



CHROME VI IN LEATHER

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World Footwear and its sister publication *World Leather* have given regular exposure to the concerns raised within the leather industry regarding claims by certain German consumer magazines of the presence of hexavalent chromium (chrome VI) in footwear. What has become abundantly clear is that there is much dispute as to the levels that were actually present, as to whether they would in fact be considered harmful and how they came to be there in the first place. In this further article on the problem, John Hubbard of the SATRA Technology Centre reviews the formation of hexavalent chromium in leather as it is currently understood.

BACKGROUND

Most of the leather used in footwear uppers, apparel, upholstery and luggage is tanned using chromium salts.

Because these salts are present at relative high quantities (around 3.5%), there exists the possibility that under certain conditions the relatively benign trivalent chromium (chrome III), which is the normal state of the chromium within the leather, can convert to more the harmful hexavalent chromium (chrome VI), with its potential as a carcinogen and a dermatological irritant.

Whilst this is a known theoretical possibility, the propensity for this to occur has never been established. Indeed, it is currently not possible to predict the precise conditions under which it would be most likely do so. However, on occasion it has been reported to have happened and sufficient concerns have been raised such that it has been suggested that some form of ageing protocol should be considered prior to conducting any tests to determine the presence of chrome VI in footwear and other leather articles.

Exposure to chrome VI in any leather article can cause dermatological irritation. This can be further exacerbated in footwear by direct contact between the foot and the leather upper, particularly in shoes with leather linings when worn without hose.

As far back as 1994, there was a requirement for leather gloves sold into the European market to demonstrate extremely low levels of chrome VI at <10ppm (parts per million) in order to be CE marked. This requirement has since been developed and extrapolated to other leather PPE (personal protective equipment) items including safety footwear. Furthermore, as analytical technology has improved, the requirement has been reduced to a level of below 3ppm.

Most assessments concentrate on testing new items to ensure products are not supplied into the market with chrome VI present. However, as there is now a concern that it can develop with age, there is interest in developing testing protocols to determine the propensity of leathers to form this potentially harmful chemical during storage or in wear.

ANALYSIS

The current method of analysis for chrome VI is specified in ISO 17075:2007 and based on colorimetric detection. The basic principle of this method involves extraction of the soluble chrome from ground leather. The extract then has the complexing agent 1,5-diphenylcarbazide added to it. This will be converted into 1,5-diphenylcarbazone by the presence of hexavalent chromium to produce a red/violet colour which can be determined by UV/visible spectroscopy at a wavelength of 540nm. The use of a longer cell length in the instrumental analysis has permitted the lower 3ppm level to be adopted.

Outside of the requirements for leather in personal protective equipment, no specific legislation exists for everyday consumer products—including footwear—across the European Union or, indeed, in any other part of the world. The German government has nevertheless adopted a policy of zero tolerance to the presence of chrome VI in leather articles being imported into the German market. There are also a large number of retailers globally who have included it in their restricted substances policies, normally adopting the detection limit of the current test method (3ppm) as their acceptance criterion. The same requirement has also been adopted by the European Eco-labelling scheme for leather footwear.

The adoption of the 3ppm limit for chrome VI was made possible by improvements in the analytical method used for determination. Previously the limit was set at 10ppm and even at this level there were no reported instances of dermatological reactions. The adoption of these low levels is intended to offer the best available consumer protection by the leather industry.

DELAYED DEVELOPMENT

Chrome VI is unusual among restricted substances in that it can be formed within the leather after manufacture,

whether or not it was originally present. Typical full-chrome leather can contain 3.5 per cent of chrome, expressed as the chrome III oxide Cr_2O_3 . This is equivalent to about 2.4 per cent by weight, which is effectively 24,000ppm (parts per million). It will, therefore, require only a very small amount (a little over 0.01 per cent or one ten-thousandth part of the chrome present) to convert to the hexavalent state and exceed the 3ppm limit specified for footwear, gloves and other leather articles.

It is therefore important to be aware that materials which are in an acceptable condition immediately following manufacture could possibly develop significant levels of chrome VI during subsequent transport, storage and use. It is also important to strictly control the process if waste leather is to be incinerated as there is a risk of oxidation of chrome III to chrome VI at high temperatures.

There is a lack of published information on the mechanism of chrome VI formation in leather, so how this might happen and the frequency with which it does so under certain conditions needs to be ascertained before considering whether additional testing is appropriate. Any method devised after this risk assessment will have to be thoroughly evaluated before it can be accepted.

RESEARCH

SATRA has conducted some limited research into the phenomenon and has been able to produce chrome VI under laboratory conditions. However, although it has confirmed the theoretical possibility, this is very different to suggesting that the generation of chrome VI is a regular or even occasional occurrence in footwear worn by the general public. Indeed, a lack of substantial medical evidence may imply there is no problem to worry about. A great deal more research will certainly be required before deciding on the need for a test.

However, the potential for it to be present in new products supplied to market should always be tested for. There is a possibility that chrome III could oxidise to chrome VI during leather production if the temperature or pH is too high during the tanning process or if the chromium source is not from a reputable chemical supplier.

In addition to the inclusion of chrome VI in safety footwear standards, many retailers are including it as a requirement on their restricted substances specifications for everyday footwear. Suppliers therefore need to include regular checks for its presence in their leather products and discuss any issues surrounding it as regards consumer goods with the tanneries where the leather is being produced.

Whether or not there is sufficient risk of chrome VI developing in aged footwear is still open to debate however and SATRA will continue to monitor the situation and to offer a testing service for hexavalent chromium as well as for other restricted chemicals included in footwear specifications. 