

LESS POLLUTING PROCESSES IN CATTLE HIDE BEAMHOUSE OBTENTION OF HIGH-YIELD LEATHERS PART II: DELIMING-BATING-PICKLING-TANNING

Cromogenia Units S.A.

This Part II is a continuation of Part I —which addressed the process up to the Unhairing phase— and completes the process up to the Tanning phase.

- 4th Deliming-Bating:
 - Free from ammonium salts.
 - Full removal of dermatan sulfate.

- 5th Pickling-chromium tanning:
 - Replacement of sulfuric acid by non-swelling organic acids.
 - Use of suitable self-basifying agents.
 - Recycling of chromium tanning baths.

- 6th Metal-free tanning:
 - Vegetal tanning.
 - Wet-White tanning.

4th.- DELIMING – BATING

a) FREE FROM AMMONIUM SALTS.- Deliming accounts for the greatest Nitrogen release into wastewater.

Ammonium salts traditionally used in deliming $\text{SO}_4(\text{NH}_4)_2$ and $\text{Cl}(\text{NH}_4)$ form the corresponding calcium salt plus NH_4OH .

The ammonium nitrogen content allowed in wastewater is quite limited; the most common limitation in Spain is:

- 25 mg/l: mean daily maximum concentration
- 85 mg/l: maximum instantaneous concentration.

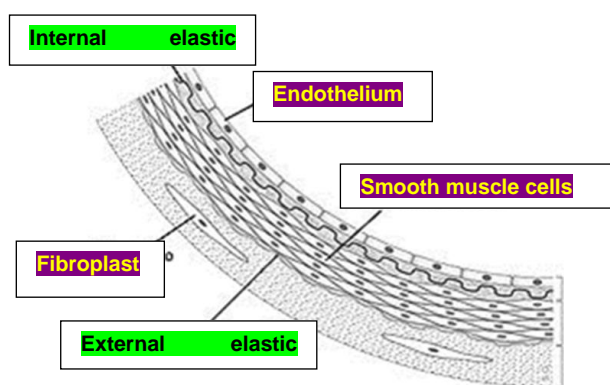
In order to reduce the environmental impact of ammonium nitrogen, ammonium salts should be replaced by alternative products which, when reacting with $\text{Ca}(\text{OH})_2$, yield H_2O —i.e. acid products, not salts.

These acids must be very weak in order to prevent acid swelling of the hides —i.e. organic acids should be used:

- Monocarboxylic acids: lactic acid, formic acid....

- Dicarboxylic acids: DELIMING AGENT (F) Bating must be performed with a specific enzyme to achieve ELASTIN hydrolyzation or solubilization: ELASTASE (G)

Should a different enzyme be used (say, a broad-spectrum protease), other proteins would also be solubilized —including Collagen—, and emptier, looser leathers would be obtained.



In the dry state, Elastin is hard, brittle and fragile.

In the wet state, Elastin is elastic, slippery and insoluble in water.

To remove veininess, the vein's main component (Elastin) must be hydrolyzed (dissolved).

The specific enzyme for hydrolysis is an ELASTASE enzyme: ELASTASE (G)

In cases where the presence of blood vessels is more troublesome, the leather must be treated already at soaking by way of ANTIVEIN (H) action.

b)DERMATAN SULFATE REMOVAL.-

Leathers repeatedly present with a number of problems:

- Greater amount of wrinkles in the necks.
- Greater hardness in the heads as compared to the rest of the hide.
- Leather hardening in final finishing plates.



These problems are due to the presence of dermatan sulfate on the scalp, and will be higher, the greater the amounts of dermatan sulphate present.

The studies conducted at **the laboratories of the British Leather Confederation** showed that:

- 1°.- The **fibrillary structure** opening during Unhairing-Liming is associated with Dermatan Sulfate or Proteoglycan removal.
- 2°.- It **takes 18 hours under high alkalinity conditions** (unhairing-liming) for the Protein to unbind from Dermatan Sulfate. The protein is attacked by OH- ions and hydrolyzed on the ionic bonds of Hyaluronic Acid.


When complete hydrolysis of Dermatan Sulfate has failed for any reason (insufficient soaking, insufficient unhairing-liming time, not crossed, very thick leather...), hydrolysis can be completed with hydrolyzing products without affecting the collagen fiber. Namely:

- 1.- With **PRODUCT(I)** in **SOAKING**
- 2.- With **PRODUCT(J)** in **DELIMITING**
- 3.- With **PRODUCT(K)** in **TANNING** and **NEUTRALIZATION**.

These three products are added in due course, and the results obtained with each will be compared:

1.- 1.- HYDROLYSIS OF DERMATAN SULFATE WITH PRODUCT (I) AT SOAKING.-

0.3% of PRODUCT (I) is added to a standard formulation of the “upper” item.”.

 UNITS SUDAMERICANA S.A. Empresa del Grupo CROMOGENA UNITS,SA (España) Sta. M. De I Buen Ayre 362/4 1277 Buenos Aires-Argentina Tel:(541)3030423/4 Fax:(541)3010030 E-mail: units@units.com.ar		Fecha: 15/08/07 Tipo de cuero: Cuero salado REMOLIO PELAMBRE 24 HORAS Peso: 8788 Cantidad: 493	PRODUCTO (I)			
Técnico:		Dosis sobre peso BARRIDO SAL				
Att.:						
PRODUCTO	%	kg/ft	TIEMPO	TEMP	Ph	obs.
			E	F	T	
AGUA AL EJE						
PRODUCTO (I)	0,3	26,364			90'	
BACTERICIDA	0,12	10,546				
HUMECTANTE (A)	0,8	70,304			30'	
SULFURO DE SODIO	0,2	17,576			4 h	

Legend: Date: 15/08/07 – Leather type: Salted leather – **SOAKING DEHAIRING 24 HOURS** – Weight: 8788 – Quantity: 493 – Dose on **BLOOD WEIGHT** – **PRODUCT – WATER AT AXIS** – **ANTIBACTERIAL AGENT – WETTING AGENT – SODIUM SULFIDE**

TRANSLATOR'S NOTE

Commas are used as decimal separators in all numeric values on all tables.

Dots are used as thousand separators in all numeric values on all tables.

DRAIN TO INITIATE UNHAIRING

The comparative results of batches with and without PRODUCT (I) are:

COMPARATIVO			
SOLTURA	muy firme	32,30%	31,10%
FLOR	firme	47,20%	48,20%
	regular	19,40%	19,60%
	mal=suelto	1,10%	1,10%
DISTRIBUCION	blando	99,38%	100%
TOQUE	normal	0,63%	-
	duro	-	-
	Resist.Tracc.	35,64	32
ANALISIS FISICOS	Elong.	62,36	63,5
	Resist.Desg.	7,38	7,59
	Tongue	8,84	9,97
ANALISIS QUIMICOS	Cromo resid.	3,09	4,77
	Cromo wb	5,15	4,94
	Cenizas	10,05	13,68
Rendimiento	ph wb	3,82	3,86
	-	-7,09	-6,66

Legend: **LOOSENESS** (very tight – tight – average – loose) – **FEEL DISTRIBUTION** (soft – normal – hard) – **PHYSICAL ANALYSES** (tensile strength – elongation – tear load – tongue) – **CHEMICAL ANALYSES** (chromium resid – chromium wb – ashes – ph wb) – yield

COMPARATIVO		
	NORMAL	PROD.(I)
SOLTURA FLOR	3,78%	0,00%
MANCHAS	0,00%	0,00%
FINOS	0,67%	0,00%
GRUESOS	0,20%	0,00%
CRISPACION LEVE	4,47%	4,74%
CRISPACION MARCADA	13,34%	16,79%
Resist. (kg)	17,91	22,62

LOOSENESS – STAINS – FINE – THICK – LIGHT SHRUNKEN EFFECT – MARKED SHRUNKEN EFFECT

Yield formula =	WB AREA	- WB
	SEMIFINISHED AREA	

INCREASE OF 0.43 (7.09 – 6.66) IN 7.09 = 6 %

As shown in the table:

- There is hardly any difference as compared to customary factory values.
- Better area yield (6%)

2.- HYDROLYSIS OF DERMATAN SULFATE WITH PRODUCT (J) AT DELIMING.

0.6% of product (J) is added to the rest of deliming products in automotive leather goods.

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		DESENCALADO	
	Tipo de cuero:	Finos	
	Peso:	8000	
	Cantidad:	626	
Técnico:	Dosis sobre peso TRIPA		
Att.:			
PRODUCTO	%	kg/lt	TIEMPO TEMP Ph obs.
			E F T
AGUA	100	8000,000	20' 30'
ESCURRIR			
AGUA	50	4000,000	20' 30'
ESCURRIR			
AGUA	20	1600,000	30'
DESENCALANTE (F)	1,5	120,000	30'
METABISULFITO DE SODIO	0,55	44,000	30'
PRODUCTO (J)	0,6	48,000	60' 8,52 ph 28°C
DESENGRASANTE (L)	0,5	40,000	10'
ELASTASA (G)	0,1	8,000	40'
LAVAR - ESCURRIR			

Legend: Date: 14/08/07 UNLIMING – Leather type: Fine leather – Weight: 8000 – Quantity: 626 – Dose on PELT weight – WATER – DRAIN – DELIMING AGENT (F) – SODIUM METABISULFITE – DEGREASING AGENT (L) – Phenolphth.; colorless ok – ELASTASE (G) – WASH – DRAIN

The comparative results of batches with and without product (J) are shown in the table overleaf:

COMPARATIVO		
	NORMAL	PRODUCTO (J)
SOLTURA FLOR	4,10%	0,70%
MANCHAS	0,10%	0%
GRUESOS	0,47%	0%
FINOS	1,58%	2,00%
CONTRACCION LEVE	6,80%	2,20%
CONTRACCION MARCADA	3,50%	0,00%
Resist. (libras)	15,29	14,69

Legend: LOOSENESS – STAINS – THICK – FINE – LIGHT SHRINKAGE – MARKED SHRINKAGE – Resist. (pounds)

COMPARATIVO			
		NORMAL	PRODUCTO (J)
SOLTURA FLOR	muy firme	32,80%	33,70%
	firme	50,60%	51,90%
	regular	14,70%	12,90%
DISTRIBUCION TOQUE	mal=suelto	1,90%	1,50%
	blando	35,50%	60,70%
	normal	54,50%	39,30%
	duro	10,00%	0
ENSAYOS FISICOS	Tracc. N	1129	994,5
	Elong.	78	86
	Resist.Desq.	20	18,28
ENSAYOS QUIMICOS	Tongue	11,78	11,81
	Cromo	4,6	4,7
	Cenizas	7,3	6,8
RENDIMIENTO	Grasas	8	6,6
	ph	4,2	
	-	-7,55	-6,72

LOOSENESS (very tight – tight – average – loose) – FEEL DISTRIBUTION (soft – normal – hard) – PHYSICAL ASSAYS (tensile strength – elongation – tear load – tongue) – CHEMICAL ASSAYS (chromium – ashes – fats) – YIELD

INCREASE OF 0.83 (7.55 – 6.72) IN 7.55 = 11 %

As seen in the table above, PRODUCT (J) provides:

- A softer feel.
- A more uniform dyeing, with defects (scratches, spots,...) dyed according to tone.
- Better area yield by 11%.
- Lower % of hides with loose grain.

3.- HYDROLYSIS OF DERMATAN SULFATE WITH PRODUCT (K) AT TANNING.-

0.4% of product (K) is added together with the tanning self-basifying agent in automotive leather goods.

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		Tipo de cuero: Finos		Peso: 8000	
		Cantidad: 581		Dosis sobre peso TRIPA	
AGUA REFRIGERADA	20	1600,000			
SAL COMUN	6	480,000			
ENGRASE (Q)	0,8	64,000	10'		
FORMICO	0,4	32,000	10'		
FORMICO	0,4	32,000	30'		
SULFURICO	0,31	24,800	10'		
SULFURICO	0,31	24,800	10'		
SULFURICO	0,31	24,800	80'		
FUNGICIDA (O)	0,08	6,400	10'		
CROMO LIQUIDO	10	800,000	90'		
AUTOBASIFICANTE (P)	0,6	48,000	60'		
AUTOBASIFICANTE (P)	0,6	48,000	60'		
PRODUCTO (K)	0,4	32,000	7 h	3,86	T°C= 42°

COMPARATIVO		
	NORMAL	PROD. (K)
SOLTURA FLOR	4,10%	0%
MANCHAS	0,10%	0%
GRUESOS	0,47%	0%
FINOS	1,58%	2%
CONTRACCION LEVE	6,80%	2,50%
CONTRACCION MARCADA	3,50%	1,50%
RESIST. (libras)	15,29	15,75

Legend: Date: 14/08/07 – Leather type: Fine leather – Weight: 8000 – Quantity: 581 – Dose on PELT weight – REFRIGERATED WATER – COMMON SALT – FAT-LIQUORING (Q) – FORMIC – SULFURIC – FUNGICIDE (O) – LIQUID CHROMIUM – SELF-BASIFYING AGENT (P)

The comparative results of batches with and without product (K) are:

COMPARATIVO			
		NORMAL	PROD. (K)
SOLTURA FLOR	muy firme	32,80%	35,30%
	firme	50,60%	51,20%
	regular	14,70%	12%
	mal=suelto	1,90%	1,50%
DISTRIBUCION TOQUE	blando	35,50%	58,50%
	normal	54,50%	41,50%
	duro	10%	0%
	Resist.Tracc.	1129	873
ENSAYOS FISICOS	Elong.	78	63
	Resist.Desg.	20	21
	Tongue	11,78	11,26
	Cromo	4,6	4,69
ENSAYOS QUIMICOS	Cenizas	7,3	6,77
	Grasas	8	5,64
	ph	4,2	4,2
	RENDIMIENTO	-	-7,55
		-6,94	

INCREASE OF 0.61 (7.55 – 6.94) IN 7.55 = 8.1 %

As seen in the table above, PRODUCT (K) provides:

- A somewhat softer feel.
- Uniform dyeing, with defects (scratches, spots) dyed according to tone.
- Better area yield by 8.1%.

These results confirm the improvement provided by products that hydrolyze Dermatan Sulfate, particularly PRODUCT (J).

Legend: COMPARATIVE RESULTS BETWEEN STANDARD FORMULATIONS IN DIFFERENT FACTORIES, ADDING PRODUCT (J) AT UNLIMING (summary of a mean exceeding 30 batches per leather type) DRUM TYPE (pegs) – SOAK-UNHAIR. PROCESS (salting 48 h-24h) – integral / pelt split – ORIGIN (Spain, Germany, Mexico, Ireland, USA, France) – LEATHER TYPE (steer, cattle, cow) – BATCH WEIGHT (kg) – NR. OF LEATHERS PER BATCH – WEIGHT (KG) / LEATHER – SURFACE INCREASE – SELECTION INCREASE (4.3% of 1st, 7.2% of 2nd...) – reason – wrinkling improvement

TIPO DE BOMBO	PROCESO REM-PEL		PROCEDENCIA	TIPO DE CUERO	PESO (KG) PARTIDAS	Nº CUEROS / PARTIDA	PESO (KG) / CUERO	INCREMENTO SUPERFICIE	INCREMENTO CLASIFICADO	motivo
estacas	salado	integral	españa	novillos vacuno	8.000	180	44,44	5,33%	4,3% de 1ª	mejora
estacas	salado	divid.Tripa	españa	novillos vacuno	7.030	185	37,84	3,56%	7,2% de 2ª	mejora
estacas	salado	integral	alemania	novillos vacuno	10.000	285	35,08	4,81%	8,1% de 2ª	mejora
estacas	salado	divid.Tripa	méxico	novillos vacuno	4.800	145	33,1	3,12%	3,5% de 1ª	mejora
estacas	salado	integral	méxico	novillos vacuno	3.000	95	31,58	3,75%	4,5% de 2ª	mejora
estacas	salado	divid.Tripa	irlanda	novillos vacuno	6.000	195	30,77	3,23%	3,7% de 1ª	mejora
estacas	salado	integral	u.s.a.	novillos vacuno	5.300	200	26,5	2,25%	2,5% de 1ª	mejora
estacas	salado	integral	españa	novillos vacuno	9.000	370	24,32	1,63%	5,2% de 2ª	mejora
estacas	salado	integral	francia	vacas	5.000	230	21,74	0%	2,2% de 1ª	mejora
estacas	salado	integral	españa	vacas	3.200	180	17,7	0,10%	5,3% de 2ª	mejora
estacas	salado	integral	méxico	vacas	3.200	180	17,7	0,10%	1,2% de 1ª	mejora
									2,4% de 2ª	mejora
									o	
									o	
									o	

This table allows drawing the following conclusions:

- Better results are obtained by using PRODUCT (J) in:
- heavy leathers, from 25 Kg/leather.
 - Short processes: 24-hour Soaking-Unhairing.
 - Unsplit hide processes.
 - Very tight structure or corneus grain leathers.

Improvements obtained in wet-blue include:

- Area increase.
- Better leather selection (no wrinkling in neck, shanks, cheeks and belly).
- High batch consistency.
- More light blue color of wet-blue.

Improvements obtained in finished leather include:

- Area increase.
- Very uniform dyeings.
- Defects dyed according to dyeing tone.
- Similar handle between heads and the rest of the hide.
- Similar handle between different batches.
- More spongy feel.
- Better selection.

Thus, a DELIMING-DEGREASING-BATING standard formula without ammonium salts and with complete removal of Dermatan Sulfate can be established:

WATER at 35°C	200%
DEGREASING AGENT (L)	0.2 %
LACTIC ACID	0.3 %

Run 15 min. Drain 15 min. under static conditions.

IN THICK LEATHER

WATER at 35°C	30 %	30%
DELIMING AGENT (F)	1.8%	2.5%
SODIUM BISULPHITE	0.4%	0.4%

Run 30 min. Run 30 min.

PRODUCT (J)	0.6%	0.6%
DELIMING AGENT (F)	0-0.7%	1 %

Run 120 min. Run 150 min.

Phenolphthalein control: neck = slight line

ELASTASE (G)	0.5%	0.7%
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DEGREASING AGENT (L)	0.2%	0.2%
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Run 20 / 30 min. Run 30/45 min.

Bating control
Drain 10 min. while running.

COLD WATER 200%
Drain while running with open valves.

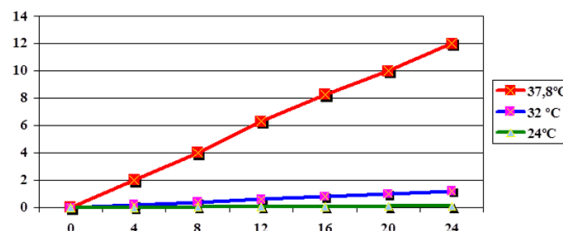
COLD WATER 200%
Drain while running with open valves.

5th.- PICKLING AND CHROMIUM TANNING.-

a).- SULFURIC ACID REPLACEMENT BY NON SWELLING ORGANIC ACIDS.

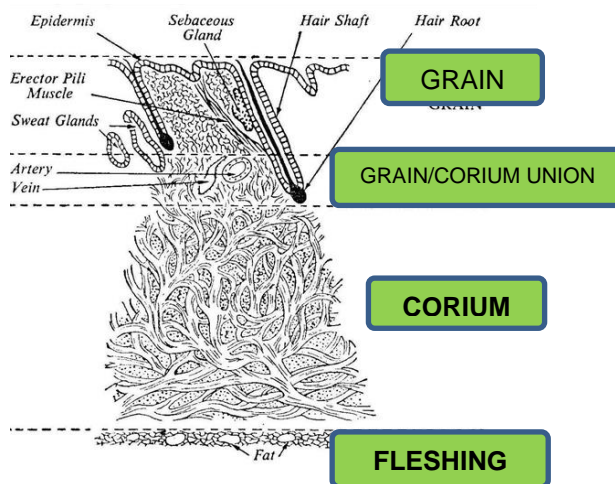
- Many countries exercise tight control over the consumption of Sulfuric Acid on account of its use in illegal drug manufacturing.

- In warm countries, water at room temperature exceeds 27°C. This, added to the heat of sulfuric acid dissolution, leads to a temperature increase in the drum that results in Collagen protein dissolution, as shown in the graph below:



The factors that have an influence on the higher hydrolysis of the collagen protein include:

- pH
- time
- temperature.

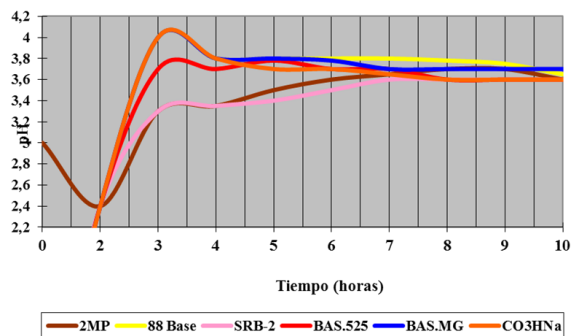


In order to avoid collagen fiber solubilization on account of the hide undergoing high temperature and low pH conditions for a long running time, a sulfuric acid-free tanning system with weak acids and less running time can be used: SULFONIC ACID (LL).

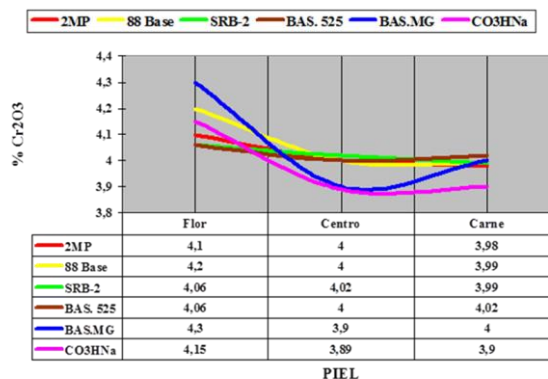
b).-USE OF SELF-BASIFYING AGENTS IN CHROMIUM TANNING.-

The use of self-basifying agents in the tanning process allows maximum chromium exhaustion and better stratigraphic chromium distribution.

Different basifying agents (formulated, magnesium oxide-based and sodium bicarbonate-based self-basifying agents) were compared in a chromium tanning process. No variations in final pH or chromium oxide content (gr/l) in residual bath were observed with each product adjusted for alkalinity, as shown in the graph below.



However, the choice of the basifying agent is indeed important regarding its stratigraphic distribution. As shown in the graph



minimum differences in Cr2O3 % between grain, middle and flesh were obtained with SRB/2 and BAS. 525.

The worst distribution is obtained with sodium bicarbonate and magnesium oxide.

Regarding difference figure:

	5 DAYS			10 DAYS			15 DAYS		
	pH	pH (1:10)	Δ pH	pH	pH (1:10)	Δ pH	pH	pH (1:10)	Δ pH
2MP	3,64	4,16	0,52	3,60	4,04	0,44	3,65	4,25	0,6
88 Base	3,60	4,06	0,46	3,58	3,87	0,29	3,62	4,13	0,51
SRB- 2	3,60	4,15	0,55	3,63	4,02	0,39	3,62	4,05	0,43
525	3,52	4,06	0,54	3,50	3,88	0,38	3,59	4,10	0,55
BAS.MG	3,62	4,08	0,46	3,58	4,10	0,52	3,60	4,12	0,52
CO ₃ HNa	3,67	4,22	0,55	3,72	4,21	0,49	3,75	4,34	0,59

ΔpH is the difference between one solution (1 g of leather at 20 g of water) and that solution diluted 10 more times; this value indicates the presence or absence of strong acids and bases in the leather.

Of note, the difference figure must always be lower than 0.7.

c) BATH RECYCLING AND CHROMIUM RECOVERY. -

This issue has been previously approached by means of the two systems available:

- Bath recycling after filtration and pH adjustment.

- Cr₂O₃ precipitation with NaOH after filtration and further redissolution with SO₄H₂.

6th.- METAL-FREE TANNING: VEGETAL AND WET-WHITE.-

Needless to say, avoiding the use of chromium is the best way to prevent chromium pollution. Non-chromium tanning procedures include vegetal and wet-white tanning.

Vegetal tanning is not as eco-friendly as it would seem (no chromium is used) due to the deforestation it involves.

The most frequently used Wet-White tanning procedure includes GLUTARALDEHYDE (M) supported by a DIHYDROXIDIPHENYL SULFONE (N).

This tanning technique allows reaching a shrinkage temperature of 76°C.

7°.- MOULD PREVENTION.-

Hides can be attacked by a number of different moulds.

Indeed, green, green yellowish and even red mould colonies can appear in hide surfaces. Moulds grow in colonies and reproduce by spores under high-humidity and high-temperature conditions and at pH greater than 4.

Moulds feed on hide fat.



TCMTB (thiocyanomethylthio benzothiazole): ANTIFUNGAL AGENT (O) is the most frequently used fungicide after the ban of Pentachlorophenol.

Experiments have shown that a Minimum Inhibitory Concentration (MIC) is required under which TCMTB exerts no action on moulds: in a PRODUCT with 30% of active matter, the minimum dose is 0.08% on pelt weight.

The dose should be increased to 0.1 – 0.15 % for long-term storage.

TCMTB breaks down at a pH greater than 4, and does so to a greater extent and faster with increasing pHs.

The following recommendations should be observed to avoid TCMTB breakdown:

- Do not store the product above 40°C to prevent TCMTB breakdown.
- Add the emulsified product together with chromium salt addition or at pickling.
- Degrease thoroughly.
- Previously ensure that product emulsion is stable (always add the product to water at a 1:3 ratio).
- Prepare the emulsion immediately before adding to drum.
- Wash final tanning in new bath with 0.1 % Formic Acid for 10 min until surface pH = 3.6 / 3.7

Should unreacted residues of basifying agent remain in the bath and fail to be thoroughly removed at the final washing, pH would rise above 4 when piling up, resulting in further TCMTB breakdown and increased hide vulnerability to moulds.

To prevent this, a new bath is prepared after draining the tanning bath and possible excessive amounts of basifying agent are made to react with formic acid.

Because restrictions in the use of TCMTB are currently being applied worldwide, two new, equally effective fungicides have already been developed:

- IPBC (3 iodoprop-2 ynyl N-butylcarbamate).
- DIMPTS (Diiodomethyl-p-tolysulfone).



pH=3,8/3,9

pH<3,6/3,7

CONCLUSIONS

- The use of dicarboxylic organic acids instead of Ammonium Sulfate at deliming allows decreasing the conductivity (SO₄⁼) and the nitrogen of residual baths from the deliming bath.

PRODUCTS USED BY CROMOGENIA UNITS S.A.

F.- DELIMING AGENT.....	DELIMING AGENT SE-01
G.- ELASTASE.....	VERDITAN EL
H.- ANTI BLOODVEIN AGENT.....	VERDITAN CV
I.- PRODUCT I.....	HUMECTOL MAX
J.- PRODUCT J.....	DECALIM PLUS
K.- PRODUCT K.....	PLENATOL IS
L.- DEGREASING AGENT.....	CELESAL DLA
LL.- SULFONIC ACID	RETANAL SCG
M.- GLUTARALDEHYDE.....	RETANAL GL-50
N.- DIHYDROXYDIPHENILSULFONE....	RETANAL SUL
O.- FUNGICIDE (TCMTB).....	ASEPTANTE WB
P.- SELF-BASIFYING AGENT.....	PLENATOL SRB/2
Q.- FATLIQUOR.....	UNIX P-48

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