Prevention of carcinogenic Cr (VI) formation in leather – A three pronged approach for leather products

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Antioxidants, based on chemical, natural and bio origin, have been used for the prevention of hexavalent chromium formation in leather. Formation of Cr (VI) is monitored in the leathers after processing and after accelerated ageing. Gallic acid and ascorbic acid are found to be more effective in the pre tanning process in the prevention of oxidation of Cr (III) to Cr (VI). Myrobalan and tara play an effective role in the chrome tanning process and prevent the formation of hexavalent chromium. The study shows that chromium based leathers can be easily classified in to benign material for manufacturing of consumer products, if these strategies are used.

Keywords: Ageing, Antioxidants, Chromium, Hexavalent chromium, Leather

Chromium is a transition metal located in group VI-B of the periodic table. Although it is able to exist in several oxidation states, the most stable and common forms are the trivalent Cr (III) and the hexavalent Cr (VI) species having different chemical properties1. Hexavalent form is five hundred times more toxic than the trivalent2,3. Basic chromium sulfate is the most popular tanning agent in global leather production. Chromium remains as a highly effective tanning agent for producing leather with high dimensional stability, mechanical strength, durability, resistance and fastness making it suitable for many end uses. There are instances where carcinogenic Cr (VI) compounds have been found in leathers tanned with benign Cr (III) compounds. Acute exposure to Cr (VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage, and respiratory problems4. Inhalation may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma)5-7. The possible direct sources of Cr (VI) are contaminations in Cr (III) tanning agent, certain class of metal complex dyes and inorganic pigments based on lead chromate8-10. Apart from the direct sources many tools, substances, auxiliaries, chemicals and process parameters could contribute significantly to the conversion of trivalent chromium into hexavalent chromium11-14. The oxidizing agents present in the specialty chemicals used for leather making can lead to the formation of Cr (VI) under storage conditions well above the permissible limits15-17.

The fatliquors based on vegetable or animal oil such as fish oil, rapeseed oil and soya oil are normally used for making soft leathers and have the potential to trigger chromium (VI) formation and induce changes in the physico-chemical characteristics of leather on ageing8-21. Cr (VI) was formed up to 46 ppm on subjecting the leathers to a heat treatment of 80°C for 16 hr. Any chemical containing potential oxidizing group can, in principle, lead to the conversion of considerable quantities of Cr (III) to Cr (VI) even under unfavorable pH conditions.

Ageing normally starts with the adverse reaction on fatliquor as the double bonds in fatliquor base are prone to be attacked by oxygen. Auto oxidation leads to formation of radicals and hydro peroxides22-24. Radicals formed in the process are highly reactive particles and can lead to the protein chain scission25-27. This may be the main reason for the deterioration of mechanical properties of leather matrix. Peroxides formed are likely to react with the trivalent chromium and converting into hexavalent during ageing. Many attempts and research works have been carried out on the prevention of hexavalent chromium in leather. The concomitant changes in various physico-
chemical properties of leather limit the choice and use of various known organic and inorganic reducing agents for prevention or remediation of Cr (VI) in leather.

Hence, an attempt has been made to develop a process methodology using products having antioxidant property. Ascorbic acid, myrobalan, tara, gallic acid and protein hydrolysate have been used in the process to prevent the formation of hexavalent chromium in leather. Earlier studies and approaches have used the vegetable tanning materials and reducing agents in the wet finishing stages of leather processing which have not provided satisfactory results. In the present work, the antioxidants are used in the pre tanning, tanning and wet finishing stages of leather processing. Hence, the present work is aimed at studying the prevention and reduction of Cr (VI) in leather.

**Experimental Procedure**

**Reagents**

Basic chromium sulfate used in the tanning is procured from Anand Chrome Pvt Ltd. Ascorbic acid, gallic acid and other reagents used in the analysis are of Analar grade. Myrobalan, tara and chemicals used in leather processing are of commercial grade. The commercial fish oil based fatliquor has been used for the study.

**Process adopted for experimental trials**

Experimental trials were carried out in three stages, viz pre-tanning, tanning and wet finishing of leather processing. Ascorbic acid and gallic acid were used in pre-tanning and chrome tanning. Myrobalan, tara and protein hydrolysate (prepared by acid digestion of keratin) were used in the chrome tanning. Finally, myrobalan and tara were used in the wet finishing process to prevent the oxidation of trivalent to hexavalent form. Initially the samples were analyzed for Cr (VI) content. The sample was cut into 15×10 cm each. Then the leathers were subjected to thermal ageing for 24 h at 80°C and 20% relative humidity in humidity chamber. The aged leather samples were analyzed for Cr (VI) content.

**Studies on chrome tanned hide powder**

Hide powder was first soaked in beaker with a 300% float (based on the weight of hide powder) for overnight. The soaked hide powder was squeezed lightly to remove excess water and the moist weight was noted. The chemicals used in the process were based on the soaked weight of hide powder. The hide powder was conditioned (pickled) with 80% water containing 8% sodium chloride and 0.5% sulphuric acid for 1h and the pH was adjusted to 2.5 followed by the addition of 8% basic chromium sulphate. The tanning solution was basified with 1% sodium formate and 1% sodium bicarbonate diluted with 10 times of water and shaken for another one hour with a final pH of about 4.0. After washing in 200% water, the chrome tanned hide powder was squeezed lightly to remove excess water. A part of chrome tanned hide powder was treated with 5% phenolic synthetic tanning agent and 5% synthetic base fatliquor. Other part of chrome tanned hide powder was treated with 30% fish oil base fatliquor.

**Studies on chrome tanned leather**

The wet salted goat skins of Indian origin approximately weighing one kilogram per piece were used for the experiments. Conventional pre tanning operations were carried out for the skins. Three sets of experiments were done on the chrome tanned leather to study the influence of pH on the formation of Cr (VI). The chrome tanned leather pH values were adjusted to 3.5, 3.8 and 4.0. Then the chrome tanned leathers were converted into crust by treating with 5% phenolic synthetic tanning agent and 5% synthetic base fatliquor. Cr (VI) was determined in the crust leathers before and after ageing. Thermal ageing of leathers was carried out by subjecting the leathers to 80°C for 24 h at 20% relative humidity in a hot air oven.

**Trials in pre tanning process**

The wet salted goat skins of Indian origin approximately weighing one kilogram per piece were used for the experiments. Conventional beam house operations such as rehydration, hair and flesh removal were carried for the skins. Deliming trials were carried out with 0.5% and 1% [on the pelt weight (w/w)] of ascorbic acid and gallic acid separately. The experimental trials done with 0.5% of ascorbic and gallic acid results in incomplete deliming, hence 0.5% formic acid is added. However, use of 1% ascorbic and gallic acid results in the completion of deliming. Completion of deliming was checked with phenolphthalein indicator. After the completion of deliming the conventional pickling and chrome tanning was carried out. Another set of experiments was carried out on pickling stage. Conventional pickling process was done and followed by the
addition of 0.5% and 1% ascorbic acid and gallic acid for 1h followed by chrome tanning. Conventional deliming, pickling and chrome tanning are carried out without addition of antioxidant materials as control leathers.

**Experiments in chrome tanning using anti-oxidants**

Different trials were done on the products in chrome tanning process. Initially the products were used separately to study the anti–oxidant property and in combinations in the chrome tanning process. Conventional deliming and pickling process was carried out followed by chrome tanning. Chrome tanning process was carried out with 8% basic chromium sulphate (BCS) on the pelt weight (w/w). The BCS was added in two installment. Initially 4% BCS is added and after 45 min remaining 4% BCS was added. The anti-oxidant materials were added in between the two installment of BCS. Ascorbic acid, gallic acid, myrobalan, tara and protein hydrolysate were used individually and in combination in-between the two installment of basic chromium sulfate in chrome tanning process. Another set of trials was carried out with myrobalan, tara and protein hydrolysate at the end of the chrome tanning process. Conventional chrome tanning process is carried out without the addition of antioxidant materials as control leathers. All the chrome tanned leathers were converted into crust by treating them with 30% fish oil base fatliquor to promote the oxidation of Cr (III) to Cr (VI) during ageing to study the behavior of aforementioned products on ageing.

**Myrobalan and tara in wet finishing**

The experimental trials were carried out with myrobalan and tara in the retanning stage. Conventional chrome tanned leather was neutralized and treated with 30% fish oil followed by the addition of 1% and 2% myrobalan separately and in combination with tara.

**Determination of hexavalent chromium in leather**

Initially the chrome tanned leather samples were analyzed for hexavalent chromium content. The aged leather samples were analyzed for hexavalent chromium content. There exists four official methods for analysis of leather for hexavalent chromium. They are EN 420, DIN 53314, SLC 22 and IUC 18. SLC 22 method is identical to IUC 18. With few differences, the other two methods are very similar to these two. Basically all these are colorimetric methods in which the colour is developed using 1,5-diphenylcarbazide. The chromium (VI) in solution oxidizes 1,5-diphenylcarbazide to 1,5-diphenylcarbazone to give a red/violet complex (measured at 540 nm.)

Ion chromatography (IC) with novel sample purification technique by membrane dialysis of leather extracts was used. Since the technique is reliable in presence of chromium (III), the IC technique with post column derivatization using 1,5-diphehylcarbazide (DPC) and photometric detection at 520 nm has been adopted. The procedure by ion chromatography supported with dialysis sample purification technique is serving the best for the determination of hexavalent chromium in the case of strongly coloured finished leathers. The method is excellent for trace level detection of Cr (VI) down to 0.3 mg/kg for finished leathers.

Hexavalent chromium determination was carried by ion chromatography, using anion exchange columns. Samples were injected into IC using 100 µL loop. The elution was done with 25 mM ammonia-ammonium buffer solution and on the post column derivatization with 1, 5-diphenyl carbazide (DPC) reagent filled in the post column reactor followed by monitoring at 540 nm using photometric detector.28,29

**Results and Discussion**

Different reducing types of anti-oxidants have been examined in order to determine their efficiency in preventing the oxidation of Cr (III) to Cr (VI). These include chemical, natural and bio products such as ascorbic acid, gallic acid, myrobalan, tara and protein hydrolysate. The addition is made in the pre tanning, tanning and wet finishing process. Experiments are carried out on the hide powder and the chrome tanned leather to study the conditions for the formation of hexavalent chromium by treating the hide powder with fatliquors with unsaturated double bonds and by varying the pH in the chrome tanned leather. The Cr (VI) content of the chrome tanned hide powder is given in Table 1. The results imply that the Cr (VI) content of the wet blue leathers and crust leathers are below the detection limit, however the fish oil treated crust powder shows higher amount of Cr (VI) of 20ppm on ageing conditions. This may probably be due to the presence of oxidizing agent present in the fish oil. Experiments on chrome tanning are carried out by adjusting the pH at 3.5, 3.8 and 4.0. Cr (VI) is determined in the wet blue leathers and in the crust leathers before and after ageing to study the influence of pH on the formation of hexavalent chromium and
the results are tabulated in the Table 2. From the results it is observed that when the pH is 3.5 the chance of formation of hexavalent chromium is more when compared with other chrome tanned samples at pH 3.8 and 4.0. This could be due to the presence of large amount of unbound chromium in the chrome tanned sample at pH 3.5.

Use of ascorbic acid for prevention of Cr (VI)

Ascorbic acid (vitamin C) is an important non-toxic biological reductant ubiquitous in humans and animals. An amount of 0.5% and 1% (w/w) ascorbic acid has been used on the pelt weight in deliming, pickling and chrome tanning and the Cr (VI) is analysed in the wet blue leathers. From the results (Fig. 1) the complete elimination of Cr (VI) is observed in the ascorbic acid treated wet blue leathers as compared to that in control samples. All the samples are treated with fish oil base fatliquor to promote oxidation. They are then made into crust and subjected to the thermal ageing. Then the samples are analysed for Cr (VI) content before and after ageing and the results are given in Fig. 2. The results in the figure indicate that the ascorbic acid used in the deliming stage is unable to reduce the Cr (VI) on the crust samples on ageing conditions. The control sample shows Cr (VI) content of 40 mg/kg treated with fish oil on ageing. The experimental sample pretreated with ascorbic acid in the pickling stage and processed

Table 1—Experiments on chrome tanned hide powder

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr₂O₇²⁻</th>
<th>Cr(VI) in CTPH mg/kg</th>
<th>Cr(VI) in CHP mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrome tanned hide powder</td>
<td>4.4</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>Treated with fish oil</td>
<td>4.0</td>
<td>0.3</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>

BDL – Below detection limit. CTHP – Chrome tanned hide powder. CHP – Crust hide powder

Table 2—Experiments on chrome tanned leathers

<table>
<thead>
<tr>
<th>pH</th>
<th>Cr(VI) in chrome tanned leathers mg/kg</th>
<th>Cr(VI) in the crust leather mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before ageing</td>
<td>After ageing</td>
</tr>
<tr>
<td>3.5</td>
<td>2.1</td>
<td>0.5</td>
</tr>
<tr>
<td>3.8</td>
<td>1.5</td>
<td>0.3</td>
</tr>
<tr>
<td>4.0</td>
<td>1.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Use of ascorbic acid for prevention of Cr (VI) with fish oil base fatliquor has shown Cr (VI) values of 5.0 and 7.3 mg/kg on ageing. Ascorbic acid used in the chrome tanning process has shown the Cr (VI) content of 10 and 11.1 mg/kg. A drastic difference is observed on Cr (VI) content of control and experimental samples. The result implies that ascorbic acid is more efficient in the pickling stage in the prevention of oxidation of trivalent to hexavalent chromium. The reaction of ascorbic acid and dichromate is illustrated in the following stoichiometry equation using alkaline and acidic condition:

\[
\text{Cr}_2\text{O}_7^{2-} + 3\text{ascorbic acid} + \text{H}_2\text{O} \\
\rightarrow 2\text{Cr(OH)}_3 + 3\text{dehydroascorbic acid} + 2\text{OH}^- \\
\text{Cr}_2\text{O}_7^{2-} + 3\text{ascorbic acid} + 8\text{H}^+ \\
\rightarrow 2\text{Cr}^{3+} + 3\text{dehydroascorbic acid} + 7\text{H}_2\text{O}
\]
Use of gallic acid for prevention of Cr (VI)

Gallic acid is simple phenolic compounds of lower molecular weight, which are abundantly found in plants, especially in dead tissues and dying cells and is known as powerful anti oxidant. They are soluble in water, ethyl alcohol, glycerol, and acetone and in dilute alkalis. Gallic acid is used at 0.5% and 1% on the pelt weight in deliming, pickling and chrome tanning and the Cr (VI) analysed in the wet blue leathers. The results are indicated in Fig. 3. It is observed that the Cr (VI) content is similar to that in control samples in wet blue leathers. They are made into crust and subjected to the thermal ageing. Then the samples are analysed for Cr (VI) content before and after ageing and the results are given in Fig. 4. From the figure it is found that the gallic acid used in the deliming and picking completely eliminates the formation of Cr (VI) however with the increasing amount of gallic acid the Cr (VI) content decreases. Similar results are observed in chrome tanning also. The results show the effectiveness of gallic acid as an anti oxidant in preventing the Cr (VI) content.

Use of myrobalan for prevention of Cr (VI)

Myrobalan contains about 30% of the hydrolysable tannins, which consist of chebulinic acid, chubulagic acid and D-galloyl glucose. It contains free tannic acid, gallic acid, ellagic acid and resin myrobalan. They exhibit a variety of biological activity including anti oxidant, free radical scavenging anticancer, anti-diabetic, anti-mutagenic, anti-bacterial, antifungal and antiviral activities. Myrobalan is used in the chrome tanning and retanning process individually and in combination with tara and protein hydrolysate. The addition of myrobalan is done in between the two installments of basic chromium sulfate and at the end of the chrome tanning process. The wet blue leathers are converted into crust leathers. Hexavalent chromium content of the wet blue leathers and crust leathers before and after ageing is given in Table 3. From the results it is found that the myrobalan treated wet blue leathers show improved resistance to the formation of Cr (VI). When it is used independently the Cr (VI) content is controlled to 1.0 from 42 mg/kg on ageing. However, the combination of tara and protein hydrolysate shows the absence of hexavalent chromium. The obtained results are in the prescribed limits of Cr (VI) in leather. Myrobalan and tara can be used effectively in controlling the Cr (VI) in leathers. Myrobalan and tara are also employed in the wet finishing process to study the influence in retanning process. The results are shown in the Fig. 5. It is found that both these products are very efficient in the tanning stage than in the wet finishing stage.

Use of tara for prevention of Cr (VI)

Tara is a vegetable tanning agent belonging to the pyrogallol tannin group. Tara is used in the chrome tanning process separately and in combination with myrobalan and protein hydrolysate. Tara is found to be inefficient when used individually in chrome tanning process, however when used in combination with myrobalan it plays more effective role in controlling the oxidation of trivalent chromium to hexavalent chromium.

Interpretation of myrobalan, tara and gallic acid materials used in the process

The protective effect should be ascribed to the anti oxidant character effect of the tannins. Most tannins...
Table 3—Cr (VI) content for the experimental wet blue samples

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Quantity</th>
<th>Quantity %</th>
<th>Cr(VI) in wet blue leather mg/kg</th>
<th>Cr(VI) in crust leathers mg/kg Before ageing</th>
<th>Cr(VI) in crust leathers mg/kg After ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>0.2</td>
<td>1.0</td>
<td>42.7</td>
<td></td>
</tr>
<tr>
<td>Myrobalan</td>
<td>5</td>
<td>0.1</td>
<td>0.5</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Tara</td>
<td>5</td>
<td>BDL</td>
<td>1.1</td>
<td>28.2</td>
<td></td>
</tr>
<tr>
<td>Protein hydrolysate</td>
<td>5</td>
<td>0.2</td>
<td>7.3</td>
<td>35.0</td>
<td></td>
</tr>
<tr>
<td>Myrobalan + protein hydrolysate</td>
<td>2.5</td>
<td>0.2</td>
<td>0.6</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Tara + myrobalan</td>
<td>2.5</td>
<td>0.1</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Tara + protein hydrolysate</td>
<td>2.5</td>
<td>0.3</td>
<td>0.3</td>
<td>24.0</td>
<td></td>
</tr>
<tr>
<td>Myrobalan + tara</td>
<td>2.5</td>
<td>BDL</td>
<td>0.2</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Protein hydrolysate + tara</td>
<td>2.5</td>
<td>0.3</td>
<td>0.6</td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>Protein hydrolysate + tara + myrobalan</td>
<td>2.5</td>
<td>BDL</td>
<td>0.3</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Myrobalan</td>
<td>2.5</td>
<td>0.1</td>
<td>0.6</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Tara</td>
<td>1.25</td>
<td>0.3</td>
<td>0.6</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Protein hydrolysate</td>
<td>1.25</td>
<td>0.5</td>
<td>0.5</td>
<td>35.0</td>
<td></td>
</tr>
</tbody>
</table>
* Myrobalan | 5 | 0.3        | 0.4                             | 1.5                                        |
* Tara      | 5        | 0.3        | 1.7                             | 39.0                                       |
* Protein hydrolysate | 5 | 0.5        | 0.5                             | 35.0                                       |

The materials are added between the chrome tanning process. *The materials are added at the end of the chrome tanning process.

The materials are antioxidants since they inhibit the propagation of free radicals. The tannins act as a radical scavenger capturing the most reactive radicals and transforming them into stable substances. Thus, the chain propagation of free radicals is interrupted and as a consequence the oxidation of Cr (III) to Cr (VI) is stopped. Use of these vegetable extracts with antioxidant property studied is a simple, efficient and economical way to eliminate or minimize the formation of Cr (VI) in leathers. The mechanism is shown below:\n
\[ \text{TH} + L \cdot t \rightarrow + LH \]
\[ \text{TH} + \text{LOO} \cdot t \rightarrow \text{T} \cdot + \text{LOOH} \]
\[ \text{T} \cdot + \text{LOO} \cdot \rightarrow \text{LOOT} \]
\[ \text{T} \cdot + \text{HO} \cdot \rightarrow \text{TOH} \]

where,
TH—tannin molecule
t—tannin radical (non – oxidant stabilized radical)

Conclusion
Gallic acid used in the pre tanning process is able to control the formation of Cr (VI) in the crust leathers during ageing. Ascorbic acid is more efficient in pickling and chrome tanning process and ineffective in deliming stage. Myrobalan and tara used in combination in chrome tanning process show more resistance to hexavalent chromium formation and prevent the oxidation of trivalent chromium to hexavalent chromium on accelerated ageing conditions. The present investigation made on the pre tanning and chrome tanning process by employing various materials with anti oxidant property in combination to prevent the oxidation of trivalent chromium has provided encouraging results. Hence, it is now possible to make leather and leather products through chrome tanning which may not produce carcinogenic hexavalent chromium in leather even under extreme ageing conditions by using combination of chemical, natural and bio products at appropriate stages of leather making.

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