

# **FUTURE TECHNOLOGIES FOR LEATHER MANUFACTURE**

**LERIG  
2016**





# Biotechnology

## KEY TECHNOLOGY

of the 21<sup>st</sup> century

**Biotechnology is recognized the world over as the technology of the future.**

- With environment and cost issues surrounding conventional chemical processes being subjected to considerable scrutiny, biotechnology rapidly is gaining ground due to the various advantages it offers over conventional technologies.

**Enzymes represent an important component of biotechnology processes.**

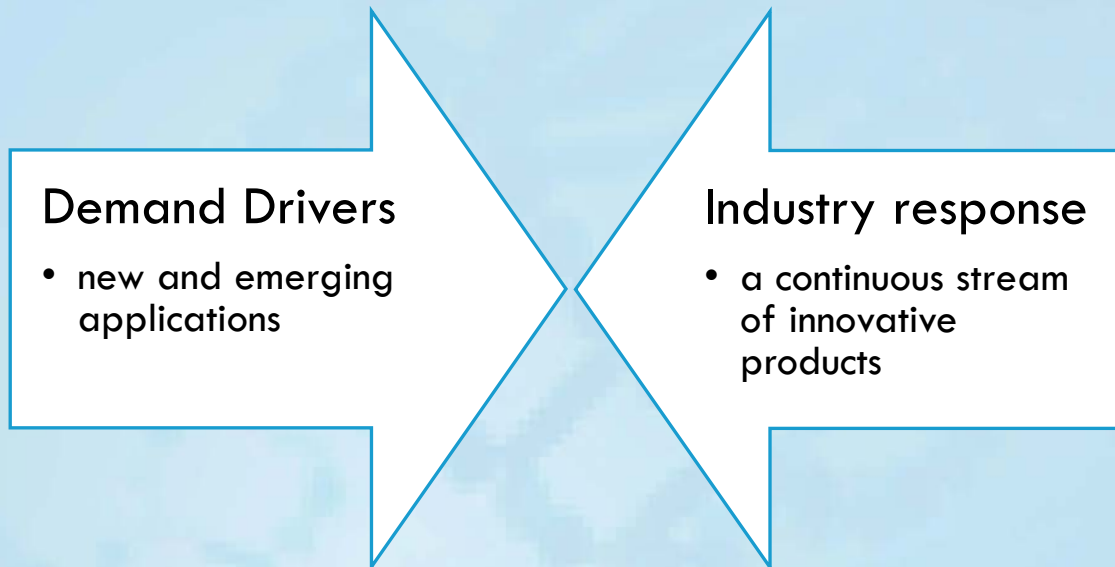
- The field of industrial enzymes now is experiencing major R&D initiatives, resulting both in the development of a number of new products and in improvement in the process and performance of several existing products.



# Biotechnology

## KEY TECHNOLOGY

of the 21<sup>st</sup> century



Significant future growth will require investments by all participants in research and applications development.

# MARKET OVERVIEW

The global industrial enzymes market is estimated at US\$2.90 billion

- Growing at 6% to 8% annually.

The Indian industrial enzymes market is in a growth phase:

- The industrial use of enzymes generated total revenue of US\$100 million in 2009, and is estimated to grow at a CAGR of 7.2% during the forecast period.

## Industrial Applications of Enzymes



Note: Others include leather, biomass and biofuel applications.



# MARKET OVERVIEW

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The key end-user segments in the Indian market are detergents and pharmaceuticals, which constitute about 50% of the total Indian market. This research service covers the use of enzymes in the detergent, pharmaceutical and textile sectors.

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The Indian enzymes market is dominated by Multinational's

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Key domestic manufacturers for the Indian enzymes market are predominantly formulators.



# ENZYMES

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Special Proteins found in all living matter

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Vital for life but are not living substances

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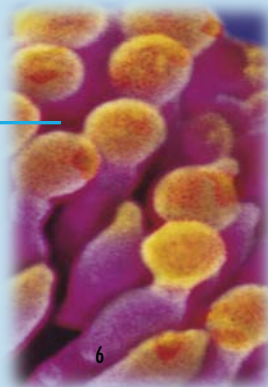
Catalysts and in very small amount speed chemical reactions without being changed in the reaction

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Very specific i.e. synthesis or break down of organic matter

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Non-toxic, biodegradable and soluble in water



# INDIAN LEATHER INDUSTRY

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India Ranks 1st in livestock population

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Leather Export 8th Largest Foreign Exchange earner to tune of USD 12 billion

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60% Skins / Hides processed in Tamil Nadu

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Second largest manufacturer of leather garment & footwear

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Large number of ISO certified leather companies

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Strong accessories and component industry

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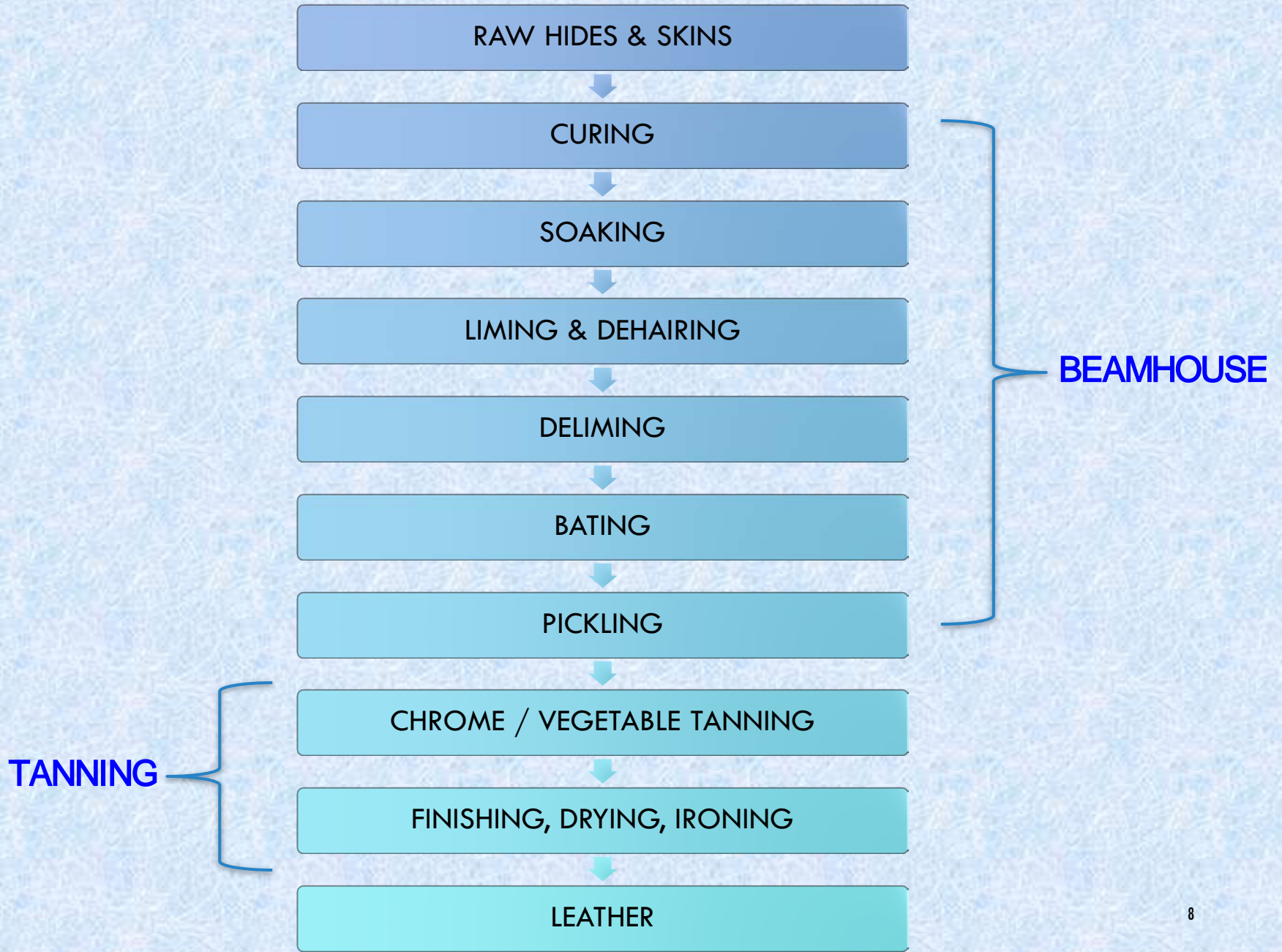
Rich experience in producing leather

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100% overseas investment allowed in tanning and footwear



# LEATHER PROCESSING - FLOWCHART





# CONVENTIONAL LEATHER PROCESSING

## REPORTS SAY:

**Tanning** which involves 7 to 8 Steps (like Soaking, Liming etc..) accounts for nearly 90% of total pollution from tannery

“Do – Undo Process” with wide variations in pH

Acids/ Alkalis/ Salts usage, Toxic gases (Ammonia/ Hyd.Sulphide) besides sludge generation

Liming-Reliming contribute 60-70% of total pollution load in leather Processing

Conventional unhairing with Lime and Sodium Sulphide is responsible for 84% of BOD, 75% of COD, 92% of Suspended solid and 100% Toxicity of total pollution from tannery

# CHARACTERISTICS AND AMOUNTS OF WASTEWATER PRODUCED IN TANNING PROCESSES

Operation	Volume	pH	Total Solids	TSS	BOD
<b>Soaking</b>	2,500 To 4,000	7.5 To 8	8,000 To 28,000	2,500 To 4,000	1,100 To 2,500
<b>Liming/ Dehairing</b>	6,500 To 10,000	10 To 12.5	16,000 To 45,000	4,500 To 6,500	6,000 To 9,000
<b>Washing/ deliming</b>	7,000 To 8,000	3 To 9	1,200 To 12,000	200 To 12,000	1,000 To 2,000
<b>Vegetable tanning</b>	2,000 To 4,000	5 To 6.8	8,000 To 50,000	5,000 To 20,000	6,000 To 12,000
<b>Pickling</b>	2,000 To 3,000	2.9 To 4	16,000 To 45,000	600 To 6,000	600 To 2,200
<b>Chrome Tanning</b>	4,000 To 5,000	2.6 To 3.2	2,400 To 12,000	300 To 1,000	800 To 1,200
<b>TotalU<sup>a</sup></b>	30,000 To 50,000	7.5 To 10	10,000 To 25,000	2,500 To 6,000	2,000 To 5,000

Source : S. Rajamani Setting up tannery effluent treatment plants in India- Practical experience and lesson Learnt - a paper presented at the eleventh session of the Leather and Leather Products Industry Panel, held in Nairobi from 29 Nov TO 3 Dec 1993 - ( ID/ WG. 536/7(SPEC)

Note: Units in mg/l except for pH values and for the total volume of wastewater, the latter is given in litres per ton of hide

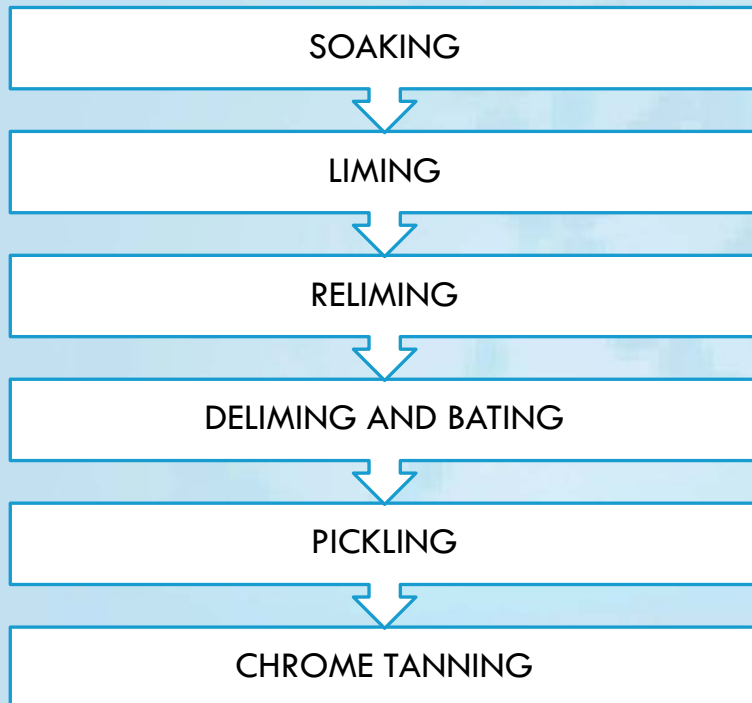
a/ The values presented in this row take into account (a) the dilution and neutralization which occurs when streams from several processing steps are mixed

# RELATIVE CONTRIBUTIONS OF THE BASIC TANNING OPERATION TO WASTE LOADING (%)

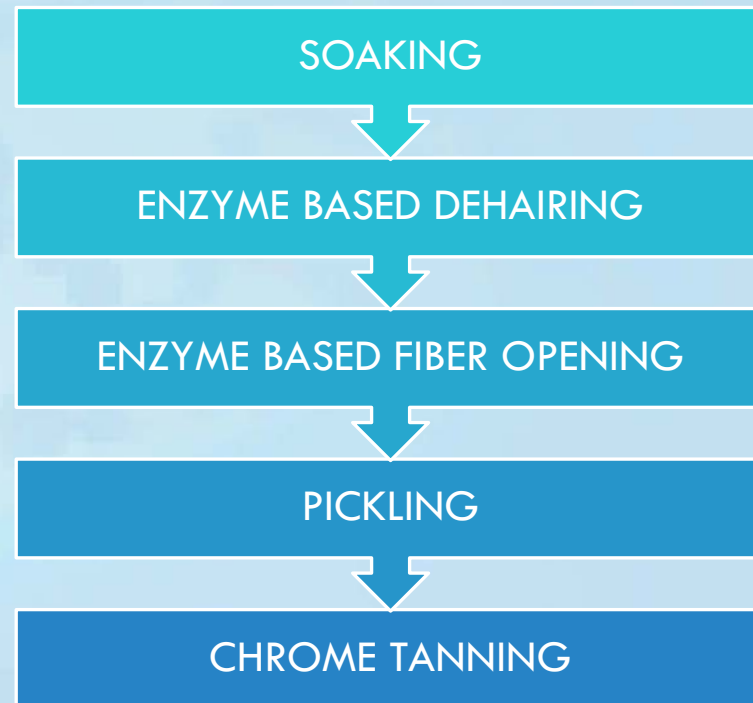
Operation	Wastewater	BOD	Solids	Chromium	Sulphides	Ether Soluble Material
Soaking	18	18	30	Nil	Nil	25
Dehairing	24	45	40	Nil	99	50
Fleshing	2	5	10	Nil	Traces	20
Bating	20	15	10	Nil	Traces	Traces
Pickling and tanning	5	4 each	1 each	95	Traces	Traces
Sammying	1	Traces	Traces	5	Traces	Traces
Retanning, dyeing and fat - Liquoring	20	7	6	Nil	Nil	5
Finishing and auxiliary Operation	10	2	2	Nil	Nil	Traces

# CONVENTIONAL AND FUTURISTIC ENZYME BASED LEATHER PROCESSING

## CONVENTIONAL



## ENZYME BASED



# ENZYMES IN LEATHER

**SOAKING**

**DEHAIRING**

**FIBRE  
OPENING**

**BATING**

**DEGREASING**



# SOAKING- SYNKROZYME-SEZ

To remove applied salt from the hide

Better removal of blood, dirt and dung

Loosening of scud

Non-fibrillar proteins are eliminated

Facilitates better penetration and equal distribution of chemicals in the subsequent step

## Recommended enzymes- Proteolytic & Lipolytic Enzymes (neutral & alkaline)

PROCESS	W/O ENZYME	W ENZYME
For Salted raw stock	24 hrs	4 hrs.
For Dried raw stock	46-48 HRS	8-10 HRS

Temp. 30-35°C & pH- 7.5 to 9.5 in Pits / Paddle / Drums.

# LIMING/DEHAIRING- SYNKROZYME-DEH

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REMOVAL OF HAIR FROM SKINS (Dissolution of hair & epidermis & to slacken the corium by alkaline swelling)

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OPENING OF HIDES, DEGRADES & REMOVES THE RETICULIN NETWORK, ELASTIN FIBRE AND MUROID FROM SKINS& HIDES.

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FREE FROM COLLAGENASE. PREPARATION OF HIDE FOR TANNING.

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SULPHIDE FREE & SULPHIDE ASSISTED DEHAIRING.

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CONVENTIONAL - USING LIME & SODIUM SULPHIDE

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ENZYMATIC- ALKALINE BACTERIAL PROTEASE ( alkali stable)  
Attacks secondary protein ( proteoglycans)

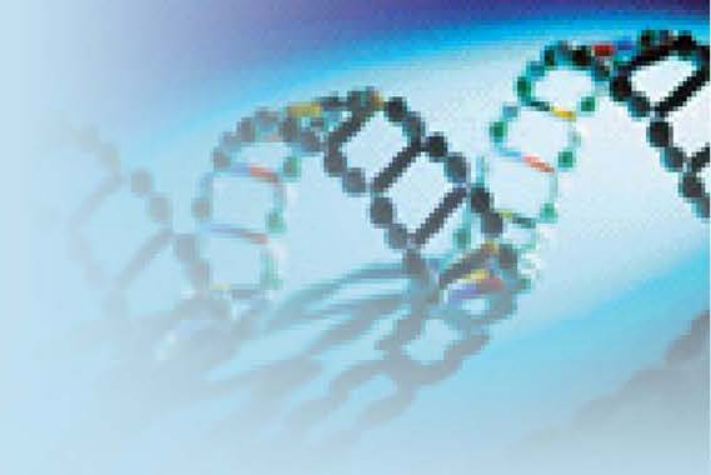
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Process - Paste Liming or Paddle liming.

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Temp. 25 to 40°C. & pH- 7.5 to 11.0 for 24 hrs.

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# ENZYMATIC FIBRE OPENING

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It will almost replace Lime which is used in conventional process for fibre opening.

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Thus reducing the Lime sludge up to maximum extent, ultimately reducing the pollution load by 60-70%.

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This enzyme will speed up the reaction and will help to achieve the desired result with minimum amount of water and energy.

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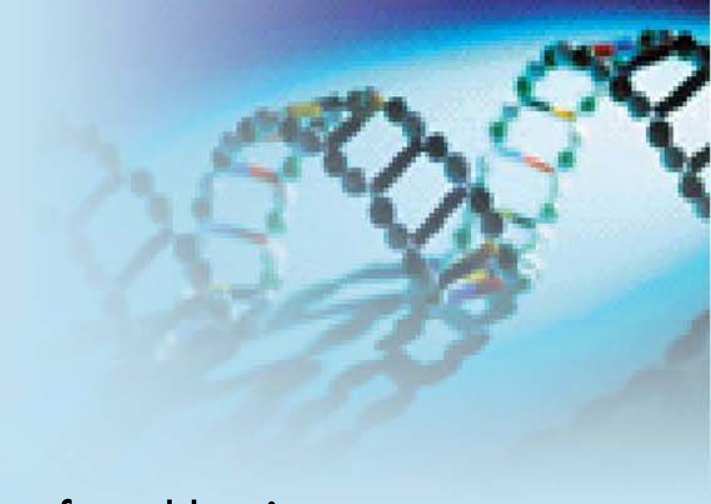
Since Lime will be almost eliminated, deliming chemicals may not be required.

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Enzymes used predominantly consist Carbohydrases which degrades specifically the proteoglycans.

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Substantial increase in area yield.



# ENZYMATIC FIBRE OPENING

Very suitable particularly for skins which has been found having better fullness and grain tightness compared to conventional lime-sulphide process, which will increase the physical properties of leather.

Due to maximum replacement of lime the final leather has been found having a smooth grain.

## SHORTCOMINGS IN INITIAL STAGES:

- Inadequate fibre opening
- Flatter grain and less thickness due to higher area yield
- Higher processing cost

# BATING(ALKALI) - SYNKROZYME-ALB

REMOVAL OF SHORT HAIRS, HAIR RESIDUES, PIGMENTS, SWEAT GLANDS, FAT GLANDS.

OPEN, SILKY SMOOTH AND FLACCID PELT.

IMPROVES FEEL, UNIFORMITY OF COLOUR AND GRAIN FINENESS.

IMPARTS AIR PERMEABILITY.

SLACKENS THE FIBER STRUCTURE FOR SOFT, STRETCHY LEATHERS.

RECOMMENDED COMBINATIONS OF ENZYMES.

- Neutral + alk. bacterial protease.

pH & Temp.- 8.2 at 25 to 40°C for 1 to 2 hrs.



# BATING (ACID)- **SYNKROZYME- ACB/BSG/MFL/GENX**

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DONE AFTER TANNING

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PRODUCES OPEN SILKY AND SMOOTH PELT

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SOFTNESS AND FINENESS OF GRAINS

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Enzyme- Fungal Protease (acid)

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pH- 4.0 to 6.0 / Temp.- 25 to 40°C.

# DEGREASING- SYNKROZYME-LDG

## REMOVAL OF FATTY TISSUES

- (Hydrolysis of fats, mono & di glycerides, free fatty acids & glycerol.)

DONE AFTER TANNING OF THE LEATHER.

LIPASE BASED PRODUCTS REQUIRED.

## FAT CONTENTS

- GOAT SKIN - 5 -10 %
- SHEEP SKIN - 15- 30 %
- PIG SKIN - 20 - 25 %.

UPTO 75% OF DEGREASING CHEMICALS CAN BE REPLACED.

COMPARED TO CHEMICALLY TREATED PELT LESS EMPTINESS.

LESS CONSUMPTION OF SYNTANS.

# CHARACTERISTICS OF SOAKING WASTEWATER



Volume of effluent (m <sup>3</sup> )	6 To 9
p <sup>H</sup>	7.5 To 8
BOD (mg/l)	1,100 To 2,500
COD( mg/l)	3,000 To 6,000
Total Solids (mg/l)	3,500 To 5,500
Dissolved solids (mg/l)	32,000 To 48,000
Suspended solids (mg/ l)	3,000 To 7,000
Chlorides as Cl (mg/l)	15,000 To 30,000

Source: Word Bank, UNIDO and UNEP Industrial Pollution Prevention and Abatement, Chapter on 'Leather tanning and finishing ' draft report (June 1994)

# ANALYTICAL DATA FOR SPENT SOAK LIQUOR

% Soaking enzyme used	0.1%	0.2%	0.3%	0.4%	Control
Total Nitrogen content Gm/ Lit	1.2	1.67	1.78	1.89	0.6
Salt Content (ppm)	9090	9294	9498	9673	8703.9

# CHARACTERISTICS OF LIMING AND DEHAIRING WASTEWATER

Volume of effluent (m <sup>3</sup> )	3 To 4
p <sup>H</sup>	10 To 12.8
BOD (mg/l)	5,000 To 10,000
COD( mg/l)	5,000 To 25,000
Total Solids (mg/l)	30,000 To 50,000
Dissolved solids (mg/l)	24,000 To 30,000
Suspended solids (mg/ l)	6,000 To 20,000
Chloride as Cl (mg/l)	4,000 To 8,000

Source: Word Bank, UNIDO and UNEP Industrial Pollution Prevention and Abatement, Chapter 'Leather tanning and finishing ' draft report (June 1994)



# CHARACTERISTICS OF DELIMING WASTEWATER

Volume of effluent (m <sup>3</sup> )	1 To 2
p <sup>H</sup>	7 To 9
BOD (mg/l)	1,000 To 3,000
COD( mg/l)	2,500 To 7,000
Total Solids (mg/l)	4,000 To 10,000
Dissolved solids (mg/l)	2,500 To 6,000
Suspended solids (mg/ l)	1,500 To 4,000
Chloride as Cl (mg/l)	1,000 To 2,000

Source: Word Bank, UNIDO and UNEP Industrial Pollution Prevention and Abatement, Chapter 'Leather tanning and finishing ' draft report (June 1994)

# Effect Of Variation Of % Sulfide & Unhairing Enzyme On Pollution Load Generated In Paste Unhairing Method With Goat Skins

Details Of Quantity of sulfide and enzyme (% on soaked wt)		Pollution load in spent lime liquor (ppm)		
Sulfide	Enzyme	Sulfide	B.O.D	C.O.D
0.5	0.5	21.1	2040	6000
0.5	0.75	19.7	2010	6200
0.5	1	18.9	1900	6500
0.5	1.25	18.5	2160	7600
0.75	0.5	28.2	2280	8200
0.75	0.75	27.3	2400	8400
0.75	1.0	28.9	2200	8100
1.0	0.5	28.5	2460	8700
1.0	0.75	51.2	2600	8900
1.0	1.25	51.7	2700	8800
1.25	0.5	52.3	3270	9400
1.3	0.75	50.9	3330	10000
2.5	0.00	112.8	4580	12800

# Effect Of Variation Of % Sulfide & Unhairing Enzyme On Pollution Load Generated In Dip & Pile Unhairing Method With Cow Hides

Details Of Quantity of sulfide and enzyme (% on soaked wt)		Pollution load in spent lime liquor (ppm)		
Sulfide	Enzyme	Sulfide	B.O.D	C.O.D
0.75	1.0	153.5	2400	8448
0.75	1.25	158.45	2620	8064
1.0	0.5	241.5	2845	8680
1.0	0.75	289.75	2820	8832
1.25	0.5	335.55	3040	9280
3.0 ( Control)	0.00	450.6	3200	11216

# COMMERCIAL TRIALS AT DINDUGAL

## Raw Material

- Goat Skins

## Scale of implementation

- 4000 skins

## Weight

- 4465 Kg

Parameters	Conventional process as followed in the tannery mg/Lit	Modified process using unhairing enzyme mg/Lit
Tot. Dissolved Solids	23826	15004
C.O.D	19527	13278
B.O.D	9365	6606
Sulfide	314	246

# COMMERCIAL TRIALS AT VANIYAMBADI

## Raw Material

- Sheep Skins

## Scale of implementation

- 4000 skins

## Weight

- 4250 Kg

Parameters	Conventional process as followed in the tannery mg/Lit	Modified process using unhairing enzyme mg/ Lit
Total Dissolved Solids	24100	18900
C.O.D	11340	8930
B.O.D	4956	3860
Sulfide	1032	848



# SALIENT FEATURES OF THE ENZYME BASED UNHAIRING AND FIBRE OPENING

Less usage of Sulphide & Lime thereby reducing sludge

Enables hair saving

Provides clean white pelt

Ensures fine and smooth grain

Provides 3-5% area yield

Minimizes wrinkle formation

Bating operation can be avoided

Provides significant reduction in pollution Load

Ensures saving in time, energy and chemicals

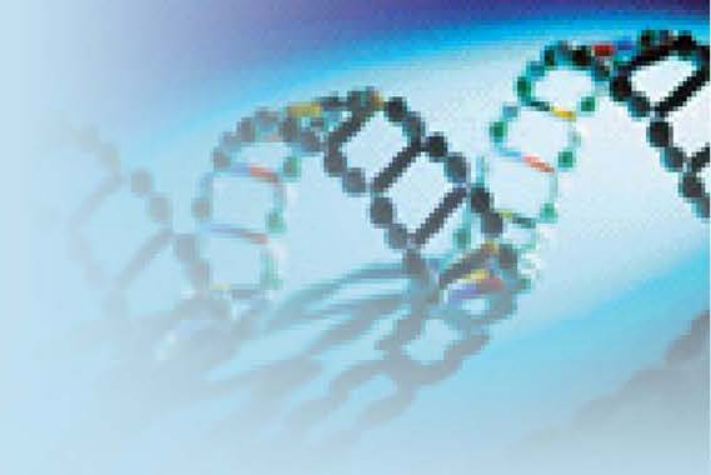
# COMPOSITE LIQUOR ANALYSIS FOR CONTROL (C) AND EXPERIMENTAL (E) PROCESS<sup>a</sup>

Process	COD (ppm)	TS (ppm)	Volume of effluent (L/t of raw hides <sup>b</sup> )	emission load (kg/t raw hides <sup>b</sup> processed)	
				COD	TS
C <sub>Cow</sub>	4624 ± 12	24652 ± 24	22600	104	557
E <sub>Cow</sub>	3618 ± 18	22850 ± 32	21000	76	480
C <sub>goat</sub>	3262 ± 12	21582 ± 28	14800	48	318
E <sub>Goat</sub>	2820 ± 14	17462 ± 22	12600	35	220

<sup>a</sup> composite liquors were collected excluding soaking;

<sup>b</sup> weight of hides before soaking

E-Lime-enzyme based dehairing followed by enzyme based fibre opening



# ENVIRONMENTAL BENEFITS

Parameters	Conventional process	Enzyme – sulphide process
B.O.D	22.78	13.31
C.O.D	50.49	23.70
Sulphide	2.9	1.36
<i>(Load in kg/ton of raw hide / skin)</i>		

# ADVANTAGES OF ENZYMATIC PROCESSING

Eco Friendly

Improve Quality

Easy Handling

Reduces Wrinkles

Growth Marks

Area Increase



# TAKE HOME



MORE FOCUS ON  
CLEANER SHOP  
FLOOR  
(FRONTYARD)



LEADING TO  
REDUCED  
INVESTMENTS IN ETP  
(BACKYARD)

# THANK YOU

## HARNESSING ECO-FRIENDLY OPERATIONS FOR BETTER LIVING

