बामर लॉरी एण्ड कं. लिमिटेड
(भारत सरकार का एक उद्यम)

Balmer Lawrie & Co. Ltd.
(A Government of India Enterprise)

SINCE 1867

GREEN CHEMICALS FOR CLEAN AND SUSTAINABLE LEATHER PROCESSING

Mr J K Basu & Dr. V.Vijayabaskar

SBU – Leather Chemicals

LERIG 2016

SINCE 1867 150 years of commitment and beyond...

BALMOL BALSYN

MEMBER OF LEATHER WORKING GROUP

Outline

BL Novel works pertaining to-

- **Improvement of Cr-fixation**
- **Cr-Free tanning –new approaches**
- **Fatliquoring- New Ideas**
- **Discussion on SCCP-A persistent quantification problems**

New green products and Application on leather

- **Pickle-free tanning**
- **Wet-white leather**
- **Fatliquor-Eco-update**
- **Syntan-Eco-update**

Future Challenge

Cr-Tanning

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The element Chromium is neither good or bad !

Elementary Chromium	⇔	Trivalent Chromium	⇔	Hexavalent Chromium
Cr(0)		Cr(III)		Cr(VI)
		 		 
chromium plated articles & stainless steel: => corrosion resistant => food contact cleared => surgical implants		Pigment Green => insoluble, not bioavailable => CLP „not hazardous"		Chromium Picolinate => soluble => essential trace element => dietary supplement		Intermediate in metallurgy & chemical synthesis => high solubility, bioavailable => acute toxic, CMR => strong sensitizer

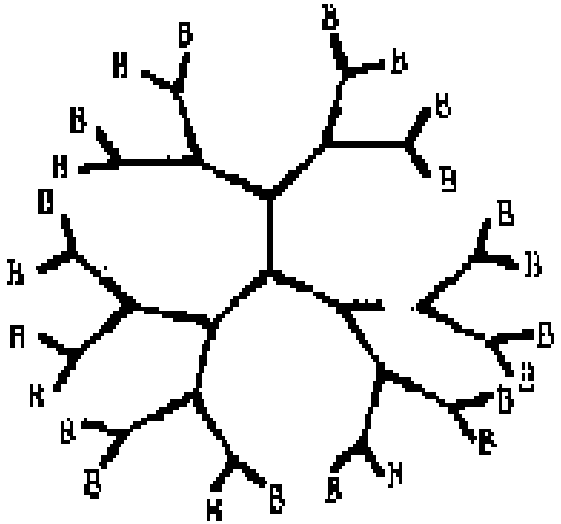
* Dr. Dietrich Tegtmeyer, Chairman IUR , IULTCS lecture Aug 2013

BL Approach-Improvement in Cr fixation

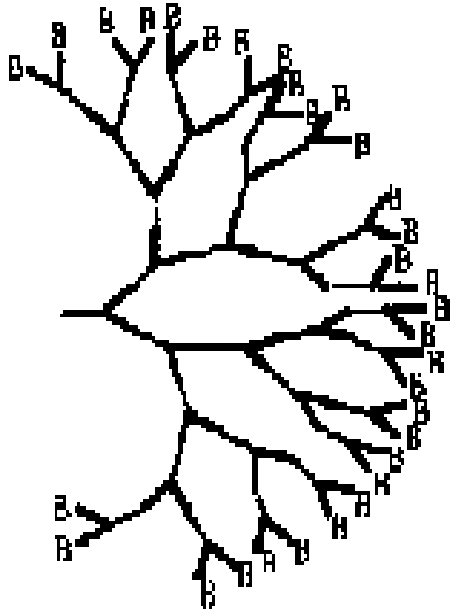
Recognize what is not absorbed and coax the unbound chromium to bind through structural modification-

- **Use of Novel concept of Hyperbranched polymers**

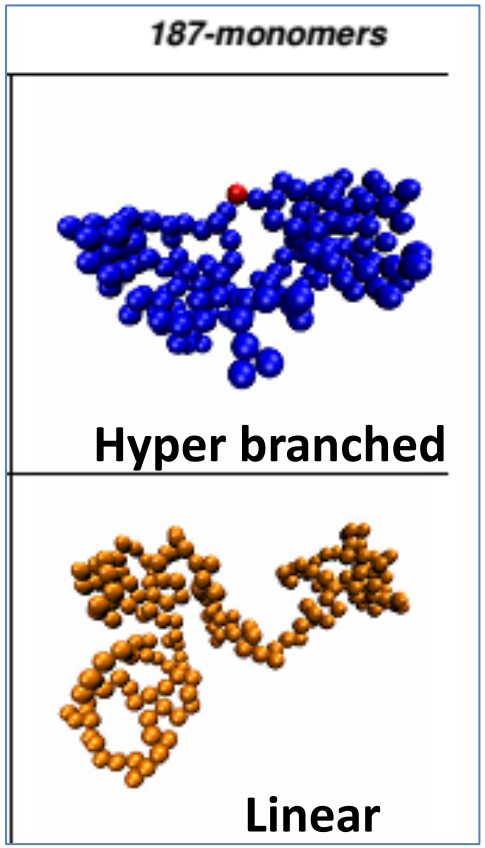
Structural representation

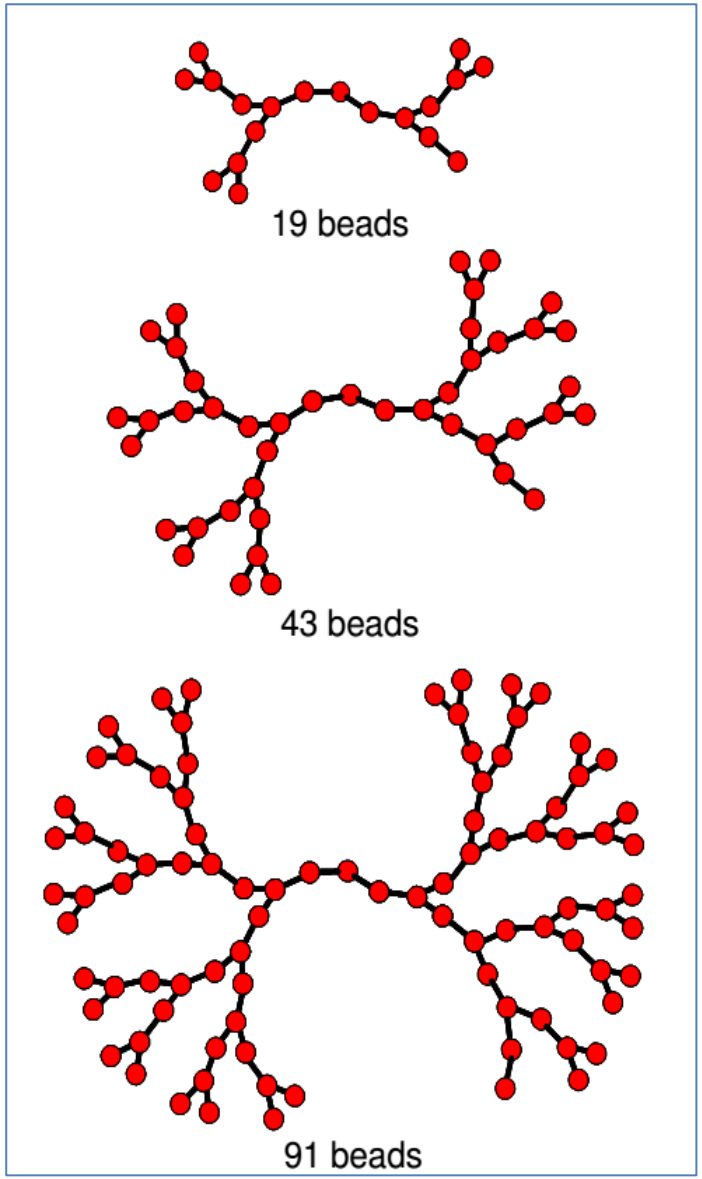


dendrimers

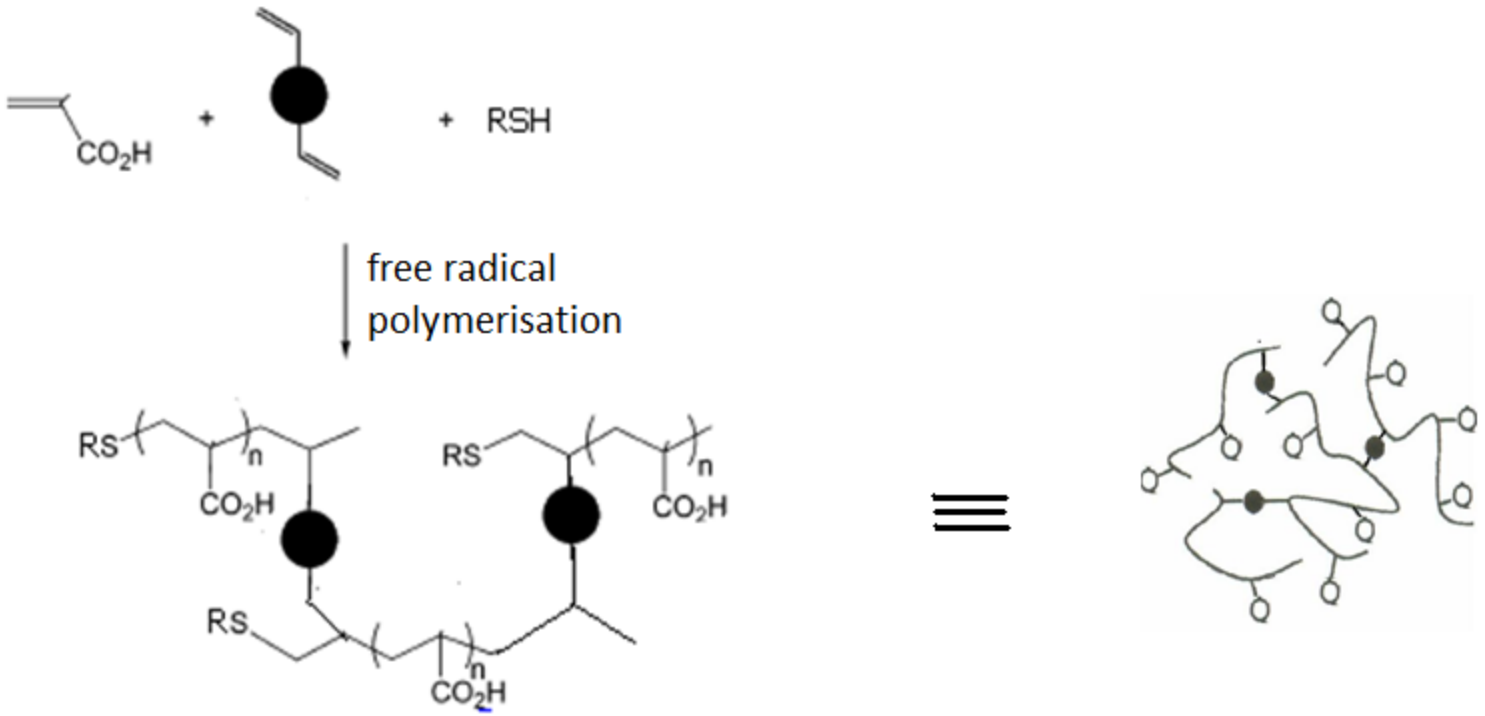


Hyperbranched polymer





Hyper branched polymers are under the class of Dendritic macromolecules. In contrast to dendrimers, hyperbranched polymers are not perfectly monodisperse. Hyperbranched polymers, are typically obtained in a one-pot reaction and as a result can be easily prepared also in larger quantities.



This is a patented process from Balmer Lawrie . This process is based on recently developeda facile and generic synthetic methodology the “Strathclyde methodology”.

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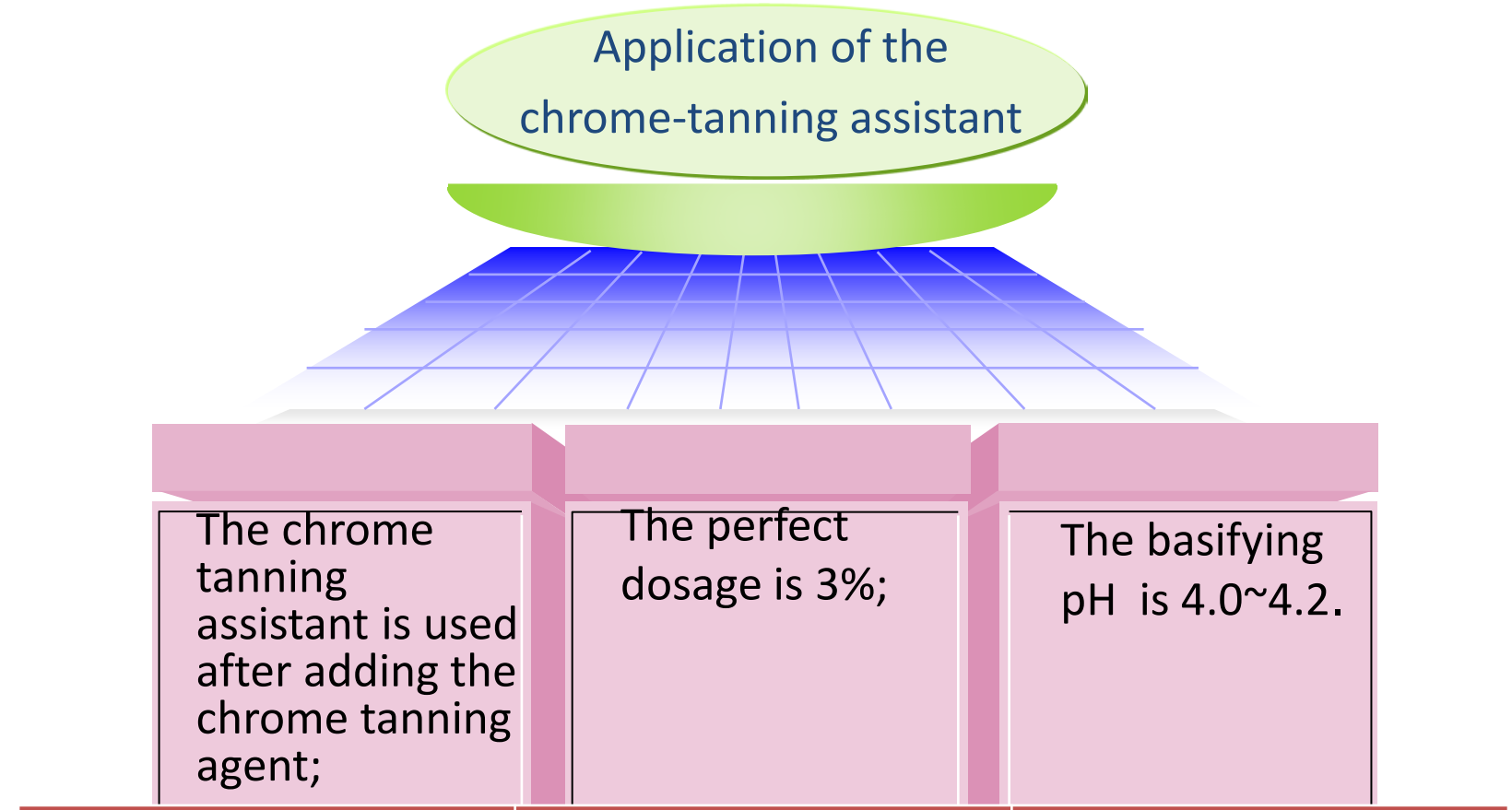


	Trial with 3% HBP	Coventional process
Chromium in the bath	3239 mg/L	4409 mg/L

There is a reduction of 25% chromium in the bath by adding HBP

* HBP- Hyper branched polymer

Chrome-free tanning

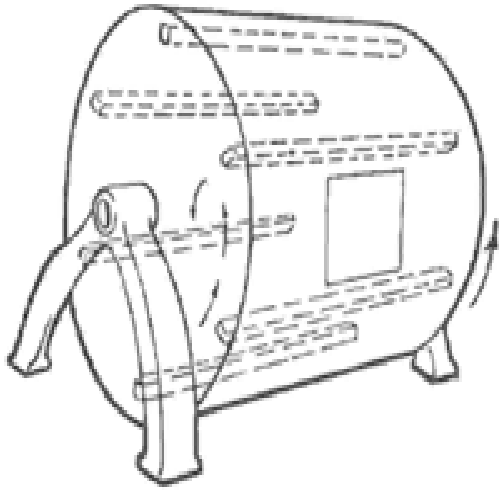
Green Chemicals in Tanning

Chrome free Tanning
Different approaches made so far

Chrome free Organic Tanning

- ❑ Phosphonium Salts
- ❑ Gluteraldehyde
- ❑ Oxozolidine
- ❑ Oil
- ❑ Vegetable tannins

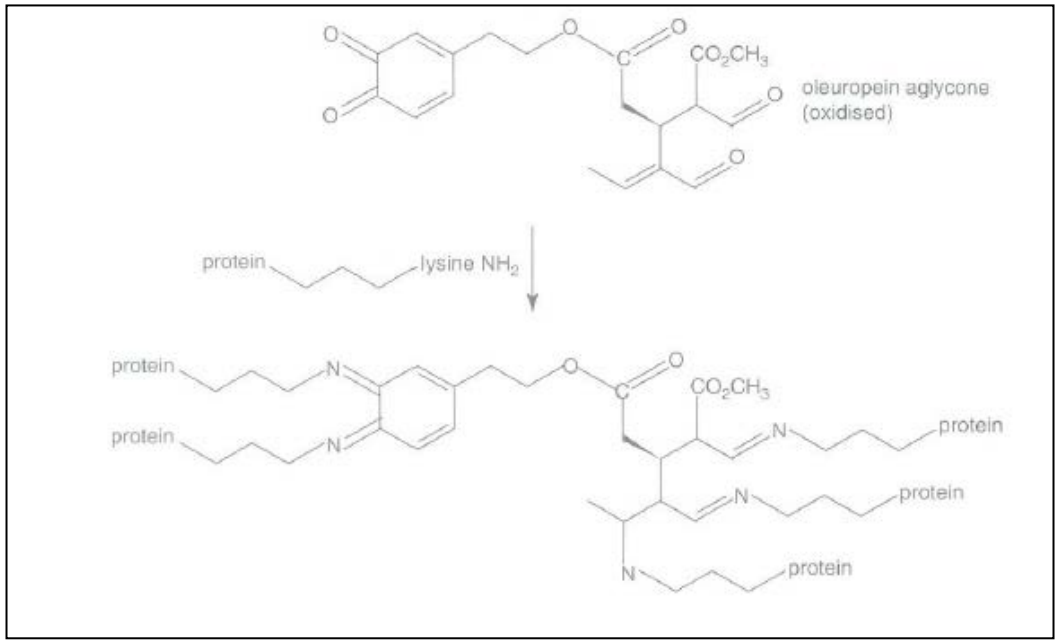
Combination Tanning



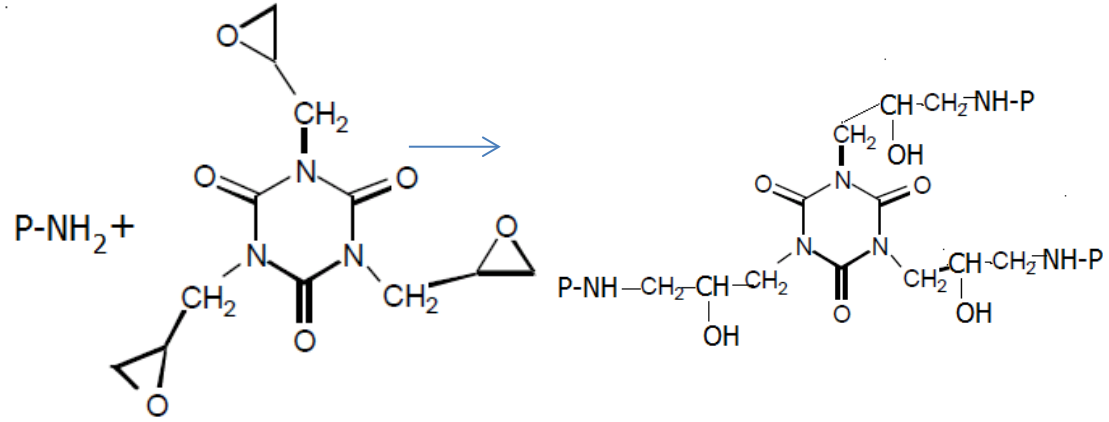
Chrome Free Inorganic Tanning

- ❑ Aluminium Tanning
- ❑ Zirconium Tanning
- ❑ Silica Tanning
- ❑

Recent developments in alternate tanning agents



Olea europea



Oleuropein is a natural product , a glycoside found in olive vegetation reacts with Lysine residues of protein.

Stabilization of collagen	**Shrinkage Temperature ^{0}c**
Control	50
Oleuropein	67
Glutraldehyde	68

This is a mineral free and aldehyde free thermal stable organic leather having

Ts > 85^{0}C. Multiple functional epoxides are known to have crosslinking ability with animal skin collagen molecules .

Patented by BLC & Loughborough Univ. US. Pat . 20090300848

Biomimetic approaches to tanning constitute a new potentially powerful aspect to applications of biotechnology in leather making.

Maillard reaction – Amadori product – Ketosamines

Fatliquor- some new Ideas

Polymeric fatliquor -Objectives

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

❖The leather treated with this retan fatliquor have desirable strength and softness qualities and significantly superior light fastness characteristics.

❖ This type of leather being particularly suitable for use in vehicle upholstery, upper leathers etc.

❖Increased Latex stabilization and resistance to freeze-thaw cycles.

❖The unsaturated fat in conventional fatliquors if not properly guarded with antioxidants lead to oxidation of Cr(III) to Cr (VI) which is carcinogenic

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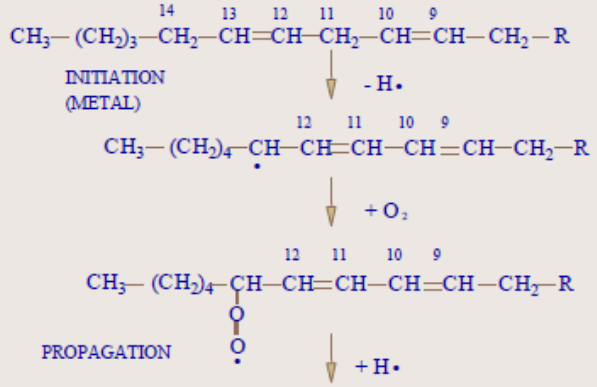
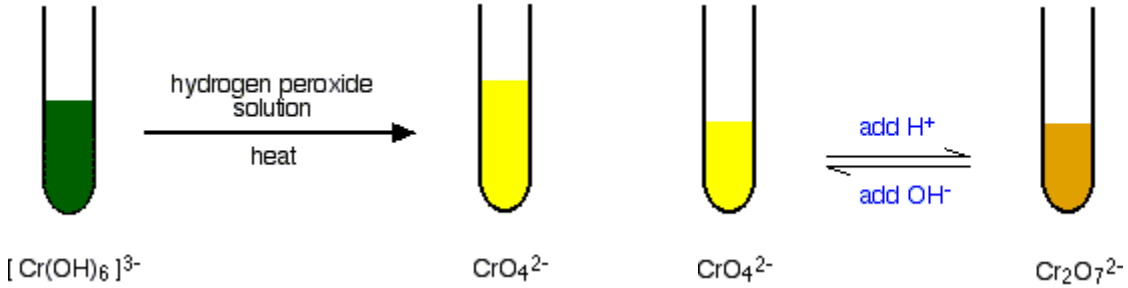
Lipid Oxidation



Oxidation of chromium (III) to chromium (VI) by unsaturated fats in the leather on ageing



There is a close relationship between the chromium and the unsaturated lipids 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

Oxidation Rates:Types of Fatty Acids

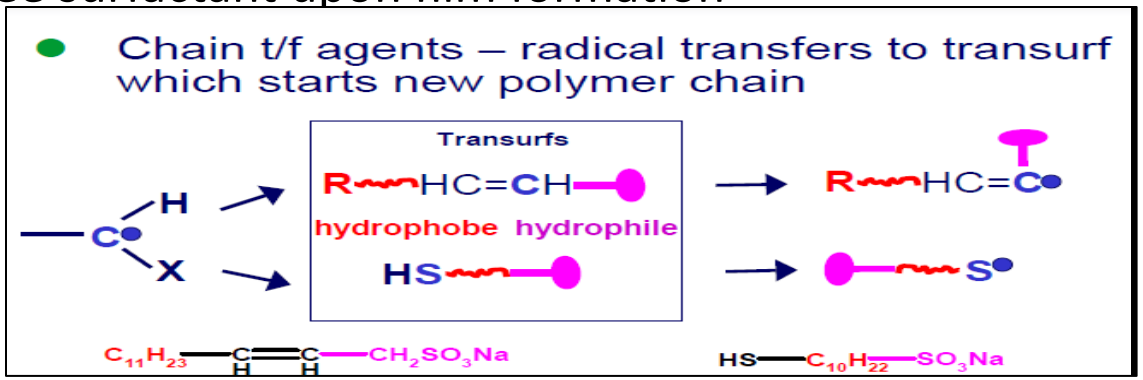
- As # of double bonds increases
  - # and reactivity of radicals increases

Type of Fatty Acid	Rate of Reaction Relative to Stearic Acid
18:0	1
18:1Δ9	100
18:2Δ9,12	1200
18:3Δ9,12,15	2500

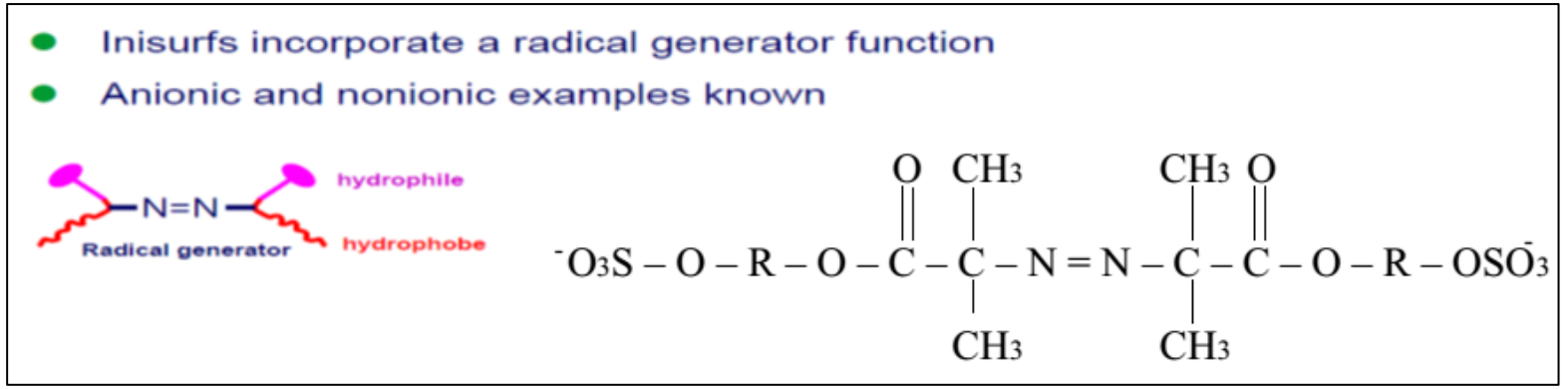
Reactive surfactants

Latexes – chemically bound surfactants- Latexes – to prevent migration and aggregation of free surfactant upon film formation

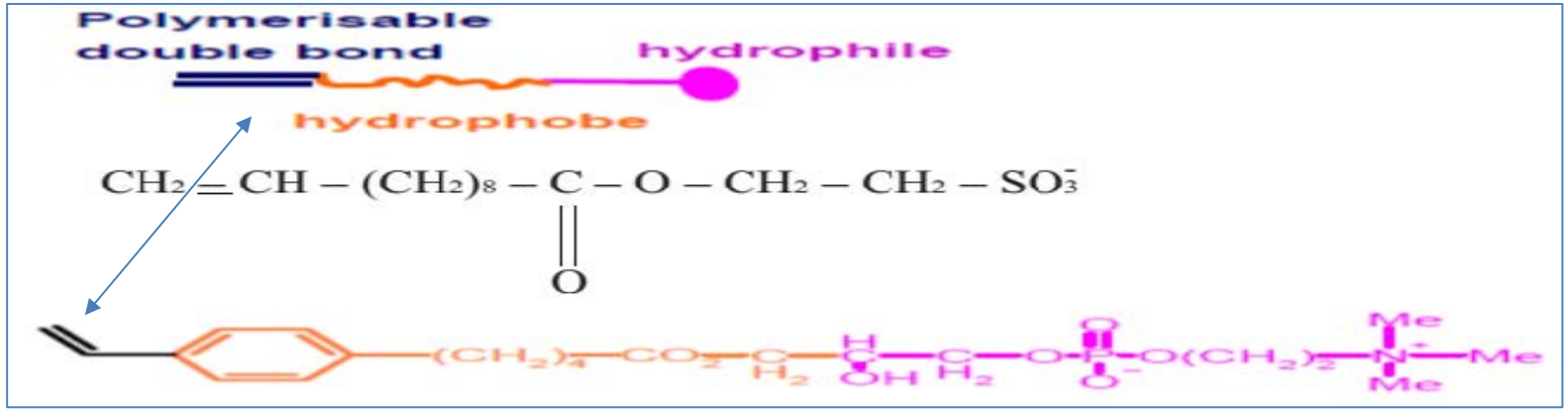
- 1. Transurfs



- 2. Inisurfs



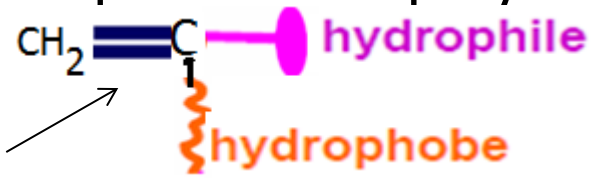
- 3. Surfmers



Polymeric Fat through Polymerisable Surfactant

One important advantage of surfmers over the other two is that their incorporation into polymer does not necessarily affect its molecular weight or the rate of polymerization

1. Preparation of polymerisable surfactant/Surfmer

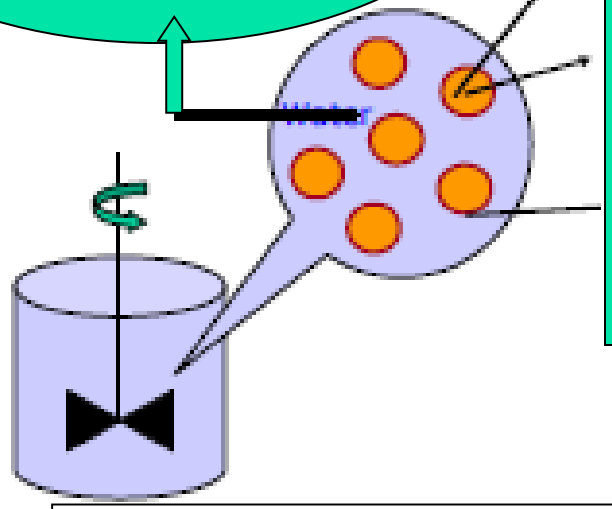


Polymerisable bond

2. Copolymerising surfmer with a hydrophilic monomer

Reactive surfactants

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



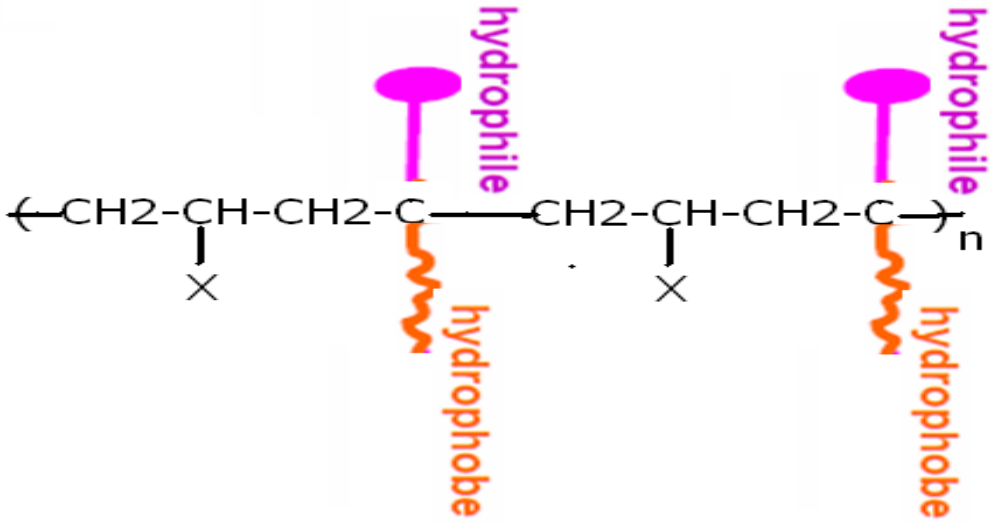
Water soluble monomer

Water soluble initiator

Here surfmer acts as a stabliser

Here surfmer acts as a Continuous phase . The copolymer is prepared by dispersing under vigorous stirring with1 mole of hydrophilic monomer in 1.2 moles of surfmer . A very little amount of water with initiator dissolved in it is added just to form the interface .

Inverse Emulsion Technique for preparing a copolymer – used as retan as well as fatliquor



pH of 10 % solution – 5.5-6
Appearance – opaque liquid and stable emulsion

- Such a high molecular weight polymer surfactant is very much useful in emulsifying most of the oils
- This methodology can be adopted to make **Reconstituted Polymerized Fats**

This work is jointly patented with IISC Bangalore

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Inference

- A synthetic route to prepare a polymeric fatliquor with maximum weight % of about 90 % of polymerisable surfactant in its copolymer composition
- This polymeric fatliquor functions both as a fatliquor and retanning agent matching the physical properties requirements of upper leathers .
- Apart from this the light fastness imparted by this fatliquor could be taken as a major advantage .
- This also minimises the loading of conventional fatliquors and solvents in the recipe which would result in less fogging.

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SCCP

A persistent quantification problem

Short Chain Chlorinated Paraffin(SCCP)

ISO/DIS 18219-IUC 30

❖ The European Directive 2002/45/EC restricted the sale and use of short-chain chlorinated paraffins (C10–C13) in product preparations for the fatliquoring of leather and were added to the Restricted Substances List (RSL).

❖C10-C13 paraffins with greater than 48% chlorination by weight. The most abundant chain lengths are C11 (33%) and C12 (38%).

❖Medium chain CPs (MCCPs) have carbon chain lengths of C14-C17 anlong chain CPs (LCCPs) have carbon chain lengths of > C17.

❖BL Products are based on long chain CPs (LCCPs) have carbon chain lengths of > C28.

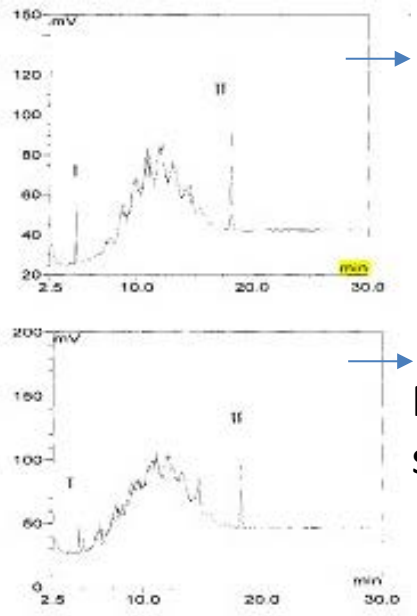
Instruments to detect and quantify

A. **High resolution Gas Chromotography with detectors of High resolution Mass Spectrometry and Electron Capture Negative Ionisation - HR GC–HR MS ECNI /NCI**

or

Liquid chromatography system with single quad (LC-MS) or triple quad mass spectrometry (LC-MS/MS) can also be used if the user has demonstrated that the accuracy of measurement is equivalent to that of the GC-ECNI-MS method.

he GC-ECNI-MS method.



SCCP sample

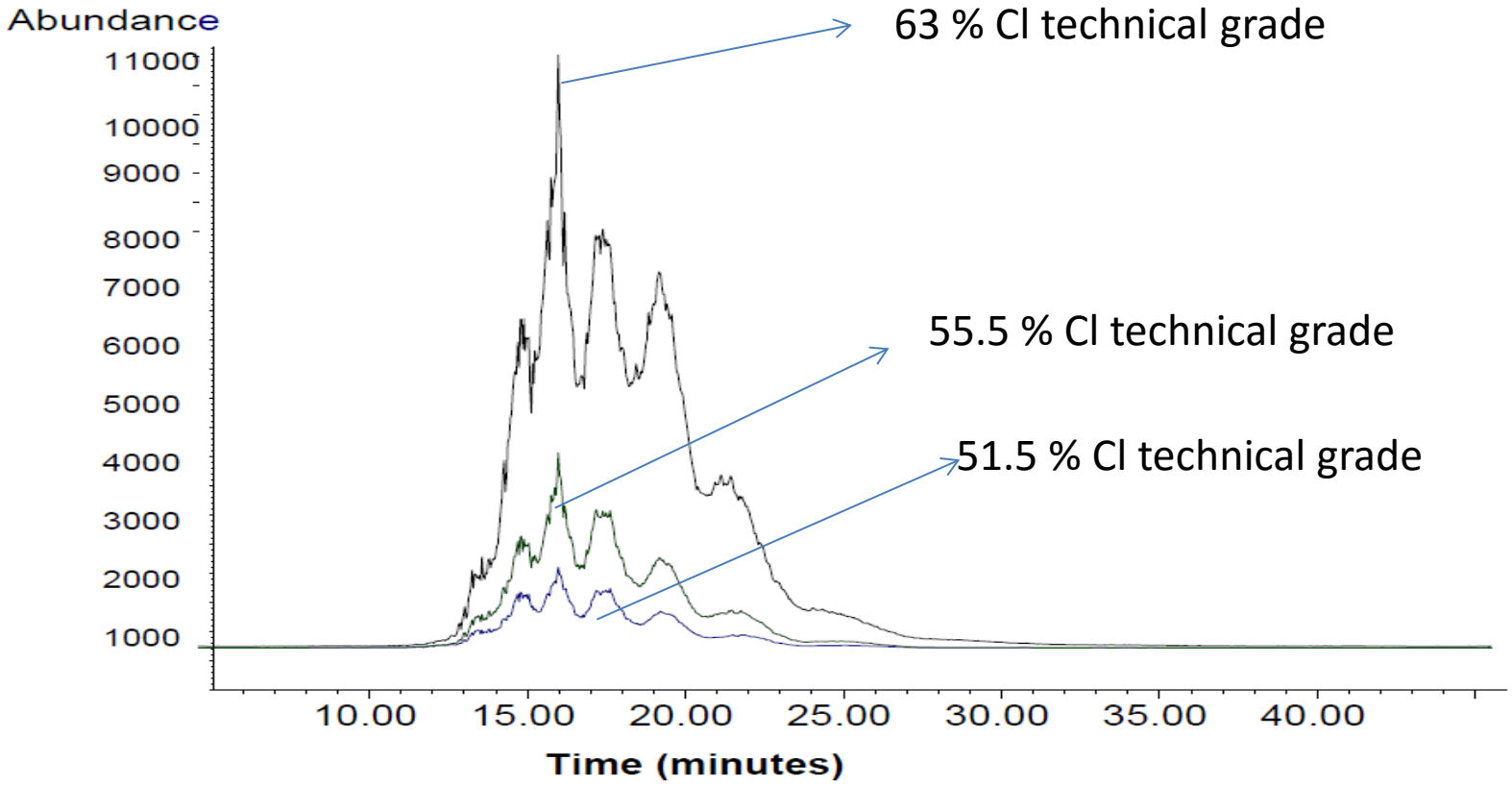
MCCP sample

B. Some Testing labs are using previous instruments with less detection and Accuracy like HR GC –ECD (Electron Capture detector). **This leads to erroneous results.**

Calibration solutions, for SCCP, C_{10}-C_{13}, with different chlorine of 51.5 ,55.5 & 63 % chlorine contents should be used . **All the three standards should be used for quantification . The pattern should be exactly matched by comparing the mass fragmentation of all 21 ions . In recent ISO method 18219-2015, SCCP standards with 59% chlorination is included**

❖**The calculated concentrations are dependent on the chlorination level of the technical mixture used in the calibrations and can vary by as much as more than 1500%.**

Figure 1 GC-ECNIMS chromatogram of three SCCP technical mixtures (51.5%, 55.5% and 63% chlorination). The response increases with chlorination level.



Systematic quantification error of CP-mixtures with 51%, 55% and 63% chlorine content.

	A	B	C
	SCCP standard		
Sample	51% Cl	55% Cl	63% Cl
51% Cl	**1500 ng**	616 ng (59 %)	159 ng (89%)
55% Cl	3655 ng (144%)	**1500 ng**	386 ng (74%)
63% Cl	14185 ng (846%)	5822 ng (288%)	**1500 ng**

The above table shows how erroneous results will be reported if samples are mismatched with a chlorine content different to that of standards

A - 51% chlorine content as standard ;

B - 55% chlorine content as standard

C - 63% chlorine content as standard

*** Coelhan, M. et.al 2000 Chemosphere 40: 685-689.**

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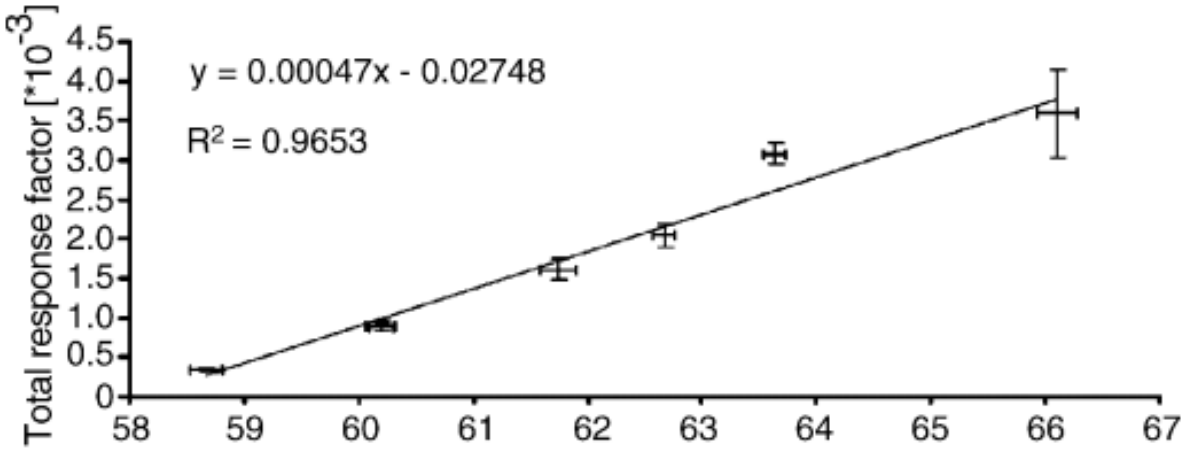
Response Factor correlates with the Degree of Chlorination



Chlorine Content %

* **Michael Oehme et.al Journal of Chromatography A, 1081 (2005) 225–231**

Tanneries, export houses should demand testing labs to provide results as per ISO/DIS 18219-IUC 30. For REACh testing has to be done as per ISO and it can be repeated across labs without any discrepancies

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Pickle-less Cr-Tanning

FLOW CHART

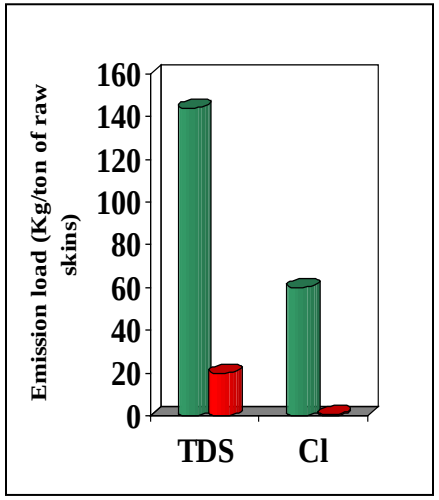
Conventional Tanning

Pickle-less Tanning

Pickle-less Chrome Tanning: Process Profile

Formaldehyde free polymeric synthetic tanning with complexing entity withpH-2-2. Ash -35-40%

Know-how transferred from CLRI to M/s Balmer Lawrie



BL process for Metal-free tanning

Wet-White process flow

Wet-White crust process flow

*** Balchem WH** is a products mainly developed to improve tanning in combination with Gluteraldehyde

Wet white Tanning-Balchem WH* & Balsyn G 50

RM : Pickled Pelt
Article : Bag Leather

Origin : India, Article- Bag Leather
Thickness : 1.1 -1.2 mm

Process	% Chemicals	Duration	Remarks
Pickle bath	50		
Balchem WH	2	90	
Balsyn G50	2	180	
Water	100	30	L/O/N
Sodium bi carbonate	1.5	5 X 15'+ 120'	Check pH 4..2
Preservative	0.2	45	Pile for 2-3 days, splitiing, shaving
Water	100		
Balgreasol HF	1	45	Drain
Water	100		
Formic acid	1	30	pH 3.2/3.5
Balchem WH	3	60	
Balsyn G50	2	90	
Sodium formate	1	20	
Sodium bi carbonate	1.5	30 + 45	pH 4.8 L/O/N , D/W

Process	% Chemicals	Duration	Remarks
Water	200		
Neutralising Syntan	2	30	
Sodium bi carbonate	2	4 X 15 + 60	pH 6.0/6.2 D/W
Water	100		
Balmol SX20	1		
Balmol BAQ	1	20	
Balsyn EAR	2	30	
Balsyn DDS	5	90	
Formic acid	2	2 X30'	D/W 10'
Water	100		
Balmol SX20	8		
Balmol BLX	7	60'	
Formic acid	2	2 X30'	pH 3.8 D/W
Water	100		
Preservative	0.1	30	D/W 5'

*** Balchem WH** is a products mainly developed to improve tanning in combination with Gluteraldehyde.

Properties Wet white and Crust leather

Leather Properties Wet White

- Excellent grain flatness
- White appearance
- Very tight grain
- Shrinkage temperature ~78C
- Cationic Character of Wet White
- Suitable for shoe upper and fancy leathers, not only for Automotive and Furniture

Properties Wet White Crust

- Less stretch and elasticity
- Less wrinkles, flatter surface
- High Whiteness may not possible
- Very tight grain
- Wide range of articles possible

Physical Properties

Strength properties are comparable with conventional system.This process is commercially running in some Tanneries

Fatliquoring

Fatliquor Eco-update

Fatliquor	Chemistry	Eco-Target	BL solution
Natural	Sulfated or sulfited natural oils (castor, neatsfoot, soya)	Recovered natural oils	Balmol BAQ , AS, LA ,FTR, CFO 04, JX20
Synthetic and Semi-synthetic	Alkylsulfosuccinates	*Use of by-products as raw materials • Higher exhaustion, lower COD values for the waste water • SCCP free	Balmol series comply with the EU Regulation of REACh norms restricting SCCP and also give high exhaustion
Polymeric	Polymeric succinates and sulfosuccinates	Higher exhaustion, lower COD values for the waste water	Balmol PGS & RKS

Retanning

Retannings Eco-update

Retanning	Chemistry	Eco-Target	BL solution
Syntan	Formaldehyde condensation of Aromatic base (Phenol, Naphthalene, cresol etc.) with sulphonate or hydroxy function	Residual content of Formaldehyde and Phenol of both < 20 ppm	All Replacement syntans, Dye Levelling ,Dye penetrating ,Chrome syntans , Alluminium Syntans are below detectable limits of formaldehyde .Balsyn RDFF, CRFF , ALFF are free from formaldehyde.
Resin	* Urea-Formaldehyde * Dicyandiamide-Formaldehyde * Melamine-Formaldehyde	Residual content of Formaldehyde and Phenol of both < 20 ppm	Balsyn SFF, MR50FF, NFS
Modified Veg	Chemically modified various vegetable tanning	More renewable resourse,avoid free phenol,PAH	Balsyn BL TARA, VQ, NC, GMR ,NPS

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Challenges for the future

- Two major issues need to recognized for leather manufactured in future

❖ A **single–tannage** system is unrealistic for the production of high quality leathers. There is a need for intelligent combinations to reach good environmental performance and to meet customers requirements

❖ The change in the perception of leather has to be realized . Leather is no longer a material simply for products for daily use , but it must be recognized as a unique and luxury material for both high quality and high-tech products where it reflects an image of originality and natural awareness

References

*Major contribution from Prof. Michael Oehme , University of Basel, Switzerland . Many Labs have followed his work for in-house their Development methods .

*Dr. Dietrich Tegtmeyer, Chairman IUR , IULTCS lecture Aug 2013
*Prof. Sherrington papers , Dept. of Chemistry University of Strathclayde ,UK, on Hyperbranched & polymermerizable surfactant.
* Prof. S Ramakrishnan papers , IPC , IISC , Bangalore

Acknowledgement-
Prof. S Ramakrishnan ,IPC, IISC-Banglore

Thank you all for your patience