From crust leather to semi-finished leather by using dense pressurized CO2

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Abstract:
In any industrial sector, dyeing is as a step which requires large amounts of water. The technology of dense pressurised fluids has the ability to create a special solution with very different qualitative properties from the ones used traditionally. One of the originality of this process is the possibility of continuously modifying the solvating power of a fluid and all of the transport properties (flow rate and mass transfer). Carbon dioxide in supercritical phases accelerates the absorption of molecules with low molecular weight on various supports.
CTC has studied the potential of this application in leather dyeing.

Trials have been made after selecting a leather support. Different dyes, additives and dyeing conditions have been optimised at labscale.
Finally, leathers have shown homogenous superficial dyeing and mass dyeing after treatment in a semi-pilot equipment.

This project has demonstrated the possibility to achieve a dry way of leather dyeing. The need to work further on the dyestuff chemistry, to improve the affinity of the dyestuff with the support, and its light stability is exposed. Applying this technology to all steps of leather manufacturing could strongly increase the interest in such an investment.
Introduction:

This study was managed to check the transfer feasibilities in the manufacturing of leather, of the dry dyeing methods already used in other industrial sectors such as the textile. This project consists on selecting a dyestuff adapted to the leather and to the conditions of the supercritical CO$_2$ and to optimise the process parameters. The pre-analyses of the industrial potential of this technology, in terms of treatment efficiency, fastness of the dyeing, reduction of effluent and energy's savings were conducted.

Theory on the supercritical CO$_2$:

The supercritical statement hold simultaneously the density of a liquid and the mobility of a gas, two parameters essentials in reaction mechanism on interfaces. CO$_2$, the more used compound presents in supercritical phases, provides very interesting solubility properties of chemical species and improve the swelling of fibres. In certain cases, the use of a recyclable additive is necessary in order to improve the product penetration in the treated support. The properties of supercritical fluids depend upon both on the pressure and on the temperature.

The following table shows the different properties of different phases of the CO$_2$. It underlines that supercritical CO$_2$ can be as dense as a liquid and less viscous and that its diffusion coefficient is better than the one in liquid phase. The critical point temperature of CO$_2$ is 31°C.

The technology of supercritical fluids represents a potential solution proposing new solvating power and impregnation properties, but also by reducing the production costs through the decrease of the amount of water and the elimination of certain post-tanning operations.

Typical properties of CO$_2$ in gas, liquid or supercritical phases:

<table>
<thead>
<tr>
<th>Properties</th>
<th>Gas</th>
<th>Supercritical</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/ml)</td>
<td>(0.6 – 2.0) $\times 10^{-3}$</td>
<td>0.2 – 0.9</td>
<td>0.6 – 1.6</td>
</tr>
<tr>
<td>Diffusivity coefficient de (cm$^2$/s)</td>
<td>0.1 – 0.4</td>
<td>(0.2 – 0.7) $\times 10^{-3}$</td>
<td>(0.2 – 2.0)$\times 10^{-3}$</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>(1 – 3) $\times 10^{-2}$</td>
<td>(1 – 9) $\times 10^{-2}$</td>
<td>0.2 – 3.0</td>
</tr>
</tbody>
</table>

Among the studies performed on textile dyeing under supercritical CO$_2$ conditions, several projects have been conducted to develop clean processes for textile dyeing. (1, 2, 3) Concerning the leather, studies have already been conducted for the degreasing of sheepskins by supercritical CO$_2$. (4, 5, 6, 7, 8). On other study from China was done on several stages of leather treatment in supercritical CO$_2$. (9)

Executions modalities:

This study was conducted into 5 phases:
Phase 1: Establishment of a book of specifications. Bibliography and selection of the dyestuffs
Phase 2: Study of the parameters that influence the dyeing procedure of leather in supercritical CO$_2$
Phase 3: Optimisation of the operating conditions of the dyeing in supercritical CO$_2$
Phase 4: Transposition in semi-pilot scale
Phase 5: Pre-industrial evaluation (Technical, environmental and economical approach).
Results obtained:

The main parameters we have studied are:
- regarding the products utilized in the process:
  - the nature of the leather: We evaluate the behaviour of 3 crust leathers (calf, kip, sheep), and the impact of their thickness.
  - the nature of the dyestuff: The dyestuff used in the textile industry where tested.
  - the nature of the additive: The current additives used for supercritical CO₂ treatment were assessed.

- regarding the equipment:
  - the temperature
  - the pressure
  - their evolution during the treatment
  - the duration of the treatment

By using a labscale equipment and a semi pilot equipment the leather has been dyed. The picture below illustrates one kind of semi-pilot equipment

Semi-pilot equipment
The following pictures illustrate the results obtained in the leather section.

The green dyestuff we used, penetrates almost the entire thickness of the leather. The variation of the colour between the external and internal sides of the leather is linked with the initial leather.

Reference before dyeing

*Picture are not given at real scale*

Same leather after the treatment

*Picture are not given at real scale*
The following picture shows the homogeneity of the treatment operated on the leather.

The impact and interactions of these parameters have been assessed through:

- Physical and mechanical tests:
  - Measurement of the evolution of the size of the piece: This parameter stay equal before and after treatment.
  - Evolution of the colour with a colormatching equipment:

<table>
<thead>
<tr>
<th>Colour parameters</th>
<th>( \Delta L )</th>
<th>( \Delta a )</th>
<th>( \Delta b )</th>
<th>( \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Values relating to the reference</td>
<td>-28.18</td>
<td>-24.93</td>
<td>-38.96</td>
<td>+53.73</td>
</tr>
</tbody>
</table>

\( L \) is the lightness  
\( a \) is the red-green colour constituent  
\( b \) is the yellow-blue colour constituent  
\( \Delta E \) is the global colour difference.

These values have enabled us to choose the best covering dyestuff. We also checked with the apparatus the homogeneity of the colour, by analysing different zones on the leather.

- The penetration of the dyestuff was assessed by a microscopal study of the cross section of the leathers.
- Colour fastness to rubbing (NF G 52301)

<table>
<thead>
<tr>
<th>Number of cycle</th>
<th>100 (DRY)</th>
<th>50 (HUMID)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average measured on grey scale</td>
<td>4-5</td>
<td>2-3</td>
</tr>
</tbody>
</table>

In dry conditions the behaviour of the dyestuff is acceptable. When water is added to the rub, the values obtained shows a lack of adherence between the leather and the dyestuff, which was not noticed after the labscale treatment (average dry value: 4-5, humid value 3-4). The semi pilot conditions, which changed a little bit (use of a rotating equipment) could explain this behaviour. The contact with the leather and the reactor during the process can have affected the diffusivity of the dyestuff inside the leather, producing a dyestuff coat on the top of the leather.

- Light fastness (NF G 52 302, Xenotest):
The average obtained on blue scale is the value of 1. These very weak value (given on the semi finished material), show the instability of the dyestuff used.

- Tear strength (NF G 52 004):
The average value obtained is 4.3 daN / mm.

- Chemical analyses:
The leather use was already assessed to the current environmental requirements. The leather, once coloured, has correct properties.

<table>
<thead>
<tr>
<th>Nature of the analysis</th>
<th>Average values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (EN ISO 4045)</td>
<td>3.85</td>
</tr>
<tr>
<td>Azodyes (DIN 53316)</td>
<td>&lt; 30 mg/kg</td>
</tr>
<tr>
<td>Water and volatiles substances (NF G 52 202)</td>
<td>11.3 %</td>
</tr>
<tr>
<td>Extractibles substances (EN ISO 4048)</td>
<td>2.1 %</td>
</tr>
</tbody>
</table>

- The natural stretch of the leather was also checked by hand and is quite similar.
From the statements we achieved at a semi-pilot scale, we transpose them to the case of a 100 kg of leather treatment in order to have an economical approach of this technology.

The main advantages of the dyeing under supercritical CO$_2$ conditions are the non use of water, which induce no effluent treatments, and the possibility of recycling the CO$_2$ and the additive. The duration of the treatment is cut in half in comparison with a traditional dyeing treatment of a crust leather. Regarding energy consumption, the power consumption per kg of leather is 0.95 kWh. The investment in such an equipment is quite important.

Conclusion

In a context in which the use of water becomes more and more controlled and restricted, finding means to avoid it, is a big challenge. The supercritical treatments belongs to the possible new clean technologies to minimise the use of water and limit problems bounded with water effluent and preservation of natural resources.

This project has shown the possibility to realise a uniform dyeing of leather (in surface and almost in the cross section). The use of the semi pilot equipment change some properties of the leather in comparison with the labscale evaluation. This reinforces the interest to work on a dedicated equipment and on the dyestuff chemistry, to improve the affinity of the dyestuff with the support and its light stability. Developing this technology for all steps of leather manufacturing could greatly increase the interest in such an investment.

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