



INTERNATIONAL UNION OF LEATHER
TECHNOLOGISTS AND CHEMISTS SOCIETIES

Cr

Chromium · 24

CHROME VI UPDATE

International Union of Leather
Technologists and Chemists Societies

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Introduction

Chromium is obtained from a natural ore called **chromite**
 FeCr_2O_4 (simplified)

From the chromite, chromium products are made:

> 90%

Stainless steel and alloys

< 10%

Chromium chemicals

2–3%

Leather production

2–3%

Other uses



Chromite ore · Google

Chromium Oxidation States

Cr(III)

TRIVALENT



Essential trace element
Low toxicity

LOW RISK

Cr(VI)

HEXAVALENT



Sensitizer · Toxic · Carcinogenic (Inhalation)
Highly mobile (yellow/orange)

HIGH RISK

Understanding the parameters governing Cr(III) oxidation is essential for process control and product stability in leather manufacturing.

Cr(VI) Can Be Reduced to Cr(III)



Bichromate ion – Cr(VI)

Chromium ion – Cr(III)

Reaction conditions:

Cr(VI) is a strong oxidizing agent

Reduction requires protons (H^+) and a reducing agent

Reaction is strongly favored under acidic conditions — Cr(III) remains soluble

* *Bichromate* is the historical name for the *dichromate* ion; *dichromate* is the term preferred under current IUPAC nomenclature

Basic Chromium Sulfate Production

Method A

Reduction of Sodium Bichromate with acid and sulfur dioxide



Sodium Bichromate – Cr(VI)

Basic Chromium Sulfate – Cr(III)



**Cr(VI)
solution**



**Cr(III) basic
chromium sulfate**

Most common manufacturing method.
Produces very well-defined
composition.

It is sold as a powder product.

Basic Chromium Sulfate Production

Method B

Reduction of Sodium Bichromate with organic compounds e.g. acid and sugars



Sodium Bichromate – Cr(VI)

Basic Chromium Sulfate – Cr(III)

This reaction also produces organic acids that work as complexing agents for the chrome, increasing the stability of the complex.

The total composition may be variable according to the reaction conditions and type of sugar (glucose, saccharose, molasses, etc.).

It is sold mostly as a concentrated liquid solution.

Cr(III) Can Oxidize to Cr(VI)

⚠ Note: The oxidation and reduction reactions are reversible

The reaction in leather requires certain conditions, but not all are necessary for oxidation.

Strong oxidizing agents	Oxygen, peroxides, ozone
High temperature	Accelerates Cr(III) → Cr(VI) conversion
High pH	Alkaline conditions strongly promote oxidation
UV light	Photochemical oxidation pathway
Low moisture	Dry heat aging conditions

Conditions that Prevent Cr(III) Oxidation on Leather

Optimal
pH

3–4

Critical control parameter

Additional protective factors:

Antioxidants: ascorbate, sulfite, phenolics, vitamin E, thioethers, etc.

Controlled humidity

Avoiding high temperatures

UV protection

Adequate lubrication in leather — minimize unsaturated fatty acids, use antioxidant-stabilized fatliquors

In Leather, Chromium Exists in Two Forms

A Bound Chromium

STABLE

- Complexed to collagen
- Insoluble
- Not easily oxidized
- Protected inside the fiber matrix

LOW RISK

B Soluble Chromium

REACTIVE — INCREASES CR(VI) RISK?

- Not fully fixed
- Exists as Cr(III) complexes (some more stable and/or unreactive)
- Mobile and exposed
- More susceptible to oxidation (?)

MONITOR

Key Compliance Practices

Five controls underpin every stage of Cr(VI) prevention and verification.

1**Routine Testing**

ISO 17075-1,2:2017 · ISO 10195:2018 · ISO 19071:2016 · ISO 4048:2018

2**Supplier Certification & Traceability**

Verified chemical inputs documented across the supply chain

3**Monitoring of Fats, pH & Oxidative Potential**

Continuous control of the key drivers of Cr(VI) formation

4**Documentation & Periodic Audits**

Records maintained and independently reviewed on a regular cycle

5**Strict Adherence to ZDHC MRSL**

Chemicals selected to meet restricted-substance requirements

Beamhouse Processing & Tanning

1 Beamhouse Processing

- Use aqueous degreasing agents only for effective degreasing
- Avoid halogenated chemicals
- Proper washing after liming and deliming to remove salts and reduce alkalinity

2 Tanning — Wet Blue Stage

- Use chromium tanning agents with no detectable Cr(VI) — ISO 19071:2016 tested
- Maintain strict inventory control and storage conditions
- Avoid or strictly control oxidizing agents — quench the oxidizer before chrome addition
- Keep natural fat levels in wet blue leather below 3% for bovine hides
- Apply final wash to remove unfixed chromium
- Give wet-blue sufficient time to “settle down” before further processing (days)

Retanning, Wet-End & Fatliquoring

3 Retanning / Wet-End / Finishing

- Select retanning agents that improve chrome fixation and stability
- No oxidizing agents to be used post-tanning — monitor oxidative potential
- Use antioxidants during retanning (e.g., hydrolysable vegetable tannins, preferably tara)
- Ensure dyes, pigments, and auxiliaries contain no Cr(VI) (ZDHC MRSL)
- Maintain proper cleaning, storage, and water quality controls

4 Fatliquors, Oils & Waxes

- Ideally use fatliquors without oxidation potential (iodine number close to zero)
- Use fatliquors and waxes formulated with antioxidants to prevent oxidation
- Make proper leather storage — control heat and UV light
- Confirm finishing oils and waxes do not contribute to Cr(VI) formation

Final Processing & pH Control

5 Final Processing Controls

- Conduct final washing after retanning/fixing to remove unfixed chromium and salts
- Adjust wash water to low pH if necessary
- Avoid UV irradiation (natural or artificial) during drying to reduce the oxidation risk

6 pH Control — Critical Factor

Maintain acidic conditions throughout tanning and retanning / dyeing / fatliquoring.

< 4.0

Final fixation
bath pH

< 4.5

Finished leather
(full cross-section)

Perform regular audits and maintain documentation throughout all processing stages.

Importance of the Cr(VI) Limit on Leather

ECHA
REGULATORY
LIMIT

3

mg/kg

Source: European Commission -
REACH, Annex XVII, entry 47 [1]

A Skin Sensitizer

Hexavalent chromium can trigger allergic skin reactions on contact. This is why limits on finished leather are tightly regulated.

REGULATORY TRAJECTORY

2014

ECHA imposes a 3 mg/kg Cr(VI) limit on leather in the European Union

Future

Ongoing scientific review will help to ensure the limit remains evidence-based

Cr(VI) Determination on Leather

ISO 17075-1 (Colorimetric) vs. ISO 17075-2 (Chromatographic — Reference Method)

Method	ISO 17075-1 Colorimetric	ISO 17075-2 Chromatographic — Reference Method
Purpose	Determination of Cr(VI) by colorimetry using the DPC reagent.	Chromatographic method (Anion IC/HPLC) with UV/PDA detection and confirmation.
Detection Principle	Cr(VI) oxidizes 1,5-diphenylcarbazine (DPC) to diphenylcarbazone, forming a red-violet complex measurable at 540 nm.	Chromate ion separated by IC. Quantified by: direct measurement at 372 nm, or post-column DPC reaction at 540 nm.
Interference / Sensitivity	High — subject to matrix effects.	Very low — preferred method.

Cr(VI) Determination on Leather

Status, sensitivity, and sample extraction

Method	ISO 17075-1 Colorimetric	ISO 17075-2 Chromatographic — Reference Method
Status	Accepted but not the reference — results must default to method 2 if both are run.	Reference method according to the standard.
Determination Limit	3 mg/kg (same as Part 2).	3 mg/kg.
Extraction Solution	Phosphate buffer at pH 8 (same as Part 2). At the end of the leather extraction, the pH must remain within the 7–8 range*.	Same extraction as Part 1; methods differ only in the analytical step.

* Why pH 7–8? The Cr(III)/Cr(VI) equilibrium is strongly pH-dependent. Alkaline conditions may promote Cr(III) oxidation; lower pH may favor Cr(VI) reduction. Holding extraction at pH 7–8 is the most conservative, technically appropriate compromise to minimize redox artifacts during analysis.

Is There a Correlation Between Soluble Cr(III) and Cr(VI)?

NO

Based on the following peer-reviewed studies:

Cannot et al. (2017) [3]

Moretto (2015) [4]

Meyndt and Germann [5]

Anderie and Schulte [6]

Current scientific literature does not support any correlation between the amount of soluble Cr(III) in leather and the presence or formation of Cr(VI).

Soluble Cr(III) and Cr(VI): Why the Old Correlation No Longer Holds

Scenario A — Traditional Chrome (SO₄ only)

- Correct processing → low soluble Cr(III) in leather
- High soluble Cr(III) signals poor process control
- Poor control cascades: bad fatliquors, oxidative conditions, wrong pH
- These downstream failures independently drive Cr(VI) formation

Conclusion: soluble Cr was a proxy for tannery quality — not a cause of Cr(VI)

Scenario B — Modern Chrome (complexed, short/zero float)

- Designed for maximum chrome exhaustion → higher extractable Cr(III) by design
- Competent tanners using these processes will show elevated soluble Cr(III)
- This does NOT indicate elevated Cr(VI) risk when best practices are followed
- Processes are more sensitive — require expert control

Conclusion: high soluble Cr(III) here is a chemistry outcome, not a quality failure

What the Science Establishes — And What It Means for Soluble Cr(III) Limits

X

There is **no scientific evidence** that a higher concentration of soluble Cr(III) in the leather increases the likelihood of Cr(VI) formation. (Cannot [3]; Moretto [4]; Meyndt & Germann [5]; Anderie & Schulte [6])

✓

Consistent soluble Cr(III) within a defined range **IS a useful indicator of batch-to-batch process control** and validates low Cr(VI) risk — as a quality signal, not a Cr(VI) predictor.

?

The safe threshold for soluble Cr(III) in leather remains **undetermined**. No data exists on whether chrome type (fresh / recycled / organically complexed) affects Cr(VI) formation.

!

Modern tanning processes (masked chrome, zero float, high exhaustion) inherently yield higher extractable Cr(III). Applying an old "low soluble = safe" threshold **penalises technically correct modern processes. Correlation-based limits are no longer scientifically valid.**

Technical and Regulatory References

1**DENMARK — Restriction on Chromium (VI) in Leather (2016) [7]**

Cr(VI) is unintended and forms by oxidation of Cr(III) in leather. Avoidable by finishing wet processes at low pH, using antioxidants and avoiding the use of ammonia prior to drying.

2**INDITEX — Protocol of Good Manufacturing Processes for Cr(VI)-free Leather 2025 [8]**

Emphasizes: achieving a final leather pH of 3.2–4.0, using antioxidants, ensuring proper wet-end processing.

3**TÜV SÜD — White Paper on Minimizing Cr(VI) in Leather (2019) [9]**

Explains how Cr(VI) forms in leather and stresses: proper tanning, correct pH control, prevention of oxidation during aging.

Leather Aging Tests

Objective: Evaluate leather resistance to Cr(III) → Cr(VI) oxidative conversion under controlled thermal stress.

1 ISO 10195 [10]

Method	Conditions	Typical Use
A1	24 h @ 60 °C, RH < 20%	General leathers (garments, gloves, leather goods)
A2	24 h @ 80 °C, RH < 10%	Critical-use leathers (footwear, automotive and upholstery)

Non-ISO Tests

2 Non-ISO

Many accredited labs (Eurofins BLC, TÜV SÜD, etc.) use UV aging or heat aging as a second stress test to simulate real-world oxidation triggers.

Typical Conditions

- UV exposure for a defined period
- Dry heat aging (similar to ISO 10195 but sometimes with different parameters)

Tests Determine Risk of Cr(VI) Formation During:

- Storage and transport
- Sunlight exposure
- High-temperature manufacturing steps

What the Scientific Data to Date Establishes (1)



Certain factors and parameters are known to reduce or prevent the formation of Cr(VI) in leather and are more effective at avoiding Cr(VI) formation on crust and finished leather. Leathers can be designed with an antioxidation property.



There is no scientific evidence that a higher concentration of soluble Cr(III) in the leather increases the likelihood of Cr(VI) formation.



The safe threshold for soluble Cr(III) levels in leather remains unknown, and no data exists on whether chrome type (fresh, recycled, or organically complexed) affects Cr(VI) formation.

What the Scientific Data to Date Establishes (2)



Maintaining a consistent concentration of soluble Cr(III) within a specific range serves as a good indicator of process control and validates the low risk of Cr(VI) formation batch to batch.



Although aging protocols such as ISO 10195 and specialized UV–heat exposure tests can reproduce several of the environmental factors known to promote Cr(VI) formation, these methods cannot fully capture the complexity and variability of real industrial conditions.



Leather that performs satisfactorily under controlled laboratory aging tests may still exhibit Cr(VI) formation during the leather article manufacturing (e.g. shoe factory), actual use or long-term service.

Bibliography

1. ECHA, Official Journal of the European Union, Commission Regulation (EU) No 301/2014 of 25 March 2014
2. ISO 17075-1,2. Leather — Chemical determination of chromium(VI) content in leather (ISO 17075:2017), 2017
3. Cannot, J.C., et al. Study of the variation of chromium (VI) content inside leathers used in footwear, CADS Seminar in Köln, 2017
4. Moretto, A., Hexavalent and trivalent chromium in leather: What should be done?, Reg. Toxicol. Pharmacol. 73:681-686, 2015
5. Meyndt, V.R. and Germann, H.P.; Zusammenhänge der Chrom (VI)-Bildung (Teil 1); Pro-Leder, 4, 12-18, 2011
6. Anderie, V.I. and Schulte, K.; Zusammenhänge der Chrom (VI)-Bildung (Teil 2); Pro-Leder, 5, 16-20, 2011
7. Restriction on Chromium (VI) in Leather, Lars Fock, Ministry of Environment and Food of Denmark, Chemical Division, Denmark, June 2016
8. Protocol of Good Manufacturing Processes for the Production of Chromium (VI)-free Leather, INDITEX, A Coruña, Spain, 2025
9. Minimising Chromium (VI) in leather products, white paper, TÜV SÜD AG, Munich, Germany, 2019
10. ISO 10195. Leather — Thermal pre-ageing of leather and determination of hexavalent chromium (ISO 10195:2018), 2018

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Thank You

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