Effect of Different Retanning Systems on Surface Properties of Leather

by

S.V. Kanth, A. Ipe, B. Madhan, R. Venba and A. Dhathathreyan*

Central Leather Research Institute
Adyar, Chennai-600020, India

Abstract

The present work attempts to analyze the surface properties of crust leathers processed using different syntans of the type phenol-naphthalene formaldehyde condensate, phenol formaldehyde, melamine formaldehyde, glutaraldehyde, styrene maleic anhydride, acrylic polymer, sulphone and heterocyclic N-methylol. Contact angles of liquid drops on the leather surfaces have been used to evaluate surface energy, acidity, basicity, polarity, work of adhesion and surface roughness. The surface energy component showed that the control crust leather without retanning is practically monopolar basic with $\gamma_s = 13.02 \text{ mN/m}$. Acrylic polymer retanned crust leather exhibited high basic character ($\gamma_s = 33.15 \text{ mN/m}$), while phenol formaldehyde retanned crust leather had the least values ($\gamma_s = 1.03 \text{ mN/m}$). The surface behavior towards rub fastness and adhesion of finish has been significantly altered by the retanning systems in leathers and showed a good correlation with the surface properties like surface charge, polarity, roughness and work of adhesion.

Introduction

Leather, being natural material has amphoteric behavior. The surface charge of the leather is a measure of its polar nature and capacity to react with polar substances. Generally surface charge densities depend decisively on the kind of tannage and are of particular importance for all post-tannage processes such as neutralization, retanning, wetting, dyeing and fatliquoring. The post tanning processes always involve treatments with compounds in their ionized form, i.e. in the form of charged particles, which react first on the surface, so that the surface charge gets modified, affecting in turn subsequent treatments. Hence the process is to be carried out in such a way that the surface charges of crusts facilities anchorage of the finishing chemicals.

Surface free energies have been correlated with many important properties of textiles. The total surface free energy of solid at equilibrium with vapor phase (indicated by $\gamma_{SV}$) can be estimated from the Young’s equation:

$$\gamma_{SV} = \gamma_{LV} \cos \theta + \gamma_{SL} \tag{1}$$

($\gamma_{SV}$ is also denoted as $\gamma_S$). The Young’s equation is also used to measure the individual $\gamma_{SL}$ (where $S$ is the solid phase or here leather and $L$ is the liquid) as shown in scheme 1.

Scheme 1: A liquid drop at equilibrium at the three phase contact line (SV, SL and LV)

Here $\theta$ is the contact angle made by any liquid in contact with the leather surface at the beginning of any operation. $\gamma_{SV}$ is the solid surface energy and $\gamma_{SL}$ is the interfacial energy between $S$ and $L$.  

* Corresponding Author - E-mail: chordchem@yahoo.co.in
Manuscript received July 14, 2006, accepted for publication November 22, 2006
TABLE I

Experimental Post Tanning Process

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>EXPERIMENTAL POST TANNING PROCESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>WASHING</td>
<td>200 % Water, 35°C 20 min pH 3.2</td>
</tr>
<tr>
<td></td>
<td>0.2 % Acetic acid, 85%</td>
</tr>
<tr>
<td>RECHROMING/</td>
<td>150 % Water</td>
</tr>
<tr>
<td>NEUTRALISATION</td>
<td>4 % Chrome syntan 60 min</td>
</tr>
<tr>
<td></td>
<td>1 % Neutralising syntan</td>
</tr>
<tr>
<td></td>
<td>1 % Sodium formate 20 min pH 4.2</td>
</tr>
<tr>
<td></td>
<td>1.0 % Sodium bicarbonate 3 x 10 min 30 min pH 5.0</td>
</tr>
<tr>
<td>RETANNING*</td>
<td>150% Water, 35°C 60 min</td>
</tr>
<tr>
<td></td>
<td>10% Retanning agent*</td>
</tr>
</tbody>
</table>

*DIFERENT RETANNING AGENTS

Experiment 1 - Control - No retanning agent
Experiment 2 - Acrylic polymer syntan
Experiment 3 - Phenol naphthalene formaldehyde condensate
Experiment 4 - Phenol formaldehyde syntan
Experiment 5 - Melamine formaldehyde syntan
Experiment 6 - Glutaraldehyde based syntan
Experiment 7 - Styrene maleic anhydride syntan
Experiment 8 - Sulphone based syntan
Experiment 9 - Heterocyclic N-methylol based syntan

<table>
<thead>
<tr>
<th>FATLIQUORING/DYEING</th>
<th>EXPERIMENTAL POST TANNING PROCESS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3% Acid black dye 60 min</td>
</tr>
<tr>
<td></td>
<td>10% Water, 35°C 60 min</td>
</tr>
<tr>
<td></td>
<td>6% Neats foot oil based fatliquor  60 min</td>
</tr>
<tr>
<td></td>
<td>1.0% Formic acid, 85% 3 x 10 min</td>
</tr>
<tr>
<td></td>
<td>10% Water, 35°C 30 min pH 3.5</td>
</tr>
</tbody>
</table>

The sample leathers were rinsed in water and piled over night followed by setting, drying, staking, trimming and buffing.

However, each of the energy term can be split into polar Lifshitz-Vander Waals and polar acid-base components. The approach of Van oss et.al.4 to evaluate the surface energies, have been used. According to this approach, surface free energy of a phase is expressed as a sum of polar Lifshitz-Vander Waals and polar acid-base components.

$\gamma_i = \gamma_i^{LW} + \gamma_i^{AB}$  \hspace{1cm} (2)

$\gamma_i$ in eqn (2) is also denoted as $\gamma_S$, $\gamma_i^{LW}$ is denoted as $\gamma_S^S$ (dispersive components) and $\gamma_i^{AB}$ is denoted as $\gamma_S^A$ (polar component).

The acid base component results from an electron donor (Lewis base) $\gamma_S^A$ and an electron acceptor (Lewis acid) $\gamma_S^A$ and is given as

$\gamma_i^{AB} = 2(\gamma_i^- - \gamma_i^+)^{1/2}$  \hspace{1cm} (3)

Therefore, the total interfacial energy between phases i and j are

$\gamma_{i,j} = \gamma_i^{LW} + \gamma_j^{LW} - 2(\gamma_i^{LW} \gamma_j^{LW})^{1/2} + 2[ (\gamma_i^- \gamma_j^-)^{1/2} + (\gamma_i^+ \gamma_j^+)^{1/2} - (\gamma_i^- \gamma_j^-)^{1/2} - (\gamma_i^+ \gamma_j^+)^{1/2} ]$  \hspace{1cm} (4)

Quantitatively surface roughness ($\Delta \theta$) is the contact angle hysteresis (variability of $\theta$ as shown in scheme 1) and is the result of the system under investigation with inhomogeneities. Work of adhesion is the attachment of substance A adhering to solid B. The work of adhesion could be defined in terms of Young’s equation $-\Delta G_{SL} = W_a = \gamma_S^A + \gamma_L^A - \gamma_S^A$ and the Young-Dupre relation $-\Delta G_{SL} = W_a = \Pi_{SV} + \gamma_L^A (1 + \cos \theta)$. The film pressure is neglected ($\Pi_{SV} = 0$), hence $-\Delta G_{SL} = W_a = \gamma_L^A (1 + \cos \theta)$, where $W_a$ is work of adhesion.
The surface charge of the skin is one of the most important factors determining the behaviors of the leather in wet operations such as retanning, fatliquoring and coloring. The dyeing processes are particularly susceptible to the nature and magnitude of the charge. Thus a variety of intensities and hues, as well as different degrees of penetration are possible. Leather acquiring a positive or negative charge will also depend on the type of fat liquor used. The charge of fatliquor is usually negative, as the most common water-soluble fatty substances are soaps or sulphates. The water-solubilising group is either the carboxyl or sulphonic group, and both convert the fatty radical with which they have reacted, into an anion. However, syntans also influence the surface charge of the leather. The physical performance of the leather is altered based on the ionicity of retanning systems.

Studies and measurements of contact angles of liquids on solids have great technological importance. Retanning using syntans is important in improving the compaction of leather and also to reduce the anisotrophiocity of leather with respect to the feel of the substance in different regions of the leather and also from one leather to another made from the same lot. There are a wide variety of syntans used in leather making and each one of them is claimed to impact certain functional property to the leather. It is of prime importance to know how each of the syntans behaves in influencing the surface characteristics of the leathers with respect to its charge, roughness and work of adhesion. An earlier work on surface energy of electrolyte solutions at air-liquid and solid-liquid interface, Maheshwari et al., suggested that electrostatic field on solid surfaces due to the presence of various ions is generally reflected in $\gamma_{SL}$. Further a number of studies on the induced effects on the interfacial energies of the solid-liquid interface have been reported. Hence in the present study an attempt was made to relate the surface interactions on leather surface in the presence of water, DMSO and hexadecane with that of the solid-liquid interfacial energy $\gamma_{SL}$.

The surface of the crust leathers is expected to be altered in terms of acidity, basicity, surface roughness. In the present study an attempt has been made to study the influence of different retanning agents on the surface characteristics of the leathers by measuring the changes in surface properties like surface free energy ($\gamma_S$), acidity ($\gamma_S^+$), basicity ($\gamma_S^-$), polarity ($\gamma_S^p$), surface roughness ($\Delta\theta$) and work of adhesion ($W_{ad}$).

### EXPERIMENTAL

#### Reagents and Chemicals

Basic chromium sulfate (BCS) and post tanning and finishing chemicals used for the manufacture of crust and finished leathers are of technical grade. Other chemicals used for the study are of analytical grade.

#### Experimental Trials

Conventional chrome tanned goat leathers (27 pieces) from a same lot of similar weight range, size and grade were selected for the study. The leathers were sammed and shaved to 1.0 mm thickness. Three samples, cut into 30 X 30 cm² size samples from the butt region were taken for each trial and the quantity

---

**TABLE II**

<table>
<thead>
<tr>
<th>Crust Material: Goat Dyed Crust</th>
<th>Coats*</th>
<th>Finish: Resin Pigmented Black</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Products</td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>Cationic Oil Ground</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cationic Wax</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cationic PU</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cationic Pigment - Black</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>800</td>
<td>480</td>
<td>500</td>
</tr>
<tr>
<td>Pigment - Black</td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wax Emulsion</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waxy Soft Protein Binder</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly Urethane Emulsion</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Medium Soft Resin Binder</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soft Resin Binder</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filler</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Based CAB Lacquer</td>
<td>500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feel Modifier - Wax Based</td>
<td>50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* - Numbers mentioned are g/L of season coat
of chemicals offered for the post tanning process was based on shaved weight. The samples were processed into upper leathers as per the process described in Table I. The effect of syntans (retanning agents) on surface charge, surface free energy, surface roughness and work of adhesion of dyed crust were studied. The samples were finished as per the process described in Table II. Finish Adhesion and fastness to rubbing was carried out on finished leathers.

Measurement of Static Contact Angle:
The contact angles of water, DMSO and hexadecane at the leather surface were measured using a custom built instrument. Measurement of contact angle was done by projecting the image of the liquid drop on a leather surface and onto a screen and the contact angle was accurately measured. The experimental error in \( \theta \) was ±0.1 degree. When the drop of liquid is resting on solid surface like leather, the drop which forms a contact angle, may be considered as resting in equilibrium by balancing the three forces involved namely the interfaced tensions between solid liquid (SL), liquid vapor (LV) and solid vapor (SV). The angle within the liquid phase is known as contact angle \( \theta \) or wetting angle 14 of the leather. Each value of \( \theta \) was the mean of at least 3 measurements taken at each point of the three numbers of leather surface. Further, at least 5 different locations were taken on the surface and the average of 15 measurements were then used.

Measurement of Surface Roughness
Roughness of the leather surface was measured by the formula \( \Delta \theta = | \theta_a - \theta_r | \), where, \( \theta_a \) is advancing angle and \( \theta_r \) is receding angle as shown in scheme 1. The hysteresis (change in \( \theta \)) formed due to inhomogeneity of the leather surface was measured using static contact angle.

Measurement of Work of Adhesion
The work of adhesion can be defined from Young’s equation and Young-Dupre relation, \( W_a = \gamma_{LV} (1 + \cos \theta) \), where \( W_a \) is work of adhesion that was measured using contact angle.

Measurement of Adhesion of Finish
Samples from all the retanned leathers of appropriate size (5 x 14 cm) were cut from the official sampling position 15 and were tested according to IUF 470 16.

**TABLE III**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water</th>
<th>DMSO</th>
<th>Alkane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control - No retanning agent</td>
<td>61</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Acrylic polymer syntan</td>
<td>38</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>Phenol naphthalene formaldehyde condensate</td>
<td>61</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Phenol formaldehyde syntan</td>
<td>83</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Melamine formaldehyde syntan</td>
<td>68</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>Glutaraldehyde based syntan</td>
<td>69</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Styrene maleic anhydride syntan</td>
<td>67</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>Sulphone based syntan</td>
<td>63</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Heterocyclic N-methylol based syntan</td>
<td>69</td>
<td>11</td>
<td>0</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSIONS**

Contact Angle and Surface Parameters of Leather
From the contact angles of the water and two liquids, DMSO (medium non-polar) and hexadecane (non-polar) made with leather surfaces as shown in Table II, surface polar component \( \gamma_{Sp} \), dispersive component \( \gamma_{Sd} \), acidic and basic components \( \gamma_{S-}, \gamma_{S+} \) of the surface energy \( \gamma_S \) of the film were determined. The pores, crevices and capillaries contributed by different retanning agents on the leather surface reflect the extent of roughness that was measured. Schwartz and Garoff 18 and Morrow 19 used capillary rise concepts to describe hysteresis due to surface roughness. Timmons and Zismann 20 attributed hysteresis to micro porosity of the solids, because they found hysteresis to depend on the size of the liquid molecules or associated cluster of molecules. The measurement of a single static contact angle to characterize the interaction is no longer thought to be adequate. For any given solid/liquid interaction there exists a range of contact angles. The work of adhesion between a liquid and a solid is actually the Gibbs free energy change per unit area upon separating the two surfaces. Work of adhesion is the work required to pull apart 1 cm² interface of solid and liquid. Good wetting will be sufficient to generate a good adhesive bond between two substances. Adhesion to an abraded or rough surface is improved because of microscopic or sub microscopic crevices and pits into which a coating could penetrate and even gain a kind of mechanical foothold. An abraded surface with many crevices, pits and irregularities has a higher surface area than the unabraded, smooth surface. Usually larger surface area of contact facilitates adhesion.

The surface related parameters viz., surface energy, acidity, basicity, roughness and work of adhesion of different retanned leathers has been calculated based on the contact angles that the leathers made with different liquids, viz., water, DMSO and
hexadecane are listed in Table IV. By observing the values obtained, it is seen that the surface free energy ($\gamma S$) is found to be highest for acrylic polymer retanned leathers (53.18 mN/m) and least for phenol based retanned leather (31.61 m N/m). For all the other samples, the $\gamma S$ values are between 35 and 45 mN/m showing the surface energy does not dramatically change in the leathers. However $\gamma S -$ show larger deviations. The $\gamma S -$ values are high for acrylic polymer (26.63 m N/m) and least for phenol based syntan (4.60 m N/m). Acrylic polymer seems to be highly polar which is indicated from the high $\gamma S -$ values.

The acidic component ($\gamma S ^+$) is more or less the same for all the retanned systems with the values ranging from 4.9 to 5.4 m N/m. $\gamma S$, where as the basicity indicator shows gradation. Here the values are in the following increasing order with values going from 1.03 - 33.15 m N/m. Phenol retained leather < sulphone retained leather < glutaraldehyde retained leather < heterocyclic N-methylol retained leather < styrene maleic anhydride retained leather < phenol naphthalene condensate retained leather < control (without retanning) < acrylic retanned leather. Surface roughness of the crust leathers influence finishing and surface related parameters. With respect to $\Delta \theta$ values, control has the highest values (62˚). The values are in the following increasing order with values ranging from 30˚ to 65˚. Melamine retained leather < phenol naphthalene condensate retained leather < glutaraldehyde retained leather < sulphone retained leather < styrene maleic anhydride retained leather < heterocyclic N-methylol retained leather < acrylic retanned leather < control. Similarly, the work of Adhesion (Wa) values is in the following increasing order.

Phenol naphthalene retained leather < Melamine and glutaraldehyde retained leather < acrylic retanned leather < sulphone retained leather < styrene maleic anhydride < heterocyclic N-methylol retained leather and control leather.

Meaningful interpretations of absolute values of surface energy can be carried out only when sampling is done on a large number of skins and different retanning combinations. However, the aim of the present study is to explore the effects of different retanning agents. Hence in the present analysis, difference in the surface energies between the control and the differently retanned leathers has been used in various plots. In order to get a clear trend of all the surface characteristics of different leathers, it was necessary to draw a correlation among various parameters as described in Figures 1, 2, and 3. Hence correlation plots are drawn by relating $\gamma S$ and $\gamma S -$; $\Delta \theta$ and Wa; $\Delta \theta$ and $\gamma S -$.

**Correlation between Surface Free Energy ($\gamma S$) and Basicity of Surface ($\gamma S -$) of Leathers Retanned with different Syntans**

Figure 1 describes the surface free energy and basicity for various retanned leathers as calculated from the static contact angle measurements. Acrylic polymer retanned leather has highest surface free energy and highest basicity compared to all the other retanned leathers. The least in the series (phenol based retanned leather) has the lowest surface free energy and basicity. Control and phenol naphthalene condensate retanned leathers show $\gamma S$ and $\gamma S -$ in the similar range. Leathers retanned with melamine, glutaraldehyde, styrene maleic anhydride and heterocyclic N-methylol can be grouped together having
surface free energy lower than control. Sulphone retanned leather form another category having surface free energy greater than phenol based retanned leather. Highest surface energy and basicity of leather will influence the adhesion of finish to leather and in turn reflect on the wet and dry rub fastness of the finished leathers.

**Correlation between Surface Roughness (Δθ) and Work of Adhesion (Wa) of Leathers Retanned with different Syntans**

Figure 2 relates the surface roughness and work of adhesion for various retanned leathers calculated from the contact angle, polarity, basicity and surface energy values. For control sample, Δθ was found to be high. This indicates that surface of leather without any syntan is rougher. This could be easily explained by the fact that the control leather is not fuller and syntans bring in filling effect to leather, which in turn can reduce the crevices and pits in the leathers. Melamine, glutaraldehyde and phenol naphthalene condensate retanned leathers have the lowest Δθ values, which indicate that they are better filling syntans. Glutaraldehyde retanned leathers show gradation for fullness in leathers. It is well known that glutaraldehyde self polymerizes and could have deposited on the grain exhibiting higher smoothness in the leathers. Styrene maleic anhydride, phenol based, heterocyclic N-methylol and sulphone retanned leathers can be grouped together to have slightly lower Δθ when compared to control and to have smoothness less than that of phenol naphthalene and glutaraldehyde retanned leathers. Sulphone based and styrene maleic anhydride retanned leathers will have better filling characteristics in leather than phenol and heterocyclic N-methylol syntan based retanned leathers among the same group. From Δθ values fullness of acrylic retanned leathers is lower than phenol based and heterocyclic N-methylol retanned leathers. Melamine retanned leathers, glutaraldehyde retanned leathers and phenol naphthalene condensate retanned leathers have similar surfaces. Hence they will contribute to more fullness in leather and are found to have significant smoother surfaces than control. The work of adhesion is the highest for heterocyclic N-methylol retanned leathers comparable to control. Phenol based retanned leathers also show higher values. These leathers have lower smoothness as seen from the roughness values. Hence, more energy is required to pull the finish out of the leather. The lowest of the values of work of adhesion is for phenol naphthalene condensate, melamine and acrylic polymer retanned leathers as they have lower Wa values. Also these leathers have more smoothness as seen from the roughness values, hence these leathers contribute to maximum fullness in leather and less energy is required to pull the finish out of the leather.

**Correlation between Surface Roughness (Δθ) and Polarity (γSP) of Leathers Retanned with different Syntans**

Figure 3 describes the surface roughness and polarity for various retanned leathers. Control has the highest Δθ value indicating that the surface is rougher. Acrylic polymer retanned leather has highly polar surface, when compared to control and has a less smooth surface (as compared to melamine retanned leather). This indicates that the acrylic retanned leather will adhere, finish better to leather better than control as the polarity of the surface is lower for control even though surface is rough. Roughness alone cannot directly influence finishing because in control piece one can have variations in pore sizes, pore size distribution and surface charge. Phenol based retanned leather on the other hand is an extreme, which has the least polar values when compared to acrylic polymer retanned leather (highest polar values) and the surface is less smoother compared to control. Phenol retanned leather is only little polar when compared to Heterocyclic N-methylol retanned leather (higher Wa) but very less when compared to control. Sulphone based retanned leather lies intermediate between phenol based retanned leather and heterocyclic N-methylol based retanned leather. Styrene maleic anhydride retanned leather has lesser Δθ values when compared to control showing that it is slightly smoother but is less polar when compared to acrylic polymer retanned leather. For phenol naphthalene condensate retanned

**TABLE V**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Finish Adhesion</th>
<th>Crust Leathers</th>
<th>Finished Leathers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wet rubbing</td>
<td>Dry rubbing</td>
<td>Wet rubbing</td>
</tr>
<tr>
<td>Control - No retanning agent</td>
<td>7.6±0.34</td>
<td>4.5±0.25</td>
<td>5</td>
</tr>
<tr>
<td>Acrylic polymer syntan</td>
<td>8.6±0.28</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Phenol naphthalene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>formaldehyde condensate</td>
<td>6.82±0.42</td>
<td>4±0.5</td>
<td>5</td>
</tr>
<tr>
<td>Phenol formaldehyde syntan</td>
<td>5.48±0.21</td>
<td>4±0.25</td>
<td>5</td>
</tr>
<tr>
<td>Melamine formaldehyde syntan</td>
<td>6.36±0.13</td>
<td>4.5±0.5</td>
<td>5</td>
</tr>
<tr>
<td>Glutaraldehyde based syntan</td>
<td>6.32±0.27</td>
<td>4.5±0.25</td>
<td>5</td>
</tr>
<tr>
<td>Styrene maleic anhydride syntan</td>
<td>6.42±0.18</td>
<td>4.5±0.5</td>
<td>5</td>
</tr>
<tr>
<td>Sulphone based syntan</td>
<td>6.12±0.43</td>
<td>4±0.25</td>
<td>5</td>
</tr>
<tr>
<td>Heterocyclic N-methylol based syntan</td>
<td>6.23±0.26</td>
<td>4.5±0.25</td>
<td>5</td>
</tr>
</tbody>
</table>

*JALCA, VOL. 102, 2007*
leathers because of less
melamine retanned leather has the smoothest surface of all the
leathers because of less $\Delta \theta$ value but $\gamma^p$ value is intermediate
between the highest polar component (acrylic polymer
retanned leather) and phenol based retanned leather, which is
lowest in polarity.

### Influence of Syntans on the Fastness and Adhesive Properties of Leather

The fastness to wet and dry rub and finish adhesion of
different retanned leathers before and after finishing are given
in Table V. It is basically mistaken to assume that the finish
formulation alone directly influences the rub fastness and
finish adhesion of the final leathers. But there are other
important factors like surface roughness, polarity and work of
adhesion, which have greater impact on the rub fastness of
leather. Therefore, for rub fastness purposes, a comparison was
made with a control leather without any retanning, which has
a rougher surface ($\Delta \theta$ was high), but basicity $\gamma^b$ was low and
work of adhesion $W_a$ was the highest. Leather with rougher
surface can be expected to exhibit better rub fastness. However
the leather (acrylic retanned leather) with slightly lower
roughness and work of adhesion but with better polarity and
basicity had the best of the rub fastness properties when
compared to control. Phenol retanned leather exhibited lowest
fastness. Also all the other leathers had comparatively lower rub
fastness than acrylic retanned leathers. This goes with the
assumption that leathers with strong polarity not only wets the
leather faster buts also anchors better to finish. The results are
synonymous to the adhesion of finish to leather as given in
Table V. Therefore the adhesion of finish to crust also plays a
decisive role based on charge than on the roughness of the
leather. Hence it is often observed that finishes well
anchored to leather exhibit better rub fastness as seen
in this also. From Table V, it is evident that adhesion of finish
to different retanned leathers is slightly lower than acrylic
retanned and control leathers. Different retanned leathers,
in general exhibited similar trend for rub fastness and adhesion.
The effect on ageing on the rub fastness properties measured after
ageing for 6 months has been found to be similar to the values
before ageing.

From the interpretations discussed we can conclude that the
different types of syntans used in the retanning process will
have definite surface characteristics and the surface properties
of these retanned leathers influence the finish properties of the
final leather. An understanding of such phenomenon is
esential to understand the finishing process as the crust carries
a surface charge or polarity, surface energy, roughness and work
of adhesion and these properties directly influence the
finish properties of leather. Hence the study of these properties
will assist the leather technologists to have thorough
understanding of the crust and develop finishes that suit their
needs and a knowledge base to improve the finish properties
of leather.

### Conclusions

The study shows that the surface energy value, made of two
components, the dispersive and polar values, can act as good
indicators to study the surface behaviour and the degree of
surface charge of the leather. Further, the polar component being
more sensitive of the two, it acts as a clear measure of the charge
contributed by different retannins to leather and has been used to
study the variation of surface charge from different retannins. The
present investigation shows that the phenol based retanned leather
has a low surface energy value, compared to acrylic polymer
retanned leathers which has highest values. Acrylic polymer
retanned leathers are highly polar. Surface of leather without
syntan is rougher. Melamine and acrylic polymer retanned
leathers have smoother surfaces and contribute to more fullness in
leather. The surface charge values that show excessively high
positive charge in the leather do not combine with the finish
properly. In the case of excessively low positive charge, the finish
may penetrate into the leather and lose its part of its hiding effect.
From the surface energy values of leathers with different retanning
agents, it can be inferred that higher the polarity and lower
surface energy, higher will be the adhesion for finishing. This is
because when the retanning agents contribute to high pH, the
leather is slightly cationic or neutral. Hence the leathers (acrylic
retanned leather) with higher polarity and basicity, moderate
roughness and work of adhesion, good adhesion of finish was
observed. Therefore the adhesion of finish to crust also plays a
decisive role based on charge than on the smoothness of the
leather. Hence it is also observed that finishes well anchored to
leather exhibited better rub fastness.

This observed difference could be an added advantage in
selecting the right type of retanning system for desired
finishing system. Thus a high quality finishing system can be
ensured by the choosing the right type of retanning systems
that contribute to the surface properties of the leather, which
will improve the cutting value of leather for better value
addition. Thus a quantification of surface charge density
through the surface energy, study of surface roughness and
work of adhesion can become innovative tools of the future
leather processing.

### Acknowledgement

The authors thank Dr. T. Ramasami, Director, Central Leather
Research Institute for his constant encouragement and
suggestions in the development of this process. Authors wish to
thank Dr. R. Rajaram for the physical testing measurements
and Ms. R. Maheshwari, Chemical laboratory for her timely
help with the contact angle measurements.

### References

1. Ortega, A. O., Jimenaz, M. E., Chibowski, E. and Caballero,
2. Jimenez, M. E. and Suarez, A. C.; Colloids and Surfaces, 97,
17. Determination of color fastness to rubbing (Croaking test); *Indian Standards*, IS 6191 (LF: 10), 1971.