

Phase-out of chromium (III) in leather tanning

This case study aims to illustrate an alternative process. It is based on publicly available information on company's experience as well as on substance hazards, alternatives to the hazardous substance and regulatory information. The case study is neither complete nor comprehensive in illustrating all substitution options of a substance but rather exemplary.

1. Case description

The conversion of hides or skin into leather involves a tanning process. In general, depending upon the end application of leather, two tanning methods are used: vegetable tanning or chrome tanning. 80–90 % of tanneries around the world today use salts of trivalent chromium for tanning.

The main chromium compound used for leather tanning is chromium (III) hydroxide sulphate, $\text{Cr}(\text{OH})\text{SO}_4$ (CAS No. 12336-95-7; EC No. 235-595-8).

Chromium is associated with several negative effects for the environment and human health. The main hazards related to chromium (III) is that it can be oxidised to chromium (VI), e.g. at very low pH values when oxygen is present. Cr (VI) is a suspected carcinogen and causes skin sensitisation. Since chromium (III) can transform into chromium (VI), its use in articles that may be in direct skin contact, should be avoided.

1.1. Hazards of chromium (VI)

Chromium (VI) causes an allergic contact dermatitis and sensitisation at very low concentrations. The risk assessment made by Denmark (also proposing a restriction to market certain articles of leather coming into direct contact with the skin) demonstrates that chromium (VI) present in shoes and other leather articles poses risks for consumers. Furthermore, Cr (VI) is a suspected carcinogen and causes acute and chronic damage to the aquatic environment.

Chromium (VI) compounds are classified for human health and environment (harmonised):

Skin Sens. 1
H317



Carc. 1
H350i



Aquatic Acute 1; Aquatic Chronic 1
H400, H410



1.2. Regulatory status of chromium (VI)

According to a report from Germany and Denmark, 30% of all tested leather articles contained chromium (VI) in concentrations above 3 mg/kg. The surveys do not report the origin of the tested articles but it is known that many of the leather articles on the EU market are imported.

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Since May 2015, REACH Annex XVII restricts Cr (VI) in leather articles or leather parts of articles that come into contact with the skin, to a concentration of less than 3 mg/kg: *“Leather articles coming into contact with the skin shall not be placed on the market where they contain chromium VI in concentrations equal to or greater than 3 mg/kg (0,0003 % by weight) of the total dry weight of the leather. Articles containing leather parts coming into contact with the skin shall not be placed on the market where any of those leather parts contain chromium (VI) in concentrations equal to or greater than 3 mg/kg (0,0003 % by weight) of the total dry weight of that leather part”.*

Unfortunately, incompliance with the restrictions do occur. Various cases of Cr (VI) in leather articles have been published under the European rapid alert system on dangerous consumer products (RAPEX).

2. Phase-out of chrome (III)

2.1. The alternative case

The alternative case about the company who never used chromium in leather tanning comes from Tärnsjö Garveri in Sweden, <http://tarnsjogarveri.com/wip/en/>.

Tärnsjö Garveri have stated the following in their company policy:

“Our predecessors used tanning acids made from oak bark. Tärnsjö Garveri still tans leather like our forefathers did, since this gives the best results. Producing leather in this way is safe for the environment and human health.”



Tärnsjö Garveri produces leather document holders, wallets, small briefcases, etc. Their vegetable tanned leather is well suitable for a versatile range of products such as saddlery for horses, furniture, interior and leather goods such as belts and bags.

2.2. Alternative description

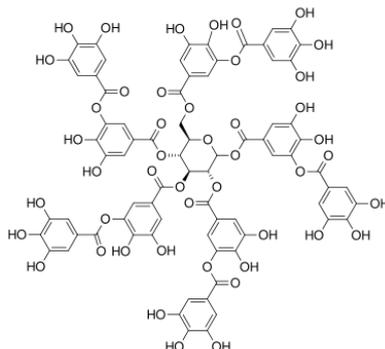
A good alternative to chrome based tanning is vegetable based tanning. Vegetable based tanning is not associated with high risks and can make the leather skin-friendly in contrast to leather tanned with chromium.

Vegetable tanning uses tannins that occur naturally in the bark and leaves of many plants. Tannins bind to the collagen proteins in the hide and coat them, causing them to become less water-soluble, more resistant to bacterial attack and also a bit more flexible. Vegetal-tanned hide could be used for luggage, furniture, footwear, belts and other clothing accessories. Chrome tanning is faster than vegetable tanning (less than a day for this part of the process) and produces a stretchable leather, which is excellent for use in handbags and garments.

Natural tannic acids can be extracted from different part of plants including woods, barks, fruits, fruit pods and leaves.

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Tannic acid, CAS No. 1401-55-4 EC No. 215-753-2



2.3. Use of vegetable based tanning agents in Tärnsjö Garveri

The compounds that are used as vegetable tanning agents instead of chromium (III) in Tärnsjö are tannins extracted from the mimosa tree.

The tannins are applied to hides after pickling. They are poured into large wooden barrels along with the hides. The barrels are then rotated for 10-12 hours, which allows the tanning agent to completely penetrate the hides. After this the hides go through the rest of the tanning process.



2.4. Costs and savings

Tärnsjö Garveri indicates that the natural tanning process with tannic acids instead of the chromium (III) is more expensive (estimation is not available). It is also more time consuming than the modern tanning.

3. Evaluation



3.1. Producing leather with chemical tanning is not safe for the environment

Tannery wastes include waste-water, carelessly disposed solid wastes and gaseous emissions. All this creates a negative image of the leather industry. Waste-water often contains hazardous chemicals such as chromium, synthetic tannins, oils, resins, biocides and detergents. The waste from leather tanneries that use chemical tanning with chromium salts is harmful to the environment and the people who live in it. Such effects

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are absent in the natural tanning industry and that is one of the reasons why the use of old technologies can be seen as an advantage.

There are numerous examples of how hazardous wastewater released from the modern tanning industry causes environmental contamination. This is especially prominent in small and medium-sized tanneries in developing countries. Kanpur, India, stands as a prime example of how tannery chemicals and wastewater can negatively affect health and ecosystems. In 2013, the city became the largest exporter of leather. About 80% of the wastewater is untreated and dumped straight into Kanpur's main water source - the River Ganges. As a result farmland is swamped with blue-tinted water, poisoned with chromium (III), lead, and arsenic. Decades of contamination in the air, water, and soil have caused a variety of diseases in the people who live in the area. Health problems include asthma, eyesight problems, and skin discoloration.

3.2. Advantages of vegetable tanning

- Vegetable tanning is environmentally friendly; wastewater coming from such tanneries is less harmful to the environment;
- Vegetable tanning is an age old tradition, since most tanneries have very skilled craftsmen producing and dyeing the leather, these methods could be applied immediately;
- Due to the natural tannins used, vegetable tanned products are unique;
- The colours that vegetable tanning produces are rich in warm tones that look completely natural;
- Vegetable tanned leathers are more valuable (thus sold at a higher average price compared to chrome tanned leathers);
- Vegetable based tanning does not require any worker's protection measures and wastewater treatment is less complex and costly;
- Workers and consumers do not have to be afraid of health damage from hazardous substances.

3.3. Disadvantages of vegetable tanning

- The average process time of vegetable tanning is longer than chrome based tanning; it can take up to 60 days to produce sole leather
- The leather can stain easily in the presence of iron; hence production processes must be free from iron - particular care needs to be taken to prevent staining
- Products that have been vegetable tanned are more expensive
- Vegetable based tanning requires a more skilled workforce
- The range of colours that can be achieved using vegetable tanning is limited
- Direct heat can cause vegetable tanned products to shrink or crack

4. References

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