



A practical evaluation of replacement white retanning syntans

D. Castiello^(†), M. Puccini^(‡), C. Rizzo^(‡), M. Salvadori^(†), M. Ventavoli^(‡), S. Vitolo^(‡)

^(‡)Dept. of Chemical Engineering, Industrial Chemistry and Materials Science, University of Pisa

&

^(†)Tanning Technology Centre, Castelfranco di Sotto, Pisa

This study presents the findings from an evaluation made on commercial replacement syntans. The technique used involved several factors that were difficult to measure directly, such as handle and tactile properties. These were assessed according to a scale of performance, then taken into account with other factors that could be measured directly.

As these different evaluations were brought together, each was given a numerical weighting or rating according to their value within the assessment. This then enabled a measurement of overall performance to be calculated. This technique has been used previously to evaluate both dyestuffs⁽¹⁾ and acrylic resins⁽²⁾ where it has proved to be a powerful tool for materials evaluation

⁽¹⁾"A practical evaluation of dyestuffs", *World Leather*, February/March 2005

⁽²⁾"A practical evaluation of acrylic resins and the development of a materials evaluation method", *World Leather*, June/July 2005

The focus of this study was on the performance of replacement white retanning syntans for chrome leather. The basic constituent of these synthetic retanning agents is the dihydroxydiphenyl sulfone molecule. These molecules are attached to one another with the aid of formaldehyde through methylene bridges. They are adjusted to the optimum degree of condensation, made water-soluble by sulfonation or sulfomethylation, and adapted using buffering systems to meet application requirements. These products are used to obtain a pale leather colour and good light fastness on chrome leather; they are used in high quantities, and have a considerable impact on the economics of the whole manufacturing cycle.

The testing methods used consisted of a comparative analysis of each product using physical/chemical methods. The handling and tactile properties of the crust leathers, and the bleaching effect associated with these products were evaluated, and physical/light fastness tests were performed. Accordingly, it was possible to create an evaluation index that takes into account the cost effectiveness of these products.

The study

Fifteen replacement white retanning syntans were used: thirteen in powder form and two as solution were selected. The leather produced was evaluated through a Global Technical Evaluation (GTE), that reflected the handling and tactile

properties of the leathers and the bleaching effect. In addition, a Light Fastness Evaluation (LGE) and a Price Evaluation (PE) were made to establish which product showed the highest level of cost effectiveness.

The physical properties were also evaluated by measuring the extension and load at grain crack and burst (*lastometer according to the Method IUP/8 and IUP/9*). Finally, the syntans were characterised by their dry solids, organic and inorganic content.

Preparation of the leather samples and characterisation of the syntans

The retannage was carried out on a series of wet blue calf leather samples split and shaved to a thickness of 1.3 mm. The samples were as uniform as possible, and excluded the lower quality areas of the skin (*belly and neck areas*).

These samples were processed using a standard formulation to the point of applying the syntan retanning agent. Fifteen pairs of samples were then separately retanned with the individual syntan. After retanning, the samples were decoupled: one series of samples were dyed and fatliquored in the same bath, the other series was fatliquored only in the same bath as shown in the procedure given in *Panel 1*.

The dry solids content was determined on Syntans 3 and 14 as these were only available in liquid form by evaporation in a drying oven at a temperature of 102°C. ➤



A PRACTICAL EVALUATION OF REPLACEMENT WHITE RETANNING SYNTANS

Panel 1: Standard procedure for retanning, dyeing and fatliquoring

	%	PRODUCT	T (°C)	pH	Operations & controls
Retannage	300	Water	30		
	0.3	Oxalic acid			
	0.3	Surface active agent for clearing			Turn 30' / Drain
	300	Water	35		
	1.7	Sodium formate		4.5	Run 30'/pH control
	1.2	Sodium bicarbonate		6.5	Run 60'/pH control/Drain
	800	Water	35		Turn 15'
	15	Syntan		6.5	Run 60'
	1.7	Formic acid		4.0	Run 30'/pH control
Dyeing/ fatliquoring	300	Water	30		
	0.2	Surface active agent for clearing			Run 20'/Drain
	200	Water	30		
	1	NH3 (35% solution diluted 1:10)		7.5	Run 15'/pH control
	2	Anionic dye			Run 90'
	2	Formic acid		3.7	Run 30'/pH control/Drain
	200	Water	30		Run 15'/Drain
	200	Water	40		
	6	Anionic fatliquor			Run 60'
	1	Formic acid		3.7	Run 20'
	200	Water	30		Turn 15' / Drain
					Dry / Stake
Fatliquoring	300	Water	30		
	0.2	Surface active agent for clearing			Run 20' / Drain
	200	Water	40		
	6	Anionic fatliquor			Run 60'
	1	Formic acid		3.7	Run 20'
	200	Water	30		Turn 15' / Drain
					Dry / Stake

Determination of the Global Technical Evaluation (GTE)

The syntan's technical performance was based on handling and tactile evaluations made on the final leather, in combination with the bleaching effect. The leather character was evaluated in two stages:

- The retanned, fatliquored and dyed samples were examined. This examination included handling and tactile characteristics such as the feel, roundness, softness, lightness, and intensity of colour
- On the fatliquored but undyed leather, the examination included the bleaching effect

The handling and tactile characteristics, and the bleaching effect evaluations were expressed numerically. An Evaluation Rating for each property was awarded on a scale of 1 to 5. These ratings were then weighted using an index relating to the relative importance of each parameter, and are shown in *Panel 2*.

These weightings reflect the main properties that white retanning syntans should provide. The measure of overall performance, (*defined as GTE*), was finally expressed as Evaluation Rating x Weighting Index.

Determination of the Light Fastness Evaluation (LFE)

The light fastness was evaluated on the fatliquored but undyed samples. Rectangular specimens, half covered with a black cardboard, were fixed on a flat support and exposed to sunlight for three weeks during the month of August. After exposure, the black cardboard was removed and the degree of variation of the white tonality of the exposed half, with respect to the corresponding covered half, was evaluated for each sample. Test method ISO 105-A03 (*Textiles-Tests for colour fastness - Part A03: Grey scale for assessing staining*) test was employed and the light fastness expressed numerically on a scale of 1 to 5.

Determination of the Price Evaluation (PE)

Market prices of the products under investigation were collected. The PE was then calculated and used, together with the GTE and the LFE, to judge the syntans under examination. The PE was calculated by attributing a value of 5 to the cheapest (*Syntan 14*), while the value of 1 was given to the most expensive (*Syntan 1*). The values of the remaining syntans were determined by the calculation as given in *Panel 3*.

Panel 2: Weightings attributed to the technical parameters of the crust leather

Parameter	Weighting
Feel	0.10
Roundness	0.15
Softness	0.15
Intensity of colour	0.20
Lightness	0.25
Bleaching effect	0.15
Total weightings	1.00



Panel 3: Price Evaluation (PE) calculations for syntans

The following formula was used where PE represents the Price Evaluation and P the price in euros per kilogramme.

$$PE - I = \frac{(5-I)}{(1.19 - 3.21)} (P - 3.21) \Rightarrow PE = -1.98P + 7.36$$

Determination of the overall evaluation

Additional weightings were attributed to the GTE, LFE and PE at 07, 0.15, and 0.15 respectively. This enabled a complete evaluation of each syntan, taking the most important factors into close account.

Findings from the investigation

PHYSICAL PROPERTIES

The physical test findings for the crust leathers are given in *Figure 4*. This shows that all of the syntans provided excellent physical properties to the retanned leathers. The extension to crack test gave a result of between 8.5 and 13 mm (*well above the lower limit of 7 mm established by the norm UNI 10594*).

GLOBAL TECHNICAL EVALUATION

The handling and tactile characteristics, and the bleaching effect evaluations are given in *Panel 5*.

The softness and colour intensity were most influenced by the type of syntan used. All of the syntans show excellent performance as far as the bleaching effect is concerned. Syntan 1, 3, 11 and 15 provided the best performance.

LIGHT FASTNESS EVALUATION

The LFE is given in *Panel 6*.

Panel 4: Lastometer test results

Syntan	Average thickness	Extension to cracking	Load to cracking	Extension to bursting	Load to bursting
n°	mm	mm	N	mm	N
1	1.28	11.50	472.90	13.00	639.50
2	1.30	10.60	251.20	13.10	442.96
3	1.44	10.41	174.56	14.00	421.65
4	1.38	8.50	122.30	13.40	465.00
5	1.37	10.21	209.75	14.00	531.50
6	1.42	10.34	304.00	13.40	591.40
7	1.48	13.13	358.44	15.10	521.73
8	1.26	10.71	363.47	13.00	628.99
9	1.47	10.69	337.61	13.00	586.37
10	1.41	10.54	216.00	13.37	435.53
11	1.48	9.24	144.39	14.30	417.82
12	1.43	12.84	347.18	14.35	455.65
13	1.40	9.62	262.66	13.23	682.62
14	1.45	11.81	523.52	13.27	811.91
15	1.45	10.27	215.75	14.07	515.70

Note: Maximum measurable load 960.84 N

The syntans based on the molecule of dihydroxydiphenyl sulfone are characterised by a trade-off between a good light fastness and a good penetration into the skin section. A good penetration may be obtained by the presence of the hydroxyl groups, as these increase the reactivity towards the collagenic structure. The amount of hydroxyl groups must, however, be optimised because of their tendency to oxidise in sunlight with a consequent yellowing/darkening of the leather. Syntan 1, 2, 5, 7, 11 and 12 show the best light fastness performance.

PRICE EVALUATION

The Price and PE for each single syntan is given in *Panel 7*. ➤

Panel 5: Global Technical Evaluation of the leather samples

Syntan	Feel	Roundness	Softness	Intensity of colour	Lightness	Bleaching effect	Global Technical Evaluation
1	5.0	3.5	5	4.0	4	4.5	4.250
2	3.5	3.5	5	4.0	5	3.0	4.125
3	3.0	5.0	3	4.5	5	4.5	4.325
4	4.0	2.5	3	2.0	5	3.0	3.325
5	4.0	4.0	4	4.0	4	4.5	4.075
6	5.0	4.0	3	3.0	5	3.0	3.850
7	3.5	4.0	4	3.5	5	3.5	4.025
8	4.5	3.5	4	3.0	5	3.5	3.950
9	4.0	4.0	3	5.0	5	3.5	4.225
10	3.5	2.5	2	1.0	5	3.0	2.925
11	5.0	5.0	4	4.0	5	3.5	4.425
12	4.5	4.0	4	3.5	5	3.5	4.125
13	3.5	3.5	2	3.0	5	3.0	3.475
14	3.0	5.0	2	4.5	5	3.0	3.950
15	4.0	4.0	5	3.0	5	5.0	4.350

Panel 6: Light Fastness Evaluation of the leather samples

Syntan	Light Fastness
1	4.5
2	4.5
3	3.5
4	4.0
5	4.5
6	4.0
7	5.0
8	3.5
9	2.5
10	4.0
11	5.0
12	4.5
13	4.0
14	4.0
15	4.0



A PRACTICAL EVALUATION OF REPLACEMENT WHITE RETANNING SYNTANS

Panel 7: Price Evaluation of the syntans

Syntan	Price (€/Kg)	Price Evaluation
1	3.21	1.00
2	2.30	2.81
3	1.96	3.48
4	1.99	3.42
5	2.50	2.41
6	2.04	3.32
7	2.65	2.11
8	1.45	4.49
9	2.20	3.00
10	1.42	4.55
11	2.05	3.30
12	1.94	3.52
13	1.25	4.89
14	1.19	5.00
15	1.93	3.54

Panel 8: Overall evaluation of syntans examined

Syntan	Global Technical Evaluation	Light Fastness Evaluation	Price Evaluation	Overall Evaluation
1	4.250	4.5	1	3.80
2	4.125	4.5	2.81	3.98
3	4.325	3.5	3.48	4.07
4	3.325	4	3.42	3.44
5	4.075	4.5	2.41	3.89
6	3.850	4	3.32	3.79
7	4.025	5	2.11	3.88
8	3.950	3.5	4.49	3.96
9	4.225	2.5	3.00	3.78
10	2.925	4	4.55	3.33
11	4.425	5	3.30	4.34
12	4.125	4.5	3.52	4.09
13	3.475	4	4.89	3.77
14	3.950	4	5	4.12
15	4.350	4	3.54	4.18

OVERALL EVALUATION

The Overall Evaluations (OE) of each single syntan are shown in *Panel 8*. A comparison of the OE and PE of each product shows that in most cases there is no correspondence between the performance and the cost of the syntan. It is observed that:

- Syntan 1, 11 and 15, show the best GTE and LFE. However, Syntan 1 has quite a low OE due to its higher price (*40% higher than Syntan 11*). Syntan 11 is by far more competitive, followed by Syntan 15;
- Syntan 14 shows an interesting trade-off between performance and price;
- Syntan 9 shows a good GTE, while the LFE appears unsatisfactory;
- Syntans 4 and 6 are very close in price to Syntan 11, but show a relatively unsatisfactory level of performance;
- Syntans 2, 5 and 7 are higher in price than Syntan 11 and

show the worst performance;

- The performances of the cheapest Syntans 8, 10, and 13 are comparable, or better than, those of Syntans 4 and 6;
- Syntans 3 and 12 show either a good GTE, or a good LFE, and an interesting PE.

CHARACTERISATION OF THE SYNTANS

The dry solids, organic, and inorganic content of the syntans is shown in *Panel 9*. Over and above syntans 3 and 14—being in liquid form—their organic content related quite closely to their active substance content.

When the organic matter content is directly related to the performances of the syntan it is also a measure of the active substance content:

- Syntans 2, 4, 5, 7 and 13 have a lower organic content and show the worst results when compared with Syntans 1 and 11 which gave the best performance.



HIDE PROCESSORS AND EXPORTERS

SYDNEY • MELBOURNE • TASMANIA

Quality and service at a competitive price

SOUTHERN HIDE EXPORTS Pty Ltd

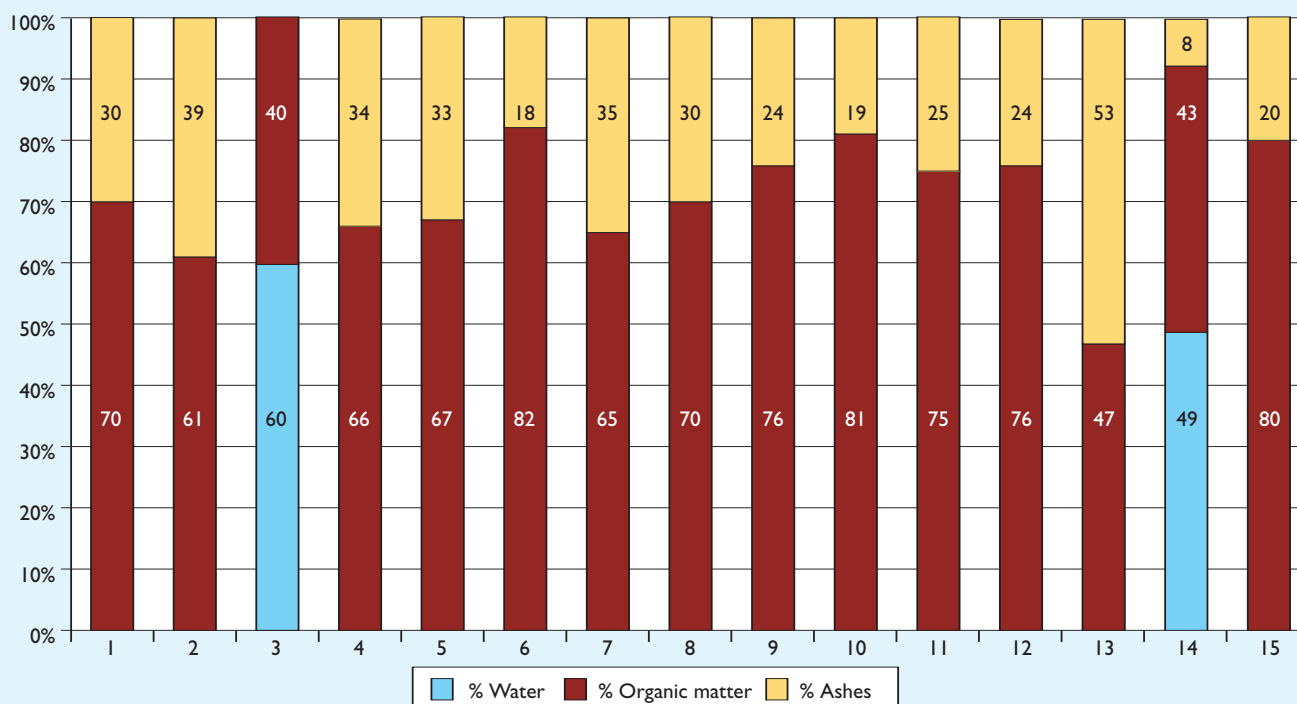
Tel +612 9261 4665
Fax +612 9261 0678
Email isb@southernhide.com.au

Wet Blue hides & splits
Salted raw hides
Salted calfskins

www.southernhide.com.au



Panel 9: Dry solids content and organic matter content of syntans examined



- Syntans 3, 9, 12, 14 and 15, with a high organic content, show interesting performances.

When the organic matter content is not related to the performances of the syntan, it may be that other inactive organic materials have been added to the formulation. In this situation they neither contribute nor detract from the performance. Syntans 6, 8, 10 are characterised by a high organic matter content, but the performances are unsatisfactory.

Conclusions

In this particular study it can be seen that:

- Various syntans show characteristics and performance levels that are often very different from one another.
- High cost is not necessarily equivalent to high performance.



ARIES VICTORIAN SHEEPSKINS PTY. LTD.

P.O. Box 12, Essendon North 3041 Melbourne

Tel: 61 3 9370 7437 Fax 61 3 9375 3290 Mobile: 0419 483868