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Chromium and Leather Research

A balanced view of scientific facts and figures

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Introduction

The tanning step in the leather making process is something like the operating system in IT. 85 % of all leathers are produced with a chrome based process technology and it can be compared to Windows system in the computer world. Chrome tanning is one of the best inventions in leather history and was the basis for development of the leather business on an industrial scale.

On the other hand, if not correctly operated there is a potential risk involved using chromium for tanning in terms of toxicity relating to hexavalent chrome. Since leather is a component in many consumer articles, and unfortunately still by-products and waste is generated in the leather manufacturing process, it is an important responsibility of the leather industry to manage and fully control this potential risk. In order to be compliant with today's sustainability standards, it is necessary to ensure 100 % safety for tannery workers, for the environment and the end users of the leather articles.

Huge progress has been made especially in the last decade. The vast majority of tanners take this potential risk very seriously. The R&D community is continuously working on methods to avoid formation of chromium (VI) so that it will not have any negative impact on the environment or people and as much chromium will be recycled as possible. Unfortunately considerable false or misleading information about the use of chromium in leather are appearing in the media. The occasional cases of poorly operating tanneries, which are not representing the standard technologies in our industry, are taken and generalized, and an impression that chrome tanning in general is a process, which has to be stopped and forbidden immediately, is given.

Fortunately, the reality is totally different. Based on current scientific knowledge, there is no reason that any consumer should face a toxicity risk from Cr(VI) when simple guidelines and recommendations are followed.

In this paper a balanced view on concerns, risks and results of scientific studies are taken and put in relation to the potential risks for an application of chrome tanned leather. It is important not to belittle or even hide risks and dangers. However, if a risk is manageable then we should ensure that

all are correctly and accurately informed so that no false hysteria is generated. We should focus on implementation of procedures to even further reduce even any theoretical risk.

The element Chromium is neither good or bad!

Elementary Chromium	⇔	Trivalent Chromium	⇔	Hexavalent Chromium
<p>Cr(0)</p>  <p>chromium plated articles & stainless steel: => corrosion resistant => food contact cleared => surgical implants</p>		<p>Cr(III)</p>  <p>Pigment Green => insoluble, not bioavailable => CLP „not hazardous“</p> <p>Chromium Picolinate => soluble => essential trace element => dietary supplement</p>		<p>Cr(VI)</p>  <p>Intermediate in metallurgy & chemical synthesis => high solubility, bioavailable => acute toxic, CMR => strong sensitizer</p>

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Chrome is a special element, which is used in various applications. More than 95 % of chromium is used outside of the leather industry, only a small portion of all mined chrome ore ends up in leather. The vast majority finds its application in premium stainless steel and chromium plated articles. This is the reason why the overall recycling rate of chromium is very high, possibly chromium is the element in the periodic system with one of the, if not the, highest recycling rates of all.

There are different forms of chromium. The elementary and trivalent forms are important basic components for many consumer goods. Trivalent chromium is important in human body nutrition. The natural average content of chromium (III) in many woods and in soil is about 3-5 ppm - again, this is a natural occurrence and not the result of any industrial contamination or application. Chromium (III) oxide pigments are also used widely as green colour for tattoos without any harm or hypersensitive reaction to the skin or body.

The hexavalent form is an important chemical intermediate to purify chromium for the use in the manufacturing of all these applications. In this hexavalent form chromium is known to be toxic to animals and humans, so it needs to be handled under extremely high safety precautions from professional chemical companies only in in-house systems similar to many other hazardous chemical intermediates. This is a normal, potential risk a chemical company has to deal with, and it is completely manageable. The fact, that chromium (III) can be oxidized under certain condition to a hazardous hexavalent form is a similar risk to many other organic chemicals, which are used in multiple applications. Therefore, the need for a scientific risk assessment of the use of chromium for leather tanning is required, in order to exclude these oxidations during normal conditions of use. This has been done in many scientific studies and the studies are the base for legal requirements to protect consumers.

Starting mainly in the 1990s studies have been carried out to fully understand the chemistry of chrome tanning, to evaluate the potential risk and to ensure a 100 % safe use of chromium for leather tanning. The UNIDO has given clear recommendation how to run a process to avoid any Cr(VI) contamination of the environment. Especially the leather manufacturing process was the base of a thorough scientific study initiated from the EU called “chrome6less”. Results are published in the internet, and the overall outcome was summarized in a sentence: “the formation of chromium (VI) in the final leather can be efficiently prevented!”

The leather industry now has to make sure, that these requirements become standard in the entire leather industry without any exception and without any disclaimer.

The chemistry of trivalent and hexavalent chromium

Chromium VI formation can be avoided with the right process and recipe conditions

Theory about Cr (III) \leftrightarrow Cr (VI) equilibrium	
In dissolved form there exists an equilibrium between Cr III and Cr VI. The RedOx potential depends on many factors such as pH, anions, etc.	$\text{Cr III} \xrightleftharpoons[\text{f (pH, conc. etc)}]{} \text{Cr VI} + 3\text{e}$ $\gg 10.000^{**} : 1$
Fixed chromium (Cr - collagen complex) makes significantly less Cr available for the RedOx equilibrium	$\begin{array}{c} \\ \text{Cr} - \text{Cr} \\ \\ \text{fixed 3-4 \%} \end{array} \xrightleftharpoons{} \text{Cr (III)} \xrightleftharpoons{} \text{Cr (VI)} + 3\text{e}$ <p style="text-align: center;">extractable 200 ppm** < 3ppm**</p>
Solid Cr ₂ O ₃ starts oxidizing directly to Cr VI under extreme conditions only	$\text{Cr (III)} \xrightarrow[> 500 \text{ }^\circ\text{C}]{\text{---}} \text{Cr (VI)} + 3\text{e}$
Aradical mechanism* can significantly lower the reaction enthalpy and speed for the oxidation	$\text{Cr (III)} + 3 \text{R-O}\cdot \xrightarrow[> 50 \text{ }^\circ\text{C}]{\text{---}} \text{Cr (VI)} + 3 \text{R-OI}^-$

4 *Reactive Oxygen Species (ROS)



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**all values are rough estimates for illustration @ typical leather conditions

In order to manage the risk it is a pre-condition to understand the chemistry involved. For leather in particular the trivalent and the hexavalent states of chromium are important.

In a dissolved form there is an equilibrium between the trivalent and the hexavalent form. This equilibrium is influenced by several factors, such as pH or concentrations. Since Cr(VI) is an extremely strong oxidizer, which is one of the reasons for its hazard potential, the equilibrium under “normal” conditions of a leather matrix (pH 3,5 - 5, concentration of extractable Cr(III) 50 - 500 ppm, temperature below 100 °C) is nearly completely on the side of the safe trivalent form; estimations refer to a factor of significantly higher than 10.000 :1.

Most of the chromium in the leather is strongly fixed to the collagen during tanning; this phenomenon was the reason why it was selected for this purpose. Once the chrome is fixed to the fibre, the availability of it for the equilibrium of Cr(III) and Cr(VI) is dramatically reduced. Only the extractable part of Cr(III) in leather is fully available for the equilibrium.

In a standard chrome tanned leather there is a chromium content of 3-4 % fixed to the fibre. For such a leather the standard value for extractable Cr(III) will be in a range of 50 – 500 ppm, although it depends very much upon the recipe and the process conditions. This 50 – 500 ppm is the amount, which is available for the equilibrium, and according to above mentioned statements regarding the distribution of the equilibrium this leads to a safe Cr(VI) concentration in the leather far below the current detection limit of 3 ppm. Concentrations that have been shown to be a risk for the consumer are higher by some orders of magnitude.

Oxidation of Cr(III) to Cr(VI)

A direct oxidation of fixed Cr(III) to the hexavalent form under standard conditions is very unlikely because reaction speed is extremely slow. Only above temperatures of 800 °C and above the oxidation reaction starts shifting towards Cr(VI). This is for normal leather and consumer conditions not a risk at all.

There is one important fact to consider that is a potential risk: the indirect oxidation route via an intermediate of a reactive organic species (ROS). There are chemicals which are found in the leather industry, which can generate such free radicals e.g. by UV light exposure or bleaching/cleaning procedures; these radicals than can oxidize trivalent chromium into the hexavalent form even under “normal” conditions. The radicals could be generated by unsaturated groups, which are e.g. part of many cheap or low end fatliquors, waxes and oils. In order to avoid such an oxidation reaction, a necessary amount of scavengers and antioxidant auxiliaries have to be built into the leather matrix, or these troublesome chemicals should be simply avoided. Under presence of such scavengers the radicals will be caught immediately after generation and irreversibly eliminated due to transformation into stable components. If this is the case, the much slower and more difficult oxidation process of trivalent chromium does not occur at all. These scavengers are “built-in insurances” to avoid the formation of Cr(VI) via an indirect way of reactive oxygen species.

Chromium is omnipresent and environmentally persistent - “chrome-free” does not exist

Chromium: the equilibrium background and its persistancy for the environment

- Cr (VI) ions are soluble in water, Cr (III) ions have a very low solubility
- Chromium (VI) is a strong oxidizing agent, especially under acidic conditions
- Cr(VI) is highly soluble and can be reduced to Cr(III) by a variety of organic compounds
- In environment the equilibrium ends up > 99.9 % on Cr(III), and < 0.1 % on Cr (VI); it depends very much on pH and concentration
- Cr(III) components quickly age to form e. g. Cr(III) oxide. Becoming insoluble and bound to soil, the chromium is no longer bio-available and **removed from the equilibrium.**

$$\begin{array}{ccccc}
 \text{Cr}_2\text{O}_3 \downarrow & \longleftarrow & \text{Cr III} + 3 e & \xrightleftharpoons{f(\text{conc, pH})} & \text{Cr VI} + 6 e \\
 \text{insoluble} & & \text{(stable)} & & \text{(hazardous)}
 \end{array}$$

Chromium in the environment

In case dissolved chromium is released into the environment, the same rules for the equilibrium will be applicable as explained earlier. Due to their strong oxidizing power small amounts of generated Cr(VI) will immediately react oxidatively with many of the organic components present in the environment. This means the Cr(VI) becomes reduced to the safe form of Cr(III) according to the distribution of the equilibrium. In these small concentrations of Cr(VI) it works like a “self-cleaning” mechanism. Since Cr(VI) is soluble, it could be also taken up by plants. In such a case the plant again reacts in the same way and converts Cr(VI) into the safe form of Cr(III); in all studies no Cr(VI) has ever been detected in any plant.

In the trivalent form in environment, Cr(III) quickly ages to insoluble Cr(III) oxide. This is a final and fixed form of chromium under “normal” conditions, which, similar to the fixed form in leather, also is not available anymore for the equilibrium between Cr(III) and Cr(VI). So even in nature the chemical system of different valency stages of chromium automatically will work against a contamination with the hazardous form of Cr(VI), and favour the stable form of Cr(III).

There is the belief, that similar effects do play a role, if a leather is going to be extracted e.g. by human sweat. The acid pH of sweat as well as many microorganisms in the sweat are a perfect environment to reduce these possible small amounts Cr(VI) directly to harmless Cr(III).

Consumer risk from chromium in leather

The chromium (III) use in leather is without any hazard for the consumer and the worker

Important human health hazard assessments of Chromium		
Cr (III)	▪ Sensitization	No sensitizer
	▪ Acute toxicity	Nothing or harmful, depending on exposure and compound
	▪ Carcinogenicity	Non CMR
Cr (VI)	▪ Sensitization	Sensitizer
	▪ Acute toxicity	Toxic
	▪ Carcinogenicity	Carcinogenic and mutagenic

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Having understood the chemistry concerning the equilibrium of Cr(III) and Cr(VI), a realistic assessment can be done of the consumer risk of chromium in leather.

Regarding Cr(III) things are clear and without any risk as again stated in the most recent REACH Annex XV Report , Kap. B 5.8 (ECHA 2011). Cr(III) in concentrations used in leather is not sensitizing, it is proven to be harmless and not CMR classified.

Hexavalent chromium, however, has all three hazardous risks even in small dosage amounts: it is a strong allergen; it is toxic and classified as carcinogenic and mutagenic category I if inhaled. Therefore, if leather would contain significant amounts of Cr(VI) we face a potential risk, and this needs to be scientifically assessed and managed carefully. The fundamental question is, what are realistic exposure risks at which limits.

Based on the current state of science acute Cr (VI) toxicity seems to be far from a relevant leather consumer risk

Chromium (VI): acute toxicity		
<ul style="list-style-type: none"> ▪ Consumer or worker safety is not the issue of an individual chemical, but of its exposure ▪ Only a risk assessment can lead to "safe" data → Lethal Dose (LD) thresholds and No Observed Adverse Effect Level (NOAEL) ▪ There is reasonably good database available on toxicokinetics of Cr (VI) for animals. ▪ Only few data are available for humans, but there is the potential, that they are generally likely to behave in a similar manner 		
<p>Model:</p> <p>1 pair of shoe → ~ 2 sqft leather 2 sqft leather → ~ 200 g weight</p> <p>Reasonable worst case scenario: 10 ppm Cr (VI) → 2 mg/pair of shoe</p>	<p>LD_{50, oral}: 74 mg/kg* bw (26 mg Cr (VI) / kg bw = 1.8 g/70 kg) → 1.8 g = 2 mg/pair x 900</p> <p>NOAEL: 2.5 mg/kg* bw (1 mg Cr (VI) /kg bw = 70 mg /70 kg) → 70 mg = 2 mg/pair x 35</p> <p>LD_{50, dermal}: 1.150 mg/kg* bw (410 mg Cr (VI) / kg bw = 28 g/70 kg) → 28 g = 2 mg/pair x 14.000</p>	
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For a better understanding first it is important of understand a general logic regarding all harmful and hazardous chemicals:

There are many chemicals, which are classified more or less hazardous, but in order to evaluate a true risk you always have to correlate the toxicity with the exposure of the chemical in its specific application. As every scientist knows this is not a specific problem of some hazardous chemicals, this is a general logic applicable for all chemicals, because at some point of exposure all substances can become harmful or even hazardous. This logic needs to be kept in mind even evaluating the toxicity of Chromium (VI).

The classic example of table salt, NaCl, everyone knows it is necessary for life, however, in excess it is health and even life threatening. The same is true even for essential vitamins! So, when considering is sodium chloride a good or a bad chemical? The answer is it depends on the level of exposure, but for sure we should never forget our body cannot survive without salt or chromium!

This logic needs to be kept in mind even for evaluation of toxic chemicals. Based on animal studies there is always a lethal upper level and a lower no effect level defined: the life threatening level,

which is called the lethal dose (LD50 in mg/kg) is set by a 50 % mortality rate of rats fed with this dose level per kg of body weight. The lower level is called NOAEL (No Observed Adverse Effect Level), which actually marks the level of no toxicity concern.

Today, there is a reasonably good data base available regarding toxicity of Cr(VI); most of it, is of course generated from studies based on mammals, and it is widely believed that these results are largely transferrable to humans.

A simple calculation proves that if a given leather contains 10ppm Cr(VI) the NOAEL and particularly the LD50 levels are far, far beyond any potential scenario that could be of any concern to consumers. Theoretically a person would have to eat 35 pairs of shoes with this level of contamination per day, in order to be in an area above NOAEL to possibly be effected. I think it is fair to say, that based on science an acute Cr(VI) toxicity risk can be excluded, because it is far beyond any relevant consumer risk.

Based on the current state of science Cr (VI) carcinogenicity seems to be far from a relevant leather consumer risk

Chromium (VI): cancerogenicity
<ul style="list-style-type: none">▪ There is never a NOAEL for carcinogenic and mutagenic substances (CM)▪ Animal carcinogenicity studies done with Cr (VI) clearly indicate lung tumour at rats and mice by <u>inhalation</u> or intrabronchial implementation▪ There is a good reason to be concerned about a carcinogenic potential of Cr (VI) by inhalation for humans▪ Carcinogenicity study data for the oral and dermal routes on Cr (VI) compounds are not available*
<ul style="list-style-type: none">➤ Chromium (VI) is classified as cat I carcinogenic by inhalation➤ Concerns about cancerogenicity of Cr (VI) don't apply to leather consumer articles, since such effects require inhalative exposure

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* REACH Annex XV Report, Kap. B 5.8 (ECHA 2011)

Concerning the risk of carcinogenicity and mutagenicity a different viewpoint is necessary. Here currently no NOAEL's are defined, although a discussion around this is currently going on within EPA and ECHA; in today's science it is simply seen as a yes or no fact, if a chemical is CMR classified or not; and, yes, Cr(VI) is rated as carcinogenic category I, but only by inhalation. This means Cr(VI) containing vapour/dust/smoke is of relevance, which, for example, is an important safety fact for worker in electroplating industries or for people who do welding of stainless steel. A one-time contamination of some Cr(VI) containing smoke, as it could come from burning leather would be comparable in terms of cancer risk to smoking a cigarette or breathing diesel exhaust in a traffic jam. Therefore, even in such cases I think it is fair to say, that based on current state of science and reality there is no measurable risk of Cr(VI) carcinogenicity from the wearing of or even (in the case of babies, for example) having oral contact with chrome tanned leather.

Statistics show, that Cr(VI) is not the outstanding concern for dermatitis sensitization as often claimed in public

Study in Germany to investigate the Cr (VI) sensitizing potential *

28.000 patients tested over a period of 5 years
 85 with background in leather and shoes
 30 persons with special test "leather"

Findings:

- From 80 million ca. 6000 report a severe foot dermatitis
- 350 (< 5 ppm of population) reacted to Cr(VI).
- Ca. 4 times as many reacted to other chemicals used in leather

source: Information network since early 1990s, 5 year report: Koch et al., *Dermatosen in Beruf & Umwelt*, 1996;

test substance	average population	background leather & shoes	special test leather
nickel sulfate	18	21	
potassium dichromate	6	13	4
glutaraldehyde	5	16	27
formaldehyde	3	5	
mercaptobenzothiazole	1	5	10
phenylene diamine	5	10	
Cr non chromate	100	155	

selected results from the 5 year report;
 percentage of skin reaction to test substance

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Cr(VI) as a sensitizing allergen

Finally the important issue of sensitization needs to be discussed. Cr(VI) is known to be a strong allergen. As pointed out in the literature (Integrated Risk Information System, EPA: <http://www.epa.gov/iris/subst/0144.htm>) in the first step (induction) of a possible contact, chromium (VI) is absorbed into the skin and triggers the next step - an immune response (sensitization). Sensitized individuals will exhibit an allergic contact dermatitis response when exposed to chromium above a threshold level then for their life time.

This threshold level or the non-sensitizing effect level is unfortunately in a range of several ppm of Cr(VI). This means, a sensitive person can theoretically be affected by leather, which contains these amounts of Cr(VI). So how significant is this risk in reality? What we can state is, leather has been used the main substrate for shoe manufacturing and skin contact leather goods such as watch bands since decades, and scientific investigations have shown, the percentage of the population that is hypersensitive against Cr(VI) is low. It appears that there is a mechanism in place so that this risk of contact dermatitis is somehow minimized. One of the reasons could be, as explained earlier concerning the equilibrium and environmental reduction, trivalent Cr(III) is formed prior to contact and penetration of the skin. The remaining amount of Cr(VI) will be below an observed effect level. However, this is only a possible and logical theoretical explanation based on scientific observations; it is not yet proven to be scientifically correct.

The fact is, according to several scientific studies the number of people that are hypersensitive to Cr(VI) is low. Official numbers refer to 0.4 % of the population, which may react positive to chromium. This is in the same range like cases against many other metals (allergic reactions against gold are 4 times, and against Nickel even more than 10 times higher) and a magnitude lower than allergic cases against e.g. certain food, lactose, grass, etc. Once a person reacts hypersensitive

against chromium and it is known, there is an easy way to protect themselves in case some e.g. shoe upper leather would contain respective amounts of Cr(VI); they just have to wear socks in a shoe and avoid a direct contact of leather with their skin.

As a conclusion: measured cases for dermatitis sensitization to leather in today's population is not a concern as often claimed in certain media. Implementation of standard technologies and further R&D results would even lower this risk and need to be pursued

Practical ways to avoid Cr(VI) formation in leather

Therefore, to be on the safe side, it is important to produce leather without any detectable amount of Cr(VI). This is manageable, a tanner has to follow strictly certain rules and use the right chemicals. These process technology guidelines are not rocket science, actually most of the tanners do practice them already today and they require a certain manufacturing discipline.

9 key points have been developed to avoid a Cr(VI) formation during the process and to create a leather matrix, which has a built-in insurance to avoid the generation of Cr(VI) during storage and use:

1. Always use premium chrome tanning salts
2. No use of oxidation agents (i.e. bleaching) on leather after tanning
3. Finish the wet end processing at (low) pH conditions (3.5 - 4)
4. Carry out a final washing
5. Avoid the use of excess ammonia prior to the dyeing process
6. Use high performance softening chemicals (no unsaturated lipids or waxes)
7. Avoid the use of chromate pigments (yellow and orange inorganic pigments)
8. Use between 1 and 3% vegetable tannin extract as this provides antioxidant protection
9. Use of synthetic antioxidants where it is not possible to apply vegetable agents *

Following these principles a tanner is producing state-of-the-art leather, which fulfils all requirements to avoid any issues with hexavalent chromium in leather.

Testing for Cr(VI)

One important aspect regarding testing still needs to be mentioned. It is the objective to protect consumers from Cr(VI) exposure producing leathers free of chromium (VI). However, there is no test method available today to detect Cr(VI) accurately directly in the matrix leather. Every detection applied or proposed so far works on extracts generated from the leather sample in question.

The condition of phosphate-buffered pH 8 applied in ISO 17075 had been selected to avoid reduction of Cr(VI) during extraction, but if the leather contains traces of oxidizing substances in parallel to

chrome it is not unlikely that the oxidation only takes place in the extract and the reading does not indicate the concentration of Cr(VI) in the leather, but the concentration of the oxidizer.

At conditions that would better simulate consumer exposure, e.g. extraction with artificial sweat solution of pH 5.5, such an oxidation is much more unlikely, but if traces of a reducing chemical are present, reduction of Cr(VI) cannot be excluded.

So far there is no conclusive evidence that proves that the concentration in one of those extracts is identical to the situation in the leather. But if the extraction conditions from ISO 17075 are applied it is important, that no numbers below 3 ppm are reported to avoid, that artefacts from the extraction are mixed with real concentrations. This pre-condition does not change; even if a detection method is applied that is more sensitive than the currently defined UV-measurement.

Summary and conclusion

A balanced scientific view on potential risks of Chromium in leather has been done, which is in contradiction to many opinions presented in public media. As stated in the most recent REACH Annex XV Report , Kap. B 5.8 (ECHA 2011), there are no reasonable issues with Cr(III) in leather. According to a scientific investigation from the EU (Chrome6less project) the formation of chromium (VI) in the final leather can be efficiently prevented. There are standard technologies available to every tanner to produce a Cr(VI)-free leather matrix.

In case leather with slightly increased amounts of Cr(VI) are found, modelling clearly shows, that a consumer risk in terms of toxicity and cancer can be excluded; results from possible exposure scenarios are far below any detectable risk for a consumer wearing a garment made out of a leather substrate.

There is a remaining potential allergy risk for Cr(VI) containing leather for a small percentage of the population. And despite leather being the material of choice for consumer applications for decades, the level of chromium hypersensitivity cases is below many other substances such as gold, nickel, food ingredients, grass, or special organic compounds.

Replacing chromium tannage by other tanning technologies by itself, wouldn't make the world a safer place, but reduces the technical advantages. However, although huge progress has been made especially in the last decade, the international leather industry needs to further promote best practice technologies, which will result in a reliably chromium (VI)-free leather matrix.