



Companies act to keep chromium VI out

Chrome tanned leathers have been used in footwear and clothing for almost a century, and might thus be considered as fit for use. The properties of chromium compounds in both the trivalent and hexavalent forms are known, and, as the trivalent form is used in tannage the process has been considered safe.

It was first recognised in the late 1990s that under certain conditions small amounts of Cr(III) could be oxidised to Cr(VI) in leather manufacture and during storage. This was mainly due to oxygen provided by certain fatliquors, and accordingly these products were identified. Moreover, it was found that many vegetable tanning agents and scavenging products were effective in addressing these effects. The problem was no longer a technical issue. (Legend)

But, the problem of chromium VI does not appear to go away, and is being taken very seriously by fashion groups, especially those selling children's footwear. Some of the issues raised – such as Cr(VI) being 5% above a limit of 3 ppm as determined by one laboratory (+0.15 mg/l) with three other laboratories suggesting the level was acceptable – are playing with determinations on the fringe of detection. However, when health matters – and especially children's health – are considerations, any concerns of the consumer will be driven by what is perceived as opposed to any technical debate.

This article is based on a presentation given in World Footwear Jan/Feb 2008, and is a timely reminder to the industry that vigilance remains of extreme importance.

A magazine called marktXL, a consumer affairs title published by Cologne-based broadcaster Westdeutscher Rundfunk (WDR), does not mess around.

It has a reputation for being the consumer's champion in questions concerning products on sale in German shops. The thorny subjects it has embraced in recent months include satellite navigation systems, electronic gaming devices and the level of chromium VI present in the leather in children's shoes. This last analysis concluded that the footwear industry in Germany, Austria and beyond needs to make a marked improvement in its performance.

The magazine carried out tests on a small sample, 20 pairs of shoes from 16 different manufacturers and brands, to see if there were traces of hexavalent chromium (commonly called chrome VI) in the leather. Chromium, a metal salt that has become synonymous with tanning leather, is harmless in itself and in compounds involving chromium III, the commonly used tanning agent. Double the valency, however, to chromium VI compounds and toxicity becomes a real potential health-risk.

Because of this, the German federal government has imposed strict controls on the levels of chrome VI that are permissible in leather, leather shoes (children's or adults') and other leathergoods. At the moment, that level is three milligrams per kilo.

In the marktXL study five pairs of children's shoes out of 20 were over the limit, which provoked a public outcry and led to a high-level industry discussion on the subject at the autumn edition of the GDS event in

Consumers could be concerned to learn that inadmissible levels of chromium VI can be found in some shoes.
PHOTO: GDS





Düsseldorf last year.

Everyone involved—the panel included Dr Gerhard Nickolaus, head of testing and research institute PFI, and a recognised expert on harmful substances, Dr Jörg Heimbrecht—agreed that there was a problem to address and that the footwear industry needed to take action to allay any possible public concern.

Consumer concern

The focus of the marktXL study and of the GDS discussion was on children's and baby shoes because matters affecting children's health make a particularly strong impression on the buying public. Consumers "were horrified" to learn that inadmissible levels of such a strongly allergenic substance could be present in shoes, with the potential to cause skin lesions on the wearer's foot and, according to the suspicions of some experts, even cancer.

One participant in the discussion was Alf Netek, chief executive of a fashion group in Austria called Shoe&Shirt, which sells children's shoes under three brand names: Richter, Jela and Siesta. He feels it's important to put any debate about chrome VI into the wider context of awareness of all harmful materials in shoes. "Apart from anything else, I have a ten-year-old daughter who wears shoes from my company every day," he says, "so of course I'm sensitive to the industry's responsibility for the health of children's feet."

His group began its own programme to eradicate harmful materials two years ago now. This involved making sure all raw materials, every production plant and every footwear model went through checks for harmful substances (including chrome VI) by external experts. Now, every supplier of leather to the company has to present documentation for every delivery showing that their leather has passed these tests.

He adds: "Our own quality control people are also doing a fine job at our production lines and I'm happy to say that, in these last two years, no models under the Richter brand have been shown to have harmful materials. We had some problems with cadmium in the outsole of some Jela shoes, but we managed to hold the shipment in quarantine in India before it got into retail in Europe."

Chrome domination

The challenges facing companies such as Shoe&Shirt over harmful substances are unlikely to vanish any time soon. The traditional craft of using vegetable tanning agents to produce leather has survived and—in some parts of the market, notably the high end—is growing again. Nevertheless, the truth is that chrome-tanning processes make it possible to produce industrial quantities of high-quality leather and account for an estimated 80% of all leather produced globally at the moment.

Tanners and their customers in footwear manufacturing have worked hard to stop using or prevent the formation of chrome VI. Salts containing this form of the metal have fallen out of use almost completely in the tanning industry, even though the metal—in its safe format—is still at the heart of the production process. This has led to a debate about how the marktXL random study could have produced negative results.

There are several possible factors, the most obvious of which is that the source of the shoes, or at least the leather they were made from, may have been countries or companies that have been less rigorous in eradicating chrome VI.

Interestingly, though, scientific doubts abound. There are suggestions that exposure to air, heat and light during the

footwear manufacturing process may be transforming chromium III into its (allegedly) carcinogenic cousin. Others believe that the aqueous adhesives that some shoe manufacturers are using are the cause of this chemical change. The footwear faction, for its part, has pointed to some of the fatiguoring processes that take place in tanneries as another possible catalyst in this change in the valency of the metal.

No guarantees

Either way, the problem remains and more intensive and more sensitive testing methods make it all the more urgent for footwear and leather producers to take action. Alf Netek acknowledges the reality of chrome VI cropping up in leather that has already been tested and approved, adding "imperfect cleaning" to the list of possible causes. His company has begun retesting leather before production begins, starting with leather that will come into direct contact with a child's feet, for example in insoles.

"But even this provides no guarantee," he continues. "We just had a discussion with one of our largest (and best known) leather suppliers in Italy because one external test showed up a chrome VI problem; the level was 5% above the limit [or 0.15mg per kilo]. However, three independent retests with different European laboratories suggested that the level was alright. So this is another problem, different tests show different results and the error ratio is high—maybe too high."

The German and Austrian shoe industries have set up a joint working group called Cooperation for Avoiding Toxic Substances in Shoes (CATS). The new organisation's work will include lobbying suppliers in the leather sector to help them keep chrome VI out of their footwear.

The member companies recognise that this is a global issue and has already held events in Asia to explain the position to tanners there. This comes at a cost, but they are of the firm belief that companies that act quickly and are able to convince consumers of their commitment to combat the problem will have an advantage in the long term.

"Quality producers are doing the maximum to prevent consumers from any harm," Alf Netek concludes. "We believe our group is doing the maximum possible. We accept and want to meet our responsibilities." 

Legend

The following papers that are technically pertinent to the conversion and avoidance of chromium III to chromium VI and their analysis have been published in previous editions of World Leather:

- *Investigations on a possible formation and avoidance of chromate in leather:* C.Hauber, H-P German, Lederinstitut Gerberschule Reutlingen: World Leather, October 1999.
- *The influence of the relative humidity of air during storage on the formation lowering of Cr(VI) in chrome tanned leathers:* D.Graf, Dr Boehme, Germany: World Leather, May 2000.
- *Avoiding Cr(VI) in leather manufacture:* G.Wolf, B. Wegner, BASF, Germany: World Leather, Aug/Sept 2000. Also see amendments: *Avoiding Cr(VI) in leather manufacture:* G.Wolf, B. Wegner, BASF, Germany: World Leather, Aug/Sept 2000.
- *The many faces of aging:* V.Candar, J.J. Palma, Y.Eryasa, I.Reetz, Cognis: World Leather, Dec/Jan 2002.
- *Comments on the determination of Cr(VI) by test method IUC18/CEN/TS14495:* R. Meyndt, C.Hauber, H-P German, Lederinstitut Gerberschule Reutlingen, Germany: World Leather, Dec/Jan 2005.
- *The determination of chromium (VI): Standardisation status:* R.Meyndt, Lederinstitut Gerberschule Reutlingen, German.: World Leather, October 2007