ACRYLIC RESINS IN WET WHITE

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Abstract. The purpose of this paper is to study the influence of acrylic resins on the properties of the hide when added at the pickling-tanning stage of a wet white process. In this study, 9 resins with different molecular weights and different monomer compositions were selected (Table 1). Resins were applied to pelt leathers of Spanish origin split at 3.5 mm. Hides were cut along the backbone. A standard process was applied to the left halves and the same process adding the resin was applied to the right halves. The resin was added at two points of the process: after adjusting the salt of the bath and after adding the pickling acids. The COD of both processes was assessed as compared to the resin-free process, and the shrinkage temperature and the degree of whiteness of the tanned hide were assessed. Hides were retanned and fatliquored with a standard process, and degree of whiteness, thickness and organoleptic properties (sponginess and leveling) were assessed. Hide shrinkage under temperature was also assessed, and images of hide sections were obtained by scanning electron microscopy (SEM). While acrylic resins did not increase shrinkage temperature, they did fix and/or deposit themselves on the interfibrillary spaces of the hide; indeed, highly reduced COD values were observed. This study showed that homopolymer acrylic resins provided fuller and fluffier hides, while the rest of resins practically did not improve the physical and organoleptic properties of the hides. Hide properties also improved more when resins were applied together with the salt, although at this point these products are less stable, particularly if working with semi-hard or hard waters.

Key words: tanning, retanning, wet white, acrylic resins.

Table 1. Products, monomers used, and molecular weights.

Product	Monomers	Molecular weight (Da)
AC 1	Acrylic acid	4,500
AC 2	Acrylic acid	4,400
AC 3	Acrylic acid	154,000
AC 4	Acrylic acid	500,000
ACN 1	Acrylic acid / Acrylonitrile	120,000
EST 1	Styrene / Maleic	10,000
EST 2	Acrylic acid / Styrene /Maleic anhydride	25,000
EST 3	Acrylic acid / Styrene / Maleic anhydride	450,000
MAL 1	Maleic anhydride	900

1 Introduction

Acrylic resins are very frequently used in wet blue tanning and retanning processes because they lend very good properties to the hide on account of their high affinity for chromium.

The acrylic resins used in tanning processes are usually polymers of high molecular weight, and the properties conferred to the hide depend basically on the type of monomer used during synthesis and on the molecular weight of the resins. The most frequently used monomers are acrylic acid, acrylonitrile, styrene, and maleic anhydride.

When applied at the wet blue retanning stage, many and varied properties are provided by these resins, from compactness or softness to a certain degree of water repellency. When applied during chrome tanning, these resins provide the hides with high fullness and high chrome salt exhaustion

on account of the strong interaction of the carboxylate groups of acrylic resins with chromium. These products also provide light fastness and lower leather degradation because they are chemically stable and do not supply phenol or formaldehyde to the hides.[1,2]

While extensive bibliography is available on the application of acrylic resins in wet blue, less information is found when these products are applied in wet white tanning.

Heidemann, E.[3] and A'mma, A.[4] described acrylic resins and their reactivity in chrome tanned leather. They discussed how acrylic resins have no tanning capacity but are able to form covalent complexes with chromium and react as polycarboxylates.

Dequing, Wei et al.[5] addressed wet white pretanning of a pig hide with a polymethacrylate resin. They concluded that the interactions between the acrylic polymer and collagen are electrostatic. Indeed, when the product is applied at pH=5.0 and then reduced to pH=3.0, a greater fiber separation is observed as compared to a product-free reference sample, which translates into higher fullness. Madhan, B. et al.[6] studied the effect of a methacrylic resin in vegetable tanning on a collagen substrate and determined that acrylic resins are fixed on collagen through electrostatic forces and favor opening, thus improving the penetration of the products added afterwards.

This paper studied the influence of different resins applied in wet white tanned leathers. To this end, 9 resins with different molecular weights and different monomer compositions were selected and applied in wet white tanning at two different points of the process: together with the salt and after pickling acid addition.

2 Materials and methods

2.1 Materials

Nine resins from different monomers (acrylic acid, acrylonitrile, styrene and/or maleic anhydride) with different molecular weights were selected (Table 2).

Pelt leathers of Spanish origin split at 3.0-3.5 mm were used. Bating and deliming were performed according to a standard formula. The hides were then cut in half and divided into 40 x 100 cm pieces. The left halves were taken as (resin-free) references and the product was applied to the right halves. Resins were applied at pickling together with the salt (process I) and after adding pickling acids (process II). The application formula is shown in Table 3. Finally, the product without glutaraldehyde was applied to determine the tanning power of the resin (Table 4).

Table 2. Products, monomers used, and molecular weights.

Product	Monomers	Molecular weight (Da)
AC 1	Acrylic acid	4,500
AC 2	Acrylic acid	4,400
AC 3	Acrylic acid	154,000
AC 4	Acrylic acid	500,000
ACN 1	Acrylic acid / Acrylonitrile	120,000
EST 1	Styrene / Maleic anhydride	10,000
EST 2	Acrylic acid / Styrene / Maleic anhydride	25,000
EST 3	Acrylic acid / Styrene / Maleic anhydride	450,000
MAL 1	Maleic anhydride	900

Table 3. Process description.

Process I	Resin application together with the salt
Pickling-tanning	80% Water at 25°C, 8% of salt. Run 10'. °Bé=7 **(Product-free) reference. Run 120'** **0.5% Resin (active matter). Run 120'** 1% Formic acid. Run 60' 1.2% Sulfuric acid. Run 120'. Control pH=3.0 and cross with vbc 2% Glutaraldehyde at 50%. Run 120' 1% Sodium formate. Run 30' 0.5% Sodium bicarbonate. Run 120'. pH=5.0 – crossed. Night in bath
Process II	Resin application after pickling acids
Pickling-tanning	80% Water at 25°C, 8% of salt. Run 10'. °Bé=7 1% Formic acid. Run 60' 1.2% Sulfuric acid. Run 120'. Control pH=3.0 and cross with vbc **(Product-free) reference. Run 120'** **0.5% Resin (active matter). Run 120'** 2% Glutaraldehyde at 50%. run 120' 1% Sodium formate. Run 30' 0.5% Sodium bicarbonate. Run 120'. pH=5.0 – crossed. Night in bath

Table 4. Application formula to determine resin tanning power.

Process	Resin tanning power before acidification
Pickling-tanning	80% Water at 25°C, 8% of salt. Run 10'. °Bé=7 **(Product-free) reference. Run 120'** **5.0% Resin (active matter). Run 120'** 1% Formic acid. Run 60' 1.2% Sulfuric acid. Run 120'. Control pH=3.0 and cross with vbc
Process	Resin tanning power after acidification
Pickling-tanning	80% Water at 25°C, 8% of salt. Run 10'. °Bé=7 1% Formic acid. Run 60' 1.2% Sulfuric acid. Run 120'. Control pH=3.0 and cross with vbc **(Product-free) reference. Run 120'** **5.0% Resin (active matter). Run 120'**

2.2 Methods

2.2.1 Bath analysis

The chemical oxygen demand (COD) of the residual baths of processes I and II was determined at the following stages: in process I, 120 min after product application and after acidification; in process II, 120 min after resin application. The CODs of the products under the same bath conditions were also measured.

Analysis was performed with 1-1500 mg/l vials heated under reflux for 2 hours at 150°C, and COD was measured with an Aqualytic AL100 spectrophotometer.

2.2.2 Hide analysis

In pretanned hides, the degree of whiteness was measured with a Color Data Spectraflash SF-30 colorimeter, the shrinkage temperature (Ts) was measured according to IUP 16, and photographs were taken with a scanning electron microscope (SEM) equipped with EDX detector (Phenom Pro-X).

Once hides were assessed at this stage, they were retanned, dyed and fatliquored according to a standard formula. Color intensity, resistance to dry heat, physical properties (degree of softness, thickness, tensile strength, tear load, grain burst) and organoleptic properties were determined.

The degree of softness was determined according to IUP 36, thickness according to IUP 4, tensile strength according to IUP 6, tear load according to IUP 8 by means of Zwick TMZ2.5/TN1S, and grain

bursting strength according to IUP 9 by means of Satra STM 463. Leather resistance to dry heat was analyzed under the following conditions: oven at 90°C for 48 h and 400 h. Finally, the organoleptic properties (sponginess and leveling) were evaluated by 5 technician specialists.

3 Results and discussion

3.1 Bath analysis

In general, a decreased COD was observed at the end of tanning in both processes, before and after acidification, although this decrease was more pronounced when the resin was applied before acidification (process I).

In alkaline medium, the carboxyl groups of collagen are mostly negatively charged and the amine groups are deprotonated. At this point, resins can penetrate without interaction with collagen. When the medium is acidified, amine groups are protonated and the carboxyl groups of the resins interact with collagen by means of electrostatic charges. On the other hand, acrylic resins are less soluble in acidic medium and therefore an acidic pH also favors resin fixation.

The percentage values of resin fixed on the hide are obtained from the relationship between the residual bath COD and the product COD (Fig. 1). While these results suggest acrylic resin fixation or deposition on the skin, this fixation is improved when the resin is applied in neutral medium together with the salt.

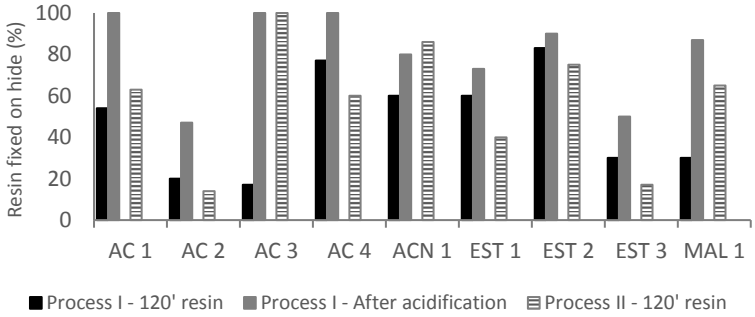

Fig. 1. Resin fixed on hide in processes I and II.

3.2 Hide assessment

3.2.1 Determination of tanning power, degree of whiteness and SEM images of the resins in pretanned hides

The Ts of the resin applied alone (application formula of Table 4) was assessed to determine the tanning power and was also assessed in the two processes (described in Table 3) to determine whether the resin had any influence on or synergy with the tanning product (glutaraldehyde). The results obtained are shown in Table 5. When the product was applied alone, none of the studied resins increased shrinkage temperature significantly. These results suggest that acrylic resins are not strong enough to bind two collagen chains and therefore provide no tanning or very little tanning, increasing Ts by 2-8°C as compared to the reference. Significant differences were also not observed between the Ts values obtained in the two processes, thus suggesting that Ts is determined by glutaraldehyde.

On the other hand, no significant differences were obtained in the degrees of whiteness of pretanned hide samples, that is, acrylic resins neither increase nor decrease the degree of whiteness. Finally, SEM was performed to deeply observe effects on skin fibers after tanning. SEM

imaging shows more structured fibers in the samples containing resin than in the respective references, in both processes I and II. The SEM imaging of the samples tanned in the two processes with products AC 3 and AC 4 are shown in Fig. 2. Fiber structuring is more prominent for the samples in process I as shown in Fig. 2 (A, B, E, F), fibril bundles are more structured and fibers are separated. This higher degree of opening up allows the fatliquoring agent to penetrate easily and leather becomes more flexible, soft and spongy. Regarding process II, it is observed that the fibers are also more structured but less separated than process I.

Table 5. Ts of the resin, process I and process II, and degree of whiteness.

Sample	Resin alone		Process I				Process II			
	Ts (°C)		Ts (°C)	Degree of whiteness			Ts (°C)	Degree of whiteness		
	I	II		L*	a*	b*		L*	a*	b*
Reference	57	56	78	88.28	0.02	10.15	80	82.57	5.82	29.91
AC 1	56	60	79	91.61	0.09	9.00	80	79.07	6.01	27.19
Reference	57	56	79	76.56	-0.60	10.25	80	84.88	4.41	27.51
AC 2	54	56	77	82.42	1.32	14.57	80	82.69	5.74	31.08
Reference	57	56	80	87.66	0.11	9.15	79	84.56	4.00	25.52
AC 3	63	62	78	89.13	0.16	8.90	79	85.13	3.97	23.06
Reference	57	56	80	89.38	-0.05	9.36	79	83.90	3.00	24.86
AC 4	62	64	79	83.32	1.01	10.85	80	88.11	3.80	21.62
Reference	57	56	80	82.84	-0.08	9.42	80	83.63	5.70	26.50
ACN 1	63	59	81	88.49	0.46	11.14	80	86.13	4.24	25.32
Reference	57	56	80	90.53	0.18	10.85	80	83.58	4.21	26.55
EST 1	60	61	82	72.86	0.72	11.33	82	82.21	5.14	29.27
Reference	57	56	80	87.60	-0.04	11.25	80	80.13	5.34	27.36
EST 2	60	58	83	87.38	-0.33	10.29	83	84.69	4.02	25.11
Reference	57	56	80	81.69	-0.21	9.32	79	85.16	3.54	21.94
EST 3	59	59	80	82.61	-0.01	10.08	83	77.64	3.62	25.26
Reference	57	56	80	87.71	0.45	11.76	80	80.69	7.21	30.89
MAL 1	56	57	80	91.52	0.51	10.62	80	85.16	3.54	21.94

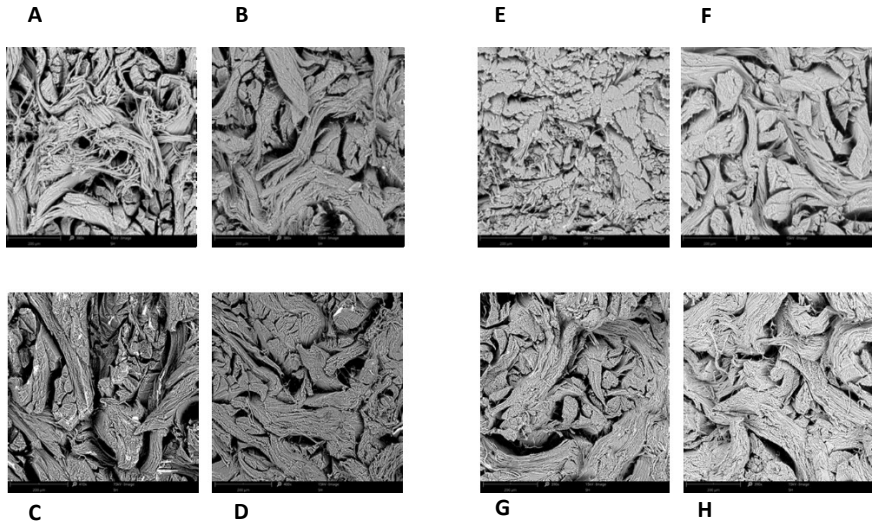

Fig. 2. SEM images of fiber cross section (x400). of resins AC 3 and AC 4 with their reference. **A:** AC 3 reference of process I. **B:** AC 3 of process I. **C:** AC 3 reference of process II. **D:** AC 3 of process II. **E:** AC 4 reference of process I. **F:** AC 4 of process I. **G:** AC 4 reference of process II. **H:** AC 4 of process II.

Table 6. Thickness and softness in crust hides.

Sample	Thickness (mm)		Softness (d=30)	
	I	II	I	II
Reference	2.8	2.2	3.4	2.6
AC 1	2.9	2.3	3.7	2.7
Variation	+3.6%	+4.5%	+8.8%	+3.8%
Reference	2.9	2.4	3.7	2.7
AC 2	2.9	2.4	3.8	2.5
Variation	0%	0%	+2.7%	-7.4%
Reference	3.0	2.3	3.9	3.1
AC 3	3.2	2.4	4.3	3.3
Variation	+6.7%	+4.3%	+10.3%	+6.5%
Reference	2.9	2.3	3.7	3.6
AC 4	3.0	2.4	4.0	3.8
Variation	+3.4%	+4.3%	+8.1	+5.6%
Reference	3.1	2.3	3.2	2.4
ACN 1	3.1	2.2	3.1	2.5
Variation	0%	-4.3%	-3.1%	+4.2%
Reference	2.9	2.5	3.1	2.8
EST 1	3.0	2.5	2.9	2.7
Variation	+3.4%	0%	-6.5%	-3.6%
Reference	3.1	2.5	3.1	2.9
EST 2	2.9	2.3	3.1	2.8
Variation	-6.5%	-8.0%	0%	-3.4%
Reference	3.1	2.4	3.8	2.7
EST 3	3.0	2.5	4.1	2.8
Variation	-3.2%	+4.2%	+7.9%	+3.7%
Reference	3.0	2.5	3.3	2.9
MAL 1	2.9	2.6	3.4	2.9
Variation	-3.3%	+4.0%	-3.0%	0%

3.2.2 Determination of resistance and other properties in crust hides

The thickness and degree of softness in crust hides are shown in Table 6. Homopolymer acrylic resins AC 1, AC 3 and AC 4 increased the degree of softness. While resin AC 2 is also a homopolymer acrylic resin, it is an acidic resin and therefore behaves differently. The degree of softness was not increased by the rest of resins. Homopolymer acrylic resins AC 1, AC 3 and AC 4 slightly but not significantly increased thickness. No significant changes in thickness values were observed with the rest of products. The values were slightly higher when the resin was applied in process I.

The results obtained in physical resistances (tensile strength, tear load and grain burst) are shown in Table 7. Although it was expected an improvement of strength in the final leather due to the positive correlation between softness and strength[7], no significant differences were observed. The products applied had no influence on tensile strength, tear load and grain burst.

The resistances to dry heat assessed, measured as surface decrease, at 48 h and 400 h in processes I and II are shown in Fig. 3. The resistances are higher for AC 1, AC 3 and EST 2, which means that these products improve shrinkage surface vs. their references. The rest of the products did not change the leather surface.

Table 7. Physical resistances in crust hides.

Sample	Process I				Process II			
	Tensile (MPa)	Elong (%)	Tear (N)	Burst (mm)	Tensile (MPa)	Elong (%)	Tear (N)	Burst (mm)
Reference	28.02	45.67	535.8	10.76	34.66	15.88	202.2	7.21
AC 1	30.99	41.35	459.5	10.71	32.44	17.56	203.4	8.01
Variation	+11%	-9%	-14%	0%	-6%	+11%	+1%	+11%
Reference	28.45	31.12	401.2	11.28	25.65	16.78	271.2	6.54
AC 2	30.54	34.67	386.0	12.54	28.30	18.90	273.1	6.21
Variation	+7%	+11%	-4%	+11%	+10%	+13%	+1%	-5%
Reference	26.44	35.58	432.3	11.03	30.35	12.50	267.4	6.81
AC 3	26.64	29.81	368.5	10.32	29.05	15.38	218.6	6.68
Variation	+1%	-16%	-15%	-6%	-4%	+23%	-18%	-2%
Reference	27.22	35.10	448.2	10.52	30.94	12.02	267.3	6.71
AC 4	26.26	33.65	348.4	10.23	30.70	14.42	241.7	6.93
Variation	-4%	-4%	-22%	-3%	-1%	+20%	-10%	+3%
Reference	30.51	51.29	400.1	9.45	27.88	15.90	300.4	7.91
ACN 1	31.45	48.32	396.7	8.64	24.76	14.56	287.1	8.24
Variation	+3%	-6%	-1%	-9%	-11%	-8%	-4%	+4%
Reference	24.66	47.58	379.0	8.88	47.91	16.99	276.8	7.83
EST 1	25.88	44.25	376.5	7.43	45.83	15.64	305.4	7.42
Variation	+5%	-7%	-1%	-16%	-4%	-8%	+10%	-5%
Reference	25.53	36.71	450.4	10.66	29.66	18.55	300.5	8.14
EST 2	23.89	34.76	437.5	9.65	30.67	19.44	298.5	9.15
Variation	-6%	-5%	-3%	-9%	+3%	+5%	-1%	+12%
Reference	32.66	35.40	400.6	10.89	28.88	20.55	298.55	8.15
EST 3	31.78	31.78	387.1	10.54	31.90	21.67	279.43	8.39
Variation	-3%	-10%	-3%	-3%	+10%	+5%	-6%	+3%
Reference	34.66	42.80	476.51	8.67	29.54	16.88	215.1	9.77
MAL 1	39.65	40.79	481.90	9.66	31.76	19.52	210.5	8.32
Variation	+14%	-5%	+1%	+11%	+8%	+16%	-2%	-15%

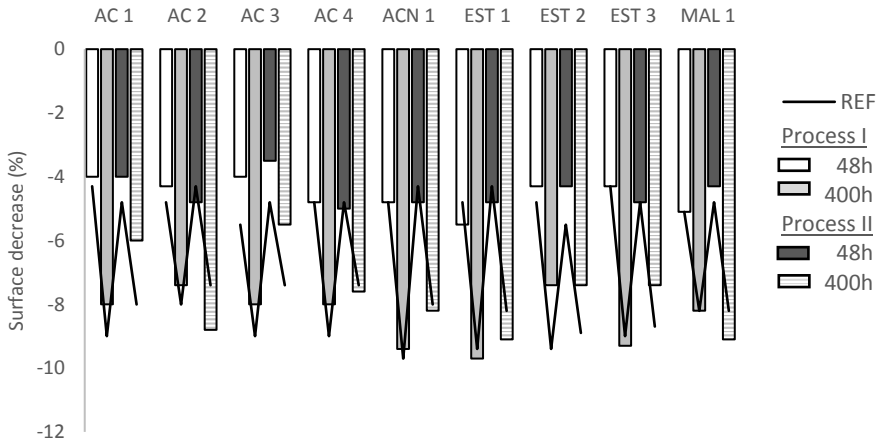

Fig. 3. Surface decrease in processes I and II.

Table 8. Sponginess and leveling in crust hides.

Sample	Sponginess		Leveling	
	I	II	I	II
Reference	2	2	1	1
AC 1	4	3	3	4
AC 2	3	2	2	2
AC 3	5	4	5	5
AC 4	3	5	3	4
ACN 1	3	2	4	3
EST 1	1	2	4	3
EST 2	2	3	3	3
EST 3	3	2	3	4
MAL 1	2	2	3	3

Finally, the organoleptic properties assessed in a 1-5 scale (in ascending order) are shown in Table 8. The values of the reference are an average of all references. The results suggest that the resin providing greater sponginess and leveling to the hides is homopolymer acrylic resin AC 3, followed by AC 4 and AC 1. Sponginess results are consistent with softness results, the better the softness the higher the sponginess.

Conclusions

The resins that provided the best properties to wet white tanned leather were homopolymer acrylic resins AC 1, AC 3 and AC 4, improving softness, surface decrease with temperature, sponginess and leveling. No significant changes in hide properties were observed with the rest of resins.

The results obtained suggest that acrylic resins interact with the amine groups of collagen by means of electrostatic charges because the COD decreases as pH is decreased. These results are consistent with the bibliography.

As shown in the SEM photographs, resin fixation increased fiber structuring and fiber separation, thus providing better sponginess and softness.

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