



A practical evaluation of acrylic resins and the development of a materials evaluation method

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This study describes a method for evaluating commercial acrylic resins as used in retannage. By means of in-house tests, this technique can prove useful to tanneries in the selection of resin retanning agents that, from a cost-effectiveness point of view, best suit their purposes. The technique has been used previously in an evaluation of dyestuffs and, furthermore, it is believed that this method can be used as a powerful tool within any manufacturing process as part of product or component evaluation.*

*A practical evaluation of dyestuffs", World Leather February/March 2005.

Tanners are becoming more aware of the need for rationalisation in the use of chemical products employed during leather manufacture. This is due to the growing costs of the materials used in tanning and retanning processes, the stringent restrictions on the discharge of treated effluents, and on the market demand for leathers of increasingly high standards.

This study falls within the context of optimising the products used in wet processing. This is by providing simple methods to evaluate the quality of products used, to help make better decisions regarding the performance of the finished leathers, and with regard to the degree of cost-effectiveness.

In particular, the focus is on acrylic resins used in the retanning phase. These resins are used to give the leather fullness with selective filling of the structure, and provide a tight and uniform grain surface for leather finishing. These products are used in high quantities, and have a considerable impact on the economics of the whole manufacturing cycle.

The testing methods consisted of a comparative analysis of the individual product using physical-chemical-instrumental analyses. The handling and tactile properties of the leathers made using these products were evaluated, and physical tests performed. Accordingly, it was possible to create an evaluation index that takes into account the cost-effectiveness of these products.

The Study

Eleven acrylic resins currently used in the form of aqueous solution were selected and consistency tests carried out. A Performance Index and Price Index were extrapolated to establish which product showed the highest level of cost-effectiveness.

Consistency tests

The consistency tests were performed to classify the resins into homogeneous groups, and then sub-divide them according to their different properties. It was then possible to begin to make comparisons.

ACID STABILITY

This test determined the behaviour of a resin in an acid environment. It was performed by gradually adding a 10% formic acid solution to a 10% resin solution, with the resins classified as stable or unstable.

THE DRY SOLIDS CONTENT

The resin solution was evaporated to dryness in a laboratory oven at a temperature of $102 \pm 2^\circ\text{C}$.

INFRA RED SPECTROPHOTOMETRY

This analysis was performed to identify specific chemical groups that might be associated with properties of the resin.

Determination of the Performance Index

The resin performance within retannage was based on tactile evaluations made upon the final leather in combination with its physical testing performance. The retannage was carried out on a series of wet blue calf leather samples split and shaved to a thickness of 2mm. The samples were as uniform as possible, and excluded the lower quality areas of the skin (belly and neck areas).➤

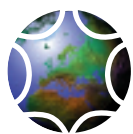


Figure 1: Standard procedure for retanning, dyeing and fatliquoring

%	PRODUCT	T (°C)	pH	Operations and controls
500	Water	30		
0.5	Oxalic acid			
0.5	Surface active agent for clearing			Turn 30' / Drain
500	Water	35		
2.8	Sodium formate		5.5	Run 30'
1.2	Sodium bicarbonate		6.5	Run 45'
10	Acrylic resin		6.5	Run 40'
1.7	Formic acid		4.3	Run 20'
500	Water	40		
13.3	Anionic fatliquor			Run 60'
2.5	Formic acid			Run 20' / Drain
500	Water	25		Turn 15' / Drain
				Dry / Stake
1000	Water	40		
1	Surface active agent for clearing			
1	Sodium bicarbonate		6.5	Run 20' / Drain
500	Water	40		Run 5' / Drain
400	Water	40		
2	Anionic dyestuff			Run 30'
2	Formic acid			Run 30' / Drain
500	Water	20		Run 10' / Drain
				Dry / Stake

These samples were processed using a standard formulation to the point of applying the resin retanning agent. Samples were then retanned with the individual acrylic resin, fatliquored, dried and staked as shown in *Figure 1*.

A sample of each type of leather was physically tested using a lastometer to measure both extension and load at grain crack and burst (*Method IUP/8 and IUP/9*). A second sample of each of the leathers was then dyed under standard conditions to evaluate the impact of the different resins on colour development.

The handle and leather character was evaluated in two stages.

- The retanned and fatliquored but undyed leathers were examined. This examination included appearance, cleanness and colour of the grain, as well as tactile characteristics such as the feel, fullness, roundness, softness and lightness.
- On the dyed leather the study covered colour change and colour intensity.

These evaluations were expressed numerically. A 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 as shown in *Figure 2*.

These weightings reflect the main properties that acrylic resins should provide—such as lightness, fullness and roundness. The measure of overall performance as per the Performance Index was finally expressed as a calculation (*Evaluation Rating x Weighting Index*).

Figure 2: Weightings attributed to tactile parameters of finished leather

Parameter	Weighting
Lightness	0.25
Fullness	0.2
Roundness	0.13
Feel	0.06
Softness	0.06
Appearance of Grain	0.06
Colour	0.06
Cleanness of Grain	0.06
Colour change	0.06
Colour intensity	0.06
Total weightings	1

Determination of the Price Index

Market prices of the acrylic resins under investigation were collected. A Price Index was calculated and used, together with the Performance Index, to judge the resins under examination.

The Price Index was calculated by attributing a value of 1 and 5 respectively to the resins of the highest and lowest cost. The other nine resins were then set between these values according to their cost.

When the Performance and Price Index had been calculated, additional weightings were attributed to both. These were set at values of 0.8 for the Performance Index and 0.2 for the Price Index. This enabled a complete evaluation of each resin taking the most important factors into close account.

Findings from the investigation

CONSISTENCY TESTS

It was found that the commercial acrylic resin samples examined could be divided into two homogeneous classes.

From the acid stability test, resins numbered 1 to 7 were classified as unstable as they precipitate between pH values 3.3 and 3.6. Resins numbered 8 to 11 remained stable within the same pH range.

Analysis using Infra Red Spectrophotometry showed that acid stability depends strongly on the presence of particular functional groups linked to the resin. All the unstable resins (1-7) presented a frequency peak of around 2200cm⁻¹. This ➤

Panel I

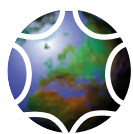
Price index calculations for resins

With reference to Panel 6, the values for the unstable resins were on a linear scale. The following formula was used where *I* represents the index and *P* the price in euros per kilogramme.

$$I - 1 = \frac{(5 - 1)}{(1.19 - 1.50)} (P - 1.50) \quad \diamond \quad I = -12.9P + 20.35$$

The formula for calculating the values for the stable resins is therefore:

$$I - 1 = \frac{(5 - 1)}{(1.45 - 2.71)} (P - 2.71) \quad \diamond \quad I = -3.17P + 9.60$$



corresponds to the nitrile group, being absent in the stable resins.

The dry content of the resins is shown in Figure 3, where it can be seen that the stable resins, with the exception of resin 9, have an average dry solids content of around 30%. The unstable resins show values of 40%.

Figure 3: Dry solids content of resins

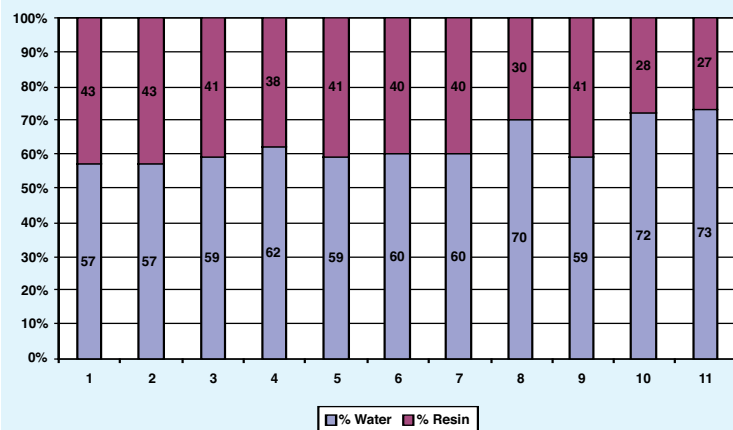


Figure 4: Lastometer test results

Test n°	Average thickness mm	Extension to cracking mm	Load to cracking N	Extension to bursting mm	Load to bursting N
0	2.02	11.50	960.84	12.79	960.84
1	2.15	12.67	799.46	13.90	960.84
2	2.15	10.63	534.68	12.72	816.70
3	2.05	11.59	960.84	11.59	960.84
4	2.20	11.00	552.37	13.50	803.50
5	2.08	11.28	617.98	13.00	960.84
6	2.25	11.34	664.91	13.49	960.84
7	2.18	10.62	565.78	12.89	960.84
8	2.25	12.00	807.13	12.90	960.84
9	2.17	12.00	883.29	12.67	960.84
10	2.08	10.71	691.72	12.11	960.84
11	2.30	12.06	632.34	14.00	960.84

Note: Maximum measurable load 960.84 N

The Performance Index

Results of the physical tests are given in Figure 4. This shows that all of the resins provided excellent physical properties to the retanned leathers. The extension to crack test gave a result of between 10 and 13mm (well above the lower limit of 7mm established by the norm UNI 10594). The load to cracking test was above 500N.

Due to these excellent physical properties, it was not appropriate to attribute a significant Weighting Index to the Evaluation Rating. Consequently, the Performance Index is the same as the Evaluation Rating.

The evaluation—in terms of handle and leather character—of the retanned, fatliquored and dyed leathers has been sub-divided into unstable resins (samples 1 to 7) and stable resins (8 to 11). These evaluations are given in Figure 5.

The price and Price Index for each single resin is given in Figure 6.

The Price Index was calculated separately for the two classes of resins. For the unstable resins, a value of 5 was given to the cheapest (Resin 7), while the value of 1 was given to the most expensive (Resins 4 and 5). Similarly, for the stable resins an index value equal to 5 was given to Resin 9 and a value of 1 to Resin 11. The values for the both the unstable and stable resins were determined by the calculation as given in Panel 1.

The final product evaluation

The final evaluations of each single resin are shown in Figure 7.

A comparison of the Performance and Price Index of each product shows that in most cases there is no correspondence between the performance and the cost of the resins. As far as the unstable resins are concerned, it is observed that:

- Resins 5 and 7, although giving similar results in terms of properties, have the highest and lowest prices in their class. The differences, therefore, show quite varied results in the final evaluation.
- Resin 2 shows the best evaluation in terms of tactile and handling properties among the unstable resins. The price is reasonable, so this is the best resin from a cost-effectiveness point of view.

Figure 5: Evaluation of retanned, fatliquored and dyed leathers

Resins	← Unstable →							← Stable →			
Sample	1	2	3	4	5	6	7	8	9	10	11
Feel	5	3/4	3	3/4	3/4	4	4/5	4	4	5	4
Fullness	4	4	4	4	4	4	4	4	4	4	5
Roundness	5	3/4	3	4/5	3	4	4/5	5	4	4	5
Cleanness of Grain	3	5	4	4/5	3/4	3	3/4	4	5	5	4
Colour	3	5	4	4/5	3/4	3	3/4	4/5	3/4	5	3
Appearance of Grain	4	4	5	4	4	3	3	4/5	4/5	3/4	5
Softness	3/4	5	3/4	3/4	4/5	4/5	4/5	3/4	5	5	5
Lightness	5	4/5	2/3	3	5	3	5	5	5	5	5
Colour change	2/3	3	3	3	3	2	2	1	2	2	2
Intensity of colour	3	4	4	4	3/4	2	2	1	2	2	2
Evaluation	4.14	4.15	3.41	3.76	3.97	3.36	4.02	4.05	4.13	4.22	4.40

**Figure 6: Price Index for resins**

	Resin n°	Price in (€/Kilo)	Price index
Unstable resins	1	1.44	1.77
	2	1.22	4.55
	3	1.29	3.71
	4	1.50	1
	5	1.50	1
	6	1.20	4.87
	7	1.19	5
Stable resins	8	1.91	3.55
	9	1.45	5
	10	2.40	1.99
	11	2.71	1

Figure 7: Final evaluation of resins examined

	Resin n°	Performance Index	Price Index	Final evaluation
Unstable resins	1	4.14	1.77	3.67
	2	4.15	4.55	4.23
	3	3.41	3.71	3.47
	4	3.76	1	3.21
	5	3.97	1	3.38
	6	3.36	4.87	3.66
	7	4.02	5	4.22
Stable resins	8	4.05	3.55	3.95
	9	4.13	5	4.30
	10	4.22	1.99	3.77
	11	4.40	1	3.72

- Resin 5, on the contrary, has a very high sales price and a relatively unsatisfactory level of performance. This is therefore the worst in the class.

Regarding the stable resins:

- Resin 11 shows the best tactile properties, but does not show the best results in the final evaluation because of its high selling price. This does mean, however, that such resins cannot be used for treating high quality leather that might achieve a higher selling price.

Findings from the investigation

In this particular study it can be seen that:

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

However, one aim of the study was to develop a method that would enable better product choice. In this case the technique has been shown to be capable of very flexible application.

This is because the various weightings can take specific needs into account, so an evaluation can be applied to any type of finished leather. For example, if a leather is required at a low price, then the cost of the product will be dominant. In this situation a higher weighting will be given to the Price Index. If, however, the objective is to have a leather with a particularly soft feel, a higher weighting will be given to the softness parameter.

It is seen that a powerful tool has been developed to help within the evaluation and choice of products. This is particularly important where properties that are difficult to express mathematically—such as tactile properties within leather-making—need taking into account within a judgement. 🌀