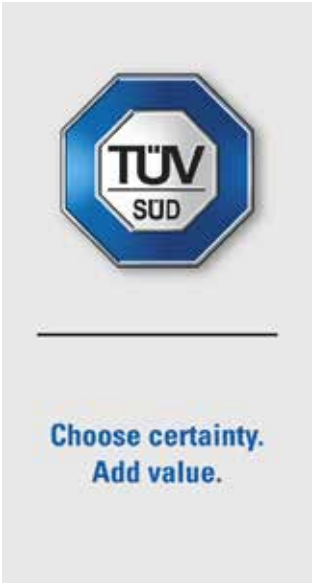
Minimising Chromium (VI) in leather products

Ensuring safety and quality in leather production



White paper

Abstract

In this white paper, we will discuss on the formation of chromium (VI) in the leather tanning process, the current chemical regulations applicable to chromium (VI) in leather materials and products, and the steps that manufacturers and producers of leather materials can take to reduce the risk of exposure to chromium (VI) in their products.

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Contents

About the TÜV SÜD expert

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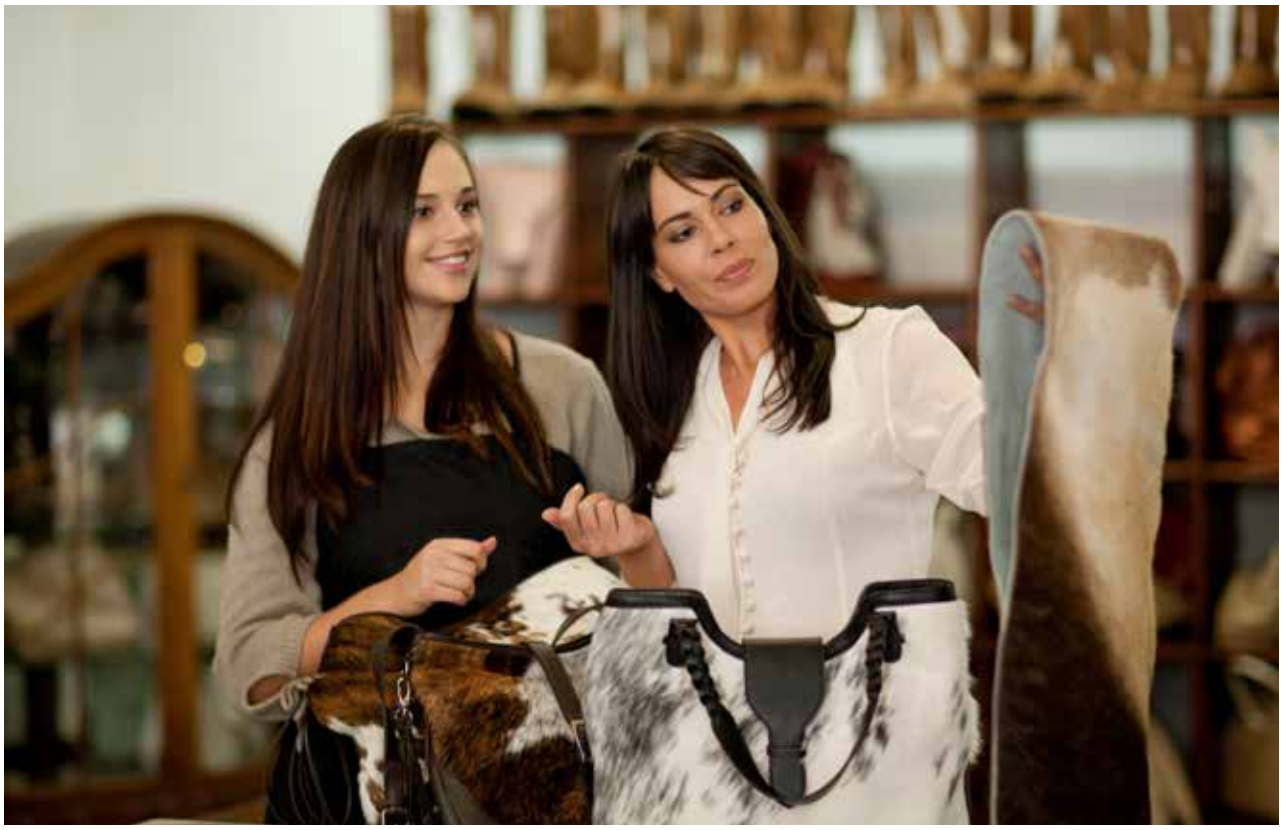
Dr Raymond Lui has over 20 years of experience that covers a broad range of interrelated topics with a strong research focus on fabrication and characterisation of exotic materials. His key responsibilities are to manage and grow the business line for the retail sector in TÜV SÜD. He is the creator of the TÜV SÜD Footwear Mark, a comprehensive quality assurance programme for footwear that has received wide acceptance by major brands in the United States of America (U.S). and the European Union (EU). Dr. Lui obtained Postdoctoral Fellowships in Chemistry (UoH), Electrical and Electronic Engineering (CUHK), and Physics (CUHK).

Introduction

Chromium is a tasteless, odourless inorganic substance naturally occurring in rocks, plants and soil, as well as in volcanic gases and dust. Chromium is the 24th element in the periodic table with an atomic weight of 52. It is also the 21st most abundant element in the earth's crust. Some forms of chromium, chromium (III) for example, are essential for human health, and can be commonly found in food and nutritional supplements. Other chromium compounds, such as chromium (0) and chromium (VI), are generally produced through industrial processes. Chromium (0), a metal chromium, is used in the manufacture of steel, while chromium (VI) and some chromium (III) compounds are used for chrome plating, dyes and pigments and wood preservation, as well as for leather tanning.[1]

Chromium tanning is one of the most frequently applied methods used in the processing of raw leather materials, with more than 95 percent of leather found in footwear tanned with chromium-based agents. In tanning chromium is used as a tanning agent in the form of basic chromium sulphate with about 33% basicity. The unreduced chromium in the basic chromium sulphate is one of the sources of hexavalent chromium. Apart from the direct source of chromium, trivalent chromium present in the leather after tanning may undergo oxidation induced by various substances, chemicals and factors. Chromium tanning is preferable to other tanning methods since it gives leather increased strength as well as greater elasticity and suppleness. Chromium (VI), referred to as hexavalent chromium, is often a component in dyes and other chemical agents used to colour leather and textile materials used in footwear, handbags and other fashion products.

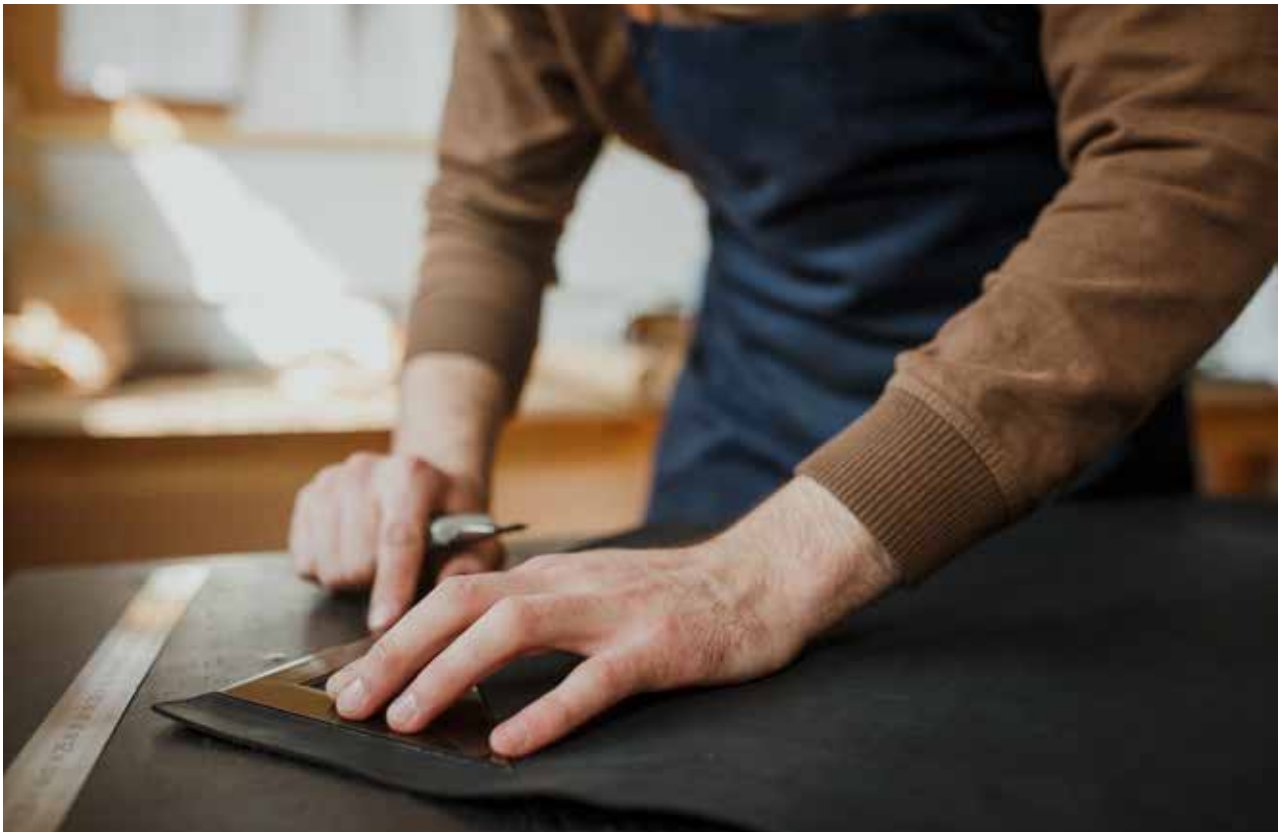
However, exposure to chromium (VI), either through inhalation, ingestion or direct contact with the skin, has been associated with numerous adverse health effects. Depending on the extent and duration of exposure, chromium (VI) can produce skin irritations and rashes, skin allergies, dermatitis and ulcerations and have gastrointestinal and pulmonary effects, perforations of nasal septum and bronchial carcinomas. Futhermore, chromium (VI) has also been associated with fertility and reproductive issues, as well as an increased risk of lung cancer.[2]



How does leather become contaminated with chromium (VI)?

The leather tanning process involves treating raw animal hides with a variety of chemicals throughout a series of processes. In chromium tanning, specific chemicals used include chromium (III) salts and other agents which bind to collagen fibres within the hide. This processing helps to strengthen the hide, making it more durable in finished goods.

It is essential to identify the possible sources of Cr(VI) and the possible generation of the same during the leather and product manufacturing process. The possible direct sources of Cr(VI) are the Basic Chromium Sulfate (BCS) used as a tanning agent, certain class of metal complex dyes and inorganic pigments. Particularly in the case of pigments based on lead chromate is a possible source of hexavalent chromium. Unreduced chromium present in the leather auxiliaries are the direct source of Cr(VI). Apart from the direct sources many tools, substances, auxiliaries, chemicals and process parameters could contribute significantly to the conversion of trivalent chromium into hexavalent chromium. Some of the possibilities of generation of Cr(VI) are neutralisation, ammonia treatment, thermal and photo ageing, fatliquors, adhesives used in product making. Oxidation of Cr(III) to Cr(VI) by oxygen in air during the processes carried out at higher pH in leather and footwear manufacturing process is an important cause of Cr(VI) generation.



Chromium (VI) contamination during the tanning process generally occurs either as a result of penetration from outside sources, or from the formation of chromium (VI) within the leather hide itself. Potential outside sources of production-related chromium (VI) contamination include:

- Contaminated chromium tanning salts from new production;
- Contaminated chromium tanning salts produced through the recycling or recovery of previously used chromium (III); or
- Contaminated tanning liquors containing chromium (VI).

Production-related chromium contamination from outside sources can also include the use of certain pigments and dyes that contain chromium (VI). For example, some yellow, orange and red pigments include chromium (VI) as an ingredient. Chromium (VI) can also be introduced into the production process through the use of contaminated water containing chromium (VI), or from contaminated tanning tubs that have not been thoroughly cleaned between production batches.

In addition to its introduction from outside sources, chromium (VI) contamination can be a result of chemical processes that occur during the tanning process itself. For example, interaction between the multiple chemicals in tanning can produce an oxidising effect, which may be sufficient to convert chromium (III) salts into chromium (VI). This oxidising effect can be exacerbated by the fluctuation in pH values, an essential aspect of the tanning process, thereby increasing the potential for chromium (III) to chromium (VI) conversion.

Finally, aside from chromium (VI) contamination attributable to production-related causes, contamination can form or further develop after tanning has been completed, and leather materials are being transported, stored or subject to further processing. This is because chromium (III) salts embedded in tanned materials may continue to oxidise, particularly when exposed to light, temperatures and other environmental conditions different than those encountered during production.

Which regulations are applicable to chromium (VI) in leather materials and products?

The concern regarding the potential harmful effects associated with exposure to chromium (VI) stems from a growing public awareness about the impact of chemicals on human health and the environment. This growing awareness has resulted in regulations in the European Union (EU), the U.S., China and other countries that bans or restricts the use of certain potentially harmful chemicals in a range of materials and products. The following sections provide a brief summary of some legislation related to the presence of chromium (VI) in leather.

Chromium (VI) requirements for leather protective gloves in EN 420

The EN 420 test method and specifications for PPE gloves applies to all CE marking for all PPE hand gloves, the presence of chromium (VI) restricts to 2 mg/kg.

Chromium (VI) requirements for leather materials and products in the European Union

The EU's REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Regulation (Regulation (EC) No 1907/2006) applies to any company/person that places products on the EU market, including manufacturers, importers and retailers of products. The Regulation sets primary requirements for the use of chemicals, and Annex XVII of the Regulation restricts the use of certain substances in particular materials or products.

The presence of chromium (VI) compounds in leather articles and articles containing leather parts that come in contact with the skin is restricted under entry 47 of Annex XVII. Starting from 1 May 2015, concentrations of chromium (VI) must be less than 3 mg/kg of the total dry weight of the leather material, and the recommended test method to demonstrate compliance is EN ISO 17075. This limit applies to products placed on the market on or after the effective date. It allows exemption to second-hand products which were in end-use before 1 May 2015.

Among the EU Member States, Germany is the pioneer imposing its national legislation to regulate chromium (VI) in leather products. Under German Consumer Articles Ordinance (BedGegstV), leather products intended to come in contact with any part of the human body must not have any detectable chromium (VI). Germany represents a significant economic interest within the EU. Since manufacturers are unlikely to develop different varieties of criteria fortheir products in individual markets, German restriction equates to a de facto ban against detectable chromium (VI) in leather products sold anywhere in the EU.

Chromium (VI) requirements for leather products in China

In China, concentrations of chromium (VI) compounds are restricted in leather and fur materials used in children's footwear. Under GB 30585-2014, China's safety technical specification for children's footwear, chromium (VI) concentrations are limited to not more than 10mg/kg. Assessing chromium (VI) concentrations is determined by the test method, GB/T 22807-2008. Chromium (VI) concentration limits for children's footwear in China came into effect on 1 January 2016.

Chromium (VI) requirements and restrictions in the U.S.

Currently, there is no U.S. national regulation directly applicable to chromium (VI) in leather materials and products. However, the California Proposition 65 requires businesses to provide consumers with a "clear and reasonable" warning before exposing them to excessive concentrations of one or more of over 800 listed chemicals associated with cancer, birth defects or other reproductive hazards. Chromium (VI) is one of the 800 listed chemicals. Proposition 65 requirements apply to all types of product sold in the state, regardless of whether or not they are intended for use by children. California is the leading state economy in the U.S, and the 12th largest economy in the world. As chromium (VI) in leather can be a potential hazard to human health, it is worthy to pay special attention to this restricted substance.

Other market considerations regarding chromium (VI) in leather materials and products

In addition to various national or regional restriction of chromium (VI) in leather products, a number of major retailers have developed their own proprietary lists of restricted substances. Their restricted substances lists (RSLs) usually include chromium (VI) as well as other substances that may be banned or restricted. In addition to compliance various legislations, leather manufacturers should observe the changes in the RSLs to meet requirments from the brands.

How can the formation of chromium (VI) be minimised or prevented?

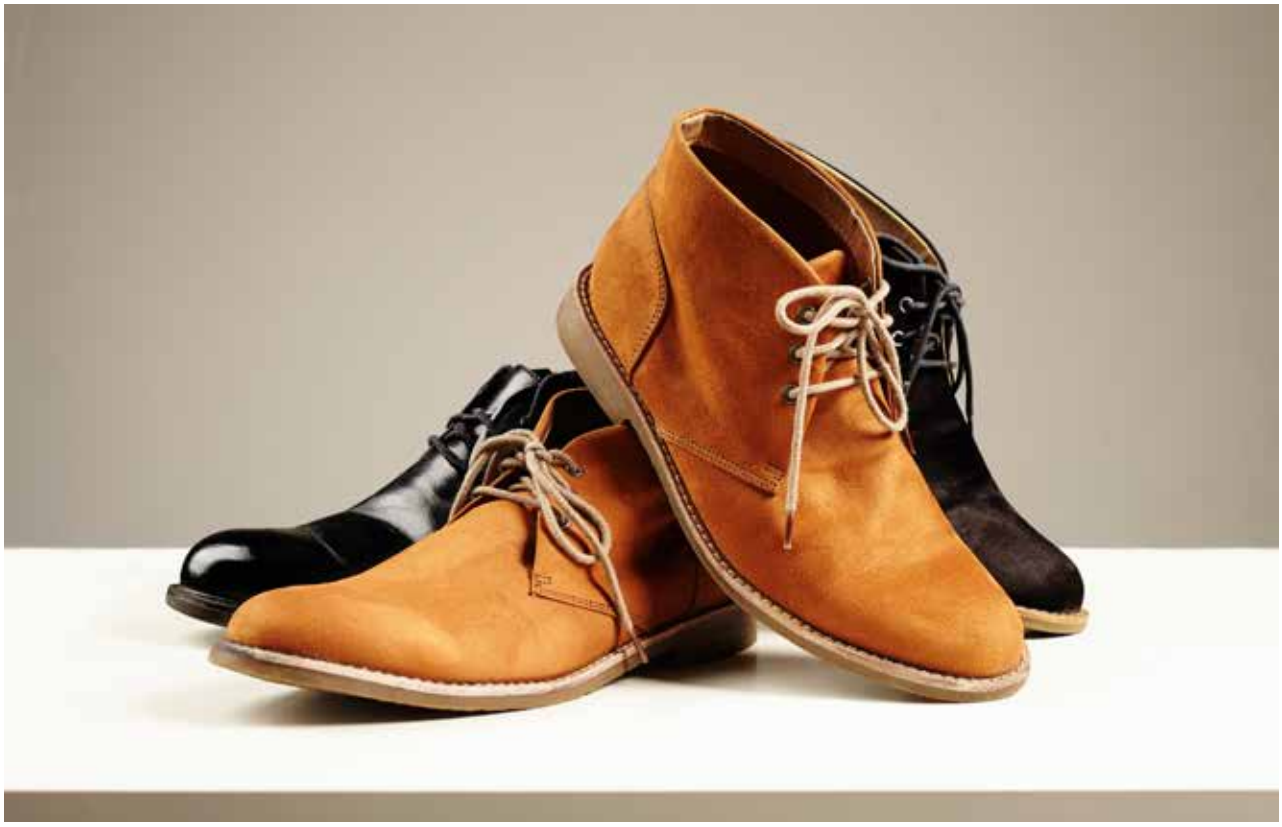
Chromium (VI) can be introduced into leather materials during the tanning process, but the formation of chromium (VI) can also occur during normal transportation and storage of materials that have already been processed. According to the German footwear manufacturers' association CADS[3] leather tanneries and manufacturers can try to minimise the potential introduction or formation of chromium (VI) during the entire lifecycle of leather materials and products made of leather by taking some or all of the following specific steps:

- Raw skins/hides—Carefully degrease raw skins and raw hides to remove all traces of tanning agents;
- Bleaching agents—Avoid or reduce the use of bleaching agents prior to the tanning process. Never use bleaching agents after leather has been tanned;
- Chromium (VI)-free agents—Use chromium (VI)-free tanning agents and chemicals;
- pH values—Neutralise leather materials to the lowest possible pH values. Avoid pH peaks during neutralisation;
- Wet blue preservation—Preserve wet blues with sufficient amounts of biocidal agents that have been certified for the purpose;
- Vegetable tanning agents—Use 1-3 percent vegetable tanning agents to provide additional protection against oxidation;
- Neutralising agents—Use neutralising auxiliaries with reduction capability in neutralisation and wetting back of crusts.
- Oxidation-stable fatliquors—Use fatliquors that are oxidation-stable rather than polyunsaturated fatliquors;
- Reducing agents—Use reducing agents such as sodium bisulfite, sodium metabisulfite may be used in the final washing of leather. However it may please be noted that such treatments may alter the shade and colour intensity of the leather and hence accordingly the process of dyeing needs to be restandardised.
- Pigments—Do not use pigments or dyes that contain chromium;
- Ammonia—Avoid ammonia or chemicals containing ammonia when neutralising and purging or dyeing. Use dispersing dyes instead;
- Finishing—Finish the wet finishing at pH values of between 3.5-4.0;
- Supplemental washing—Where feasible, carry out an additional washing procedure;
- Mould formation—Avoid the formation of mould throughout the entire tanning process;
- Post-production checks—After prolonged periods of storage, check leather for post-production formation of chromium (VI).

What are some additional steps to prevent chromium (VI) contamination?

In addition to the process-specific steps previously noted, leather producers can also reduce the risk of chromium (VI) formation in their materials by instituting specific policies and procedures intended to ensure overall quality throughout the entire production process. At a minimum, an effective quality programme would include:

- Proper documentation of the processes involving the use of chemicals, batch/log numbers of production and other forms of identification, to provide efficient traceability when required and to help ensure complete transparency;
- Thorough training for production employees on the safe use of all chemicals used in leather production, along with information on the potential hazards associated with misuse. Easy access to current material safety data sheets for all chemicals used;
- Rigorous management of chemicals used in leather production processes or stored in inventory. Regular inventory audits to ensure that chemicals are not stored or used past their expiration date;
- Periodic internal audits and inspections of production processes to ensure that established quality processes are being maintained and that overall quality objectives are being fulfilled;
- Regularly-scheduled, formal audits of production facilities and suppliers conducted by independent third-parties, and follow-up action plans to address quality system gaps and non-conformities;
- Proactive procurement policies to reduce or eliminate completely the use of chemicals containing chromium (VI) or chemicals that contribute to the formation of chromium (VI) in leather during or after production.



How can TÜV SÜD help leather producers reduce the risks of chromium (VI)?

The testing of leather materials and products for the presence of chromium (VI) is essential to help ensure the safety of those products in the hands of consumers and demonstrate compliance to legislation of major markets. Leather tanneries and manufacturers who fail to evaluate their products for concentrations of chromium (VI) risk market exclusion, product recalls and litigation, as well as negative impact on brand reputation.

TÜV SÜD is recognised for its extensive experience in the evaluation of leather and leather products for the presence of unsafe chemicals, including chromium (VI). We are a trusted industry partner for the independent chemical evaluation of leather materials, and can validate compliance of chemical requirements in the EU, the U.S., China and most other important jurisdictions. Our comprehensive training programmes can assist tanneries, leather manufacturers and suppliers on the proper methods to minimise the presence or limit the formation of chromium (VI) during leather processing, storage and transportation. Our active involvement in leather industry associations, including CADS, gives us direct and timely access to emerging compliance issues and challenges, for the benefit of all of our clients.

Conclusion

The growing global demand for leather products has been accompanied by the implementation of strict regulations in major markets around the world intended to help protect consumers against potentially dangerous chemicals. As the awareness of hazards to chromium (VI) increases, leather manufacturers and producers should plan for comprehensive testing and quality assurance measures. Reducing the risk of chromium (VI) contamination can ease market access and increase acceptance of their products by consumers.

TÜV SÜD is a leading international service organisation providing one-stop global solutions for product quality and safety testing and inspections, engineering support, management system certification, and training. With over 24,000 employees, TÜV SÜD operates worldwide at more than 850 locations. As partners in our customers' processes, our specialist teams ensure that technology, systems, and know-how are optimised, thus strengthening our customers' global competitiveness.

For additional information regarding TÜV SÜD's testing, training and advisory services for chromium (VI) and other harmful chemicals, go to http://www.tuv-sud.com/cps. Or contact cps@tuv-sud.com.

GLOSSARY OF ACRONYMS

PPE - personal protective equipment
CADS - cooperation at DSI

FOOTNOTES

[1] "Chromium," Toxic Substances Portal, Agency for Toxic Substances & Disease Registry, U.S. Centers for Disease Control. Available at http://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=17 (as of 1 September 2016).
[2] "Chromium Compounds," website of the U.S. Environmental Protection Agency. Available at https://www.epa.gov/sites/production/files/2016-09/documents/chromium-compounds.pdf(as of 1 September 2016).
[3] "The Guide for Leather Manufacturers: Recommendations for the avoidance of chromium (VI) formation," CADS, Cooperation at DSI, 2011.

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