**SMA® Resins: A Wet Blue Suppleness & Softening Agent for Leather**

**Introduction**
This bulletin presents the advantages of using SMA® Resins for retanning to produce a supple and soft touch leather.

**Leather Retanning**
Retanning is an important step during the transformation of a hide into leather. The goal of this step is to give to the leather its final appearance and properties, which include hand, softness and mechanical properties. Optimal properties can not be obtained by a simple tanning with chromium.

As more tanners standardize their production methods, at a specific step (generally after the tanning), the batches are split according to the types and qualities of the different final products desired. Retanning confers to each hide its specific properties. Also, it can serve to homogenize the product, despite an input of different hides. Finally, retanning prepares the hide for the end treatments of dyeing, fatliquoring and finishing.

The tendency of the market is to make leathers more and more supple, with a fine and homogeneous grain which allows a soft finishing, such as aniline finishing for luxurious leather. The use of retanning agents like the SMA® Resins can help to obtain these kinds of properties.

**Introduction To SMA® Resins**
SMA® Resins are low molecular weight copolymers of Styrene - Maleic anhydride. SMA® 1000 and 2000 are copolymers with a styrene / anhydride ratio equal to 1/1 and 2/1, respectively.

The resins used for the retanning are aqueous solutions of the sodium salts of the SMA® Resins.

<table>
<thead>
<tr>
<th>Properties of SMA® Resins:</th>
<th>SMA® 1000 HNa</th>
<th>SMA® 2000 HNa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Clear and fluid liquid</td>
<td>Yellowing, transparent and fluid</td>
</tr>
<tr>
<td>Charge</td>
<td>Anionic</td>
<td>Anionic</td>
</tr>
<tr>
<td>pH</td>
<td>9 - 11</td>
<td>9 - 11</td>
</tr>
<tr>
<td>Solids (%)</td>
<td>39 - 41</td>
<td>34 -36</td>
</tr>
<tr>
<td>Viscosity at 30 °C (mPa.s)</td>
<td>&lt; 500</td>
<td>&lt; 500</td>
</tr>
</tbody>
</table>

SMA® NHa solutions are fully miscible with water. They are sensitive to strong acid and can precipitate at pH below 7.

SMA® Resins are compatible with the principal tanning agents, vegetal and synthetic products, sulfited or sulfonated fat-liquors and anionic dyestuff at pH conditions greater than or equal to 7.

**Advantages Of Using SMA® Resins**
1) The principal properties of a leather retanned with the SMA® Resins are:

- a very improved suppleness with
- a specific touch, softness and silky
- a particularly fine grain

Moreover the SMA® resins give a good and deep penetration of dyes and fat liquors. Mechanical properties obtained with the first Chrom tanning are not diminished after the retanning step.
These properties can be adjusted, depending on the final article needed, by the choose and the quantity of resins SMA® 1000 HNa or 2000 HNa, used.

<table>
<thead>
<tr>
<th></th>
<th>SMA® 1000 HNa</th>
<th>SMA® 2000 HNa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplesiness/flexibility</td>
<td>+++</td>
<td>++++</td>
</tr>
<tr>
<td>Smooth Grain</td>
<td>++++</td>
<td>+++</td>
</tr>
<tr>
<td>Touch/Softness</td>
<td>+++</td>
<td>+++</td>
</tr>
</tbody>
</table>

2) Interaction between SMA® Resins and Chromium: The measurement of the quantity of Chrome, released during the retanning treatment and after the acidification of the leather demonstrates that SMA® Resins are able to complex and fix the free Chromium present in the inter-fibrillar space. Figure 1 shows the release of chromium salts during the retanning treatment at different times.

When SMA® Resins are used, the amount of Chromium released decreases. For quantities of SMA® Resins higher than 2%, the Chromium released stays at the lower limit.

Clearly, SMA® Resins fix a large amount of the free Chromium in the leather.

3) Interactions Between SMA® Resins and Leather: Tanning with Chrome can promote the formation of linkages between the fibers of collagen. These linkages give the leather improved thermal stability and mechanical properties. The thermal stability of leather can be evaluated by the measurement of the temperature of denaturation, which is proportional to the level of crosslinking of the leather fibers.

The levels of fixation by SMA® Resins are higher than with the acrylics resins, during the retanning treatment, acidification, and after the fatliquoring.

The temperatures of denaturation of different samples (measured by DSC) are reported in Table 3.

In trials, the hides retanned with SMA® Resins have a temperature of denaturation lower than those of Wet-Blue but much higher than the crude hides. This indicates, SMA® Resins make linkages between the collagen fibers.

<table>
<thead>
<tr>
<th></th>
<th>Crude Hide Tanned with SMA® Resins</th>
<th>Hide Tanned with Chromium (WET - BLUE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of Denaturation °C</td>
<td>103</td>
<td>134</td>
</tr>
</tbody>
</table>
These interactions allow one, during a retanning with the SMA® Resins, to preserve the mechanical properties due to the initial Wet-Blue treatment with a good suppleness and silky touch.

Optimization of different process parameters is necessary to obtain the best results during retanning with SMA® Resins.

**Optimal Conditions For Using SMA® Resins**

By studying the kinetic absorption of SMA® Resins, the optimal time of reaction for a good fixation in the hide can be found.

After 30 minutes of drum rotation, the level of consumption reaches its maximum no matter the initial concentration of the SMA® Resin.

After 30 minutes of drum rotation, the level of consumption reaches its maximum no matter the initial concentration of the SMA® Resin.

The length of bath, on bath level, between 50% and 100% of total hide weight gives a good penetration of the SMA® Resins and increases their performances.

The initial neutralization, before retanning, at pH=5 is the best preparation for a total efficiency of the retanning with the SMA® Resins.

**Examples of the Use of SMA® Resins With Other Retanning Agents**

The trials performed in our laboratory show the existence of a synergy between the SMA® Resins and other types of retanning agents. Under the conditions of our evaluations: 2% of SMA® Resin and 5% of other retanning agents on a calf WET-BLUE 1.6/1.8 mm, we obtain consistency improved suppleness with the SMA® 1000 HNa or 2000 HNa.

**Conclusion**

The optimal conditions for using SMA® Resins for retanning, are:

- pH of neutralization (bath) = 5
- Length of bath 50 - 100%  
- Concentration of SMA® Resins = 2%  
- Time of rotation = 30 minutes

---

The information in this bulletin is believed to be accurate, but all recommendations are made without warranty since the conditions of use are beyond Cray Valley Company’s control. The listed properties are illustrative only, and not product specifications. Cray Valley Company disclaims any liability in connection with the use of the information, and does not warrant against infringement by reason of the use of its products in combination with other material or in any process.