

Chromium (VI)

Other Names	Hexavalent Chromium, Cr(VI)
CAS Number	Substance
18540-29-9	Chromium VI (the element Cr in the 6+ oxidation state)

May Be Found In	<ul style="list-style-type: none"> ▪ Tanned natural leather ▪ Pigments and dyes (especially those used in wool)
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Cr (VI) is the chromium element in its 6+ oxidation state. Hexavalent Chromium can occur naturally in the environment from the erosion of natural chromium deposits or produced during industrial processes. Chromium VI can naturally occur from the transformation of Cr (III) under the right conditions such as exposure to UV light, high temperatures, low humidity, low pH-Values, or oxidizing agents. Chromium, in this oxidation state, can be extremely stable and persistent in the aquatic environment.

Uses in the Supply Chain

Within the apparel and footwear supply chain, chromium may be in use in the following applications:

Leather tanning: Leather tanning is often performed using trivalent chromium (Cr(III)). Under certain conditions such as exposure to UV light, high temperatures, and/or low humidity, Cr(III) may transform into Cr(VI).

Pigments and Dyes: Cr(VI) may be used as a mordant after dyeing, especially for wool, or in lead-chromate pigments, inks, plastics, and surface coatings.

Why Cr(VI) is Restricted

- Exposure to hexavalent chromium has been linked to many health problems in humans. Acute and long-term exposure to Cr(VI) has been linked to allergic skin reactions, gastrointestinal and respiratory issues, and damage to the male reproductive system. Cr(VI) is considered a carcinogen by the International Agency for Research on Cancer (IARC).¹
- Cr(VI) is regulated in textiles and leather products in multiple regions globally, including Egypt, Europe, South Korea, Taiwan and China.²

Sourcing Compliant Materials from Your Suppliers

Contact your suppliers and explain that you require materials with extractable Cr(VI) values that do not exceed current AFIRM RSL listed limits.³

In chrome tanned leather where Cr(III) is added to the hides, Cr(VI) may occur under certain circumstances. To help mitigate the risk of Cr(VI) generation, see the following guidance:



Chemical Information Document

- Use of chromium-based colorants and/or chromium-based after-treatments may fail the AFIRM limits. Compliance of chromium-based colorants available on the market must be checked with suppliers as described in the sections below.
- Share this guidance sheet with your material suppliers and instruct them to work with their chemical suppliers to source Cr(VI) compliant chemical formulations using the “Sourcing Chromium VI-Compliant Chemical Formulations” guidance section below.
- Have your suppliers verify that their manufactured materials meet the Cr(VI) limits with a certification or, if necessary, by providing a test report from a third-party laboratory experienced in analyzing the specific material.
- Perform risk-based checks of your suppliers’ materials by submitting samples to a third-party laboratory for testing to ensure the Cr(VI) limits are not exceeded.
- Since the Cr(VI) limit is equal to the method quantification limit (3 mg/kg), every fail with values falling into the 3-5 mg/kg range should be confirmed by a different third-party qualified laboratory.
- Check with your customer regarding brand specific requirements for application of the ageing test to leather samples, and consider applying it whether your customer requires it or not. This additional sample processing step will artificially age the leather in conditions that will drive Cr(VI) generation, giving an indication if changes in the leather over time might result in Cr(VI) generation.

Preventing Cr (VI) Formation through Leather Tanning

- Roughly 80% of global leather production is chrome tanned. Alternatives are generally more expensive and produce different leather characteristics. Viable alternatives include:
 - Metal salts of aluminum, zirconium or titanium.
 - Synthetic organic compounds such as glutaraldehyde, tetrakis hydroxymethyl phosphonium sulfate (THPS), polymeric syntans or poly(carbamoyl)sulfonate (PCS).
- When tanning with Cr(III), the formation of Cr(VI) can be reduced by following these steps:
 - Utilize Cr(VI) free tanning products, tested for Cr(VI) and procured from a reputable supplier.
 - Avoid use of highly unsaturated fats:
 - If the raw material has a high level of natural grease, degrease thoroughly.
 - Avoid fat liquors or finishing oils with natural fats (e.g., fish, animal or vegetable).
 - Maintain pH below 6.5 and avoid use of ammonia, sodium bicarbonate and bleach during and after the tanning step.
 - Avoid the accumulation of free chromium on leather surfaces by washing after neutralization step, after any wet-end waterproofing treatment, and at the end of wet processing.
 - Add antioxidant chemicals in the re-tanning process (e.g., vegetable tannins).
 - Finish the wet end processing at low pH conditions (3.5 - 4)
- The transformation of the residual Cr-III into Cr-VI should also be prevented for finished goods. Recommendations include:
 - Avoid storage and transport of leathers in air polluted heavily with oxidizing gases like ozone, nitrogen oxides, sulfur oxides.
 - During transport, manufacture and use of leather items, avoid the prolonged exposure to low humidity, high temperatures and direct sunlight.
 - Avoid heating chrome-tanned leather to apply prints or set adhesives.

Sourcing Compliant Formulations from Your Chemical Suppliers

- Contact your chemical suppliers and explain that you require chemical formulations with no intentionally-added Cr(VI). Any residual concentration should comply with the ZDHC MRSL limit whenever applicable.⁴
 - Pay special attention to suppliers of wool after-dyeing mordants, metal-complex dyes and pigments and chromium leather-tanning powders.
- Have your chemical suppliers verify that their chemical formulations meet the ZDHC MRSL limit with a certification or, if necessary, by providing a test report from a third-party testing laboratory whenever applicable.
- Check the Safety Data Sheets (SDS) of all chemical formulations to ensure that Cr(VI) and chromate salts, including dyes and pigments, are not listed as ingredients.
- Perform risk-based checks of your chemical suppliers' formulations by submitting samples to a third-party laboratory for testing to ensure the the ZDHC MRSL limit is not exceeded whenever applicable.
- Discuss with your chemical supplier whether the below safer alternatives are suitable substitutes for your production needs.

Safer Alternatives

- As mentioned previously, there are alternatives to the chrome tanning process, but these may result in leather with distinctly different performance properties.
- There are many alternatives to chromate pigments and dyes. Most major chemical suppliers have discontinued production of these dyestuffs.
- There are many after-dyeing mordant alternatives to chromate, including potassium aluminum sulfate, aluminum acetate and ferrous sulfate. Work with your chemical and dye suppliers to confirm that any chosen alternative is ZDHC MRSL compliant whenever applicable.

Additional Information

Visit ECHA's Candidate List of substances of very high concern to view dossiers for many restricted substances <https://echa.europa.eu/candidate-list-table>.

References

¹ World Health Organization, International Agency for the Research on Cancer. "IARC Monographs on the Evaluation of Carcinogenic Risks to Humans: Chromium, Nickel and Welding." Volume 49 (1990).

<http://monographs.iarc.fr/ENG/Monographs/vol49/mono49-1.pdf>

² Hohenstein Institute & Textile Exchange. *Chemical Snapshots – Heavy Metals*. 03/17/2017, Revision 0.2.

Links: www.hohenstein.com, www.textileexchange.com

³ Apparel and Footwear International RSL Management Group (Ed.). (2018, January 31). Restricted Substances List (RSL). Retrieved <http://afirm-group.com/afirm-rsl/>

⁴ Manufacturing Restricted Substances List (Publication). (2015, December). Retrieved

<http://www.roadmaptozero.com/programme/manufacturing-restricted-substances-list-mrsl-conformity-guidance/>