UNEWS. Leather

Information Bulletin Nr. 27

CROMOGENIA UNITS
YOUR SPECIALIST FOR SPECIALTIES

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PRESENTATION

The second technical meeting of 2016 was held at the H10 Marina Barcelona, attended by more than 50 technicians from countries like Spain, Portugal, Argentina, Brazil, Mexico, Colombia, Chile, China and Italy. This meeting lets the commercial technical developments of new products and studies.

Moreover, it is given priority to the presentation and comments of the commercial technicians

Designed, Edited and published by Cromogenia's Leather Department

This bulletin is addressed to all technicians, Representatives, Customers and Friends who wish to keep themselves updated about our new products and releases.

For further information or suggestions, please contact: **oballus@cromogenia.com**

UNEWS. Leather, Nº 27.

The Interview

In this new section, a prominent figure of our Company will be interviewed. The purpose of this new section is to disseminate different opinions and views about different technical and commercial aspects of our Industry, particularly that developed outside Spain.

In this issue we interview Units Sudamericana. S.A. CEO Carlos Szalai.

Question: ***How did Units Sudamericana came about?***

In 1986 Cromogenia Units, SA entered the Southern Cone market through an Argentinian family company, Ardennes, SA.
Joint work by the two companies yielded very good results, and "Units Sudamericana" was created in 1997 with the team that reached those results.

Question: ***What countries do you have a special relationship with?***

We are a growing company in the Cromogenia Units group and we operate in Argentina, Chile, Peru, Uruguay, Bolivia and Brazil. With highly qualified and committed personnel in every sector, we believe in teamwork and give weight to each individual's best efforts and dedication at their workplace.

Question: ***What is your relationship with Cromogenia Units. S.A.?***

A strong and interesting synergy has developed among our our Company and the technical and development team of Cromogenia Units. This has allowed us to grow considerably and to pioneer in many developments which, today, are used in all the countries where we operate.

Question: ***What is the current situation of the Southern Cone market?***

From our very beginnings, the leather market has often been suffocated, mainly due to change of ownership between leather owners. While all countries were affected, Argentina and Brazil bore the brunt of these changes. To a greater or lesser extent, the quantity of hides is the same

and a lower quantity of tanned hides are distributed, thus making competition very strong and voracious.

Question: ***Is it difficult to remain in the current market?***
Thanks to the professional work of our technical and human team we have been able to remain in the market and position Units Sudamericana and its subsidiaries Units Brazil and Units Chile as members of the selected group of supplying companies in the leather market, with service and quality being our hallmarks. This would not have been possible without the unqualified support of Cromogenia Units, SA and its entire commercial, technical and human infrastructures.

Question: ***What is your Company's past, present and future?***
Some of the pioneers are not with us anymore, but the new generation is!
On behalf of the entire staff of Units Sudamericana, I wish to thank you for the opportunity to provide some insight into the Southern Cone. You're all welcome to visit us!

Carlos Szalai

RETANAL ML

RETANAL ML is a melamine resin-based retanning agent with a good filling effect.

This is a product in liquid form at approx. 50% of active matter.

RETANAL ML is a non-astringent product that enhances grain firmness and leather fullness and provides a very fine grain.

High fastness to light and temperature is obtained

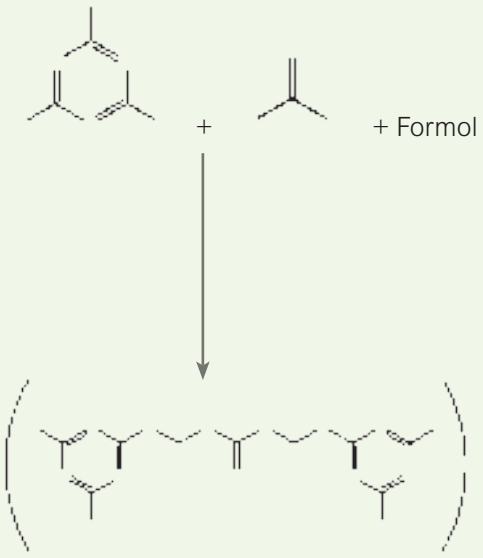
SYNTHESIS OF MELAMINE RESINS

Melamine resins used in tanning are synthesized by polymerization between melamine, urea and form under alkaline or acid conditions. Polymerization is based on three sequential reactions:

1) Reaction leading to the formation of methylol: involves the addition of formol to melamine or to urea.

2) Reaction leading to the formation of the pre-polymer or chain or chain polymerizatioin.

3) Crosslinking or curing of polymer.



New Wet end Products

These resins bind to collagen by means of hydrogen bridges, reactions of the amine groups of the resin with Cr^{3+} and finally by Van der Waals' forces.

Because these are amphoteric products that may increase collagen cationicity at the end of the process, they do not decrease color intensity as strongly as acrylic or phenolic resins.

IINFLUENCE OF NAPHTHALENESULFONIC ACID DERIVATIVES ON THE DYEING PROPERTIES OF LEATHER. PART II

1. Introduction

The first part of this study was presented at a former meeting held in July 2015. At this meeting, the dyeing properties provided by the different naphthalenesulfonic derivatives to the hide when tanned separately with dyes Acid Brown 83 and Acid Black 210, were assessed. It was concluded that the higher the molecular weight, the higher the penetration. In terms of intensity and leveling, no clear tendency was observed.

In this second part we shall study the behavior of a mixture of equal parts of the above-mentioned two dyes and we shall compare them in parallel studies to an amine ethoxylate (Colorfix US) to assess its effect on the dyeing.

2. Experimental Part

2.1. Process

PROCESS			WEIGHTW.B. (2 m.m.)		Minutes	
WASHING	35	200	Water			
		0.2	Acetic acid			
		0.2	Celesal DL		10	pH=3.20
						Drain and wash
NEUTRALIZATION	35	150	Water			
ANIONIZATION		2	Sodium formate		30	pH=4.20
		0.3	Sodium bicarbonate		60	pH=5.2
		2.5	NAPHTHALENE SULFONIC		60	Drain and wash
DYEING	45	100	water			
VARIABLE WITH	1.5	2	COLORFIX US		20	
	1.5	1.7	Acid Brown 83			
		1.7	Acid Black 210		60	
		5	Fosfol SC-10			
		5	Fosfol 50		60	
		1	HCOOH		60	pH=3.8 - 4.0
						Drain and wash

Formula 1. *Application process*

2.2. Products used

PRODUCT	CHAIN LENGTH	MEAN MW	SO_3 / MOLECULE MEDIUM	pH (10/100)
RETANAL A-50	long	3.000	11	7
RETANAL A-4	medium	1.400	6	6
RETANAL A-40	medium	1.300	5	7
RETANAL HD	medium	1.200	5	7
RETANAL NS	medium	1.200	5	7
RETANAL NK	short	600	3	7

Table 1. *Products used*

2.3. Results

2.3.1. Penetration – anionic part

Penetration is assessed by differential dyeing with methylene blue.

Maximum anionicity penetration is obtained with RETANAL A-50 followed by RETANAL A-4, and minimum penetration is obtained with RETANAL NK.

Figure 1. *Penetration - anionic part*

RETANAL A-50 —i.e. the product with highest molecular weight and larger number of SO_3, groups— has a helicoidal structure which, together with its spatial size (15 Å), allows it to penetrate and bind to the spaces of chrome-tanned hides

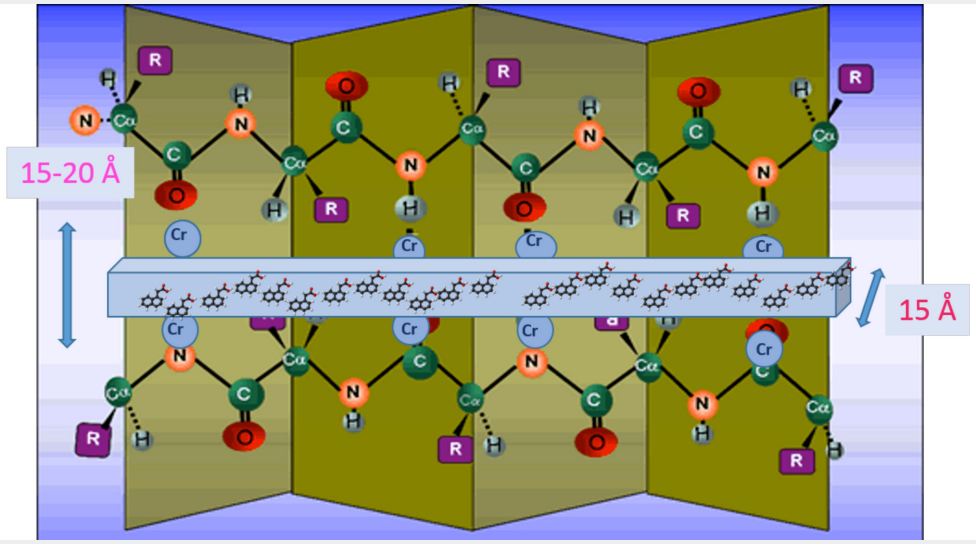


Figure 2. *Simulation of RETANAL A-50 binding*

2.3.2. Dye penetration

Dye penetration (mixture of the two dyes) shows good levelness at hide section, with a somewhat grayer tonality.

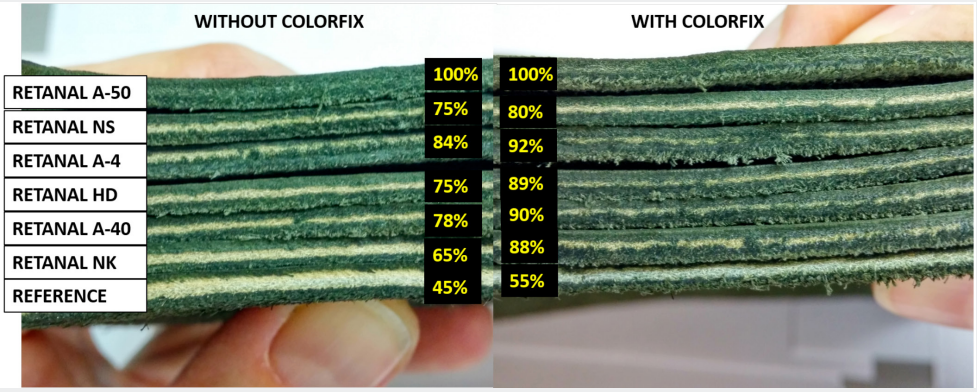


Figure 3. *Influence of COLORFIX US on dye penetration*

COLORFIX US significantly increases dye penetration. A comparison between the penetrations **WITH and WITHOUT COLORFIX US** shows that RETANAL A-50 does not influence penetration, while the latter is significantly increased in the rest of products and the Reference.

PRODUCT	ANIONICITY PENETRATION (%)	PENETRATION WITHOUT COLORFIX (%)	PENETRATION WITH COLORFIX (%)	% OF PENETRATION VARIATION WITHOUT-WITH COLORFIX	MEAN MW
RETANAL A-50	100	100	100	0	3000
RETANAL NS	70	75	80	6.6	1100
RETANAL A-4	85	84	92	9.5	1400
RETANAL HD	60	75	89	18.6	1200
RETANAL A-40	60	78	90	15.4	1200
RETANAL NK	50	65	88	35.3	600
REFERENCE	0	45	55	22.2	

Table 2.

Influence of COLORFIX US on dye penetration

2.3.3. Color intensity

When color intensity (L*) is compared on the grain side, the REFERENCES (without RETANAL) have the highest values (lower L*).

The comparison of the values WITH and WITHOUT COLORFIX US shows that RETANAL A-50 and RETANAL A-4 strongly increase intensity, while no significant differences are found in the rest of products and in the REFERENCE.

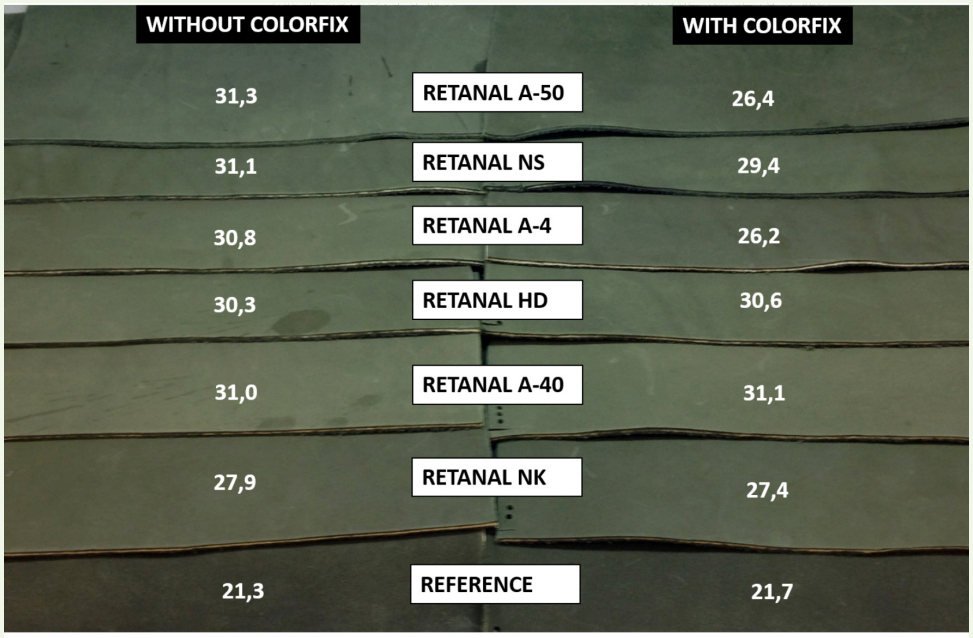


Figure 4. *Influence of C COLORFIX US on dyeing intensity*

PRODUCT	L* (WITHOUT COLORFIX)	L* (WITH COLORFIX)	% OF PENETRATION VARIATION WITHOUT-WITH COLORFIX	MEAN MW
RETANAL A-50	31.3	26.4	15.6	3000
RETANAL NS	31.1	29.4	5.4	1100
RETANAL A-4	30.8	26.2	14.9	1400
RETANAL HD	30.3	30.6	-0.9	1200
RETANAL A-40	31	31.1	-0.3	1200
RETANAL NK	27.9	27.4	1.7	600
REFERENCE	21.3	21.7	-1.87	

Table 3. *Influence of COLORFIX US on dyeing intensity (quantification)*

2.3.4. Bath exhaustion

Impregnate filter paper with residual bath, allow to dry and measure color intensity (L*).

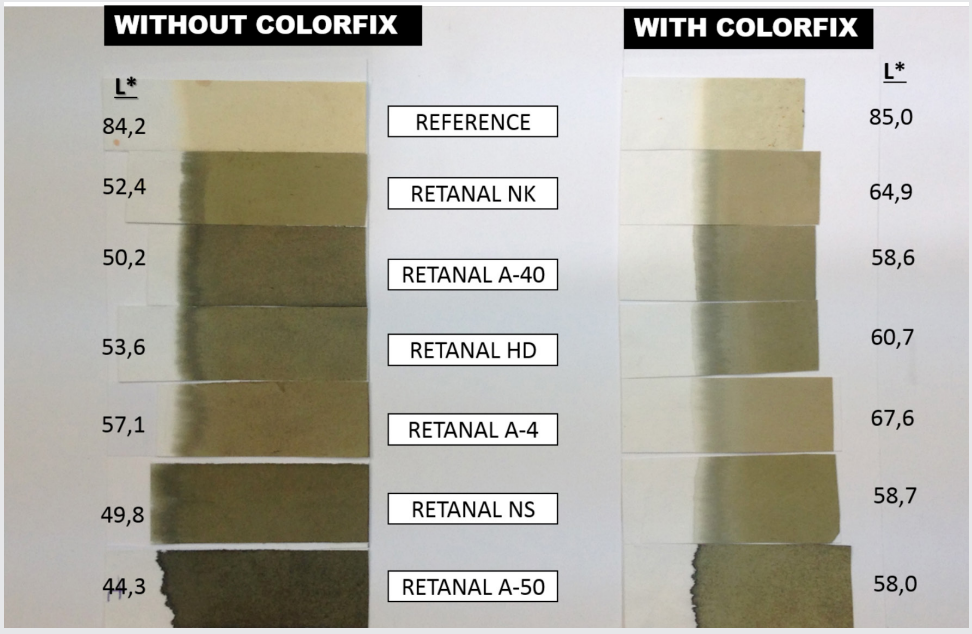


Figure 5. *Influence of COLORFIX US on dye bath exhaustion*

All dye bath exhaustion values are strongly increased by the action of COLORFIX US; only the Reference shows little variation (+5%).

PRODUCT	EXHAUSTION WITHOUT COLORFIX US (%)	EXHAUSTION WITH COLORFIX US (%)	% VARIATION WITHOUT-WITH COLORFIX US
RETANAL A-50	44.3	58	30.9
RETANAL NS	49.8	58.7	17.8
RETANAL A-4	57.1	67.6	18.3
RETANAL HD	53.6	60.7	13.2
RETANAL A-40	50.2	58.6	16.7
RETANAL NK	52.4	64.9	23.8
REFERENCE	84.2	85	0.95

Table 4. *Influence of COLORFIX US on dye bath exhaustion*

2.3.5. Chemical oxygen demand (COD) of the residual baths

As seen in each column (different RETANAL), RETANAL NK (lower molecular weight) yields the highest value (54,700 ppm), i.e. doubling and/or tripling the rest of RETANAL. The Reference yields a significantly lower value and the difference with each of them indicates the quantity left in the bath.

The comparison of the two columns (WITHOUT and WITH COLORFIX) shows a small increase except when using RETANAL NK (27% increase).

PRODUCT	COD without COLORFIX US (mg O_2/L)	COD with COLORFIX US (mg O_2/L)	% of COD Variation WITHOUT-WITH COLORFIX US
RETANAL A-50	20500	22600	10.2
RETANAL NS	22400	24400	8.9
RETANAL A-4	13000	13500	3.8
RETANAL HD	14800	15700	6
RETANAL A-40	16200	16800	3.7
RETANAL NK	17900	18700	4.4
REFERENCE	6000	6400	6.6

Table 5. *Influence of COLORFIX US on the COD of dye baths*

2.3.6. Color leveling

Color leveling was assessed by measuring total color (E*) at a reference point and at another ten points on the grain side. The ΔE*values vs. that reference were calculated and these values were averaged (DE*). This value represents color “leveling” for each naphthalenesulfonic and for the Reference.

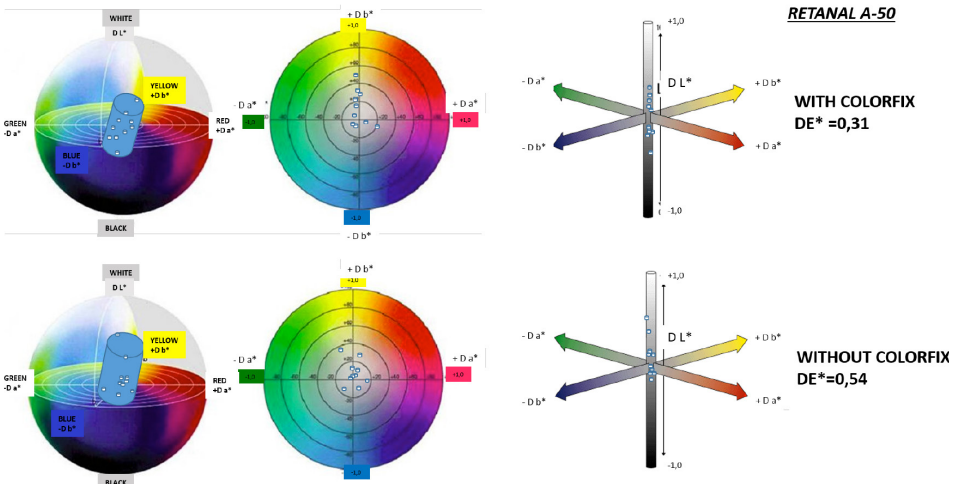


Figure 6. *Trichromatic representation of color leveling*

PRODUCT	COLOR LEVELING WITHOUT COLORFIX US (DE)	COLOR LEVELING WITH COLORFIX US (DE)	% of color leveling variation WITHOUT-WITH COLORFIX US
RETANAL A-50	0.54	0.31	42.5
RETANAL NS	0.44	0.38	13.6
RETANAL A-4	0.64	0.47	26.5
RETANAL HD	0.6	0.37	38.3
RETANAL A-40	0.14	0.12	14.2
RETANAL NK	0.8	0.44	45
REFERENCE	0.94	0.88	6.3

Table 6. *Relation between color leveling and product properties*

Each RETANAL and the REFERENCE are depicted in a graph with three levels. On the first level, L* (Luminosity) depicts the values of the White-Black component; the second level includes the values of the chromatic component (Green-Red; Yellow-Blue); and the third level includes a tridimensional sphere that contains the two first levels.

In this sphere, the center is the value of reference. ΔE*values are inside a cylinder whose size indicates the degree of value dispersion: the higher the cylinder volume, the higher the dispersion.

The worst leveling are found with the REFERENCES. A comparison of the values of the two columns shows that, in both columns, RETANAL NK has the worst leveling both with and without COLORFIX US. Also, leveling is quite similar in the rest of products. However, the addition of COLORFIX US significantly improves leveling (by 13 to 47%) in all RETANAL. A low influence (+6%) is found in the Reference.

3. Conclusions

An overall assessment of the influence of COLORFIX US on dyeing is shown in the table below:

VARIATION OF THE PROPERTY (%) WHEN ADDING COLORFIX US						
PRODUCT	PENETRATION	INTENSITY	BATH EXHAUSTION	LEVELING	MW	SO_3 / MOLECULE
A-50	0	+16	+32	+45	3,000	11
A-4	+9.5	+15	+20	+26	1,400	6
A-40	+15.3	+0.3	+17	+14	1,300	5
HD	+18.6	-2.3	+14	+38	1,200	5
NS	+6.6	+5	+19	+13	1,200	5
NK	+35	+0.1	+48	+47	600	3
REF	+12	+0.18	+5%	+6		

Table 7. *Influence of COLORFIX US on color properties*

Studies

The larger dye exhaustion when using COLORFIX US translates into:

3.1. Increased color intensity when using RETANAL A-50.

3.2. Increased color intensity and increased penetration when using RETANAL A-4.

3.3. Increased penetration in the rest of RETANAL and in the Reference.

FATLIQUORING AGENTS IN WET WHITE TANNING

1. Introduction

The parameters that define when a chrome-tanned leather has the optimal conditions to be fatliquored are well known and are based on criteria of reactivity of that leather at different pH, degrees of neutralization and anionization, and type of retanning agent.

In general, in terms of anionic fatliquoring agents, the fatliquoring agent remains on the surface when the leather has an acid pH. In case of strong anionicity, normally at retanning, the fatliquoring agent is less fixed but penetrates more easily.

Tanning and retanning a wet white leather provides it fatliquoring agents is different from that of a wet blue leather.

So far, usual practice has been to use the same fatliquoring products with (in principle) positive results.

The purpose of this study was to assess the comparative behavior of different fatliquoring products from different families by measuring the degree of softness, the thickness and the COD (exhaustion) of the bath.

2. Operational method

2.1. Raw material

The origin is an entire hide pickeled at pH=3.2 and tanned with RETANAL CX-90 according to Formula 2.

2.2. Fatliquoring products

The products applied in this study are shown in Table 8 classified by families.

SULFITED/ SULFONATED	SULFATED	SULFOCHLORINATED	PHOSPHORIC ESTERS	LECITHINS	POLYMERS
FOSFOL AUT C-3	FOSFOL 50	FOSFOL SC-10	REPELAN WR-25	FOSFOL CL	RETANAL PR-165
FOSFOL AUT	FOSFOL 51	FOSFOL SC-20		FOSFOL LC-80	REPELAN HC
FOSFOL DF-20					
FOSFOL AUT 09					

Table 8. *Fatliquoring agents used*

2.3. Processes

2.3.1. Tanning

OPERATION	ºC	%	PRODUCT	g /Kg	TIME	REMARKS
	25	80	Water 6°Be, pH=3			
		5	**RETANAL CX-90**		**180**	
		1	Sodium formate			
		1	UNIX P-48		60	pH=
		0,5	Sodium bicarbonate		60	pH=4,5 - O/N
		2,5	RETANAL XD		60	
		2,5	RETANAL XD		60	pH=4,5
						Tc=75°C - @ bm
			drain, shave 1,2 mm			

Formula 2. *Wet white tanning with RETANAL CX-90*

2.3.2. Retanning Fatliquoring

The left halves are used as REFERENCES fatliquored with FOSFOL AUT 09.

The right halves are fatliquored with the selected products showed in Table 8.

OPERACIÓN	ºC	%	PRODUCTO	g /Kg	TIEMPO	OBSERVACIONES
	40	300	Water			
		0,2	EDTA		10	
		0,1	ASEPTANTE BF			
		0,8	Formic acid		2x30	pH=4,2.Control=
						Drain
	30	200	Water			
		3	NEUTRAGENT NT		60	pH=4,5. Drain
	30	100	Water			
		3	RETANAL XD			
		7	RETANAL AOX		60	
		3	A.B. 83		120	@
		3	RETANAL XD			
		7	RETANAL AOX		120	
	45	40	Water		5	
		3	RETANAL RST		30	pH=
		0,6	Formic acid		2x15	pH=4,2. Drain
	45	300	Water		10	Drain
	45	200	Water			
LEFT - REF		**12**	**FOSFOL AUT 09**		**90**	
RIGHT - PROD		**x**	**PROD**		**90**	
					60'	pH=
		0,6	Formic acid		2x15'	pH=4. Drain

Formula 3. *Retanning/Fatliquoring*

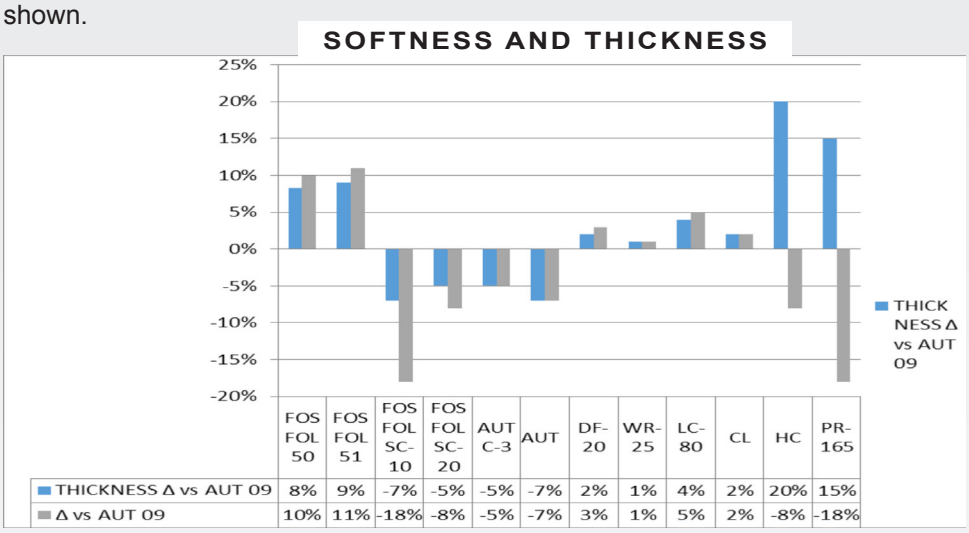
NOTE: **FOSFOL AUT 09** was applied at 12%. The rest of oils were applied with equal amounts of active material.

2.4. Assessments

All assessments were made with FOSFOL AUT-09 as Reference; therefore, they all are variations in respect of FOSFOL AUT-09.

2.4.1. Degree of softness and thickness

In Graphic 1, variations in softness and thickness in respect FOSFOL AUT 09 are shown.

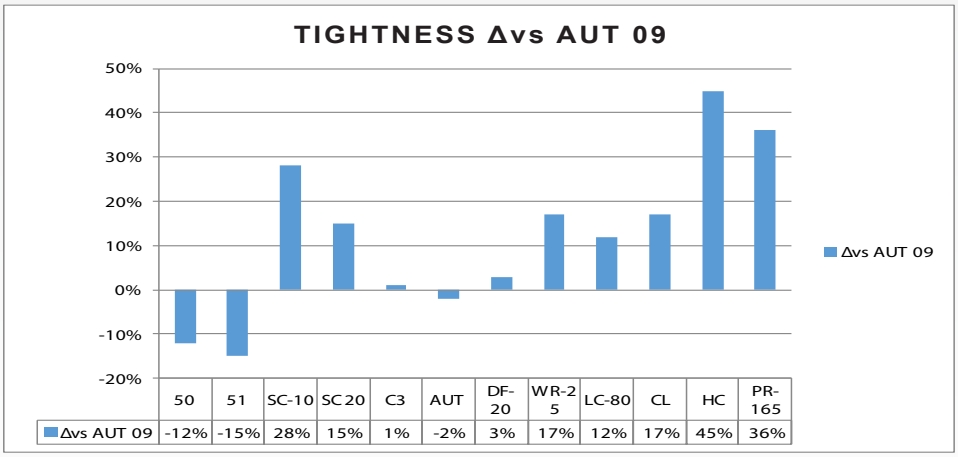


	FOSFOL 50	FOSFOL 51	FOSFOL SC-10	FOSFOL SC-20	AUTC-3	AUT	DF-20	WR-25	LC-80	CL	HC	PR-165
THICKNESS Δ vs AUT 09	8%	9%	-7%	-5%	-5%	-7%	2%	1%	4%	2%	20%	15%
Δ vs AUT 09	10%	11%	-18%	-8%	-5%	-7%	3%	1%	5%	2%	-8%	-18%

Graphic 1. *Variations in softness and thickness*

2.4.2. Tightness

In the graphic 2, variation in tightness in respect FOSFOL AUT 09 is shown.

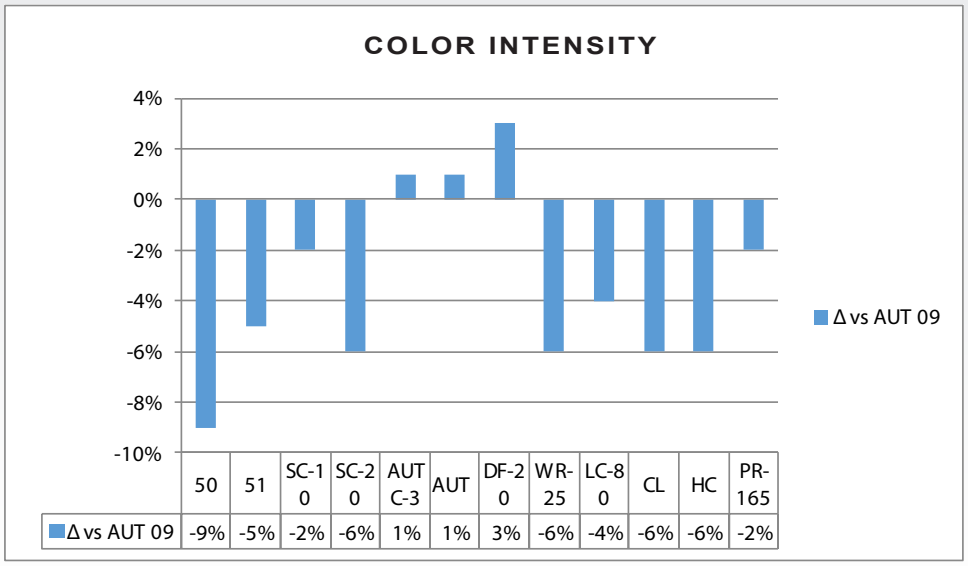


	50	51	SC-10	SC 20	C3	AUT	DF-20	WR-25	LC-80	CL	HC	PR-165
Δvs AUT 09	-12%	-15%	28%	15%	1%	-2%	3%	17%	12%	17%	45%	36%

Graphic 2. *Variation in tightness*

2.4.3. Color intensity

In the Graphic 3, variation in color intensity in respect FOSFOL AUT 09 is sown.



	50	51	SC-10	SC-20	AUT C-3	AUT	DF-20	WR-25	LC-80	CL	HC	PR-165
Δ vs AUT 09	-9%	-5%	-2%	-6%	1%	1%	3%	-6%	-4%	-6%	-6%	-2%

Graphic 3. *Variations in color intensity*

3. Conclusions

1.º Sulfated oils have high softening power but very low grain tightness.

2.° FOSFOL AUT C-3 and FOSFOL 50 have the highest thickening power.

3.º Importantly, REPELAN WR-25 and FOSFOL CL do not alter softness but do increase tightness.

4.° To be emphasized is the high tightening power of REPELAN HC.

5.° Lethicins behave well on wet white, with high softening and tightening power.

6.º Color intensity undergoes only minor variations.

NEW WET WHITE PROCESS WITH RETANAL A-WW

1. Introduction

For the past 15 years, many studies have been conducted and many products have been developed at C.U. to meet the demand for chrome-free articles, particularly in car upholstery.

Currently, the most frequently used product of our range is RETANAL CX-90, which in general meets part of the market requirements. Its formulation, however, contains an aldehyde. According to the current policy for the development of new products, this aldehyde should be eliminated.

The present study developed a new wet white process based on a tanning material originating from a strongly anionic and helicoidal polymer we have called RETANAL A-WW.

2. Experimental part

2.1. Tanning process

ºC	%	PRODUCT	TIME	REMARKS
25	80	Water 6ºBe, pH=3		
	1.5	FOSFOL AUT 09	20	
	5	RETANAL A-WW	60	control
	5	RETANAL A-WW	60	control
	5	RETANAL A-WW	60	control
	5	RETANAL A-WW	60	control Ts= 72-74ºC
				Drain - wash
Penetration control with methylene blue Shave 1.2mm				

Formula 4. *Wet white tanning with RETANAL A WW*

2.1.1. Controls performed

2.1.1.1. (Final) pH=4.5

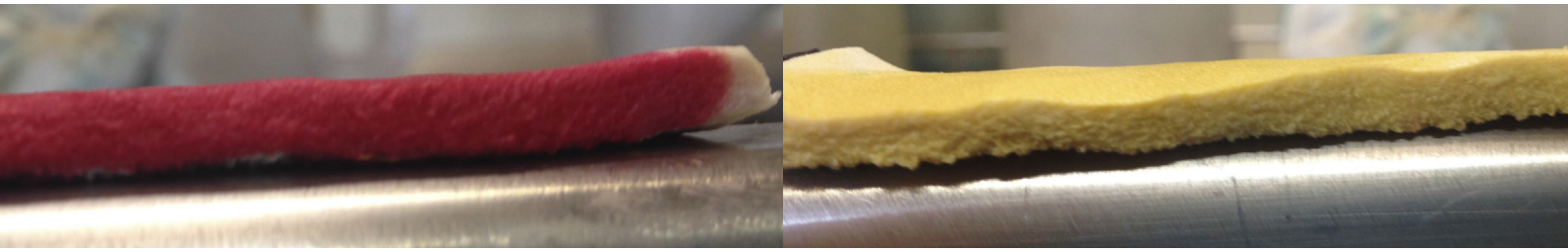


Figure 7. *(Left) Universal Indicator section. (Right) Bromocresol Green section*

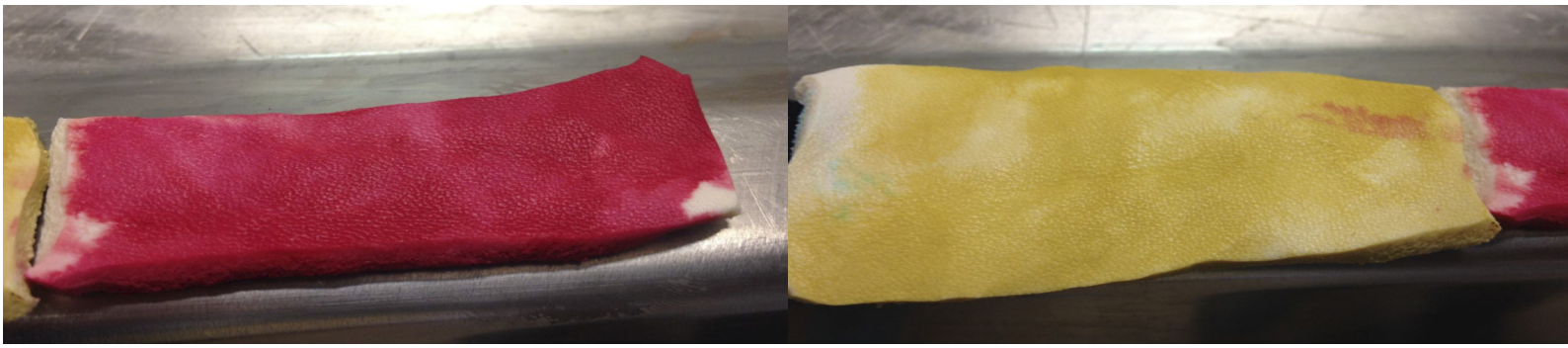


Figure 8. *(Left) Universal Indicator grain. (Right) Bromocresol Green grain*

2.1.1.2. Degree of anionization

- **Section penetrated 100%**
- **Even surface**

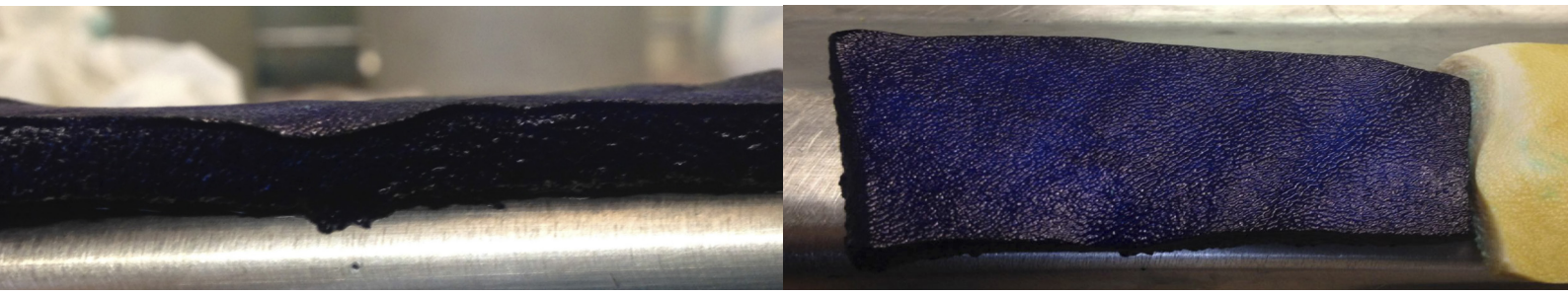


Figure 9. *(Left) Section anionicity. (Right) Grain anionicity*

2.1.1.3. Shrinkage temperature

Tanning with RETANAL A WW gives Ts=75ºC.

Ts = 75ºC	Shrinkage: 20%

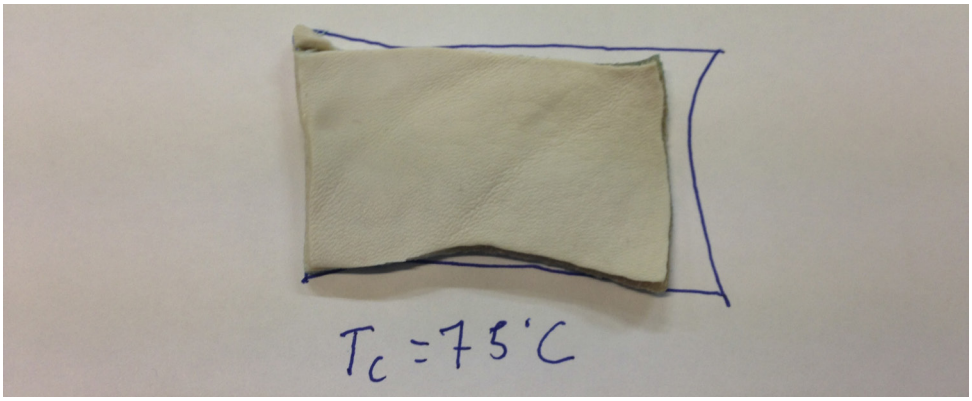


Figure 10. *Shrinkage temperature*

Figure 11 shows the aspect of a tanned leather with RETANAL A WW.

Figure 11. *Appearance of entire tanned hide*

2.3. Comparative processes

The ultimate purpose is to replace current processes based on glutaraldehyde and chrome tanning. We thus designed a comparative study using two hides; the left halves were tanned with the prior process with RETANAL A-WW (Formula 4); one right half was tanned with glutaraldehyde (Formula 5) and the other right half was tanned with chrome (Formula 6).

ºC	%	PRODUCT	TIME	REMARKS
25	80	Water 6ºBe, pH=3		
	2	**RETANAL GL-50**	**180**	
	1	Sodium formate		
	1.5	**FOSFOL AUT 09**	60	pH=
	0.5	Sodium bicarbonate	60	pH=5.0 - O/N
	2.5	**RETANAL XD**	60	
	2.5	**RETANAL XD**	60	pH=4.5 Ts=78-80ºC
Drain - wash Shave 1.2mm				

Formula 5. *Applicative formulation for glutaraldehyde tanning*

ºC	%	PRODUCT	TIME	REMARKS
25	80	Baño de píquel	15	
	1,5	**FOSFOL AUT 09**	20	
	7	**CROMOTAN RAPID 33**	120	
	0,7	**PLENATOL HBE**	**8 h**	pH=3.9-4.0
Drain - wash Shave 1.2 mm				

Formula 6. *Applicative formulation for chrome tanning*

The two left halves, tanned with RETANAL A-WW, were retanned and fatliquored according to Formula 7.

ºC	%	PRODUCT	TIME	NOTES
		on ww + 30 % weight		
40	300	Water		
	0,2	EDTA		
	1	**FOSFOL AUT 09**	15’	
	0,1	**ASEPTANTE BF**		
	0,8	Formic acid	2x30’	pH= 4,2
				Drain
30	200	Water		
	3	**NEUTRAGENT NT**	60'	pH=4,5
				Drain
30	100	Water		
	3	**RETANAL XD**		
	7	**RETANAL AOX**	60'	
	2,5	**FOSFOL AUT 09**	30'	
	3	**BLACK DERMACUIR 234**	60'	cross section
	3	**RETANAL XD**		
	7	**RETANAL AOX**	120'	
	2,5	**FOSFOL AUT 09**	60'	
45	40	Water	5'	
	3	**RETANAL RST**	30'	pH=
	0,6	Formic acid	2x15'	pH= 4,2
				Drain
45	300	Water	10'	
				Drain
45	200	Water		
	1	**FOSFOL AUT C-3**		
	12	**FOSFOL AUT 09**	90'	
	0,6	Formic acid	2x15’	pH= 4
				Drain - wash

Formula 7. *Retanning fatliquoring for wer white tanning with RETANAL A WW*

The right half tanned with glutaraldehyde was retanned and fatliquored according to Formula 8:

ºC	%	PRODUCT	TIME	NOTES
		on ww + 30 5 weight		
40	300	Water		
	0,2	**EDTA**		
	1	**FOSFOL AUT 09**	15'	
	0,1	**ASEPTANTE BF**		
	0,8	Formic acid	2x30'	pH= 4,2
				Drain - wash
30	200	Water		
	3	**NEUTRAGENT NT**	60'	pH= 4,5
				Drain - wash
30	100	Water		
	5	**RETANAL XD**		
	10	**RETANAL AOX**	60'	
	2,5	**FOSFOL AUT 09**	30'	
	3	**BLACK DERMACUIR 234**	60'	cross section
	5	**RETANAL XD**		
	10	**RETANAL AOX**	180'	
	2,5	**FOSFOL AUT 09**	60'	
45	40	Water	5'	
	3	**RETANAL RST**	30'	pH=
	0,6	Formic acid	2x15'	pH= 4,2
				Drain
45	300	Water	10'	
				Drain
45	200	Water		
	1	**FOSFOL AUT C-3**		
	14	**FOSFOL AUT 09**	90'	
	3	**RETANAL XD**	60'	pH=
	0,6	Formic acid	2x15'	pH= 4
			Drain - wash	Drain - wash
		RETANAL XD	60'	pH=
	0,6	Fórmic acid	2x15'	pH=4.
				Drain - wash

Formula 8. *Retanning/Fatliquoring for RETANAL GL-50 tanned leather*

ºC	%	PRODUCT	TIME	NOTES
		% on shaved weight		
40	300,0	Water		
	0,6	Formic acid		
	0,2	**CELESAL DL, (1:3)**	60'	pH= 3,2-3,4
				Drain - wash
30	150,0	Water		
	0,4	**FOSFOL AUT C-3**	10'	
	3,0	**RETANAL PNB**	30'	
	0,5	Black dyestuff	15'	
	3,0	**RETANAL CNE**		
	3,0	**CROMOTAN RAPID 33**	120'	
	3,0	Sodium formate	30'	pH= 3,8-4,2
				Drain - wash
30	200,0	Water		
	0,2	Black dyestuff	20'	
	2,0	**NEUTRAGENT NT**	20'	
	1,2	Sodium formate	30'	
	0,2	Sodium bicarbonate	20'	
	2,0	**FOSFOL AUT C-3**	60'	pH= 5,0 - check
				Drain
30	250,0	Water	10'	
				Drain
30	100,0	Water		
	1,5	**FOSFOL AUT C-3**		
	1,0	**FOSFOL AUT C-9**	30'	
	2,0	**RETANAL RCN-40**		
	2,0	**RETANAL RC-200**		
	2,0	**RETANAL CLE**	30'	
	10,0	Tara		
	6,0	**RETANAL A-75**		
	3,0	**RETANAL PNB**	50'	
	2,0	**RETANAL A-4**	10'	
	3,0	Black dyestuff	80'	cross section
50	150,0	Water	5'	
	4,5	**FOSFOL AUT 09**		
	1,0	**FOSFOL AUT C-3**	60'	
	2,0	**RETANAL XD**	30'	
	1,0	Formic acid	20'	
	1,0	Formic acid	20'	
	1,0	Formic acid	40'	pH=
				Drain
40	200,0	Water		
	0,1	Formic acid	10'	
				Drain - wash

Formula 9. *Retanning/fatliquoring for chrome tanned leather*

2.3. Comparative results

2.3.1. RETANAL A-WW/Glutaraldehyde Tanning

At the retanning-fatliquoring phase of tanning with glutaraldehyde, 10% more fatliquoring agents and 30% more synthetic retanning agents are used, with the same quantity of RETANAL RST.

Free formol values are practically the same.

RETANAL A-WW	GLUTARALDEHYDE
18% FOSFOL AUT 09	*20% FOSFOL AUT 09*
23% SYNTHETICS	*33% SYNTHETICS*
3% RETANAL RST	*3% RETANAL RST*
FREE FORMOL (IUC 19-1)	
11 ppm	10 ppm

Table 9. *Product and free formol comparison*

PRODUCT	COLOR (L*)	SOFT. (IUP-36	THICK (mm)	TENSILE STRENGTH (N/mm^2)	ELON (%)	TEAR LOAD (N)	TEAR LOAD (N/mm^2)	GRAIN BURST (mm)	OBS.
RETANAL A-WW	*DARKER*	*4.4*	*1.4*	*14.83*	*26*	*66.15*	*45.76*	*10.1*	*Fine grain*
RETANAL GL-50		*4.8*	*1.2*	*12.27*	*21*	*67.41*	*44.70*	*8.30*	*Fine grain*
VARIATION		*-8%*	*+17%*	*+21%*	*+24%*	*-6%*	*+2.4%*	*+22%*	

Table 10. *Physical properties of hides*

2.3.2. RETANAL A-WW/CHROME Tanning

At the retanning-fatliquoring phase of tanning with chrome, 50% less fatliquoring agents and 49% less synthetic retanning agents are used. Free formol values are half the above.

RETANAL A-WW	CHROME
18% FOSFOL AUT 09	*10,4 % OILS*
23% SYNTHETICS	*11 % SYNTHETICS*
3% RETANAL RST	*8% ACRYLIC RESINS*
	10 % TARE
FREE FORMOL (IUC 19-1)	
11 ppm	6 ppm

Table 11. *Product and free formol comparison*

PRODUCT	COLOR (L*)	SOFT. (IUP-36)	THICK. (mm)	TENSILE STRENGTH (N/mm^2)	ELON (%)	TEAR LOAD (N)	TEAR LOAD (N/mm^2)	GRAIN BURST (mm)
RETANAL A-WW	*DARKER*	*4.4*	*1.3*	*15.5*	*25*	*40.49*	*35.93*	*Fine grain*
CHROME		*4.9*	*1.1*	*12.7*	*23*	*34.14*	*30.86*	*Medium grain*
VARIATION		*-10%*	*+18%*	*+22%*	*+9%*	*+19%*	*+16*	

Table 12. *Physical properties of hides*

In these first tests and as comparted to standard wet blue and wet white with glutaraldehyde tanning, RETANAL A WW provides leathers with the following characteristics:

1º- More intense COLOR

2º- BETTER tensile strength and GRAIN BURST

3º- INCREASED THICKNESS

4º- INCREASED TIGHTNESS

5º- DECREASED SOFTNESS

6º- FINER, SMOOTHER GRAIN

VERY GOOD RESULTS HAVE BEEN OBTAINED,
BUT MORE WORK IS NEEDED!

DECREASED SULFIDE-HYDROSULFIDE CONTENT IN EFFLUENTS AND LEATHERS

The poor reputation of tanneries worldwide, mainly due to the foul odor of rotten eggs generated by tanneries working with raw hides, is well known.

In Arzignano (Italy), an eminently tanning city with a whiff of sulfide, they say that this is the "smell of money" because tanners made money by the sackful. This, however, took place during the 20th Century. Things have changed in the 21st Century and authorities care much more about the environment and try to promote laws that force tanneries to create as little smell as possible.

Among the chemicals used in tanneries, the Sulfide and Hydrosulfide used in leather unhairing accounts for most of this smell.

Besides the environmental issue, a new test —the smell test— is to be complied with by leathers. The relationship between the amount of sulfide used at unhairing and the creation of more or less smell in crust leathers is under study, and there does seem to be a relationship between the two.

That is why we must try to work with:

1º.- Processes using fewer sulfides (our ECO process, with 0.6% sulfide + 0.6% Riberzym ECO C).

2º.- Decalim SS, a product that significantly reduces sulfide content in wastewaters and leathers

1.º Processes using fewer sulfides: ECO UNHAIRING

The progress made in industrial tests performed on this process and the results obtained already suggest a quite safe formulation.

The following must be borne in mind:

SOAKING.- SWe know that not any soaking is valid, even if it is the factory standard. Indeed, a number of (not yet identified) SURFACTANTS partially inhibit the action of Riberzym ECO C and provide insufficient UNHAIRING

For the process to be successful, SOAKING must be performed with HUMECTOL ECO A and can be reinforced with CELESAL CN in case of wetting difficulties.

Soaking pH should not be excessively raised to fully prevent grain swelling. Reaching a crossed pH=8 is sufficient. In case of very fatty leathers, add a small quantity of alkali (caustic soda or sodium carbonate).

Studies

UNHAIRING.- The pH obtained at UNHAIRING (11.7) with 1.2% lime from immunization and 0.6% sulfide is sufficient to obtain good UNHAIRING. Because the addition of caustic soda is not required, the process is more convenient than the previous ones.

Temperature is crucial, and should be maintained at 28ºC ± 1 throughout the process. A decrease of 3ºC significantly slows down the process.

Because leather fat in the UNHAIRING bath slows down the activity of RIBERZYM ECO C, it is important to add CELESAL BE-50 as an emulsifier of leather fat.

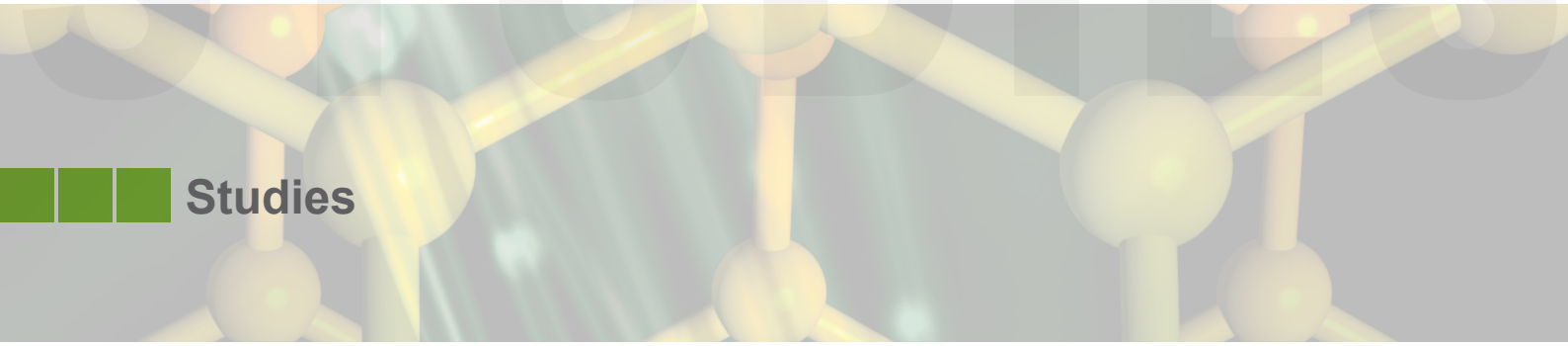
VERDITAN CV is used as anti-wrinkle and anti-vein product.

The process is as follows:

ULL!!
He canviat **vacuno** per **bovine**.
És correcte?

Item: ENZYMATIC UNHAIRING WITH 0.6% Na_2S AND IMMUNIZED HAIR			
Type of hide:	bovine	**Origin:**	Italy
Hide size:	32 Kg/leather	Drum process	
State:	Salted		
Dose on weight:	Salt sweeping weight		

OPERATION	ºC	%	PRODUCT	TIME	REMARKS
WASHING	27º	150	Water		
		0.05	ASEPTANTE DMC	15’	
				10’	Drain
SOAKING	27º	120	Water		
		1	HUMECTOL ECO A		
		0.10	CELESAL CN		
		0.10	ASEPTANTE DMC	420	pH=7.8 (Cross section (1/3)
		0.15	NaOH (30%)	180	pH=8/8,1
O/N (Autom 5’/30’)					
FOLLOWING DAY: pH=7.6 ; 25 ºC; 2/3.5 ºBe					
				15'	Drain
UNHAIRING	27º	40-60	Water		
		0.05	Sodium sulfide		



Studies

OPERATION	ºC	%	PRODUCT	TIME	REMARKS
		0.80	VERDITAN CV		
		0.10	CELESAL BE-50	45'	
		1.20	LIME	40'	pH= 11.5 Phenolphthalein control hair root
		0.60	RIBERZYM ECO C		
		0.30	SODIUM SULFIDE	45'	Ph=11.7; T= 28.2 ºC
					Hair starts loosening
		0.25	SODIUM SULFIDE		
		0.90	LIME		
		0.10	CELESAL BE-50	60'	pH=11.7 ; T= 27.7 ºC
			FILTER	120'	pH=11.7 ; T= 27.5 ºC
					UNHAIRING CONTROL: OK
					Hair fully loose in bath. Very white, clean, keratin-free grain surface
		0.80	LIME		
		0.20	VERDITAN CV		
		0.05	CELESAL BE-50	120'	pH=11.8 ; T= 28.5 ºC
					LIME PENETRATION CONTROL (some crossing missing in thick cheeks)
				60'	STATIC
					crossed lime
LIMING	27º	40	WATER	10'	O/N (autom. 5'/25')
			TOTAL 8H MINIMUM SINCE AUTOMATIC		
FOLLOWING DAY (after 8 hours)					
				5'	DRAIN
WASHING	25º	60	WATER	15'	DRAIN
	25º	60	WATER	10'	UNLOAD

Formula 10. *ECO unhairing process*

Leathers pass smoothly through the fleshing machine

Pelt leathers are as follows:

- Very clean and keratin-free.
- Very light in color, both grain and flesh.
- Fine turgidity, flesh easily removed.
- Very open and extended
- No wrinkles in necks, heads or shanks.
- No blood veins

Studies

2.º DECALIM SS: a product that reduces and eliminates sulfide from unhairing/liming wastewaters and leathers

- This white powder is a combination of several oxidative products with special additives, with (10%) pH of 11
- Leathers of a slightly lighter color are obtained
- Decalim SS is added to the final unhairing/liming bath, one hour before washing. Washing is performed as usual after running for one hour.
- The amount will depend on the quantity of sulfide used. Decalim SS at between 0.5 and 0.8% will be used with 1.5% sulfide.

NEW BOOK

LAMBSKIN AND CATTLEHIDE DEGREASING

1. Introduction

Natural fat extraction from skins and leathers is mandatory to avoid the appearance of undesirable effects in finished items. Non-extracted natural fat is responsible for hard feel, decreased physical resistance and dye stains, and is also partly responsible for the appearance of the dreaded repousse —the appearance of a white veil on the skin surface due to the efflorescence of certain free fatty acids and/or triglycerides of the skin. Natural fat content in ovine skins is highly variable and depends on the animal's origin, diet, surrounding climate, etc.

EFat amount is much lower in cattle hides. It is estimated at 2-3% and its distribution in the leather is different from that in lamb skins. However, its removal before tanning is also mandatory to avoid problems similar to those found in lamb skins.

The advantages of degreasing before tanning are obvious; indeed, metal soap formation is prevented and natural fat is eliminated from the interfibrillary spaces, thus allowing a better and larger penetration of tanning liquids, fatliquoring agents, dyestuffs, etc. In the past few years, great progress has been made in the field of degreasing in an aqueous medium, both regarding the use of less polluting surfactants and the application technology of these products.

Lambskin degreasing

- Natural fat skin content
- Surfactants
- Enzymes
- Experimental part I. Variables optimization

NEW BOOK

- Experimental part II. Process optimization
- Experimental part III. Comparative study of surfactants made in CU

Cattlehide degresasing
- Natural fat skin content
- Soaking
- Experimental part
- Material and Methods
- Conclusions

2. Lambskin degreasing

The amount of natural fat contained in the skin varies depending on its origin, and has differential distribution according to their topographic distribution and thickness (Figure 1).

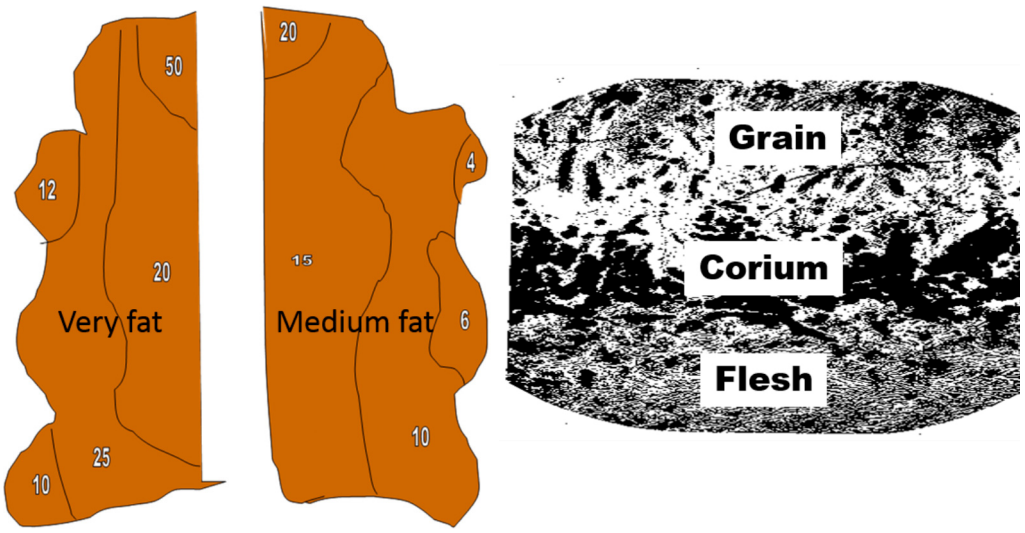


Figure 12. *Superficial distribution (left) and internal dsitrbution (right)*

The fat contained within the skin is inside cells whose walls are formed by a protoplasmic sheath surrounded by a mesh fabric. Any degreasing process must be proceeded by the rupture of the envelope (Figure 12).

NEW BOOK

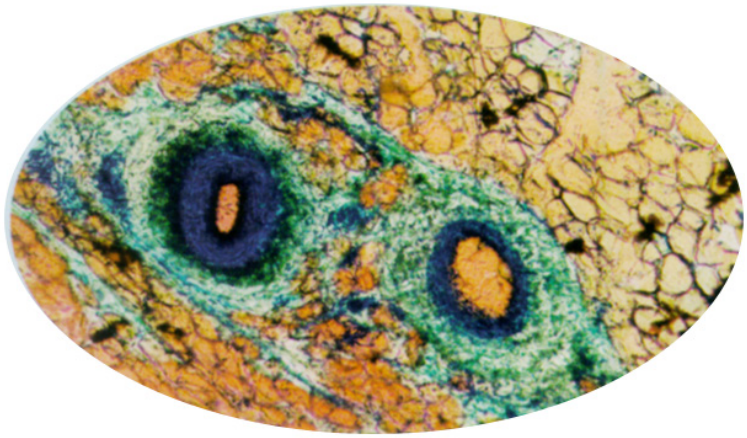


Figure 13. *Distribution of fat in lambskin*

According to the ionic character, surfactants are classified into anionic, nonionic, cationic or amphoteric. Table 13 shows the chemical structure of the anionic and nonionic products of CU classified by families.

NON IONICS	
NATURE	Ethoxylated fatty alcohols
STRUCTURE	$R\text{-}CH_2\text{-}(OCH_2)_xOH$
PRODUCTS	CELESAL DL
	CELESAL K-3
	CELESAL K-6
	CELESAL K-7
	CELESAL K7 CONC
	CELESAL INP
	CELESAL CN
ANIONICS	
NATURE	Sulphated
STRUCTURE	$R\text{-}O\text{-}SO_3^-M^+$
PRODUCTS	DETERPIEL PF-14
	DETERPIEL CT-20
NATURE	Sulphonated
STRUCTURE	$R\text{-}SO_3^-M^+$
PRODUCTS	HUMECTOL AS-21
	CELESAL BE-50

Table 13. *Classification of tensoactives by chemical structure*

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According to the hydrophile-lipophile balance (H.L.B) surfactants can act as defoamers, emulsifiers, wetting agents, detergents or solubilizers (Table 14).

HLB	Aplication
2-3	defoamers
3-6	emulsifiers w/o
7-9	wetting agents
8-16	emulsifiers w/o
13-15	detergents
15-18	solubilizers

Table 14. *Classification of tensoactives by physical affinity*

Formula 11 shows the applicative formulation once all the experimental variables and experimental process were optimized. Formula 1 were applied for the comparative study of surfactants.

OPERATION	ºC	%	PRODUCT	TIME	NOTES
PRETANNING	35	200	Water 6ºBe, pH=3		
		2	**RETANAL DFS NEW**	15'	
		2	Sodium formate	15'	
		4	Sodium bicarbonate	180'	pH= 6.5 Ts=60ºC
					Drain - wash
DEGREASING	40	100	Water		
		5	PRODUCT		Drain - wash

Formula 11. *Applicative formulation*

The products applied in this study are shown in Table 15 indicating active matter, nature and efficacy of each one.

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NON IONICS			
PRODUCT	**ACTIVE MATTER (%)**	**NATURE**	**EFFICACY (%)**
CELESAL DL	85	ALM (medium)-MOE (low)	57
CELESAL K-6	50	ALM (medium)-MOE (low) +ad1	62
CELESAL K-3	43	ALM (medium)-MOE (Md-high)	70
CELESAL K-7	65	ALM (medium)-MOE (Md-high) +ad2	75
CELESAL K-7 Conc.	80	ALM (medium)-MOE (Md-high) +ad3	80
CELESAL INP	32	ALM (medium)-MOE (Md-high) +ad4	59
CELESAL INP	32	ALM (medium)-MOE (Md-high) +ad4	59
ANIONICS			
PRODUCT	**ACTIVE MATTER (%)**	**NATURE**	**EFFICACY (%)**
HUMECTOL AS-21	50	Dialkyl sulfosuccinate +ad5	55
CELESAL BE-50	40	Benzenic derivative + ad6	40
DETERPIEL PF-14	27	Lauryl ether +ad7	77
REFERENCE	without product		12
Notes			
ALM= C_{12}-C_{15} MOE(low)= 4.5-5.5 MOE(Md-high)= 11-12 Additives: ad1, ad2, ad3, ad4, ad5, ad6, ad7			

Table 15. *Classification of tensoactives by physical affinity*

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CONCLUSIONS

Maximum effectiveness of the surfactants currently manufactured by CROMOGENIA UNITS corresponds to:

THE LAST… THE BEST…

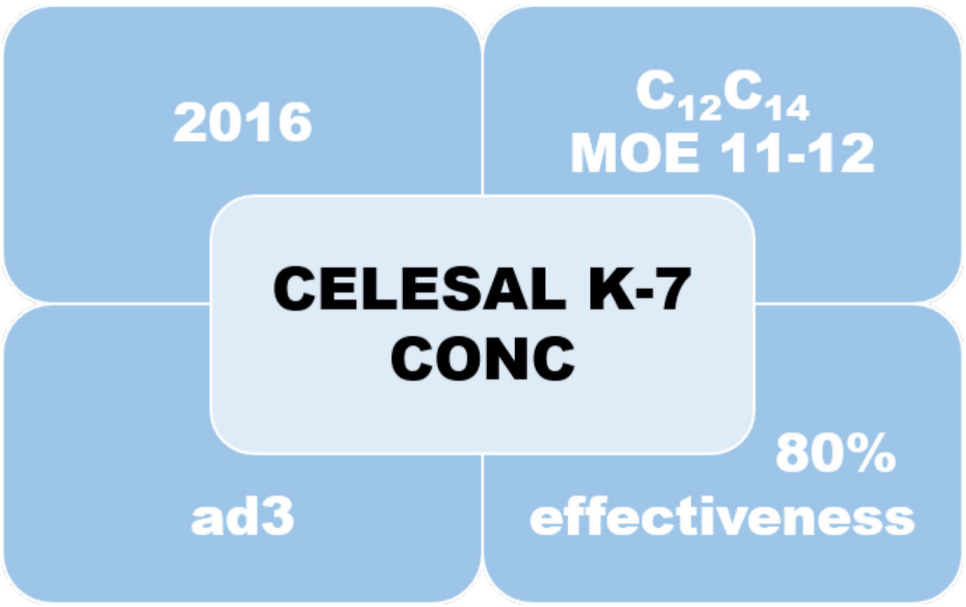

Figure 14. *Surfactant with the maximum effectiveness*

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