Modified Polyacrylates as a New Leather Retanning Agents

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Abstract. Acrylic resins have affinity for chrome tanned leather, for this reason, they are widely used as a retanning products. Its main use as a retanning agents is to produce full leathers. However, the leathers retanned with them have lower colour intensity and poorer structural properties because of their high anionicity which change the cationic surface of the leather causing a lower interaction of dyeing and fatliquoring agents with leather. This study proposes the use of modified polyacrylates as a new retanning agents. They were applied in leather versus traditional acrylic resins. The properties of the retanned leathers were evaluated concluding that this type of resins improve some leather properties avoiding the dyeing and fatliquoring problems of the traditional acrylic resins. The structure and the molecular weight of the modified polyacrylates play an interesting role in the improvement of the fixation of dyes and fatliquors, but also its lower anionic charge in comparison to the traditional acrylic resins. It has been observed that final leathers have a better colour intensity and softness. Moreover, its use as retanning agents favours the absorption of dyes and fatliquors which means an environmental improvement for the wet end process.

1 Introduction

Retanning process is one of the important steps in the manufacture of leather. It influences directly in the final steps (dyeing, fatliquoring and finishing) and, at the same time, defines the final properties of the leather. It is based in the treatment of the tanned leather with one or more chemical products to complete the tanning process and to give the end properties to the leather like fullness, softness, elasticity, colour levelness, etc.[1-3]

The products used as retanning agents can be based on different chemical natures: mineral agents (chromium, aluminium and zirconium salts); vegetable tannins (mimosa, tara, chestnut, etc.); synthetic tannins (based on naphthalenics, phenolics and sulfones); resins (based on urea, melamine, dicyandiamide, acrylic) and others (aldehydes, polyphosphates, etc.). Each product provides different properties to the end leather.[1]

Nowadays, the acrylic resins are extensively used because of its high affinity for chrome tanned leathers.[4-7] The acrylic resins used as a retanning agents in the wet end process are homopolymers or copolymers of acrylic acid and its derivatives synthetized by free radical polymerization.[9] They are linear chains with a number of carboxyl side groups that give resins an anionic charge.[5] This negative charge density allows them to react by ionic ligands with chrome tanned leather which has a cationic charge.[8,10,11] The resulting leather shows better properties such as fullness, flexibility and tensile strength.[4,12] However, this reaction with chrome reduces the cationic charge on the surface of the leather which is an inconvenience for dyeing and fatliquoring steps. In these stages anionic chemical products are mostly used, so, they can't react with the surface of the leather and the result is a leather with rigid grain (low fatliquoring) and lower colour intensity (low dyeing).[1,13]

In other fields, a polyalcoholic branched polyacrylates are being used because of the presence of a backbone chain with one chemical nature and a multiple side chains with another chemical nature.[14-19] This structure suggests that maybe this products can work as a retanning agents acting similar to the acrylic resins because of their backbone chain and introducing some advantages for their side chains.[15]

In this work, a new modified polyacrylate is tested as a retanning agent to analyse if the fixation of the fatliquors and dyes is better than that obtained using acrylic resins.

2 Experimental

2.1 Material and Chemicals

To make the retanning tests, it was chosen two Cromogenia's products. On one hand, an experimental modified polyacrylate that is composed of a polyacrylic acid with polyalcohol branches with a molecular weight (Mw) of 35000g/mol. On the other hand, and because of the good performance as a retanning agent in comparison to other commercial acrylic resins, it was chosen a standard acrylic resin produced by Cromogenia that is composed of a polyacrylic acid with a molecular weight (Mw) of 615000g/mol.

The other chemicals used for the retanning tests apart from those of common use in the tanning industry were: chrome sulfate with a basicity of 33% and a richness of 25% in Cr_2O_3; anionic dyestuff (colour index Acid Brown 83); sulphated neatsfoot oil (75% of active matter); sulfochlorinated paraffin (67% of active matter).

The retanning test were performed with split wet blue sheepskins from France shaved at 1.1mm.

2.2 Equipment

Simplex DF-2 Inoxvic drums with a dimension of 50cm in width and 100cm in diameter were used to carry out the retanning tests. All of them equipped with velocity and temperature regulators.

2.3 Retanning tests

To avoid the anisotropic effect and to be able to make the comparison between the hides retanned with the two products, retanning tests were carried out splitting the sheepskins through the backbone. The right side was retanned with the experimental modified polyacrylate meanwhile the left side was retanned with the acrylic resin (both products were applied at 5% of active matter). The retanning procedure applied is listed below in Table 1.

Table 1. Retanning tests formula

Process	Chemical	%	time (min)	T (ºC)	pH
Washing	Water	200		35	
	Non-ionic surfactant	0.2	30		
	Formic acid	0.2			
Drain					
Rechroming	Water	100		35	
	Chrome sulfate	5	30		
	Sodium formate	1.5	30		4.1
Overnight. Drain and rinse					
Neutralization	Water	150		30	
	Sodium formate	2	15		
	Sodium bicarbonate	0.5	60		5.0
Drain and rinse					
Retanning	Water	50		35	
	Retanning Agent (5% of active matter)	5	60		
Dyeing	Dispersing agent	2			
	Dyestuff	2	45		
Fatliquoring	Water	50		50	
	Sulphated neatsfoot oil	5	60		
	Sulfochlorinated paraffin	5			
	Formic acid	2	60		3.7
Drain and rinse					

2.4 Leather Characterization

To evaluate the leather physical properties, it was used the IUP (physical test methods) standard leather rules defined by the International Union of Leather Technologist and Chemists Society (IULTCS). These rules have an equivalence with the International Organization for Standardization rules (ISO).[20]

Before the analyses of the physical properties, leather samples were cut and conditioned during 48h at 20±2ºC with a 65% of relative humidity following rules IUP 1 & IUP 3 (ISO 2419:2012) and IUP 2 (ISO 2418:2017).

The physical properties evaluated were:
- Softness degree according to IUP 36 (ISO 17235:2015) using a Softness Tester. Seven measures are done in belly, backbone and middle doing an average of the 21 values.
- Thickness value according to IUP 4 (ISO 2589:2016) using a thickness gauge. Seven measures are done in belly, backbone and middle doing an average of the 21 values.
- Colour intensity using a colorimeter Color Data Spectraflash SF-30 based on chromatic model CIELAB for colour measures. Three measures in three leather different points are done obtaining an average value from the colorimeter.

All the leathers obtained in the retanning tests were checked by organoleptic tests carried out by experts in the field. The properties evaluated were fullness, visual colour levelness and colour intensity, grain tightness and superficial touch.

3 Results

The performed retanning tests were done following the methodology explained in the Experimental part to obtain comparative results between the leather retanned with the acrylic resin and those retanned with the modified polyacrylate.
In table 2 are described the values obtained for the physical retanned leather properties for three of the retanning tests done.

The physical property to be highlighted is the colour intensity. Acrylic resins are characterized by decreasing the colour intensity of the leathers because of their high anionicity. In this case, all the leathers retanned with the modify polyacrylate have a better colour intensity as it can be seen in the lightness (L*) values of table 2 (highest values mean more lightness and, consequently, less colour intensity). These values are logical because the modified polyacrylate is less anionic than the acrylic resin, basically because of their side chains. Therefore, the retanned leather with the modified polyacrylate is more cationic and favours the fixation of the dyes on its surface.

Regarding the other two properties, practically no difference is appreciated in thickness, but it does concerning softness. Leathers retanned with the modified polyacrylate are softener than the other ones. Apart from the influence of charge, the modified polyacrylate is less anionic which means more fatliquors fixation, it seems that the polyalcoholic side chains play an important role too. On one hand, the chemistry nature of these lateral chains can lubricate the collagen fibrils and, on the other hand, these lateral chains can produce a different distribution or packaging of the modified polyacrylate resin inside the leather which favours an increase of softness in leather.

Table 2. Physical properties values for retanned leathers of PCE A vs AR

		Colour intensity (L*)	Thickness [cm]	Softness [mm]
Test 1	AR	65.03 ± 1.30	1.1 ± 0.1	5.3 ± 0.2
	PCE A	54.22 ± 1.09	1.1 ± 0.1	5.6 ± 0.2
	Variation	19.9%	0.0%	5.7%
Test 2	AR	61.09 ± 1.22	1.1 ± 0.1	4.3 ± 0.2
	PCE A	52.99 ± 1.06	1.0 ± 0.1	5.0 ± 0.2
	Variation	15.3%	10.0%	16.3%
Test 3	AR	57.54 ± 1.15	2.1 ± 0.1	2.3 ± 0.1
	PCE A	50.58 ± 1.01	2.1 ± 0.1	3.0 ± 0.1
	Variation	13.8%	0.0%	30.4%

These laboratory results were confirmed by experts in the leather field who analysed the organoleptic properties. Leathers retanned with the modified polyacrylate have a silky and soft touch while those retanned with the acrylic resin have a rough and hard touch. Fullness has similar values, but the visual colour intensity and the colour levelness are greater for those retanned with the modified polyacrylate. Both of the retanned leathers are similar in that they have low grain tightness (typical for acrylic resins or derivatives).

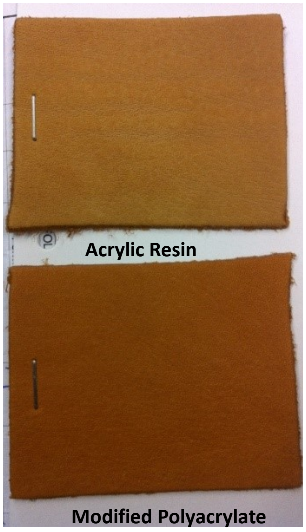

Figure 1. Colour intensity for leather retanned with acrylic resin and leather retanned with the modified polyacrylate.

After all the wet end process (retanning, dyeing and fatliquoring), it could be observed that the drums float of the modified polyacrylate test was more exhausted than the acrylic resin. It means that the products used in the retanning, dyeing and fatliquoring processes, are better absorbed using as a retanning agent the modified polyacrylate. This better absorption, which is traduced to an environmental improvement of the process, is probably linked to the structure, conformation and the charge of the modified polyacrylates.

4 Conclusions

Modified polyacrylates were evaluated as new retanning agents. They improve the fixation of dyes and fatliquors avoiding the principal problem of the acrylic resins used as retanning agents. The use of these new products as retanning agents will provide leathers with increased softness and colour intensity. Moreover, their use favours the absorption of the retanning, dyeing and fatliquoring agents which means the use of less quantities of these products and the presence of less quantities of them in the drum's float. Therefore, the use of modified polyacrylates means an environmental improvement for the retanning, dyeing and fatliquoring processes.

New studies will be done to complete the explanation of the positive effects of the modified polyacrylates on the physical retanned leathers properties.

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