Possibilities of Hexavalent Chromium Generation and Plausible Preventive and Corrective Measures

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Introduction

Chromium is the 24th element in the periodic table with an atomic weight of 52. Chromium is the 21st most abundant element in the earth's crust [1]. The toxicity and mutagenity of hexavalent chromium is well known. Exposure to compounds of hexavalent chromium can cause skin allergies, dermatitis and ulcerations. These compounds can cause perforations of nasal septum and bronchial carcinomas[2,3]. Trivalent and hexavalent chromium are in mutual dynamic equilibrium. Trivalent chromium is less permeable in whole cells and has lower redox potential compared to hexavalent chromium and hence less toxic[4]. Due to its high mobility and toxicity hexavalent chromium gain more importance than trivalent chromium. In tanning chromium is used as a tanning agent in the form of basic chromium sulphate with about 33% basicity. The unreduced chromium in the basic chromium sulphate is one of the sources of hexavalent chromium. Apart from the direct source of chromium, trivalent chromium present in the leather after tanning may undergo oxidation induced by various substances, chemicals and factors. Because of the toxicity associated with hexavalent chromium, restrictions have been enforced to minimise the presence of hexavalent chromium in leather and leather products. Therefore, minimising the possibility of chromium VI during manufacturing processes and scavenging the hexavalent chromium that is generated during the process gain much importance to the tanners. This paper deals briefly with the standards pertaining to chromium VI, possible generation and its prevention and tools to scavenge chromium VI formed.

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Requirements

The presence of Chromium(VI) is one of the parameters of EN420 and of European Eco-label for footwear. Various limit levels prescribed by different institutions are presented hereunder.

Table 1: Specifications for Cr (VI)

Specification / Label	Application	Limit
EN 420: 1998 Standard	Leather Protective Gloves	2 mg/kg
European Eco-label	Footwear	10 mg/kg
Toxproof (TUV - Rheinland) label	Textiles, Leather	Undetectable
Öko-tex 100 Label	Textiles, Leather	Undetectable
SG Label	Textiles, Leather, Paper, Wood	Undetectable
LGR Label	Leather	Undetectable

It can be seen from the table that many Eco-labels demand undetectable level of Cr(VI). The detection level provided by öko-tex 100 Label for Cr (VI) is 0.5 mg/kg of leather. The IULTCS test protocol pertaining to the determination of Chromium VI in leather - IUC 18, may not be sensitive for such detection levels. Inter-laboratory disagreements have arisen due to the mismatch between the restrictions imposed and the sensitivity of analytical tools and techniques[5]. It is much more difficult to obtain true estimation results if the sample is dyed in dark colours. The interference of colourants in the estimation of chromium VI is

severe. It has been observed; presence of colourants in substantial quantity could bring about both false positive and false negative results.

There arises a need for common test protocol for such sensitive limits and harmonization among various test houses. A method[6] developed by CLRI using Ion-Chromatography after membrane separation of colourants is gaining recognition with reproducibility and reliability at more than 95%. This method overcomes the shortcomings associated with the official test ptotocol with reference to both false positive and false negative results.

Chromium (VI) – the source

It is essential to identify the possible sources of Cr(VI) and the possible generation of the same during the leather and product manufacturing process. The possible direct sources of Cr(VI) are the Basic Chromium Sulfate (BCS) used as a tanning agent, certain class of metal complex dyes and inorganic pigments. Particularly in the case of pigments based on lead chromate is a possible source of hexavalent chromium[7]. Unreduced chromium present tin the leather auxiliaries are the direct source of Cr(VI). Apart from the direct sources many tools, substances, auxiliaries, chemicals and process parameters could contribute significantly to the conversion of trivalent chromium into hexavalent chromium. Some of the possibilities of generation of Cr(VI) are presented below. Oxidation of Cr(III) to Cr(VI) by oxygen in air during the processes carried out at higher pH in leather and footwear manufacturing process is an important cause of Cr(VI) generation[8].

Neutralization

Chromium (III) undergoes oxidation into Chromium(VI) in presence of strong oxidizing agent in acidic condition. Oxidation can also occur at higher pH with the help of mild oxidizing agents. The aforesaid conditions prevail during neutralization of wetblue leather. Direct correlation between the final pH and the Cr(VI) conversion could not be established. However it was reported that there was a clear correlation between the netralisation pH and Cr(VI) generation in the

wetblue. Cr(VI) was found to increase with the increase in neutralization pH. But it was reported that the leathers after finishing did not show the presence of Cr(VI)[8]. It was concluded that the Cr(VI) content was independent of neutralization pH. Whereas it was also reported that regardless of the chemical chosen for neutralization the Cr(VI) in the finished leathers after heat treatment were found to be in direct proportion with the pH of neutralization. Therefore it can be construed that there is a direct correlation between the Cr(VI) content in leather and the neutralization pH[9]. It was also found out that in the extreme conditions such as carrying out neutralization at 80^{o}C for 24 hrs showed presence of Cr (VI)[10].

Ammonia Treatment

Treatment of crusts prior to dyeing with ammonia, sodium bicarbonate, cationic auxiliaries aiming better leveling and penetration may promote the oxidation of Cr (III). It was reported that the Ammonia and sodium bicarbonate treated samples when heated to 80^{o}C for 24 hours showed the presence of Cr(VI).

Thermal and Photo-ageing

Thermal ageing or exposure to UV light can induce the formation of large amounts of Cr(VI). It is also reported that the natural light or UVA light (UV light produced by lamps of 366 nm) can induce the formation of Cr(VI)[11].

Fatliquors

Fatliquors have a significant role in the formation of Cr(VI). The kind of fatliquors known to cause the formation of Cr(VI) are sulfated fish oils, sulfited fish oils, fatliquoring products with single or multiple unsaturated fatty acids either free or esterified. The free radicals that are released by the unsaturated lipids in presence of UV light can significantly cause the formation of Cr(VI). Sulphited vegetable oils were also found to cause Cr(VI) formation[12].

Adhesives Used in Product making

There appear possibilities of Cr(VI) formation when alkali Glue is used for binding (in the Shoe making). The levels of Cr(VI) in leather increased significantly after using the said adhesive and heat setting. The degree of conversion of Cr(VI) reported to be higher if the extractable Cr(III) level is high ie more than 50 mg/kg.

Avoidance and Mitigation

The background of the possible sources of Cr(VI) and possibilities of Cr (VI) formation torches the pathway of solution to the problem. It is obvious and principally important to avoid the direct sources of Cr(VI).

- The BCS used for tanning needs to be screened for the level of Cr(VI) and avoided if found to contain significant mass of Cr(VI).
- The process of Chrome tanning needs to be controlled and monitored so as to minimize the level of leachable chromium. As more amount of leachable chromium enhances the Chromium conversion into Cr(VI).
- Similarly the Dyes and Pigments shall be chosen for processing only if they contain no or undetectable levels of Cr(VI). The yellow colored anionic pigments that are based on chromate are most likely to contribute to Cr(VI). The problem becomes much serious if the pigment contains Ammonia or Carbonates. It shall be ensured that such pigments are screened and avoided for use in the finishing operation.
- Fatliquors including synthetic or natural, especially fish oil based fatliquors with single or multiple unsaturated fatty acids shall be avoided.
- Exposure to direct sunlight for drying may be avoided.
- Alkaline glue (as adhesive) shall be avoided in shoe making operations.

The points to be pondered for the mitigation of Cr(VI) are presented below.

- It is preferable to use neutralizing auxiliaries with reduction capability in Neutralization and wetting back of crusts.
- Treatment with vegetable tanning agents proved to reduce the presence of Cr(VI). The vegetable tanning agents that show marked influence in reducing the levels of Cr(VI) are Wattle, Quebracho, Chestnut and Tara. Tara however understood to be the best in the said characteristic among all. Even treatment with 1% of Tara proved to reduce the risk of presence of Cr(VI) significantly.
- Reducing agents such as sodium bisulfite, Sodium metabisulfite[13] may be used in the final washing of leather. However it may please be noted that such treatments may alter the shade and colour intensity of the leather and hence accordingly the process of dyeing needs to be restandardised.

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