Upgradation of leathers: Masking defects using pigments in pre-finishing processes

R Aravindhan¹, B Madhan¹, P Thanikaivelan¹, Swarna V Kanth¹, J Raghava Rao¹*, C S Gnanasekaran² and Balachandran Unni Nair¹*

Central Leather Research Institute, Adyar, Chennai 600 020
²C Kalyanam & Co., Chrompet, Chennai 600 044,

Received 20 February 2007; revised 27 December 2007; accepted 14 January 2008

Inferior quality East India (EI) leather was upgraded by using a water-soluble pigment, which provides better coverage of defects during post tanning. Effect of fatliquors and wet as well as dry milling on covering defects on leather was also studied. Leathers have required strength and bulk properties apart from looking natural.

Keywords: Defects coverage, Leather, Pigment dyeing

Introduction

Leather and leather products produced in India contribute to 10% of global production on volume terms; the value it could fetch is only around 2.4% of global business¹. One of the main reasons for India’s low share is poor raw material quality (30% from fallen or dead animals). Quality of raw material is affected either due to ante-mortem defects (scratches, rub marks or horn rake, yoke mark, scabies, pox brand marks etc.) or post-mortem defects (flay cuts, fleshing cuts, grain crack, etc.). While post-mortem defects are controllable to a certain extent, ante-mortem defects pose serious challenges to the tanner:²,³. Finishing of leather significantly increases aesthetic appeal and sale value of the product⁴.

Generally, using pigments in finishing operations cover deep defects in grain on full grain leathers. Although, this approach provides good covering, it reduces aniline characteristics or natural look of leather, which in turn reduces its potential value and returns to the tanner⁵. Earlier, there had been attempts in using chitosan as an auxiliary in dyeing process to enhance the depth of leather shade, which can also facilitate covering of defects to some extent⁶-¹². However, recent developments in dyeing process, through special application of pigments, which are compatible with selected dyes, offer an alternative approach¹³,¹⁴.

Advantages of careful blending of pigment and dyestuff may be summarized as follows¹⁵: opaque, uniform shade with level coloration; masking of grain damage; increase in the depth of shade; upgradation of leathers with moderate grain damage; full retention of aniline character; and possibility of lighter finishing for comfort leathers. Slaats et al¹⁵ reported need for the use of cationic auxiliary based on polyethylene-polyamide to change surface charge and subsequent addition of a weak cationic polymer or chrome syntan to create uniform charge over the entire grain surface and cross section¹³,¹⁵. Use of these products was necessary to obtain uniform deposition of pigments on leather matrix, especially on defects.

This study presents use of pigments for covering defects in wet finishing in combination with wet or dry milling.

Experimental Details

Materials

Low grade East India (EI) tanned buff calf with numerous open defects (1.2±0.1 mm thickness) was used. Water-soluble pigment dispersion was sourced from Allied Chemicals International Co. Ltd., Thailand. All chemicals used were of commercial grade. Chemicals used include: Alloderm Black 2B (Water soluble pigment...
dispersion from Allied Chemicals International Co. Ltd., Thailand; Basyntan DI (Phenol condensate based syntan from BASF, Germany); Vernaminol liquor ASN (Synthetic oil based fatliquor from Clariant Ltd., India); Luwet 40 (Wetting agent from Textan Chemicals, India); Catalix GSIN (Cationic fatliquor from Clariant Ltd., India); Derminol NLM-LE (Lecithin fatliquor from Clariant Ltd., India); Luganil black FBO (Acid black dye from BASF, Germany); Rodobind casein 4080 (Cationic casein binder from TFL, Germany); Rodoground KCF 647 (Cationic casein binder from TFL, Germany); and Rodopur K 8727 (Cationic polyurethane binder from TFL, Germany).

Characterization and Effect of Pigment

Particle size and zeta potential of pigment were measured using Malvern Zetasizer 3000HS A. For comparison, a commercial pigment (dispersible in water), used for conventional finishing, was also subjected to these measurements. Measurements were taken using 0.01% (w/v) pigment concentration using water as solvent.

EI tanned buff calf leathers were post tanned (Table 1). All process steps were same for control (C) and experimental (P) post tanning process except that black pigment (Alloderm black 2B) was used in experimental process. Crust leathers were evaluated based on visual assessment for defects coverage, color intensity/depth, uniformity of color and overall improvement.

Effect of Milling of Leathers

In addition to the use of pigment in post tanning (Table 1), milling (wet and dry) of leathers was performed in two experiments. In experiment M1, after post tanning operation, leathers were sammed, set, hooked to dry, conditioned, staked and then finally dry drummed for 3 h. In experiment M2, leathers after post tanning were sammed, set, and then rotated in a drum without float, wet milling, for 3 h. Then, leathers were hooked to dry,
staked and dry drummed for 3 h. Leathers were evaluated by visual assessment for defects coverage, color intensity/depth, uniformity of color, uniformity of milling pattern and overall improvement.

Selection of Fatliquoring for Post Tanning
Three types of fatliquors (synthetic, lecithin and vegetable based) were used for post tanning after making following experimental samples: F1 (synthetic, 10; lecithin, 5; vegetable, 5%); F2 (synthetic, 5; lecithin, 5; vegetable, 10%) and F3 (synthetic, 5; lecithin, 10; vegetable, 5%). While other unit processes/operations in the processing of leathers remained same [Table 1 (experimental)], milling operation was similar to that adopted for experiment M2. The leathers were evaluated by hand and visual assessment for fullness, milling effect, uniformity of milling, fluffiness, defects coverage and general appearance.

Finishing of Leathers
A cationic protein finishing system (dye stain coat/cationic coat), which was adopted for control and experimental (F3) leathers, had following parameters: Rodobind casein 4080, 160 parts; Rodoground KCF 647, 80 parts; Rodopur K 8727, 48 parts; water, 580 parts; disperser/penetrator, 50 parts (2x spray coat); cationic black dye solution, 20-30 parts (plate @ 100-120°C, 3.5 kg/cm² pressure) and formalin, 100 parts (1 x spray coat). Finished leathers were then evaluated for rub fastness and visual assessment.

Physical Testing of Leathers
Samples for various physical tests from experimental (F3) and control (C) crust leathers were obtained as per IULTCS method. Specimens were conditioned at 25±4°F and 65±2% relative humidity over a period of 48 h. Physical properties (tensile strength, percentage elongation at break and tear strength) were examined for the specimens. Dry and wet rub fastness tests were carried out for finished leathers from F3 and C.

Hand and Visual Evaluation of Leathers
F3 and C finished leathers were assessed for fullness, grain tightness or break, defects coverage and general appearance by hand and visual examination. Functional properties of leathers in a scale of 0-10 points was rated by four experienced tanners and average values were reported. Higher values indicate better property.

Reflectance Measurements
Reflectance factor measures amount of light reflected from surface of opaque specimen at a number of wavelengths throughout the visible spectrum as a fraction of that reflected by a white standard identically illuminated. Reflectance measurements were carried out on dyed crust leathers from C and P using a Mitton Roy Color Mate HDS instrument.

Results and Discussion
Characterization and Effect of Pigment
Average particle size of pigment is estimated to be 188.7 nm as against 320.2 nm for commercial pigment used for finishing of leather. Pigment chosen in this study for application during post tanning has lower particle size compared to the pigment used for finishing. It is expected that lower particle size pigment would mask the defects effectively without covering hair pores and grain structure. Zeta potential of both pigments is estimated to be –12.2±5.6. Higher numbers indicate better stability while minus or positive sign indicates charge of the chemical. This means that both pigments are anionic and stable.

Crust leathers treated with pigment during post tanning exhibit low reflectance values throughout the visible wavelength region compared to C leathers (Fig. 1). Low reflectance denotes high absorption and darker pigmented leathers. Thus, experimental leathers show greater covering of defects when compared to conventional post tanned leathers, and use of pigment
in post tanning process gives good coverage of defects and improves color of final leathers. This is in good agreement with the results obtained from particle size analysis. Uniformity of color of crust leathers is comparable, while leathers treated with pigments showed a high degree of coverage (Table 2). Comparatively, better depth of shade is observed with leathers treated with pigments, hence improvement in quality of the final leather. Visual assessment data are in agreement with reflectance and particle size results.

**Effect of Milling Operation**

Milling is usually done for lower grade leathers in order to break grain of leathers uniformly, so that defects get hidden and leathers obtain a unique pebbled grain pattern. Visual assessment data (Table 2) show that both milling experiments resulted in leathers with good coverage of defects compared to control. Particularly, leathers underwent wet milling followed by dry milling operation, showed better defects coverage, uniformity of color and uniformity of milling pattern, and compared to leathers that had dry milling alone (Fig. 2). Hence, for subsequent experiments, leathers were processed through both wet and dry milling (M2).

**Modification of Fat liquoring Process**

Process F3, where higher amount of lecithin based fatliquor offered, resulted in leathers with better characteristics (Table 3). The leather (F3) that has shown better fluffiness is also found to possess better milling effect as expected. Bold and uniform milled pattern, of the leathers processed using higher lecithin based fatliquor, assisted in good covering of defects. Hence, F3 employing pigment along with high offer of lecithin fatliquor followed by wet milling and dry milling has been chosen as an optimum process for effective coverage of defects.

**Effect of Upgradation Process on Strength Properties**

Strength properties of control and processed leathers were found as follows: tensile strength, C, 270±6, F3, 259±5 kg/cm²; elongation, C, 43±2, F3, 57±3%; and tear strength, C, 40±2, F3, 43±2 kg/cm. Experimental leathers possess

---

**Table 2—Visual examination of leathers for the effect of pigment addition and milling**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Defects coverage</th>
<th>Intensity/Depth</th>
<th>Uniformity of color</th>
<th>Uniformity of milling pattern</th>
<th>Overall improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (Without pigment and milling)</td>
<td>1±0.2</td>
<td>6±0.2</td>
<td>8±0.5</td>
<td>-</td>
<td>1±0.2</td>
</tr>
<tr>
<td>P (Pigmented without milling)</td>
<td>4±0.5</td>
<td>7±0.3</td>
<td>9±0.2</td>
<td>-</td>
<td>4±0.5</td>
</tr>
<tr>
<td>M1 (Pigmented with dry milling alone)</td>
<td>6±0.5</td>
<td>6±0.3</td>
<td>7±0.5</td>
<td>6±0.5</td>
<td>5±0.5</td>
</tr>
<tr>
<td>M2 (Pigmented with wet and dry milling)</td>
<td>7±0.2</td>
<td>7±0.3</td>
<td>8±0.5</td>
<td>8±0.5</td>
<td>7±0.3</td>
</tr>
</tbody>
</table>

---

Fig. 2. Photographs showing the milling pattern of leathers treated with pigment in post tanning followed by dry milling alone (M1) and both wet and dry milling (M2)
Table 3—Organoleptic properties of leathers treated with various fatliquoring combination

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fullness</th>
<th>Milling effect</th>
<th>Uniformity of milling</th>
<th>Fluffiness</th>
<th>Defect coverage</th>
<th>General appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>6±0.2</td>
<td>7±0.5</td>
<td>6±0.5</td>
<td>7±0.3</td>
<td>7±0.2</td>
<td>7±0.5</td>
</tr>
<tr>
<td>F2</td>
<td>8±0.2</td>
<td>6±0.3</td>
<td>6±0.5</td>
<td>6±0.3</td>
<td>7±0.2</td>
<td>7±0.5</td>
</tr>
<tr>
<td>F3</td>
<td>7±0.5</td>
<td>9±0.2</td>
<td>8±0.5</td>
<td>8±0.5</td>
<td>8±0.5</td>
<td>9±0.2</td>
</tr>
</tbody>
</table>

Fig. 3. Photographs showing milling pattern and defects coverage of final leathers processed using optimized (F3) and control process without pigment (C)

Fig. 4. Organoleptic properties of finished leathers processed using optimized (F3) and control process without pigment (C)
comparable or similar tensile and tear strength compared to control leathers. Slight decrement in tensile strength of experimental leather could be attributed to the opening or loosening of compact fiber structure on milling. Although, control leathers showed slightly better tensile strength characteristics, percentage elongation was better in experimental leathers owing to further opening up. Thus, selected upgradation process has little or no effect on strength characteristics of processed leathers.

**Effect of Finishing on Upgradation of Leathers**

Conventional upgradation system employs resin based finishing system for defect coverage resulting in sealing or covering grain rather than defects, protein based finishing provides open or naked grain resulting in natural leather look. Hence for comparison, both F3 and C leathers were applied with stain coat, which contains a mixture of protein and PU binders, wax and dye solution. Leathers after application of finish film were plated at high temperature (100-120°C) in order to give a glossy look. Wet and dry rub fastness for both C and F3 leathers has a value of 4/5 in the grey scale. Thus application of pigment during post finishing and grain tightness of C and F3 leathers are comparable (Fig. 3), indicating that wet and dry milling carried out during experimental process do not lead to any grain damage. Defects coverage is significantly better in F3 leathers. Overall, unit value realization for F3 leather can be significantly improved using upgradation methodology.

**Conclusions**

Leathers can be upgraded significantly before finishing through a series of post tanning process/operations. The coverage of defects is high, mainly facilitated by milling effect and it is feasible to use a protein based finishing, which is not employed in conventional upgradation methodologies. Developed upgradation process can improve unit value of leathers substantially.