Exploring New Chemistries for Sustainable Leather Processing

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SBU – Leather Chemicals
Balmer Lawrie’s efforts towards sustainability

Input raw materials

Improving chemicals manufacturing processes

New products for sustainable leather

- All restricted Substances has been removed
- Suppliers are to be comply with sustainable standards
- Zero Liquid Discharge
- Minimising water and effluents
- No emission
- Safe and Healthy environment (OHSAS)
- No restricted substances
- No health hazards
- Maximising use of renewable raw materials
This presentation will highlight some of the new approaches not pertaining to just change of substrates but new reactions with possible different outcomes-BL inhouse works.

Technological Translations, new chemistries from other research institutions in various fields with an intention to be adoptable is highlighted.
Fatliquor- some new Ideas
Reactive Surfactants

1. Transurfs

![Transurfs diagram]

2. Inisurfs

![Inisurfs diagram]

3. Surfmers

![Surfmers diagram]

Chemically bound surfactants to Latexes – for enhanced stability and performance.
1. Preparation of polymerisable surfactant/Surfmer

Polymerisable bond

Itaconic acid is used to generate the surfmer. Lauryl itaconate was synthesized and used as a surfmer.

Our commercial products, Balmol SWG, PG1, UP101 are formulated with modified surfmers.
or PEG Itaconates

can undergo Michael Addition

* Ref: Prof. Sherrington papers, Dept. of Chemistry, University of Strathclyde, UK, & Prof. S Ramakrishnan papers, IPC, IISC, Bangalore on Hyperbranched & polymermerizable surfactant.
The unsaturated vegetable fat if not properly guarded with antioxidants lead to oxidation of Cr(III) to Cr (VI)

The oxidation of lipids could accelerate the oxidation of chromium (III) to chromium (VI). Likewise, the presence of chromium (VI) ions could accelerate the oxidation of lipids.

The oxidation rates of fatty acids:

- As the number of double bonds increases, the rate of reaction increases.

<table>
<thead>
<tr>
<th>Type of Fatty Acid</th>
<th>Rate of Reaction Relative to Stearic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>18:0</td>
<td>1</td>
</tr>
<tr>
<td>18:1Δ9</td>
<td>100</td>
</tr>
<tr>
<td>18:2Δ9,12</td>
<td>1200</td>
</tr>
<tr>
<td>18:3Δ9,12,15</td>
<td>2500</td>
</tr>
</tbody>
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Syntheisized fat based fatliquor – Another application of surfmer

Indian Patent No. 282682

- This work describes the method for treating leather with excellent light fastness with a retan fatliquor containing a dispersion of a selected amphiphilic copolymer, substantially free from organic solvents.

- It is formed from a predominant amount of at least one hydrophobic monomer/surfmer and another copolymerizable hydrophilic monomer.

- This type of leather being particularly suitable for use in vehicle upholstery, upper leathers etc.
Inverse Emulsion Technique - copolymer with surfmer as co monomer

Sodium salt of surfmer, a polymerisable surfactant
( C12-C18
Esters with polymerisable vinyl end groups)

Water soluble monomer
Water soluble initiator
Here surfmer acts as a stabiliser

Here surfmer acts as a Continuous phase. A very little amount of water with initiator dissolved in it is added just to form the interface.

2. Copolymerising surfmer with a hydrophilic monomer
Mole ratio of surfmer : Acrylic acid is 1.2:1
The Copolymer structural formula prepared above has a maximum loading of 80% by weight ratio of surfactant in its copolymer composition.

The structural elucidation have been done with $^1$H NMR.

Such a high molecular weight polymer surfactant is very much useful in emulsifying most of the oils.

“Surfmer based” Patent No. 282682, granted.
- To Improve Cr-fixation (in Leather and exhaust bath)
- To avoid Cr-VI formation
Hyperbranched polymers are under the class of Dendritic macromolecules. In contrast to dendrimers, hyperbranched polymers are not perfectly monodisperse.
Synthesis approach

Here the diacrylate is a surfmer

Hyper branched polymer - HBP

This is a patented process from Balmer Lawrie. This process is based on recently developed a facile and generic synthetic methodology the “Strathclyde methodology”. The Hyper branched polymer is crosslinked with surfmer.

Leather trial results

<table>
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<tr>
<th></th>
<th>Trial with 3% HBP</th>
<th>Conventional process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium in the bath</td>
<td>3238.5 mg/L</td>
<td>4409.0 mg/L</td>
</tr>
</tbody>
</table>
Polycarboxylates – Free Chrome Binding agent in Leather

Example for *surfmer* application - **Polycarboxylate ether** - For avoiding Chromium (VI)

Polymerisable bond

Allylether of PEG (**APEG**) ester copolymerized with other monomers to make **Polycarboxylate ether**

Other acrylic monomers used for copolymerizing are Acrylamido 2- methyl propane sulphonic acid-

The vinyl ends in the APEG can form Michael Adduct with Collagen
Application of the Chrome fixing agent Polycarboxylate

"Hyperbranched Acrylic Copolymers ” Patent No. 286195

Our product in this range is Balfix PAC 20

Polycarboxylate is used after adding the chrome tanning agent;

The perfect dosage is 2%;

The basifying pH is 4.0~4.2.

In leather, Cr (VI) after ageing not detected and free chrome oxide is reduced to less than 50 ppm
BL process for wet white tanning
Wet-White process flow

Pickling  →  Glut- Tanning  
5 hrs   -  4 %  →  Organic Tanning  
1-2 hrs  
WW* -  6 %  →  Basification

Wet-White crust process flow

Neutralisation  →  Fatliquoring  →  Retanning  →  Fixing

* WW-  Wet white special combination of Balsyn DRW and Balsyn DDS  -  products to improve tanning in combination with Gluteraldehyde
Properties  Wet white and Crust leather

Leather Properties
Wet White

- Excellent grain flatness
- Whitish appearance
- Very tight grain
- Shrinkage temperature ~94 C
- Suitable for shoe upper and fancy leathers, Lining and softer articles

Physical Properties
Strength properties are comparable with conventional system. This process commercially running in some Tanneries in Ambur and other parts of India.
Finishing - new chemistries related to sustainability
New chemistries in finishing chemicals towards sustainability

Urethanes are made by using different blocked isocyanates and diols.

\[
\begin{align*}
&\text{OCN} - R - \text{NCO} + \text{HO} - R' - \text{OH} \rightarrow \\
&\quad \text{R} - \text{NCO} - \text{R'} - \text{O} - \text{C} - \text{R} - \text{NCO} - \text{R'} - \text{O} \quad _n
\end{align*}
\]

Yoshida et al have also reported synthesis of carbamates through the one-pot reaction of amines with alkyl halides using gaseous CO\(_2\).


A mixture of amine and alkyl halide was placed in a 100 cm\(^3\)-autoclave under pressure of carbon dioxide (40 atm;) at 70 °C for 48 h.

\[
\begin{align*}
\text{Et}_2\text{NH} + \text{CO}_2 & \rightarrow \text{Et}_2\text{NCOO}^- + \text{H}^+ \\
\text{Et}_2\text{NCOO}^- + \text{R} - \text{X} & \rightarrow \text{Et}_2\text{NCOOR} + \text{X}^- 
\end{align*}
\]
Formation of tri urethanes by this reactions with gaseous CO$_2$

Bio based urethanes
Urethanes can be made from sugars which will reduce carbon foot print

Ref: Dr. Berta Vega et.al from Covestro, NVVT Symposia 2016

Ref: Manoj R. Nair and V.C.Malshe, Paint India, November 1999
Gabriel Synthesis for Amination

Catalytic amination of alcohols involves the synthesis of amines by means of the so-called borrowing hydrogen methodology,

Ref: Matthias Beller et al. ChemCatChem 2011, 3, 1853 – 1864
The possible pathway for amination would be borrowing hydrogen methodology.

Ref: Matthias Beller et.al ChemCatChem 2011, 3, 1853 – 1864
Preparation of polyester diols from CO$_2$.

CO$_3^{2-}$- promoted C–H carboxylation

C–H + M$_2$CO$_3$ \rightleftharpoons M$^+$C$^-$ + MHCO$_3$

M$^+$C$^-$ + CO$_2$ \rightarrow C–CO$_2$M

C–H + CO$_2$ \rightarrow C–CO$_2$H

C–H + CO$_2$ + ROH \rightarrow C–CO$_2$R + H$_2$O

Fructose

\[ \text{HO} \quad \text{O} \quad \text{C} \quad \text{OH} \]

HMF

\[ \text{O} \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \]

Furfural

Oxidation

\[ \text{HO} \quad \text{O} \quad \text{C} \quad \text{OH} \quad \text{CO}_2 \quad \text{OH} \]

2-furoic acid

\[ \text{HO} \quad \text{O} \quad \text{C} \quad \text{OH} \quad \text{CO}_2 \quad \text{OH} \]

FDCA

Lignocellulose

\[ \text{Industrial} \quad \text{process} \]

\[ \text{Difficult} \]

2-furoic acid, from furfural, PEF, substitute of PET
Researchers have shown that \( \text{Cs}_2\text{CO}_3 \) can deprotonate alkynyl, allylic, and activated heteroaryl C–H bonds with \( \text{pK}_a \) values of up to 27. In this synthesis it is possible to deprotonate C-H bonds of \( \text{pK}_a \) value- 35 with carbonates.


\[
\text{C–H} + \text{M}_2\text{CO}_3 \rightleftharpoons \text{M}^+\text{C}^- + \text{MHCO}_3
\]

RMgX – Grignard reagent – Carbon centred nucleophile

Caesium salts do typically have lower melting points
CO$_2$ utilization cycle

It is similar to an un-substituted furan, the pKa of the C–H at the 5 position of furan-2-carboxylate is \(~35\).

In this synthesis it is hypothesized that CO$_3^{2-}$ would deprotonate furan-2-carboxylate if the reaction were performed in a molten salt with a high concentration of alkali cations to stabilize the conjugate base by ion pairing.

When we launched the first indigenous rocket SPV 3, when we successfully sent Agni and tested nuclear weapons in Pokran, I was really very happy. But today when I see children run around and cycle with the artificial limbs we designed, it is sheer bliss.

Dr. A.P.J Kalam

"I had seen these children struggling with the artificial limbs that weighed at least 4 kg. My team made one with composite heat materials used for rockets. This one is 10 times lighter,"

Technological translation from ISRO
Rockets to Polio Crutches
Photochemistry of Vision

rhodopsin $\xrightarrow{h\nu}$ rhodopsin* (+ nerve impulse?)

opsin $\xrightarrow{-H_2O}$ retinal isomerase

11-cis-retinal $\xleftarrow{\text{retinal isomerase}}$ all-trans-retinal

several dark processes $\xrightarrow{H_2O - \text{opsin}}$

G.Wald (Nobel Laureate in Physiology and Medicine, 1967)

Molecular Switches

Visible light

retinal

$\text{cis}$
A rotaxane consists of a "dumbbell shaped molecule" which is threaded through a "macrocycle"

These molecules can be considered for film formation. They are formed by different approaches like capping and clipping

Ref: https://en.wikipedia.org/wiki/Rotaxane
Ref: Soong-Hyun from Department of Chemistry, Michigan State University, 2004
Ref: Nobel lecture: Bernard L. Feringa, Nobel Laureate in Chemistry 2016
Plausible Applications in Leather for Future
Second Generation Molecular Motor

Molecular Design

enhancing the speed

from 1 rotation/hour to more than 10 million rotations/sec
The above is a photocurable Rotaxane with excellent mechanical properties and self-healing capabilities. This concept can be applied for exotic and costly leathers.

Ref: US patent 20140080936
New chemistries Discussed So Far

- Polymerisable surfactants – Surfmer in fatliquors
- Hyper branched polymers as chrome fixing agents & acrylic syntans
- Utilization of CO2 in making polyester polyols and isocyanates from Biosources for making PU
- Rotaxanies in self healing finishing
Surfmer - Reactive surfactants applications from Balmer Lawrie - BL

- Reconstituted fat was synthesized with better light fastness and less fogging.

- Hyperbranched polymers based on surfmers helps in penetration of free chrome and helps in binding chromium with collagen. These surfmer based polymer avoids Cr(VI) formation.
Thank you all for your patience