4 Chromate Testing in Leather: EN ISO 17075

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4.1 Chromium in Leather Articles: Allergenic Potential

Allergic reactions to leather products are quite common in the population. Skin rash and allergic symptoms, caused by wearing leather articles, can be observed in sensitized people. There is a broad range of articles made from leather for everyday use such as shoes, jackets, gloves, belts, purses, dog leashes, chairs, sofas, or auto interiors, and the risk of sensitization is omnipresent. One of the major allergens described for leather is chromium(VI) [1, 2]. The potent leather allergen chromium(VI) represents one of the oxidation states of the elemental chromium. In general, most of the chemical elements exist in different oxidation states, varying in energy level and chemical reactivity.

The most important oxidation states of chromium are chromium(0), chromium(III), and chromium(VI):

- Chromium(0) is the metallic form and a component of several metallic alloys.
- Chromium(III) is a component of chromium salts, which are used for leather tanning. Chromium(III) does not induce skin irritation, as its permeation through human skin is very low. Under certain conditions, even chromium(III) can cause allergic reactions (see Chap. 27). In the aqueous environment, chromium(III) is present at acidic pH values below pH 7.0.
- Chromium(VI) is very reactive and often used for chemical-induced oxidation processes. Chromium(VI) salts are toxic and highly caustic, and direct skin contact leads to skin damage and poorly healing ulcers. Chromium(VI) is a potent allergen, and sensitization due to repeated skin contact is possible. In the aqueous environment, chromium(VI) is present at alkaline pH values above pH 7.0.

Chrome tanning is the most commonly used method to preserve leather. Around 80% of the leathers produced worldwide are chrome tanned. The tanning process requires a lot of expertise, as the procedure is very complex and different chemicals need to be used. In a preliminary step, the hide is cleaned of meat leftovers, hair, and fat. The tanning process is carried out then by using chromium(III) salts or by using a combination of chromium(III) salts and further tanning agents, like vegetable or synthetic tannins. Chrome-tanned leathers contain huge amounts (10,000–80,000 mg/kg) of chromium(III), which is needed for the tanning process. During the leather tanning process, chromium(III) intercalates with the collagen fibers of the wet skin. This creates a stable skeletal structure and allows drying of the

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skin without shrinking. The resulting chrome-tanned leathers are durable and are characterized by a high strength and extremely good ductility and malleability. Thanks to its special properties, chrome-tanned leather can be found in diverse uses for almost all kinds of leather goods, among others footwear, clothing, furniture, or car leather. According to current knowledge, the use of chromium(III) salts for leather tanning is safe. If leathers are produced according to the best available technologies using modern high-end chemicals, there is nearly no risk for the generation of chromium(VI) in leather or leather articles [3, 4].

Under certain conditions, chromium(III) in leather can be oxidized to the potent allergen chromium(VI) [5, 6]. However, the use of obsolete technologies and chemicals in leather production and leatherworking, poor storage and transport conditions, heat, low relative humidity, light, and mold can lead to the formation of the potent allergen chromium(VI) out of the chromium(III) tanning salts in leather and leather articles [2, 7, 8]. Therefore, if chromium(VI) is detected in a leather article, its source is in most cases not clear. As shown in Fig. 4.1, this chemical process is reversible, and already-generated toxic chromium(VI) can be converted back to chromium(III) by using reducing agents, minimizing the generation of chromium(VI) during tanning, and creating a so-called reductive potential in the leather. This protects the leather against oxidation, leading to drastically decreased formation of chromium(VI) during the manufacturing process, storage, and transport. This treatment is not only suitable for the raw material leather, but it is also possible to post-treat already-finished leather or leather articles with reducing agents either to prevent chromium(VI) generation or to remove chromium(VI) [5]. Leather items should not form chromium(VI) beyond the period of marketability. Wearing leather goods may also trigger leather aging processes, which could lead to oxidation to chromium(VI). Wearing of leather items should be possible without risk to health for a reasonable period of time. A preventive treatment of leather or leather products with a reducing agent is recommended.

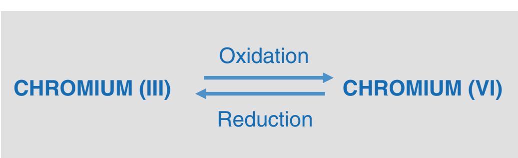

Fig. 4.1 Schematic representation of the conversion process of chromium(III) into chromium(VI)

4.2 Legal Regulation of Chromium(VI) in Leather Articles

Due to its potent allergenic potential, German health authorities enforced a national limit for chromium(VI) in 2010 [9]. The same limit was proposed by Denmark for the EU as well. The limit entered into force within the EU with regulation [10] as amendment of Annex XVII of the REACH Regulation [11]. Since May 2015, it is forbidden to bring leather products to the market that contain chromium(VI) above 3.0 mg/kg. Despite this legal regulation, there are nearly each week recalls of chromium(VI) containing articles published in RAPEX, a European Internet platform created for customer protection to warn consumers about dangerous products. The high number of non-compliant articles shows that the issue of chromium(VI) analyses in leather is still highly relevant [12].

4.3 Treatment of Leathers or Leather Articles with Reducing Agents for the Elimination of Chromium(VI)

Chromium(VI)-containing products are not marketable. The main cause of chromium(VI) generation in chrome-tanned leathers over time is the transformation of chromium(III) into chromium(VI) due to oxidation. This process is reversible, as chromium(VI) and chromium(III) are interconvertible by oxidation-reduction processes (Fig. 4.1). This reversibility is utilized in posttreatments of leathers and leather articles with reducing agents. Usually spray applications of reducing agents (e.g., ascorbic acid) are applied to the chromium(VI)-containing leather items. This posttreatment eliminates chromium(VI) from the raw material leather and also from already-produced leather articles like a shoe or a jacket [8]. Professional re-conditioners are able to provide this service for complete product batches, which allows the trader to bring the revised leather articles back to the market. This posttreatment may not be successful in some cases. Depending on the worked-up leather and further materials on a given article, a rework might not work or lead to stains on the product. Whether chromium(VI) elimination by posttreatment leads to long-term success needs to be discussed carefully for each contaminated leather product.

4.4 Methods for the Measurement of Chromium in Leather

Several chemical methods and different parameters are available to receive more detailed information on the chromium content of leather. Some of the methods take into account the intended use and try to simulate the wear situation. Some of the extraction solutions used for determination have a sweat-like salt composition, and some extraction methods are carried out at temperatures between room temperature (20 °C) and body temperature (37 °C). On the other hand, some methods simulate exposure to heat and light during production, storage, and transport of leather articles and may give hints as to whether chromium(VI) generation due to oxidation of chromium(III) may occur in the life cycle of a leather.

4.4.1 Determination of Chromium(VI) Content According to EN ISO 17075

This method is used to determine whether the legal limit for the potent allergen chromium(VI) of 3.0 mg/kg is adhered to. Direct determination of chromium(VI) content in the leather matrix is currently not possible. Therefore, according to the standard EN ISO 17075, an extraction of the leather has to be executed prior to the determination of chromium(VI) in leather. The leather is either milled or cut into small pieces, then placed into an extraction vessel, and shaken within a buffer solution for 3 h. Afterwards, the leather parts are filtered off, and the content of chromium(VI) within the extract is determined. Determination of extracted chromium(VI) can be carried out by two different methods, photometry and ion exchange chromatography.

4.4.1.1 Photometry

For photometric measurement, the colorless reagent 1,5-diphenylcarbazide is added to the extract. In the presence of chromium(VI), the reagent is oxidized to a pink-colored chromium complex, which allows the quantitative photometrical determination of chromium(VI). A critical point of this method is the parallel extraction of dyestuffs from the leather that results in heavily colored extracts. The dyestuff may interfere with the photometrical determination of the pink-colored chromium complex. In that case, interfering substances need to be removed by solid-phase extraction (SPE) before adding the 1,5-diphenylcarbazide reagent.

4.4.1.2 Ion Exchange Chromatography

The determination of chromium(VI) content with ion exchange chromatography is state of the art, and modern technical equipment is needed. The technique allows determination of chromium(VI) content directly from the extraction solution. Chromium(VI) is separated on an ion exchanger column and the amount determined, after formation of the above-described pink-colored chromium complex or without derivatization directly at the corresponding UV-wavelength of chromium(VI) absorption. Due to the separation on the ion exchanger column, usually no interference of dyes occurs, and therefore no purification with solid-phase extraction is needed.

The amount of chromium(VI) found in the extract measured by photometry or by ion exchange chromatography refers to the amount of chromium(VI) in the leather, and the content can be calculated. The detection limit of this method is 3.0 mg of chromium(VI) per kg of leather. The conditions for extraction must be followed exactly as described in EN ISO 17075; otherwise, there is a risk of false-positive or false-negative findings. The extraction should always be carried out in a single test, and extraction of mixed samples with more than one leather for chromium(VI) determination is not recommended. Incorrect false-negative results may occur if one of the leathers in a mixed sample has a reductive potential, which may prevent the identification of a possible chromium(VI)-loaded leather by reduction to chromium(III).

4.4.2 Spot Test

Recently, Danish scientists [13] described a spot test for the determination of chromium(VI) in leather and metal alloys, which should allow the detection of chromium(VI) directly on a leather article, without sample preparation. They used the reagent 1,5-diphenylcarbazide for direct application on a leather and determined chromium(VI) presence by observing a color change on the leather to pink. Based on our experience, handling the reagent 1,5-diphenylcarbazide is complicated, and colored leathers may lead to false interpretation of color change. Furthermore, the leather is damaged at the spot where the reagent was applied. In order to avoid false-positive or false-negative results, the determination of chromium(VI) according to EN ISO 17075 under controlled conditions in a test lab is advised [14, 15].

4.4.3 Determination of Recovery Rate According to EN ISO 17075: Influence of Leather Matrix

During the tanning process, the leathers are treated with several reagents to obtain the required characteristics. Some of them may have a reductive potential, which may influence chromium(VI) determination. In addition, even finished leather or leather articles may be treated with reducing agents, either to prevent chromium(VI) generation or to destroy chromium(VI) in contaminated leathers. Influences of the leather matrix can be detected by measuring the recovery of a known concentration of chromium(VI), which has been added to the extraction solution from EN ISO 17075. After the addition of a known amount of chromium(VI), the sample is worked up identically to the methods described in Sect. 4.4.1, using photometry or ion exchange chromatography. In normal cases, the recovery rate should be above 80%. In leather samples that were treated with reducing agents, the recovery rate may even drop to 0%, indicating that the reductive potential of the leather was strong enough to reduce the added chromium(VI) directly to chromium(III).

4.4.4 Determination of Chromium(VI) Content: Aging

Chromium(VI) may be generated in leather under certain stress conditions like heat and light. Heat and light influence the leather matrix. Due to these heat and/or light aging processes, the skeletal leather structure may disrupt, leading to an increase of unbound chromium(III) and its oxidation to chromium(VI) (Fig. 4.3). Another effect of heat and light aging may be degradation or inactivation of reducing agents, which were added to the leather to prevent oxidation. These processes may increase chromium(VI) formation and lead to concentrations above 3 mg/kg [16]. In their life cycle, leather and leather articles are often exposed to higher temperatures or light, e.g., via outdoor storage in the sun, the heat setting during production, transport in an overheated container, or storage in hot warehouses or behind showcases. To simulate these aging processes under lab conditions, the leathers can be aged artificially by heat and UV light:

- Heat aging: Leathers are heat-aged for 24 h at 80 °C in an incubator with a relative humidity below 5%. Thereafter, the above-described determination of chromium(VI) according to EN ISO 17075 is performed.

- UV-light aging: Leathers are aged for 24 h with xenon light in a lighting unit. Thereafter, the above-described determination of chromium(VI) according to EN ISO 17075 is performed.

Some leathers react strongly to heat aging or UV aging with increasing amounts of chromium(VI). On the other hand, a lot of leathers survive these stringent heat or UV aging processes without showing any chromium(VI). Therefore, lab tests on the raw material evaluating for chromium(VI) by applying these aging conditions can serve as a support in deciding which leather can be used for the production of leather articles.

4.4.5 Determination of Soluble Total Chromium(III) Content According to EN ISO 17072-1

Chromium(III), which is used for tanning, is usually strongly bound to collagen fibers. Washing processes after tanning remove loosely attached chromium(III) from leather, so that only small amounts of chromium(III) should be released by wearing leather articles or using leather products. Nevertheless, some persons may react to a higher soluble total chromium(III) content with skin reactions (see Chap. 27) [17]. Therefore, this parameter is usually tested only on leathers that will have direct skin contact, e.g., lining leathers. In contrast to EN ISO 17075, where chromium(VI) is analyzed, soluble total chromium content can be determined using method EN ISO 17072-1. The test method imitates wear situations. The leather is cut into small pieces and incubated at 37 °C in a sweat-like, slightly acidic solution. During incubation, the leathers are not destroyed. The release of chromium(III) is determined either by atomic absorption spectroscopy (AAS) or inductively coupled plasma (ICP).

4.4.6 Determination of Chromium(III) Content After Total Digestion According to EN ISO 17072-02 to Classify a Leather as "Chrome Tanned" or "Chrome-Free Tanned"

The complete content of chromium in leather can be determined after complete disruption of the leather by total digestion. Measurement of total content of chromium is tested according to EN ISO 17072-2 or 5398 part 1–4. The leathers need to be digested completely by using strong acidic solutions and microwave treatment. Determination of chromium in the digestion solution will be usually performed using either AAS or ICP.

4.4.6.1 "Chrome-Tanned," "Chrome-Free-Tanned," or "Chrome-Free" Leather

The content of chromium is a benchmark to classify a leather as "chrome tanned" or "chrome-free tanned." The total content of chromium in a leather depends on the tanning process, on the washing and fixation, on the leather itself, and on the properties it should have. In chromium-tanned leathers varying concentrations of chromium can be found, grading from 10,000 to 80,000 mg/kg. For leathers with total chromium below 1000 mg/kg, it can be assumed that the leather is tanned without the intentional use of chromium(III) salts (per EN 15987), and these leathers can be classified as "chrome-free tanned." Small amounts of chromium may result from contaminated equipment, water, and chemicals, e.g., chromium-based dyes [18–20]. However, these leathers should not be described as "chrome-free leather." For "chrome-free leather," the total content of chromium should be as low as possible, as is technologically feasible. Chromium is a naturally occurring trace element, which is found in animals. Therefore, each leather will have small amounts of total chromium per se. For chromium-free leathers, some requirements advise that the content of total chromium should not exceed 20–50 mg/kg.

Synthetic or vegetable alternative tanning agents are available for chrome-free-tanned leather. Currently only a few tanneries use this technology because it is difficult to produce smooth and tear-resistant synthetic or vegetable tanned leathers. However, one can observe a growing demand for these chrome-free alternatives to avoid any health risk. Nevertheless, recent studies from Thyssen et al. [21] observed in some individuals an allergic reaction caused by chrome-free-tanned leathers, indicating that the use of chrome-free alternatives must be considered carefully.

4.5 Correlations Between the Different Test Parameters for Chromium in Leather

In a research project funded by the "Deutsche Forschungsgemeinschaft," we tried to identify correlations between the different parameters for chromium in leather [8]. We expected to find some simple rules which could easily be followed by the tanneries, thereby minimizing the risk of generation of the toxic chromium(VI) in leather. Three leathers with varying total chromium contents according to EN ISO 17072-02 were manufactured. No increase of chromium(VI) could be observed with increasing the total chromium used for tanning. Nevertheless, a correlation between the content of total soluble chromium and total chromium was found, as total soluble chromium increased with higher levels of total chromium (Fig. 4.2).

As already mentioned above, heat aging and UV aging may lead to increasing chromium(VI). Both aging processes were developed to simulate conditions to which the leather can be exposed during its life cycle, such as manufacturing, transport, or storing processes. We investigated the aging effects on upper leathers and lining leathers of shoes and found an obvious difference between upper leather and lining leathers (Fig. 4.3). Upper leathers are thicker and much more stable than lining leathers, which are often very thin and very soft, indicating that the tanning process is different. Chromium(VI) generation has increasingly taken place in lining leather, under normal conditions as well as under heat or UV aging.

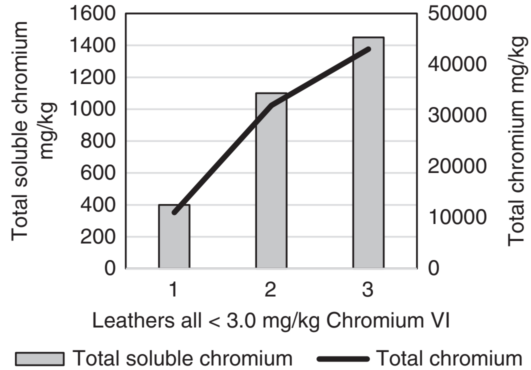

Fig. 4.2 Correlation between chromium(VI) EN ISO 17075, total chromium EN ISO 17072-02, and total soluble chromium EN ISO 17072-1 [8]

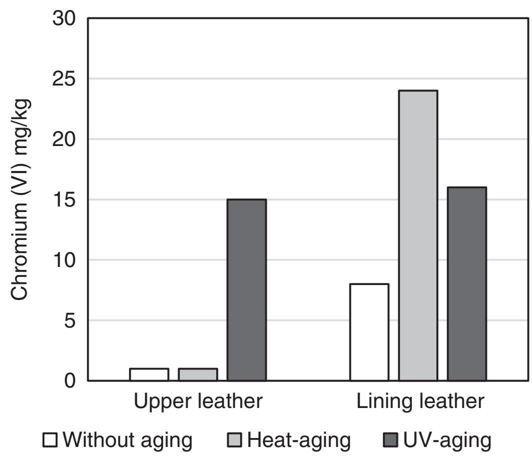

Fig. 4.3 Chromium(VI) generation in upper leather and lining leather for shoes under the influence of heat aging or UV aging [8]

Not only aging processes during the leather life cycle may lead to chromium(VI) generation in leather. Other processes during tanning are also critical, e.g., pH value, which should not be too alkaline. The pH value of the tanning baths should be controlled carefully. In addition, some posttreatments which are necessary after the tanning process are considered to induce chromium(VI) generation, like bleaching of the leather with oxidizing reagents or refatting the leather with unsaturated fat liquors.

Table 4.1 Correlation between chromium(VI), total soluble chromium (EN ISO 17072-1), and total chromium EN ISO 17072-2 [8]

Leather tanned using	Chromium(VI) EN ISO 17075	Total soluble chromium EN ISO 17072-1	Total chromium EN ISO 17072-2
	mg/kg		
Modern fat liquor	<3.0	749	37,947
Non-saturated fat liquor	8.1	787	36,005

Table 4.1 shows a comparison of leathers which were refatted by treatment with either a so-called modern fat liquor or the unsaturated fat-liquor fish oil. One could see that the amount of total chromium and total soluble chromium are nearly identical for both leathers, whereas chromium(VI) dramatically was induced by treating the leather with the unsaturated fat-liquor fish oil. Unsaturated fat liquors are easily oxidized, leading to free radicals, which may support chromium(VI) generation. Therefore, modern fat liquors should be used for chrome tanning, as they usually prevent chromium(VI) generation and protect the leather.

4.6 Prevention of Chromium(VI) in Leather and Leather Articles

The generation of chromium(VI) in chrome-tanned leathers can be avoided if some rules are followed. The leathers should be tanned with the best and latest know-how, and modern high-end chemicals should be used. Storage, transport, and processing steps at higher temperatures are unfavorable, and mold formation should be avoided during the whole life cycle of the leather or leather article [16, 22]. In recent years, the tendency has been increasingly to prepare leathers without chromium(III) salts. These so-called chromium-free-tanned leathers are either tanned with vegetable tanning agents from tree barks or fruits (e.g., oak, quebracho, chestnut) or with synthetic tanning agents. The number of different synthetic tanning agents is large, ranging from the traditionally used formaldehyde resin condensates and glutaraldehyde, to modern, lab-designed synthetic compounds. Nevertheless, even if there is a wide selection of chromium(III) alternatives, the use of some of them may be considered partially unfavorable with respect to effects on human health and the environment. However, one should also note that small amounts of up to 1000 mg/kg chromium(III) can still be present in chromium-free-tanned leathers (see above). For those sensitive to chromium, it should be ensured that the leather product is free of chromium. So far there is no protected designation with an exact specification as to how much chromium is acceptable in a so-called chrome-free leather. Leather is a natural product, and small traces of chromium will always be present.

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