in their compatibility. For special effects they can be mixed with one another or applied to the same pelt one after the other.

Due to the classical vegetable tanning characteristics only a very limited leather spectrum can be achieved with plant-extract tanning. In particular, the limited dyeability as well as the lower softness compared to chromium-tanned leather should be noted.

In order to optimize the tanning properties of the vegetable tanning agents, certain chemicals can be added during or after extraction. The concentrated plant extracts can be influenced by this form of sulfitation in astringency, solubility, penetration ability or coloring.

For the hazardous properties of the ingredients used pre-tanning and retanning substances play an important role since they are used to a great extent in vegetable tanning. Also the chemicals used during sulfitation have to be considered critically.

Vegetable tanning is a complex tanning process compared to chromium tanning, which causes high tanning material costs and leads to high water consumption and process times. By using mainly plant-based and completely non-toxic substances, pure vegetable tanning is well suited for reutilization of residual tanning material in the biological cycle. To date, however, no concepts are known which implement this concept of composting consistently.

Assessment plant extract tanning	
Hazardous properties	- Based on polyphenol compounds (e.g., quebracho, mimosa, oak) extracted from plant material. - Auxiliaries are, e.g. pre-tanning substances, bleaching agents and fatliquors, formic acid, synthetic tanning agents and resins. Some of these substances can also be considered problematic; this includes the chemical modification by sulfitation.
Material health	- During the tanning process no precarious ingredients are used which are also present in the end product. Basically, applicability is good. - Migration behavior during typical vegetable tanning by synthetic pre- or retanning is not known.
Tanning process	- Cultivation of plant material, partly on large-scale plants, is questionable from an ecological point of view. - Production of the tanning agent requires a very large amount of biomass. - Energy and especially water expenditure in vegetable tanning is comparatively high. - Large amounts of organically contaminated water may be produced.
Recyclability	- The use of vegetable tanning agents potentially opens up the possibility of compostability. However, few processes are designed for that purpose, which is a problem especially in connection with synthetic tanning agents.

Plant extract tanning: wet-green® OBE

	Tanning agents used	Auxiliaries used
	Extract of olive leaves (contain phenolic compounds)	Formic acid, sodium carbonate, fatliquors, synthetic tanning agents, fungicides

wet-green's aspiration is 100% prevention of pollution by hazardous tanning chemicals which are still used in mass production in all conventional leather production processes. The reason for this is that leather products, which are in direct contact with the skin, can sometimes contain high levels of toxic, hexavalent chromium and other allergens.

For the wet-green® OBE tanning agent only by-products from olive cultivation are needed - the leaves. For the production of the raw material no tree is felled and no new field is cultivated, thus no predatory exploitation of nature occurs.

On the basis of an aqueous olive leaf extract a plant-based concentrate is prepared, which is neither corrosive nor is it a precarious commodity, which brings clear advantages in logistics. In addition, the wet-green® OBE tanning agent is free of metals and any chemical-synthetic reactive tanning agents. Waste materials from leather production, such as shavings, can thus be returned to the value chain.

For the assessment of hazardous properties of the ingredients in the tanning process with the wet-green® OBE tanning agent, consideration of the auxiliaries or retanning agents is also an important factor. Compared to wet-white tanning (e.g. with glutaraldehyde) these are used in a reduced amount and are optimized, from an ecological point of view, by the use of the latest standards.

Because of the use of olive leaf extract, which is a 100% renewable raw material, the "wet-green® OBE" tanning agent is designed for the biological cycle. After tanning, the tanning agent is completely integrated into the product, thus as a biological nutrient it is completely biodegradable and can be returned into cycles. This is the main difference to previous tanning methods, which in some cases theoretically allow a circulating capability, but which has not been taken into account from the very beginning in the design of the tanning agent and processing steps.

Assessment wet-green® tanning	
Hazardous properties	- Tanning agent from olive leaf extract, neither corrosive nor toxic. - Reduced use of auxiliaries such as sulfuric acid, formic acid, salts and auxiliary- or retanning agents.
Material health	- No metals or materials evaluated as toxic are used and therefore they cannot be found in the final product.
Tanning process	- Low energy consumption during the production of the tanning agent. - > 50% energy use by renewable energies during production of the tanning agent. - Waste water does not contain any toxic chemicals and can be fed to the waste water treatment plant. - No resource burden for nature since it is a natural "by-product".
Recyclability	- The extract of olive leaves is 100% made from renewable raw materials and can circulate completely in the biological cycle.

Social aspects

The ecological disadvantages of chromium tanning affect the safety and health of workers in the particularly Asian production sites. A review of the working standards in these countries is challenging, however a sufficient working safety cannot be considered as a well-established standard.
The use of toxic glutaraldehyde in the tanning process can have a detrimental effect on the health of workers as well. However, in comparison to chromium tanning, the application of glutaraldehyde tanning requires more modern production facilities, so that compliance with labor standards is assessed as more likely.

Vegetable tanning does not pose a risk to the safety of workers and represents, with its limited area of use, a kind of premium tanning, which has been obtained by small production sites in Europe.
The wet-green GmbH, as part of the nature network®, goes a step further in the area of social aspects and tries to generate positive effects along the value chain beyond the expected standard requirements. Regular audits are carried out at the olive plantations to investigate the working conditions; employee projects were launched to further implement the Cradle to Cradle® principles.

Results

Assessment	Chromium tanning	Glutardialdehyde tanning	Plant extract tanning	wet-green® tanning
Hazardous properties	-	0	+	+(+)*
Material health	-/0	+	++	++
Tanning process	0	0	0	++
Recyclability	-	0	+	+(+)*
Social aspects	-	0	+	++

The chromium tanning process is characterized by energy and water efficiency, but the use of chromium, whose use in emerging and developing countries frequently leads to environmental problems, as well as the possible formation of chromium(VI) compounds in the leather and during the combustion of leather, leads to the lowest rating among the considered tanning processes. A biological recyclability of chromium tanned leather products is therefore to be excluded.

In the case of the alternative glutaraldehyde tanning, the starting material also constitutes a risk, since it is toxic. A possibly safe application of glutaraldehyde in the production process and a reduced risk for workers in advanced production sites lead to a better evaluation compared to chromium tanning. Since no residues remain in the final product, a biological recyclability is possible, but the ingredients have not been optimized for this purpose. The wet-white tanning agents X-Tan® and Granofin® Easy F-90 have improved properties from an eco-toxicological point of view compared to glutaraldehyde tanning; however, these tanning agents are based on fossil raw materials and thus from a Cradle to Cradle® perspective, can only be considered as a transitional solution.

The material health of plant extract tanning is rated as very good. When assessing the hazardous properties of the ingredients, the synthetic pre- and retanning agents as well as the chemical modification of the the tanning agent by sulfitation must be taken into account, which can partly contain problematic substances. The recyclability of vegetable tanned leather is fundamentally given, but not optimized for this purpose. From an ecological point of view the large quantity of required tanning agent is problematic, since the biological material of which it is partly produced has a critical cultivation.

The material health of the wet-green® olive leaf tanning is rated as very good. Through the use of olive leaves, whose cultivation as a "natural by-product" is not an additional burden for the environment, the wet-green® tanning agent scores through a sustainable production process. Compared to conventional vegetable tanning agents, the water consumption in the tanning process, as well as in comparison to other chrome-free tanning processes the use of synthetic retanning agents, is significantly reduced and optimized from the ecological point of view by using the most recent standards.

From the Cradle to Cradle® perspective, the wet-green® OBE tanning agent represents the best possible alternative among the evaluated tanning processes. (*) The use of ecologically harmless and for recyclability optimized synthetic retanning agents is an essential factor, which influences the evaluation of tanning processes and needs to be optimized.