Chemical Information Sheet
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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

- Chrome-tanned leather and fur
- Inorganic Pigments
- Textile dyes (special mordants used in wool)

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 it can be produced during industrial processes. Cr(VI) can naturally occur from the transformation of Cr(III) under certain conditions such as exposure to UV light, high temperatures, low humidity, high pH-values, or exposure to oxidizing agents during manufacturing processes, transportation, storage, etc.

Uses in the Supply Chain

Within the apparel and footwear supply chain, chromium in different oxidation states may be used in the following applications:

- Leather tanning is often performed using trivalent chromium (Cr(III)). The transformation of Cr(III) to Cr(VI) can occur under certain conditions:
  - Exposure to UV light, high temperatures, low humidity and oxidizing gases (ozone, nitrogen oxides, some sulfur oxides), can lead to the formation of lipid peroxides from the unprotected unsaturated fatliquoring agents or natural fats. These peroxides are molecules with strong oxidant potential.
  - The use of oxidizing chemicals (bleaching or decoloring agents such as peroxides or potassium permanganate).
  - High pH values.
- Lead-chromated pigments used during the leather finishing process: C. I. 77600 Pigment Yellow 34 and C. I. 77605 Pigment Red 104. In textile dyes Cr(VI) may be used as a mordant for dyeing wool.

Why Chromium (VI) is Restricted

- Legislation in major markets around the world restricts the presence of chromium (VI) in finished products, both textile and leather. [1,2]
- Exposure to hexavalent chromium (Cr(VI)) 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).[3]

Sourcing Compliant Materials from Your Suppliers

- Contact your suppliers and explain that you require their manufactured materials to be compliant with the current AFIRM RSL limits for extractable Cr(VI).[4]
- Require suppliers to submit a confirmation of material compliance or a test report from a third-party laboratory.
- When materials are received, consider performing risk-based testing to ensure the current AFIRM RSL limits are met.
- In chrome-tanned leather where Cr(III) is added to the hides/skins, Cr(VI) may occur under certain circumstances. To help mitigate the risk of Cr(VI) generation, see the following guidance:
  - Avoid the use of the following pigments: C. I. 77600 Pigment Yellow 34 and C. I. 77605 Pigment Red 104.
  - 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 Compliant Formulations from Your Chemical Suppliers" guidance section below.
  - Require suppliers to submit a confirmation of material compliance or a test report from a third-party laboratory that has the accreditation ISO 17025:2017 for the test methods ISO 17075-1:2017 and ISO 17075-2:2017.
  - Perform risk-based checks of your suppliers' materials by submitting samples to a third-party laboratory (with the ISO 17025:2017 accreditation for the test method ISO 17075-1:2017 and ISO 17075-2:2017) for testing to ensure the Cr(VI) limits are not exceeded. A positive result by the ISO 17075-1:2017 - colorimetric method should be confirmed by the ISO 17075-2:2017 - chromatographic method to discard any false positive result.
  - To predict the behavior of leather over time and know its propensity to develop Cr(VI), an ageing test can be applied on leather samples using the test method ISO 10195:2018. This additional sample processing step will artificially age the leather in conditions that will drive Cr(VI) generation in case the leather has not been adequately protected, giving an indication if changes in the leather over time might result in Cr(VI) generation. This will give some indication if your leather goods are adequately prepared to endure the oxidative conditions of practical or daily use of the articles over time.

Sourcing Compliant Formulations from Your Chemical Suppliers

- For all formulations, request SDS documentation that meets current GHS requirements.
- Contact your suppliers and explain that you require formulations to be compliant with current ZDHC MRSL limits whenever applicable with no intentionally added Cr(VI) compounds.[5]
- Have your chemical suppliers verify that their chemical formulations meet the current limits with a certification or, if necessary, by providing a test report from a third-party testing laboratory.
- Discuss with your chemical supplier whether any safer alternatives are available that are suitable substitutes for your production needs.
- Prior to procuring any formulation, the chemical properties must be reviewed to ensure that proper protective equipment, chemical storage facilities, facility engineering controls, and associated treatment/disposal facilities are appropriate for the chemical(s).
- Pay special attention to suppliers of wool dyeing mordants, pigments, and chromium leather-tanning powders.
- 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.
- Ensure that each of the fatliquoring agents used in the tannery processes are properly protected against oxidation such that Cr(VI) formation is not triggered. Tanners should obtain from their suppliers a declaration stating that the acquired fatliquoring agents are properly formulated and protected against Cr(VI) formation. In case you are not confident with this declaration, change to products from reputable international chemical suppliers or perform specific tests to check the propensity of the fatliquoring agents to trigger Cr(VI) formation. Information about this test is available in the JALCA Journal publication article "*A Simple Test to Determine the Propensity of a Fatliquor to Trigger the Formation of Chromium (VI) in Leather*"[6]

Preventing Chromium (VI) Formation when Leather Tanning

- Roughly 80% of global leather production is chrome-tanned. Alternatives are generally more expensive and produce different leather characteristics. Viable alternatives to chrome-tanning include:
  - Metal salts of aluminum, zirconium or titanium
  - Synthetic organic compounds such as tetrakis hydroxymethyl phosphonium sulfate (THPS), polymeric syntans, or poly(carbamoyl)sulfonate (PCS)
  - Zeolites
  - Glutaraldehyde (this substance is facing regulation under EU REACH and may not be a viable alternative for EU-based tanneries without specific authorization in the future)
- When tanning with Cr(III), the formation of Cr(VI) can be avoided by following these steps. All steps are important and must be followed one by one.
  - Utilize Cr(VI) free tanning products, tested for Cr(VI) and procured from a reputable supplier.
  - Avoid unprotected polyunsaturated fatliquors (e.g. fish, animal or vegetable oils); use stabilized oxidation-resistant fatliquors instead. Use only fatliquoring products from suppliers that guarantee that they have implemented active protocols to ensure that their fatliquoring agents do not have the propensity to form Cr(VI) in fatliquored hides or skins. Their fatliquoring agents must be suitably formulated and appropriately protected with the antioxidant required by its chemical characteristics. In case you have any doubt about this protection, add a phenolic-lipidic antioxidant agent in the fatliquoring mixture (follow TDS instructions for the application and never use after date of expiry).
  - Degreasing in the wet-end should always be done in skins and splits with a degreasing agent. In hides it should be done if the % of natural grease content is not confirmed to be under 3% by conducting fat content tests.
  - Maintain the pH of neutralization as low as possible for each article.
  - Use of ammonia should be avoided and replaced by dispersant agents. If not possible, a correct final pH and sufficient washings can counterbalance its effect. Make sure to adjust the final pH to 3.5-4.0, and leather should remain in the drum long enough during the pH adjustment process to get the pH adjusted at all cross sections.
  - Finish the wet-end processing at low pH conditions (3.5 – 4.0).
  - Avoid the use of oxidative bleaching during and after the tanning step.
  - Avoid the accumulation of free chromium on the leather surface by washing after the neutralization step, after any wet-end waterproofing treatment, and at the end of wet processing.
  - Consider the possibility of applying additional protection against oxidation using any of the following options:
    - Add antioxidant chemicals in the re-tanning process (vegetable tannins).
    - Add phenolic-lipidic antioxidant agents in the fatliquoring mixture.
    - Add reducing agents (iso-ascorbic acid based) at the end of wet-end (never wash after treatment or apply high temperatures).
    - Sodium dithionite and sodium metabisulfite (as bleaching agents) can also help to reduce Cr(VI).
- The above actions will assure the protection of leather finished goods against the transformation of the residual Cr(III) into Cr(VI), but it is strongly recommended to avoid storage and transport of leathers in air polluted heavily with oxidizing gases like ozone, nitrogen oxides, and sulfur oxides. It is also recommended to keep chrome-tanned leather / suede in sheltered areas with adequate air circulation to minimize the risk of UV light exposure and high temperature environments. This applies equally to Tier 1 and Tier 2 factories.

Safer Alternatives

- As mentioned above, there are alternatives to the chrome-tanning process, but these may result in leather with distinctly different performance properties. Alternative chemicals and processes also come with their own environmental and safety considerations.
- There are many alternatives to chromate pigments and dyes. Most major chemical suppliers have discontinued

production of these chromate dyestuffs.

- For wool materials 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.[5]

References

[1] Substances restricted under REACH. https://echa.europa.eu/substances-restricted-under-reach/-/dislist/details/0b0236e1807e2bc1

[2] Official Journal of the European Union - COMMISSION REGULATION (EU) 2018/1513. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32018R1513 Retrieved April 2019

[3] 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

[4] Apparel and Footwear International RSL Management Group Restricted Substances List (AFIRM RSL) http://afirm-group.com/afirm-rsl/

[5] ZDHC Manufacturing Restricted Substances List (ZDHC MRSL) https://www.roadmaptozero.com/mrsl_online/

[6] Journal of the American Leather Chemists Association (JALCA) Journal Vol. 117. No. 11 (2022). Pages 480-488 "A Simple Test to Determine the Propensity of a Fatliquor to Trigger the Formation of Chromium VI in Leather". I. Compte, R. Cuadros, F.Izquierdo, F. Combalia, A. Bacardit. https://journals.uc.edu/index.php/JALCA/article/view/6294