GUIDELINE FOR LEATHER MANUFACTURERS

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G-Star Raw C.V.

G-STAR RAW

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FOREWORD

For us at G-Star it is crucial to think innovatively about the impact we have on society and the environment through the activities that we undertake. Sustainability is a condition for doing business and a process of continuous improvement

The purpose of this guideline is to provide information to leather manufacturers and leather goods manufacturers to enable them to produce leather according the latest state of the art science and technology. This guideline provides targeted measure and appropriate due diligence obligations across the entire leather production process to avoid the development of chromium VI.

According to the current state of technology, leather and leather goods can be produced using suitable tanning procedures and equipment without the risk of chromium VI formation. Through Quality Assurance in the production facilities, during the course of which technical measure can be prepared and monitored, a defined quality of leather can be achieved and also retained in the long-run.

In the leather manufacturing sector, standards have been created by the 'Leather Working Group', which provide tanneries with assistance in producing leather without chromium VI formation.

However in addition to the technical standards, transparency and mutual communication within the supply chain are required in order to ensure that the leather is suitable for the intended purpose.

This guideline is created in accordance with CADS (Cooperation for assuring defined standards for shoe and leather goods production e.V.) CADS has the purpose to secure the quality of footwear and leather goods, to engage in public relations work for the manufacture and marketing of sustainable, non-toxic, environmentally compatible shoes, shoe materials and leather goods with social responsibility.
G-Star is an active member of the cooperation and is therefore striving forward to implement this standard within the industry.

SECTION 1 – CHROMIUM (VI) PROHIBITION IN LEATHER PRODUCTS

1.1 CURRENT SITUATION

In accordance with the current EU legislation, leather products contaminated with Chromium (VI) cannot be marketed.

Any person putting such goods onto the market must maintain their due diligence obligation and guarantee that the leather product accords with the legal specifications before it is placed on the market. However, it is not only the seller of the goods who is obliged to check the marketability of the product; intermediate traders are also obliged to check the marketability of a product if the suspicion arises that a product does not or no longer fulfills the legal requirements. If one of these participants within the supply chain receives knowledge that a product is not marketable or that this product generates a risk, they must notify the responsible authorities for all countries in which the product is sold.

The goods must be removed from the market, and depending on the risk potential of the product, it may be necessary to recall them from the end consumer. Notifications on hazardous products are published weekly on the webpage of the EU-wide Rapid Information System RAPEX.

The potential of Chromium (VI) formation in leather can be generated in various stages of production, which can be classified as follows:

1. Leather manufacturing process
2. Product manufacturing process
3. During storage and transport of leather or leather goods

Verifiable quantities of Chromium (VI) almost always indicate that the leather has not been produced or treated in accordance with the latest technological status. The use modern process chemicals and suitable leather manufacturing process chemicals and suitable leather manufacturing methods mean that the formation of Chromium (VI) can be avoided.

1.2 STATUTORY REGULATIONS

In Germany, Chromium (VI) has been prohibited since 2010 in consumer articles made of leather which do not only come into brief contact with the human body – such as clothing, wristwatches, shoes, bags, back packs, seating furniture or neck pouches – through the Consumer Article Ordinance (BedGegstV).

In the year 2012, Denmark mediated to the European Chemical Agency a dossier acc. Appendix XV on the initiation of a restriction procedure. In this dossier, it was proven that exposure to Chromium (VI), such as occurs in leather products of in leather parts of production which come into contact with the skin represents a risk to human health.

From 1st May 2015, a regulation on the subject of Chromium (VI) will be applicable across the entire European Union (Ordinance EU 301/2014). Due to this ordinance, Appendix XVII of the Ordinance EC 1907/2006 REACH has been supplemented through a Chromium (VI) prohibition with the following wording 'Leather products and products which contain leather parts which come into contact with the skin may not be placed on the marketed if they are found to reveal a Chromium (VI) content of 3mg/kg (0.0003% by weight) or more of the total dry with of the leather'.
Leather and leather products are thus no longer marketable across the entire European Union if they contain >=3mg/kg Chromium (VI). The limit value is oriented on the EN ISO 17075, which is stated as the test method in the Ordinance. The verification limit of the procedure according the standard EN ISO 17075 lies at 3mg/kg Chromium per kg leather (0.0003% by weight), referring to the dry weight of the leather.

The prohibition applies not only to leather and leather products newly entering the market or trade, but also concerns products which have been put on the market prior to the enforcement of the Ordinance, as well as older stored goods and remaining stocks, which have not yet reached the end consumer prior to 1-May 2015. This limit value must be maintained over the product entire life cycle.

1.3 SCIENTIFIC STATUS

Comprehensive investigations exist on the generation of Chromium (VI). All relevant knowledge on the formation and stability of Chromium (VI) indicate that tanning using Chromium salts, which is carried out in accordance with the latest technology cannot lead to the formation of Chromium (VI).

Investigations have shown that the formation of Chromium (VI) from Chromium (III) is possible at higher pH values and/or with oxidative potentials (e.g. oxidizing organic substances, oxygen in combination with elevated temperatures, light influence and low relative air humidity. Further results with regard to the investigation of accelerated aging processes confirm the influence of thermal post-treatment and UV ration on Chromium (VI) formation.

Significant includes on the generation of Chromium (VI) in leather could be verified through fat liquors. In experiments concluded using individual process chemicals, it was revealed that the use of fat liquors based on polyunsaturated fats – in particular natural fat liquors such as fish oils – can promote the formation of Chromium (VI) in leather if these products themselves have insufficient stabilization against oxidation (antioxidants).

The application of vegetable tanning agents in re-tanning with relatively low application quantities (approx. 1-3%) proved to be a highly effective method of avoiding the generation of Chromium (VI). In the same way, through the additional of reducing agents in the tub treatment, the formation of Chromium (VI) can be suppressed. In many cases, the use of reducing-effect leather agents in the field of neutralization and purging proved advantageous with regards to the avoidance of Chromium (VI).

Furthermore, the influence of the relative air humidity during storage of the Chromium (VI) content of chrome tanned leather was revealed. Here Chromium (VI) formation was promoted in the presence of atmospheric oxygen and a relative air humidity of under 35%. The tendency for Chromium (VI) formation increased as the relative air humidity dropped. Storage at high air humidity does not, however, completely exclude the formation of Chromium (VI).

In order to avoid the formation of Chromium (VI) during manufacture, dialogues between tanners and processors are necessary in order to clarify the suitability of the leather for the intended purpose.

1.4 CLASSIFICATION OF LEATHER – TENDENCY FOR CHROMIUM (VI) FORMATION

Some types of leather tend more strongly towards the formation Chromium (VI). This is exacerbated through various factors: amongst others, the animal species, the tanning procedure and the further processing. As far as the animal species are concerned, lambskin and pigskins are more at risk of generating Chromium (VI), whereas the risk of cowhide lather doing so is less high. Lambskin and pigskin have a higher proportion of skin fat than cowhides, and do incomplete degreasing during production can provide a possible explanation for this higher tendency towards Chromium (VI) formation. In terms of the leather production procedures, hydrophobic leather, leather in dark color shags and vegetable re-tanned leather are seldom subject to Chromium (VI) formation. Split leather and leathers in lighter shades are known to show higher levels Chromium (VI) formation. This list is exemplary and does not comprise all leathers.

SECTION 2 – THE USE OF CHROMIUM SALTS IN THE TANNING PROCESS

2.1 THE TANNING PROCESS – GENERAL INFORMATION

The manufacture of leather incorporates a series of complex chemical reaction and mechanical processing steps. Certain qualitative requirements are placed on the leather for shoe manufacture: here it must be sturdy and tear-resistant, but at the same time of a high elasticity and supple. These factors can be influenced through the tanning process. During the tanning process, the leather is treated with the appropriate tanning agents over several process steps. The tanning agents penetrate into the moist animal hide and link the collagen fibers with each other so that sturdy basic framework is created within the skin. For this reason, the leather does not shrink as it dries and it remains supple and strong.

The following are used as tanning agents:

TANNING AGENGT	LEATHER DESIGATION
Chromium II salts	Wet blue* Chromium leather
Vegetable ingredients	Vegetable tanned leather
Synthetic and reactive tanning agents	Wet white* Synthetically tanned leather

Depending on the leather properties to be achieved, the leather can also be tanned using several tanning agents. In this way, leather tanned using vegetable or synthetic tanning agents has a higher strength and a better elasticity if it has been tanned before or after these tanning processes with chromium salts.

**In case of wet blue and wet white, these are intermediate steps in the manufacture of leather.*

2.2 CHROME TANNING

Chrome tanning is currently the most frequently applied tanning processes; over 80% of all worldwide leather is chrome tanned. The proportion of chrome tanned leather in the shoe industry specifically even total of over 95%. The animal skins and hides first have to be fleshed, de-haired and degreased. For the subsequent tanning of the animals skins and hides chromium salts are used or combinations of chromium slats and other tanning agents. The chromium salts permanently penetrate into the collagen fibers of the animal skins and h ides, and remain fixed in the leather after tanning. This is particularly important to ensure that the leather retains its shape, strength and suppleness. The freshly-tanned, still-wet limed hide is known as wet blue, as it takes on a slightly blue tinge through the chrome tanning process. The early-stage wet blue leather can be easily stored with the use of appropriate preservatives, and can also be easily transported. Chrome tanned leather is characterized by its particularly high strength and extremely good elasticity of suppleness. Thanks to these special properties, chromium leather is used in diverse application comprising of almost all types of leather articles, such as shoes, clothing, furniture or car leather and amongst other things.

2.3 LABORATORY VERIFICATION FOR CHROME TANNING

The chromium salts are permanently fixed into the leather during tanning. The total chromium content of the leather can be determined in a laboratory using standardized methods. The EN ISO 17072-2describes the determination of the contents of different metals , amongst other things chromium, for low contents , and is suitable for confirming chromium-free tanning. The second standard, the EN ISO 5398 Parts 1-4, shows the determination of the chromium content for leather, and is also suitable for chrome tanned leather with contents of 5% chromium.

LEATHER#	TOTAL CHROMIUM CONTENT
Intended use of chromium	From approx. 1000mg/kg
Tanned chromium-free*	Up to approx. 1000mg/kg

#In cases of leather with contents of over 1000mg/kg, we can assume that the addition of chromium has been intended, for example during re-tanning or tanning.

**According to the definition according EN 15987 for chromium-free tanned leather. Dyes containing chromium can lead to chromium contents within a range of several 100mg/kg; chromium contaminated water and chromium contaminated tanning tubs and washing tanks may occasionally generate content figures with a low mg/kg range.*

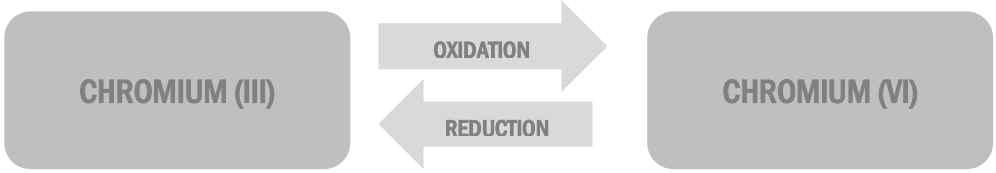
2.4 OXIDATION STAGES OF THE ELEMENT CHROMIUM

Chromium can occur in various oxidation stages:

CHROMIUM (0)
This is metal chromium, which is highly stable.

CHROMIUM (III)
The use of Chromium (III) salts is classified as harmless according current knowledge. Chromium frequently occurs in the environment in its trivalent form. The average concentration it the earth's crust lies at approx. 100mg/kg; in ore deposits, it totals up to 50%. Most Chromium (III) compounds are water-insoluble and are not biodegradable. Furthermore, Chromium (III) is an essential trave element, and can be found in all animal or vegetable tissue.

CHROMIUM (VI)
Under certain conditions, the Chromium (III) can generate Chromium (VI) through oxidation. Chromium (VI) is an allergen and can lead to allergic exanthema if it comes into contact with sensitized skin. Some Chromium (VI) compounds are classified as carcinogenic but only if inhaled.



Simplified representation of the transfer from Chromium (III) to Chromium (VI)

The low oxidation stages Chromium (III) and Chromium (VI) are mutually convertible. Depending on different factors, the conversion from Chromium (III) to Chromium (VI) takes place through oxidation. However, the conversion of Chromium (VI) back to Chromium (III) is also possible via reduction. This is useful when treating leather, which is contaminated with Chromium (VI), with antioxidants (reducing agents).

2.5 CHROMIUM MEASUREMENTS IN THE LABORATORY

There are several test procedures for chemical analysis, which can supply the parameters for the chromium content of leather:

CHROMIUM (VI) CONTENT - Inspection for maintenance of the legal limit value:
Chromium (VI) in leather is determined on a cut sample according to EN ISU 17075 standards after extraction. The direct determination of the Chromium (VI) content in the leather matrix is not currently possible. The quantity of the Chromium (VI) found in the extract Is calculated back to the content in the leather. The verification limit of the procedure is 3mg/kg Chromium (VI) per kg leather. The conditions stipulated in the standard for the extraction must be adhered to strictly, otherwise there is a risk of a false-positive result.
An extraction of composite samples for the determination of Chromium (VI) is not recommended, as it can lead to false results if one leather sample is contaminated with Chromium (VI), but the other features a reductive potential.

CHROMIUM (VI) AGING – Inspection for the formation of Chromium (VI) during the leather aging process:
Under laboratory conditions, thermal aging is simulated on the leather. To do this, the cut sample is stored according to the CADS methods at 80°C and with relative air humidity of up to 5% for 24h in a drying cabinet without ventilation, air circulation or any openings to the outside. Subsequently, the Chromium (VI) determination according to the EN ISO 17075 standards takes place as described above.

CHROMIUM SOLUBLE – Inspection as to whether a leather sample releases larger quantities of soluble Chromium under wearing conditions:
Chromium soluble is mainly tested on leather samples which may come into contact with the skin during the intended application of the respective leather product. In this test approach, wearing conditions are simulated which provide information on the possible Chromium release under realistic conditions. The determination takes place according to EN ISO 17072-1 after extraction of the leather with an acidic perspiration solution at 37°C.

TOTAL CHROMIUM CONTENT – Inspection of whether leather has been chromium tanned or has been through a chromium-free tanning process:
For the measurement, the leather is completely dissolved according to EN ISO 17072-2 or 5398 Part 1-4 (total disintegration process). The total chromium content of chromium is a piece of leather. Based on this data, conclusions can be drawn concerning the tanning method used. In case of a total Chromium content of below 1000mg/kg, the leather is classified as chromium-free tanned leather according to EN 15987.

SECTION 3 – HOW DOES BECOME CONTAMINATED WITH CHROMIUM (VI)

3.1 GENERAL INFORMATION

With increasing globalization, leather production has also undergone major changes. Whereas before leather was generally manufactured in one company, from the raw hide right up to the finished product, the process chains today have been broken up greatly and the products are in part sent around the world for different processing steps. This has led to an increasing in the formation of Chromium (VI) in leather manufacture. Due to these altered production and trade prerequisites, far better standards of communication must take place within the supply chain than is currently the case. In order to determine whether a leather sample is suitable for the respective intended use, the leather product manufacturers must be provided with information from leather manufacturers as to under which production conditions, such as for example shrinkage or color fastness, the leather does not change. On the other hand, manufacturers of leather production should also provide information of leather manufacturers as to which conditions may have a negative effect on the leather quality. Here, for example, the temperature, duration and humidity to which the leather is exposed during further processing are to be stated, so that leather manufacturers can comment on the suitability of their leather. During Chrome tanning, Chromium (III) salts are used to tan the skins and hides. So what causes Chromium (VI) contamination in leather?

3.2 CHROMIUM (VI) ENTRY EXTERNAL FACTORS

For the production of Chrome-tanned leather, the use of different process chemicals, tanning agents and tanning auxiliary agents is necessary. Here it is important to select these chemicals carefully and it is essential that the chemicals used fulfill the required quality standards.

CONTAMINATED TANNING SALTS

Chromium (VI) can occur during leather production through:

- Contaminated chromium tanning agents containing Chromium (VI) from new production
- Contaminated chromium tanning agents containing Chromium (VI) from Chromium (III) recover
- Multiple use of contaminated tanning liquors containing Chromium (VI)

DYES CONTAINING CHROMIUM (VI)

Chromium (VI) can occur during leather production through the use of pigments containing Chromium (VI). Some yellow, orange or red pigments contain Chromium (VI), for example:

- C.I, 77600 Pigment Yellow 34
- C.I, 77603 Pigment Yellow 34
- C.I, 77605 Pigment Red 104

CONTAMINATED WATER OR CONTAMINATED TANNING TUBS

Chromium (VI) contamination can occur during leather production through:

- Contaminated water containing Chromium (VI)
- Poorly cleaned tanning tubs and tools

RECOMMENDATION FOR Chromium (VI) AVOIDANCE: EXTERNAL FACTORS

- Use certified products of chemicals from well-known resources
- Do not chemicals from old inventories; observe the use-by date
- Have your chemicals guaranteed Chromium (VI)-free by the manufacturer
- Do not use Chromium tanning agents which you have recycled yourself without a preliminary test being carried out for Chromium (VI)
- Only use recycled Chromium tanning agents from preparation companies which guarantee Chromium (VI)-free preparations
- Do not use pigments containing Chromium (VI)
- Ensure thorough cleaning of the tanning tubs and tools
- Do not use water contaminated with Chromium (VI) to clear equipment, tubs, tools etc.
- Do not use water contaminated with Chromium (VI) during the tanning process

3.3 CHROMIUM (VI) FORMATION IN LEATHER

Leather which has been tanned using Chromium salts, even if this is merely a pre-tanning or retaining process, will contain Chromium (III). If quality standards are maintained and the necessary due diligence obligation upheld in the tanning and wet finishing process, the use of Chromium (III) as tanning agent is harmless. However, Chromium (III) and Chromium (VI) are mutually convertible under certain conditions. Diverse conditions permit the formation of Chromium (VI). Starting points for the avoidance of Chromium (VI) formation lie in the tanning procedure, including the pre-tanning, re-tanning and surface finishing through finishing products. During the entire tanning process, a multitude of different chemicals are used which, in part have an oxidizing effect. In the different stages of the tanning process, strong pH value fluctuations are technologically necessary; this demands sufficient knowledge of the control of pH values. High pH values over pH 8, or above all in the strongly alkaline range (approx. pH 13) and oxidizing chemicals, promotes the formation of Chromium (VI).

3.4 PRODUCTION STEPS IN CHROME TANNING – BEAMHOUSE

The term beam house refers to a series of processes which typically take place prior to the actual tanning step.

SOAKING – CLEANING AND SOAKING

The raw hide or skin is cleaned and soaked; here the water content of the hides and skins should reach their natural water content and as many water-soluble non-leather producing proteins as possible are to be removed. This takes place in rotating tubs with water, with the addition of chemicals.

LIMING – REMOVEL OF HAIR, GREASE AND LOOSENING OF THE SKIN STRUCTURE

During liming, hair adhered flesh and fat residues are removed from the raw hides. At the same time, the collagen network in the raw hide is prepared for the tanning agent in the subsequent tanning step. For the manufacture of particularly soft leather, a long liming process is required. During liming the chemicals sodium sulphide; as a de-hairing agent, calcium hydroxide; as a collagen opener and non-ionic emulsifiers; as de-greasing agents are frequently used. The limed skins and hides are referred to as limed hides. Due to the use of calcium hydroxide (lime), the pH of the limed hides is now highly alkaline, with values of approx. pH 13.

DECALCIFYING – NEUTRALIZAION OF THE HIGHLY ALKALINE LIMED HIDES

In order to remove the excess lime and for gentle des-welling, the pH value is generally lowered to a value between pH 6-8. This takes place through the introduction of CO_2, or through the addition of organic acids (e.g. lactic acid, citric acid, acetic acid, propionic acid, caproic acid), or also through the use of ammonium salts. Further liming chemicals are removed from the limed hides through subsequent washing steps.

BATING – HIDE CLEANING AND OPENING UP OF THE HIDE

Through the enzymatic degradation of problematic residual proteins and the hydrolytic degradation of the natural collagen fiber networks, the limed hide is opened up for the tanning agents subsequently used in the tanning steps, so that they can penetrate better into the deeper layers of skin. To do this, the enzymes are often used together with ammonium salts.

RECOMMENDATION FOR Chromium (VI) AVOIDANCE: BEAMHOUSE

- Check the pH values during the individual process steps
- Ensure sufficient removal of the naturally occurring residual fat, which possesses an oxidative potential
- Do not use halogenated organic degreasing agents
- Avoid products with oxidative potential, e.g. peroxide, permanganate or perborate. If using these products, check the oxidative potential with iodine-starch paper and if necessary, reduce the oxidation agent using a reducing agent prior to the addition of chromium.
- Use aqueous degreasing agents
- Reduce the excessive use of ammonia and ammonium salts
- Wash the limed hides carefully after liming and decalcifying

3.5 PRODUCTION STEPS IN CHROME TANNING – TANNING

Tanning mainly comprises of the working steps pickling and tanning.

PICKLING – PREPARATION FOR TANNING

In order to prevent the superficial bonding of the tanning agent and in order to remove the last residues of lime, the skins and hides must be placed in an acidic substance. In order to prevent excessive swelling in acids, a sufficient quantity of salt; generally table salt (NaCl) must be added. Then the pH value is added to the limed hide using acids such as sulphuric acid, hydrochloric acid, formic acid, acetic acid or lactic acid to make the hide acidic (pH 2.5-3).

TANNING OF MAIN TANNING – THE PENETRATION AND FIXATION OF THE DYE

During the actual tanning process the Chrome tanning agent is added to the limed hide in the tanning tub in the form of Chromium (III) salts. So that the Chrome tanning can penetrate quickly right into the deeper skin layers, it is necessary for the limed hides to first achieve an acidic pH value of approx. pH 2.5-3m as ensured through the pickling process. Later during dulling the pH value is raised with the addition of alkaline agents such as solid magnesium hydroxide or diluted sodium hydrogen carbonate solution to a pH value of approx. pH 4. This is required in order to fix the Chromium (III) to the collagen fibers. If the pH value were to remain too acidic, the Chromium (III) would not bond with the collagen fibers and the tanning process would be incomplete.
After Chrome tanning, the skins are referred to as wet blue. Wet blue remain permanently elastic and can be stored in moist condition, so long as sufficient preservation has been conducted over an extended period of time and also transported thus representing an important, tradeable intermediate product.

RECYCLING OF CHROME TANNING AGENTS

Chrome tanning tub liquors are frequently re-used for subsequent tanning processes. To do this, either in the remaining liquor from the previous tanning process can be used to prepare the pickling for the next tanning process, or the Chromium (III) can be obtained from the alkaline Chromium (III) hydroxide precipitates from the remaining liquor and subsequent re-dissolving. Whatever the case, an inspection of the recycled tanning agent for Chromium (VI) contamination is to be conducted (e.g. according to EN ISO 19071). If Chromium (VI) compounds are found, the tanning agent must not be used.

RECOMMENDATION FOR Chromium (VI) AVOIDANCE: TANNING

- Use certified Chrome tanning agents from well-known, certified chemical manufacturers
- Carefully check the pH values during the individual process steps
- Avoid excessively high pH value peaks over pH 8
- Ensure as complete a fixation of the Chrome tanning agent as possible
- Check the pH value of the Chrome tanning tub liquor if it is to be re-used; this should lie below pH 4
- Do not use self-recycled Chrome tanning agents without prior inspection for Chromium (VI) (e.g. EN ISO 19071)
- Only use recycled Chrome tanning agents from preparation companies who are able to guarantee that their products are free of Chromium (VI)

3.6 PRODUCTION STEPS IN CHROME TANNING – WET FINISHING

RE-TANNING, BLEACHING, DYEING, GREASING

Afterwards, the tanned skins and hides are further processed in several mechanical working steps. This includes dehydration (sammying, splitting, folding and washing). After this, follows the neutralization step, and re-tanning, sometimes known as wet finishing. The leather is then bleached, dyed, greased (fat-liquoring) and dried, depending on the intended application. After this process step, the leather is referred to as 'crust' and is now also a tradeable intermediate product.

The process of purging, bleaching, dyeing and greasing require the use of chemicals which can have an effect on the formation of Chromium (VI). Fat liquors such as oils or waxes may contain polyunsaturated fatty acids, which tend to lead to oxidation. Ammonia-based purging agents basis are highly alkaline, and can promote the formation of Chromium (VI) through their high pH value. In case of oxidative processes, we must distinguish between direct oxidation (e.g. through bleaching agents) or indirect oxidation (e.g. through fat liquors). Indirect oxidation can lead to the formation of Chromium (VI) over the full lifecycle, even if the leather was free of Chromium (VI) at the end of the manufacturing process. When selecting chemicals it must be ensure that both oxidation processes are excluded.

DRYING

The leather is dried subsequent to the wet finishing; here the drying procedure is dependent on the type of leather. The procedure ranges from gentle, slow air-drying to fast-drying procedures, such as vacuum drying. Direct solar irradiation and high temperatures are to be avoided during drying.

RECOMMENDATION FOR Chromium (VI) AVOIDANCE: WET FINISING AND DRYING

- Check the pH values during the individual process steps
- Avoid pH values over pH 8 through the use of neutralization tanning agents or buffering substances
- Carry out re-tanning using vegetable tanning agents; this can suppress the formation of Chromium (VI) during storage.
- Do not use aggressive bleaches; do not use peroxides and potassium permanganate ($KMnO_4$) as bleaching agents after tanning
- Do not use dyes containing Chromium (VI)
- Reduce your use of ammonia or its salts when purging or dyeing; use dispersing syntans instead
- The pH value of the crust should lie below pH 5, ideally at pH 3.5-4

3.7 PRODUCTION STEPS IN CHROME TANNING – FAT LIQUORS

RECOMMENDATION FOR THE SELECTION OF A SUITABLE FAT-LIQUOR

The selection of suitable fat liquors for re-tannin g is decisive for the required leather quality, and is to be regarded as a critical influence parameter concerning the possible formation of Chromium (VI).

Fat liquors with a high quantity of polyunsaturated fatty acids, such as fish oils, tend to form oxidizing intermediate stages, so called free radicals. If leather is treated with fat liquors which contains a high quantity of unsaturated fatty acids, this generally has no direct effect on the formation of Chromium (VI). As the leather and leather product age, a conversion from Chromium (III) to Chromium (VI) may occur through the generation of oxidizing free radicals. The use of fat liquors using polyunsaturated fatty acids is to be avoided.

One tip for when selecting a suitable fat liquor, can be the fat liquor's iodine count. The iodine count is a parameter which states how high the proportion of unsaturated fatty acids is in a product. The iodine count of a product should be as low as possible, unless the fat liquor supplier confirms that the fat liquor has been supplemented with sufficient stabilizers to prevent the formation of Chromium (VI)

In addition, fat liquors based on synthetic fats or plasticizing polymers can be used to prevent the formation of Chromium (VI) in leather.

RECOMMENDATION FOR Chromium (VI) AVOIDANCE: FAT LIQUORS

- Do not use fat liquors with a high proportion of unsaturated fatty acids, such as fish oils
- Use fat liquors with oxidation protection, synthetic fat liquors and/or softening polymers from certified manufacturers

3.8 PRODUCTION STEPS IN CHROME TANNING – FINAL FINISHING/FINISH

In the field of final finishing/finish, the leather is provided with additional required properties. Depending on the end product, mechanical treatment steps and also the treatment of the leather surface or even sealing of the leather through the application of a coating are conducted.

SOFTENING THROUGH MECHANICAL PROCESSING (STAKING, TUMBLING)

As the leather is dried the collagen fibers and the leather become hard. The leather is then moistened slightly, kneaded mechanically (staked) and softened once more (tumbling). These mechanical processing steps have according to the most recent findings no influence on the Chromium (VI) formation.

SURFACE TREATMENT (DRY FINISHING)

The actual finishing of the leather begins with the surface treatment. It makes the leather more robust, or lends it certain properties. Depending on the end product the leather generally receives a color coating consisting of a mixture of pigments and bonding agents. On this color coating another layer – the so called top coat – can be applied which consists of clear lacquer and cross linkers. The chemicals used can, under certain circumstances (e.g. high pH value, oxidative potential), promote the formation of Chromium (VI).

RECOMMENDATION FOR Chromium (VI) AVOIDANCE: FINAL FINISHING/FINISH

- Use suitable chemicals from certified manufacturers from safe sources
- Do not use finishing agents with alkaline adhesive coatings
- Do not use pigments containing Chromium (VI)
- Use suitable finishing products (e.g. colors and coatings) which ideally feature antioxidation properties
- Avoid excessively high temperatures during final finishing

3.9 CHROMIUM (VI) FORMATION IN LEATHER – INFLUENCES THROUGH STORAGE AND TRANSPORT

It must be ensured, over the entire leather manufacturing process, that the material properties of the leather do not change during storage and transport and that the leather is also able to withstand the processing condition to form the end product. The formation of Chromium (VI) accumulation can occur even a long time after manufacture, during the conversion of processes. The later formation of Chromium (VI) has usually already begun during the tanning process. It is recommended to take possible influences on the material through factors such as higher temperatures, artificial lighting and sunlight during leather manufacturing and processing processes accordingly. The leather should also be able to withstand longer transport distances without compromising on quality. Therefore the formation of mold must be avoided and the transportation containers fumigation with ammonia must be avoided. An inspection of the Chromium (VI) content of leather and leather products after extended storage periods is recommended.

SECTION 4 – RECOMMENDATION ON AVOIDING CHROMIUM (VI) FORMATION

4.1 GENERAL INFORMATION

In accordance with the latest findings, it is possible to produce leather that is contaminated with Chromium (VI) after the tanning process and in a way so that no Chromium (VI) formation occurs over the entire lifecycle, even after the processing of leather products.

Chromium (VI)-free tanning agents and equipment which eliminate the entry of Chromium (VI) from 'outside' thought the use of suitable products are available.

Furthermore the conditions which can lead to the formation of Chromium (VI) in the tanning process, during storage and transport or during further processing, are mainly known. According to the latest findings, the formation of Chromium (VI) in leather can be successfully countered.

4.2 A QUICK SUMMARY – GENERAL RULES

Recommendations and important approaches for the optimization of leather manufacture

The material properties of leather may not change during storage, transport and processing. The following overview contains the most important recommendations, presented in the previous chapters for the optimization of leather production with regard to the avoidance of Chromium (VI) in leather and leather products.

1. Carefully degrease the raw skins/raw hides
2. Avoid or reduce the bleaching agents used prior to the tanning process and never use bleaching agents after tanning
3. Use Chromium (VI)-free tanning agents and chemicals
4. Neutralize to the lowest possible pH value, avoid pH peaks during neutralization
5. Preserve wet blue sufficiently with the biocides certified for the purpose
6. Use 1-4% vegetable tanning agent; this provides additional protection against oxidation
7. Replace polyunsaturated fat liquors with oxidation; stable fat liquors
8. Do not use pigments containing Chromium
9. Avoid ammonia or chemicals containing ammonia when neutralizing and purging or dyeing; instead use dispersing syntans
10. Finish the wet finishing at low pH values of pH 3.5-4
11. Carry out an additional washing procedure
12. Avoid the formation of mold over the entire process
13. Check the leather for Chromium (VI) contamination after prolonged storage

SECTION 5 – INSPECTION OF QUALITY STANDARDS

5.1 SUPPLEMENTARY RECOMMENDATIONS FOR THE MANUFACTURERS OF LEATHER, LEATHER SEMI-FINISHED PRODUCTS AND FOR LEATHER TRADERS

In addition to the recommendations in this manual on the individual process steps in the manufacturing process, the following additional general measure for quality assurance can be recommended, which support the prevention of Chromium (VI) formation throughout the entire process.

1. Ensure cleanliness and good organization within your production facilities. Check storage conditions and ensure that no chemicals which are past their use by date are used.

2. Ensure that an update safety data sheet (SDS) is available for each chemical and that the employees have been trained to handle the chemicals.

3. A documentation of all process steps including the chemicals used with batch number is required and ensures transparency in the manufacturing or processing procedure. In this way, an overview is given at all times and chemicals can be traced. Traceability represents the basis for good manufacturing practice.

4. Ensure that the products which are used to degrease, tan dye or re-tan the leather are free of Chromium (VI) and have no oxidation potential.

5. Chemicals which are not free of Chromium (VI) or which the manufacturer cannot guarantee of being free of Chromium (VI) shall not be used! Ask the chemical supplier for Chromium (VI)-free alternatives!

6. Chemical suppliers shall be asked for the iodine count of the fat liquors. Only fat liquors with a low iodine count (as low as possible). Chemical supplier shall confirm that suitable stabilizers have been added in order to counter the formation of Chromium (VI).

7. Ensure that wet blue, leather intermediate products or leather fulfill the required quality criteria and material properties and that goods are able to withstand all processes.

8. Preliminary inspections with regard to quality criteria to be fulfilled in wet blue, leather intermediate products or prior to further processing are required in order to avoid the further processing of materials already contaminated with Chromium (VI).

9. An inspection of the leather after prolonged storage, for possible contamination of Chromium (VI) is to be recommended.

10. The establishment of an internal Quality Management and execution of audits at the production facilities (e.g. by LWG Leather Working Group) can assist you in the execution of the recommended measures.

SECTION 6 – APPENDIX

6.1 GLOSSARY

ACIDIC
An aqueous solution of salts or acids, the pH value lies below pH7. The lower the pH value the more acidic the solution. A pH value of 2 and below is considered as highly corrosive, i.e. the entire thickness of the skin is destroyed upon coming into contact with such a corrosive solution.

ALKALINE
An aqueous solution of alkalis, e.g. sodium hydroxide (NaOH), caustic potash KOH), ammonia (NH3) the pH value lies at pH 7 to 14, the higher the pH value, the more alkaline the solution. From pH values of approx. pH 11, the solution is considered highly corrosive, i.e. when coming into contact with the corrosive solution, the entire thickness of the skin is destroyed.

ALLERGIC
Hypersensitivity of the immune system which concerns the body's own defense system.

AMMONIA
Ammonia (NH3) is a gas with a pungent smell. Ammonia vapors can have an irritant effect even in low concentrations and corrode the mucous membranes in higher concentrations. The standard is commercially available in aqueous solutions and contains approx. 10-30% ammonia (ammonium hydroxide NH4OH). Ammonia solutions between 5-10% are skin irritants and corrosive above 10%. Ammonia is a basic production in the chemical industry and is used in the manufacturing of many chemicals. In the leather production sector, ammonia is found in disinfectants, cleaning agents and pickling agents. It is used in order to disinfect, bleach and for the adjustment of certain pH values after chlorine or formaldehyde treatments.

ANTIOXIDANTS
Antioxidants are so-called oxidation inhibitors or ageing production agents. Antioxidants are a group of very different substances which are all capable of inhibiting or even completely preventing unwanted oxidative processes caused through the effects of oxygen. One of the known oxidants is for example ascorbic acid (vitamin C). Antioxidants act as radical catchers for the 'free radicals' developed during oxidation, and thus render them harmless.

CARE PRODUCTS
The agent used for leather care after tanning in order to achieve the required properties, e.g. re-greasing, conservation, hydrophobic treatment, impregnation, oxidation protection, protection against UV radiation, odor improvement, color re-tanning agents and color intensification agents.

COATED LEATHER
Leather coated with, for example, a synthetic material such as PU (polyurethane), dye, pigments or a lacquer layer, whereby the coating has at least a thickness of 0.15mm and may total max one third of the total thickness of the product (EN 15987)

BLEACHING AGENTS
Bleaching agents are used to de-color leather, e.g. peroxide (hydrogen peroxide) and chlorine (sodium hypochlorite).

COLLAGEN FIBERS
Collagen fibers as structure proteins run though the connective tissue in animal skins and hides.

CHROMIUM (III)
Chrome tanning agents contain Chromium (III) salts. In an aqueous environment, Chromium (III) prefers acidic pH values ranges below pH7.

CHROMIUM (VI)
The leather is first 'artificially' aged under laboratory conditions through heat. To do this, the leather is heated for 24h at 80°C and with a relative air humidity of 5% in a drying cabinet. After this, the Chromium (VI) determination described above takes places according to EN ISO 17075 standard.

CHROMIUM CONTENT, SOLUBLE
For this laboratory parameter, the entire content of soluble Chromium in the leather is determined in an aqueous salt solution according to EN ISO 17072-1. The leather is not destroyed.

CROSSLINKER
Crosslinkers are bonding agents or crosslinking agents for top coats, generally on a polyurethane or isocyanate bases.

CRUST LEATHER
Crust leather is dried leather which is neither dyed nor finished.

DEGREASING
The removal of residual fat on the animal skin or hides with degreasing agents on a solvent basis or using aqueous degreasing systems. Residual fats can form free radical through oxidation and thus accelerate the formation of Chromium (VI).

EXPOSURE
Ambient influences which affect an object or a living thing.

EXTRACTION
The removal of Chromium from leather without destroying the leather.

FINISHED PRODUCT
Using finish products, the surface of leather is refined or finished.

FREE RADICAL
Free radicals are short-lived, highly-reactive intermediate products which can develop through a reaction with oxygen. Free radicals can for example be fat residues in leather which has not been degreased carefully and which therefore triggers a chain of reaction which leads to an increasing number of free radicals. Free radicals can be caught through antioxidants and thus made harmless. Free radical can promote the development of Chromium (VI). Free radicals can be caught through antioxidants and thus made harmless. Antioxidants are therefore known as radical catchers.

HIGH QUALITY
High quality chemicals or production processes based on the latest technological developments.

HYDROPHOBIC
A substance which is water-repellent is referred to as hydrophobic. In case of leather, this is achieved through the use of impregnation agents, finish products or through a colored coating (finishing, pigmenting) with a top coat (a clear lacquer coating).
IMPROTANT: G-Star does not allow any chemistry based on fluor carbons for achieving water repellency.

IODINE COUNT
The iodine count is the measurement used to measure how unsaturated a compound is. Fats with high iodine counts contain a lot of double bonds. Fat liquors with iodine counts within a range of 5-20 are ideal. Fish oils have iodine counts of between 100 an d200.

IODINE-STARCH PAPER TEST
Test of the oxidative potential by using potassium iodine starch paper (oxidation agent test). The oxidative potential is indicated through blue discoloration of the test strip.

LEATHER WORKING GROUP (LWG)
The LWG is an international association of companies, chemicals providers and manufacturers in the field of leather products, who issue environmental certificates to tanneries based on the regular audits and product documentation.

MICROBIOLOGY
It refers to microorganisms such as bacteria or fungi.

MOLD
Fungi cultures which are growing on the surface which indicate microbial infestation of the leather. Some mold fungi varieties produce toxic substances which then make the leather unfit for use by humans.

OXIDATION
The Oxidation refers to a chemical process in which the chemical charge is emitted in the form of electrons, for example when reacting with oxygen.

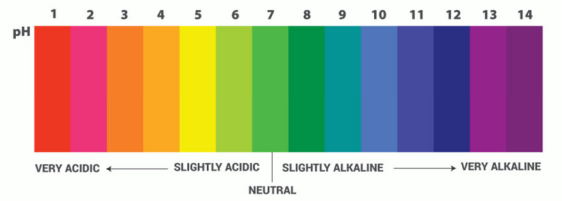
OXIDATION PROTECTION
The oxidation state tells us how many electrons surround an element such as Chromium. The more positive the number, the more electrons have been transferred. The electron density around the element is reduced and the chemical charge changes.

OXIDATIVE POTENTIAL
The oxidative potential of leather describes its capability of oxidizing Chromium (III) to form Chromium (VI).

SODIUM HYDROGEN CARBONATE SOLUTION
A weak, alkaline, aqueous solution of sodium hydrogen carbonate ($NaHCO_3$), known as baking soda or bicarbonate, with a pH value of approx. pH 8.

PEROXIDES
Oxygen compounds which are highly reactive and aggressive and which are used for oxidizing, bleaching and decoloring.

PH VALUE
The pH value provides information on how acidic or alkaline a solution is. If the pH value lies between pH 0-7, the solutions react in an acidic alkaline manner. If the pH value is pH 7, the solution is neutral. Pure water for example has pH value of pH 7. Human perspiration has a pH value of between pH 4 – 6.5 and is therefore slightly acidic.



PIGMENTS
Color particles which are used to dye leather. Pigments are insoluble and either form a layer of color on the leather, or penetrate into it, bonding with the collagen fibers.

POTASSIUM PERMANGANATE
A strong oxidation agent which can be used to bleach leather.

PRESERVATIVES
Substances which increase the durability and therefore the utilization of capability of products.

RAPEX
The European Union's legally established a rapid-warning system for hazardous substances which includes an internet platform and weekly updates.

REACH
The REACH Ordinance (EC) No. 1907/2006 (REACH Ordinance) is an EU Ordinance on chemicals which determines the limit value of hazardous substances and regulates their handling.

REDUCING AGENTS
Reducing agents prevent oxidation as they are more easily oxidized than the substance to be protected.

REGREASING
Leather is re-greased after tanning with oils or waxes so that they remain supple.

RESIDUAL GREASES
Fat residues on raw hides and skins which have not been completely removed during de-greasing. Residual fat can lead to the formation of free radicals, and therefore accelerate the formation of Chromium (VI). Residual grease can also lead to odorous leather.

SENSITIZATION
An increase in sensitivity to certain substances. A strong hypersensitive reaction occurs through increased sensitivity, for example Chromium (VI) after repeated contact with the chemical which we designate an allergic reaction.

SKIN FAT, NATURAL SKIN FATS
Animal fat on the raw hides or skins.

SYNTHETIC TANNING AGENTS
In contract to the mineral tanning agents (e.g. chromium, aluminum) or the vegetable tanning agents, which all come from natural sources, synthetic tanning agents are designed and created in laboratories.

TANNING AGENTS
Tanning agents are a group of vegetable tanning agents. They have strong tanning effect which is why they have been used for centuries for leather processing. Tanning agents can be found, amongst other things in persimmons, grapes, quinces, in wood and bark of oak trees, valonia oak (from the Mediterranean), birch, chestnuts, mimosa and quebracho.

TOTAL CHROMIUM CONTENT
For this laboratory parameter the entire content of Chromium is determined after complete disintegration, i.e. once the leather has been completely dissolved in acid according to EN ISO 5398 Part 1-4.

TOTAL DISINTEGRATION PROCEDURE
The leather is completely destroyed and dissolved in acid.

TOXIC
Poisonous

UV RADIATION
UV rays are a part of the natural radiation on our earth. The main source is the sun, and therefore normal day light, but also UV lamp and fluorescent tubes also emit UV rays, UV radiation is not visible and is high in energy. In leather the light-energy UV rays can lead to formation of extremely reactive substances and free radicals, through which Chromium (VI) formation is promoted.

VEGETABLE TANNING
Vegetable tanning agents obtained from trees, shrubs or fruits. The main groups of these tanning agents, which include oak, quebracho, chestnut, mimosa or tara.

VERIFICATION LIMIT OF PROCEDURE
The verification limit of the procedure according to EN 17075 of 3mg/kg is reasoned in the uncertainty of the extraction method. A measured Chromium (VI) content under 3mg/kg can be incorrect due to the extraction method or may not be stated in the test report.

WET BLUE
Wet blue is Chrome-tanned leather in moist condition which has neither been dyed nor finished. The Chromium dive this leather its light blue tinge.

WET WHITE
Wet white is synthetically tanned leather in a moist condition, which has neither been dyed nor finished. The leather remains white due to the lack of Chromium.

6.2 REFERENCES

The following literature has been used:

18th Ordinance on changes to the Consumer Goods Ordinance 3rd August 2010.

Final Report on the AiF Project No. 11599 N, Untersuchungen zur Entstehung und Vermeidung von Chrom(VI)-Verbindungen im Verlauf der Lederverarbeitung, Investigations on the development and avoidance of Chromium (VI) compounds in the course of leather processing PFI, Pirmasens, 9.03.2000.

Anderie I., Schulte K. Zusammenhänge der Chrom (VI)-Bildung (Teil 2). Interrelationships of Chromium (VI) formation (Part 2) PRO LEDER 5, pp.16-20, 2011.

Bundesinstitut für Riskiobewertung (Federal Institute for Risk Assessment). Gesundheitliche Bewertung von Chrom (VI)-Verbindungen in Lederwaren. Health assessment of Chromium (VI) compounds in leather goods, March 2025.

Bundesinstitut für Riskiobewertung (Federal Institute for Risk Assessment). Chrom (VI) in Lederbekleidung und Schuhen problematisch für Allergiker, Chromium (VI) in leather clothing and shoes is problematic for allergy sufferes, Press Release 10/2007, 02.07.2007.

Bundesinstitut für Riskiobewertung (Federal Institute for Risk Assessment). BfR empfiehlt, Allergie auslösendes Chrom (VI) in Lederprodukten streng zu begrenzen, Federal Institute for Risk Assessment recommends that allergic Chromium (VI) should be strictly limited in leather products, Statement No. 017/2007 by the BfR from 15th September 2006 – updated on 24th May 2007.

Danish Ministry of the Environment, Survey and health assessment (sensitization only) of chromium in leather shoes, Survey of Chemical Substances in Consumer Products No. 112. 2011.

Falbe, J., Regitz, M. RÖMPP Lexikon Chemie (A dictonary of chemistry). Vol. 1-6, 1999.

Font, J. Cuadras, R. M., Reyes, M.R., Costa-Lopez J. and Marsal, A., Influence of various factor son Chromium (VI) formation by photo-aging, J. Soc. Leather Technol. Chem. 83, 1999, 300.

Font, J. Cuadras, R.M., Lalueza, J. Orus, C. Reyes, M. R., Costa-Lopez, and Marsal, A., Presence of Chromium (VI) in sheep skins: Influence to tannery processes, J. Soc. Leather Technol. Chem. 83, 1999, 91.

Font J., Ruis A., Marsal A., Sanchez D., Hauber C., Tommaselli M. Prevention of Chromium (VI) formation by improving the tannery process. (EU-CRAFT project GIST-CT-2002-50264, Chrom6less)Leather 208, pp. 18, 2006.

Graf, D. The Influence of the relative humidity of air during storage on the formation/lowering of Cr(VI) in chrome tanned leathers, World Leather 13, May 2000, 38.

Graf, D. Formation of Chromium (VI) traces in chrome-tanned leather: Causes, preventions and latest findings, J. Am. Leather Chem. Ass. 96, 2001, 169.

Hauber, C. Und Germann, H.-P. Untersuchungen zur Entstehung und Vermeidung von Chromat in Leder (Investigations on the development and avoidance of chromate in leather), Leder- und Häutemarkt (Leather and skin market), 9-1999, 25.

Koch, R. Umweltchemikalien – Physikalisch-chemische Daten, Toxizitäten, Grenz- und Richtwerte, Umweltverhalten, (Environmental chemicals – physical-chemical data, toxicities, limit and guideline values, environmental characteristics), VCH-Verlagsgesellschaft, Wehinheim/Bergstrasse, 18989, 185 ff.

Meyndt R., Germann H.-P., Schulte K., Anderie, I. Untersuchungen zur Ermittlung der Zusammenhänge von löslichem Gesamtchrom sowie hauteigenen Inhaltsstoffen mit der Chrom (VI)-Bildung in Leder und Lederartikeln. (Investigations on the determination of the interrelationships of soluble total chromium and the skin's own sustances with Chromium (VI) formation in leather and leather articles).DFG-promoted research project: IGF-FV No. 15845 N – 15.01.2011, Lederinstitut Gerberschule (Leather Institute Tanning School) Reutlingen und Prüf- und Forschungsinstitut (Testing and Research Institute) Pirmasens.

Meyndt R., Germann H.-P., Zusammenhänge der Chrom (VI)-Bildung (Teil 1). (Interrelationships of Chromium (VI) formation (Part 1)). PRO LEDER 4, pp. 12-18, 2011.

Meyndt R., Germann H.-P.,Relationship in the formation of hexavalent chrome [Cr(VI)]. WORLD LEATHER June/July, p. 14-17, 2011.

Nickolaus, G. Untersuchungen zur Entstehung und Vermeidung von Chrom (VI)-Verbindungen im Verlauf der Lederverarbeitung, Investigations on the development and avoidance of chromium (VI) compounds during the course of leather processing) Lecture held on the occasion of the 52nd VGCT Annual Conference in Aachen, May 2000.

Saddington, M.J. Trivalent chromium to hexavalent chromium, Leather 201, Dec. 1999, 33.

Sammarco, U. Formazione di Cr(VI) nelle pelli e possibilita di elimazione, Cuoio Pelli Materie Concianti 74, 1998, 83.

Schulte K. Chromium ist nicht gleich Chromium. Schumarkt. (There is chromium and chromium) 10pp. 24-25, 2014.

Schwedt, G. Beiträge zur Frage der Umweltverträglichkeit von Chrom aus Leder, (Contributions on the question of environmental compatibility of chromium from leather) Research results from the Institute of Anorganic and Analytical Chemistry at the Technischen Universität Clausthal, 2nd edition 1994.

Tegtmeyer D., Kleban M. Chromium and leather research – A balanced view of scientific facts and figures. IULTCS. IUR-1 Aug, pp. 1-10, 2013.

Tegtmeyer D., Rabe V. Modern chrome tanning is safe. International leather maker July/Aug pp. 18-19, 2014.

Umweltbundesamt (Federal Environmental Office). Integrierte Vermeidung und Verminderung der Umweltverschmutzung (IVU) (Integrated avoidance and reduction of environmental pollution) – Reference document on the best available techniques for the leather industry, 2013.

Wolf, G. and Wegner, B. Avoiding Cr(VI) in leather manufacture, World Leather 13, May 2000, 39; and Aug./Sept. 2000, 62.

Zschimmer und Schwarz. Preventing chromium VI formation in leather. Science and Innovation. May/June p. 32,2014.

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