

SmiTools - Chrome VI

Chrome VI and leather

In this SmiTools on chrome VI you can learn about its background, its relation to wetblue, the risks, ways to avoid it and available test methods.

Introduction

The presence in leather of what is generally called 'Chrome Six' is an undesired effect related to the use of chrome tanning agents. Since tanning with chrome salts constitutes roughly 80% of the processing technology worldwide, the debate about the risk for its presence is too important to be based on hearsay instead of facts.

Chromium

What we call 'Chrome Six' is chemically known as Cr(VI) or Cr6+. Cr(VI) is one of the possible forms of the element chromium. These different forms are expressed as oxidation states. For chromium, from now onwards to be called 'chrome', they are: +6 +5 +4 +3 +2 +1 0 and -1 -2. For tanners the trivalent and hexavalent states are of importance.

During tanning trivalent Cr3+ is used. This oxidation state is causing its green



colour when the element reacts with oxygen to Cr2O3. It enables the production of green pigments and gives emeralds their incomparable colour. Cr3+ is also a trace element essential for our bodies to function.

The hexavalent Cr6+ is used as an intermediate in metallurgy and in chemical synthesis. This intermediate step strips chrome of its impurities and is necessary before chrome can be used as ingredient for the various purposes. Cr6+ has a known toxicity and is classified as CMR (Carcinogenic – Mutagenic – Reprotoxic).

The stable oxidation state in acidic conditions is trivalent. In the alkaline medium chrome can react to hexavalent compounds. For tanners it is important to be aware of this possibility. Since the formation of Cr(VI) in leather is directly related to the use of chrome tanning agents one needs to distinguish between the presence (in wet blue) and the risk of formation during further processing.

Presence: is Cr(VI) present in wet blue?

Chrome (VI) acts as a powerful oxidizer, meaning that it has a very high tendency to oxidize whatever it finds on its way. In the process of oxidizing the other compound or atom, Cr(VI) is exhausting its oxidizing power. In other words: the oxidizing power is reduced, meaning that Cr(VI) itself is reduced – to its stable trivalent state.

During a proper executed chrome tannage most of the chrome (III) offered reacts with the untanned collagen. Once this reaction is complete the source for Cr(VI) is near-empty, since it is only the unbound, extractable chrome (III) which could later react to Cr(VI). The moment the chrome tanning agent has fixed it is no longer available for oxidation into Cr(VI).

The unfixed chrome, dissolved in the aqueous medium present in wet leather, is never 100% in one state of oxidation only. An equilibrium between Cr(III) and Cr(VI) exists. Under normal conditions, however, this equilibrium is nearly completely on the side of Cr(III). Only very high temperatures and alkaline conditions could possibly cause a detectable formation of Cr(VI). Only at temperatures >500°C Cr(III) will spontaneously begin to oxidize into Cr(VI). The conditions in wet blue, where just small amounts of extractable chrome are present - when processing the pelts properly - are detrimental to the a process where Cr(III) would oxidize to Cr (VI). The low pH and the presence of oxidizable compounds guarantee that whatever Cr(VI) was formed would immediately be reduced to Cr(III) again.

When

- using chrome tanning agent from reliable sources, and
- achieving near bath exhaustion, and
- basification is carried out evenly with no excessive temporary or local pH increases

no Cr(VI) will be present in the wet blue.

The same applies to chrome in the environment. Once chrome becomes insoluble and bound to soil, it is no longer available as a source for oxidation. In addition, its strong oxidizing properties ensure that any Cr(VI) will immediately become reduced to Cr(III).

Risk: what could cause Cr(VI) formation?

Oxidizers

The most likely cause for the formation of Cr(VI) in leather is an oxidation process provoked by the presence of free radicals. Bleaching agents are a source for free radicals. Another source for such free radicals is the peroxidation process of lipids. Heat, light, metal ions or irradiation can be the initiation of this peroxidation. Formulating fatliquors is a balance between function and good stability to prevent oxidative stress.

pH increase

The common basic neutralizing agents (sodium formate, sodium acetate and sodium bicarbonate) have little or no influence on the oxidation of Cr(III). Specialty neutralizing syntans do not contribute to the formation of hexavalent chrome and are recommended to fully eliminate the risk of Cr(VI) formation induced through pH increase.

Ammonium bicarbonate and, particularly, ammonia have a more drastic effect on the pH and can increase to a point where some Cr(VI) formation becomes possible.

Pigments

Chromate pigments can be a source for Cr(VI).

What can be done to prevent formation of Cr(VI)?

- *Use chrome tanning agents from reliable sources*
- *Wash well prior to post tanning and include some formic acid to reduce the pH*
- *Use special neutralizing syntans*
- *Acidify well to pH <3.9 and give the acid time to penetrate*
- *Wash at the end of post tanning*
- *Use products that are formulated to inhibit free radical formation*
- *Veg tans actively counteract the formation of Cr(VI) and the inclusion of some quantities is advised*
- *Inorganic yellow and orange chromate pigments are to be avoided*
- *Apply synthetic antioxidants when no veg tans are used*

Levels

The maximum level allowed in leather is 3 ppm, equalling 3 mg in one kg of leather. This figure also constitutes the current official detection limit: only amounts equal or higher than 3 ppm can be detected. This means that tests resulting in figures below 3 ppm have not been carried out by reliable parties.

The maximum level is so very low, because of Cr(VI) causes allergenic reactions, is toxic and CMR classified. Its toxicity stems from the poisonous effect when swallowed and its mutagenic and carcinogenic effects when inhaled. Since Cr(VI) cannot be inhaled from leather and the amount of leather to be swallowed before reaching the LD50 of 74 mg/kg bw¹ is beyond the possibilities of human metabolism, these risks are of no concern to producers of leather.

The main cause for concern is Cr(VI) as a sensitizing allergen. Known Cr(VI) hypersensitivities are very rare, however, and remain far behind those to nickel and even gold. It is very likely, but not yet proven, that because of its instability Cr(VI) will transform into Cr(III) before it actually has skin contact. Another likely barrier against Cr(VI) formation prior to skin contact are the low pH of fresh sweat and the presence of oxidizable microorganisms in it.

Test method

The presence of Cr(VI) in leather cannot be tested in the leather itself. The analysis is carried out in a phosphate-buffered solution of pH 8 by colorimetric measurement. The quantifying method is based on a colorimetric measurement of the extract. The limit for detection for this measurement has been set to 3 ppm.

If oxidizing ingredients present in the leather are extracted with the chrome and react under these favorable alkaline conditions (pH 8) with the extracted Cr(III), Cr(VI) formation can take place in the solution. This means that even leathers free of hexavalent chrome can appear to contain Cr(VI).

¹ LD50 is the dose at which 50% of the test animal dies within a certain time period. It is expressed as an amount per kilogram body weight.

Conclusion

Apart from the fact that we neither want Cr(VI) in leather, and that levels exceeding 3 ppm are forbidden, the potential health risk represented by the presence of Cr(VI) in the final leather, is – to our current knowledge – minimal.

Yet Cr(VI), being an undesired chemical, its presence should be avoided. By avoiding certain risks during processing and by actively taking measures preventing the formation of Cr(VI), the risks of finding hexavalent chrome in the final leather can be eliminated.

The risks of formation of toxic, cancerogenic and mutagenic Cr(VI) are to be ruled out.

The reported number of persons with a known hypersensitivity to Cr(VI) remains far below that of those allergic to other metals as nickel and even gold. Chrome tanned articles have been worn for a very long time with either direct or indirect body contact. Gloves and watchstraps are worn directly on the skin and have not given rise to concern as potential cause of allergic reactions.

All the above mentioned measures and advices represent current Best Available Technologies (BAT).

Smit & Zoon strongly supports the consequent application of BAT. When consequently applied, the risk of Cr(VI) formation occurring in leathers and articles can be reduced to zero.

Contact Smit & Zoon for further information

The information given in this SmiTools is just a synopsis on the topic. We would be glad to help you further in case of questions, the sharing of information or help with choosing the right wet-end products for your application. Please feel to contact your usual relations within Smit & Zoon.

Contact details

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