

# CHROME FREE TANNING COMPOSITIONS AND PROCESSES

by

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## ABSTRACT

Totally organic tannages that start with an aromatic composition that lends itself to secondary reactions or crosslinking are one approach to the reduction or elimination of chrome as the primary tanning agent for leather. Our approach was to focus on the preparation of low molecular weight methacrylic acid copolymers with methacrylate comonomers in order to maintain a rigid-rod structure with functional groups extending from the rod. In one series we developed polymerization procedures with an aminomethacrylate monomer, to impart cationic functionality to the tanning molecule, and hydroxyethylmethacrylate to provide hydroxyl functionality for the second stage reaction. In another series, methacrolein was the only comonomer thus providing aldehyde functionality for the second stage reaction. For evaluation shrinkage temperatures were measured before and after the addition of crosslinking agents to the experimentally tanned stock. The best result for the hydroxyl functionality was 86°C obtained with glutaraldehyde, while for the aldehyde functionality the best result was 84°C obtained with oxazolidine. While lower than shrinkage temperatures obtained with chrome tanning, these values are high enough for automotive upholstery leather. Samples of these systems were retanned with a typical upholstery formulation and evaluated. These leathers met the physical requirements for automotive leathers, but we feel the retanning formulations and polymer compositions would need adjustments to improve color matching and to be certain the fatliquors are suitable for fogging tests.

## INTRODUCTION

Chromium has been used as the primary tannage for many leathers for over 100 years. In the early days the tanning

form, Cr(III), was produced from Cr(VI) in the form of bichromate by reduction of the chrome in the tanning bath by sugars at low pH. When basic chrome sulfate was introduced as a product ready to be used for tanning, tanneries changed to the use of these products either as an aqueous solution or as a dry product.<sup>1</sup> Environmental concerns about the effects of Cr(VI) and other heavy metals resulted in strict guidelines as to the amount of soluble chrome that could be discharged in a tannery waste stream, and disposal of waste leather from shavings, trimmings and buffing dust was limited to contained landfills.<sup>2</sup> Even so, the possibility of oxidation of chrome in the landfill to Cr(VI) with leaching into the environment has been a concern to Environmental Protection Agencies. However, the disposal of leather from worn out shoes, garments, gloves and upholstery, particularly automotive upholstery, and the possibility of ingestion of chrome containing leather by children has been addressed only recently.<sup>2</sup>

Several approaches to alleviate the problem have depended upon reducing the amount of chrome used in the tanning process and reducing the amount of waste leather containing chrome. The most significant was the "Wet White Process" developed by M. Siegler and Dr. W. C. Prentiss.<sup>3,4,5,6,7,8,9</sup> In this process pickled stock ready for tanning was tanned with a specially masked Aluminum Sulphate sufficiently to raise the shrinkage temperature (Ts) high enough to permit splitting, shaving and trimming. The waste product here was readily disposable or converted to a usable protein. Only the grain and split layers were tanned with chrome. Others introduced variations to produce a wet white.<sup>10</sup> Another development was a self basifying chrome composition.<sup>11</sup> With this product it was possible to reduce the chrome feed by about a third of the normal, achieve the full characteristics of a chrome leather and produce a discharge easily meeting effluent guide lines. The problem with these approaches is that they still require chrome as the primary tanning agent.

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The development of a leather free of chrome would solve the problem entirely. There have been two routes followed. One was the replacement of chrome by other less toxic metals such as titanium.<sup>12,13,14,15</sup> The other which has shown promise was the replacement of chrome with an organic tanning composition stabilized (crosslinked) with a small amount

t of aluminum and/or zirconium or a polyfunctional organic cross linking agent.<sup>16,17,18,19,20,21,22</sup> Many of these approaches utilize vegetable extracts, melamine/formaldehyde condensates or other materials not suited to making leathers with the heat and light stability required particularly for automotive upholstery. Our research was to build on the inherent stability of acrylic polymers to provide a new technology for products and/or processes to be able to produce by regular leather making processes leathers which would have a  $T_s$  approaching 100 °C. and properties meeting the performance requirements particularly of automotive upholstery. Because low molecular weight, water soluble polymers of methacrylic acid (MAA) do tan and raise the  $T_s$  of hides and skins, we conjectured that if functional groups such as hydroxyl or aldehyde were to be introduced in the polymer chain then a post tanning reaction with organic cross linkers such as glutaraldehyde, oxazolidine or polyamines would provide a leather with  $T_s$  much higher than the  $T_s$  achieved by the base polymer alone. We reasoned that such functional groups could be introduced by copolymerizing with suitable comonomers, and that these comonomers should be methacrylate based so the rigid spiral chain structure of polymethacrylic acid would not be disrupted, and the functional groups would stand out from the chain to be more readily available for subsequent reaction. One series included amine functionality to make a polyampholyte which is insoluble within its isoelectric range and could be more receptive to dyes, fatliquors and other anionic retanning agents.

## EXPERIMENTAL

### A. Polymerization Recipes

The general procedure follows. In a polymerization vessel equipped with a reflux condenser, a stirrer, a thermometer and a temperature controlled heat source  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  is dissolved in water at 90 °C. To this solution is added dropwise over a period of 1 1/2 hours the monomer mixture simultaneously with a solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  dissolved in water. This batch is maintained at 90 °C for 1/2 hour and then cooled to 60 °C. before it is then carefully, partially neutralized by slowly adding a sodium hydroxide solution with stirring.

This procedure was modified depending upon the monomer mix being polymerized and the results obtained in test runs.

For the polyampholyte polymers dimethylaminoethyl methacrylate (DMAEMA) was the preferred amino monomer, and it was necessary to introduce enough hydrochloric acid to maintain the pH of the polymer solution below the isoelectric range and to form the amine hydrochloride. Comonomers for the first tests were methacrylic acid (MAA), ethyl acrylate (EA) and hydroxyethyl methacrylate (HEMA). Subsequently to insure freedom from gelation during processing, MAA was increased, DMAEMA was reduced and EA was eliminated. The preferred procedure with all weights in grams was:

Monomer Composition:

MAA/DMAEMA/HEMA//81/9/10.

Initiator Mix: Distilled Water/1N HCl/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ //76.4/14.4/16.8.

Reaction Vessel Content: Distilled Water/1NHCl/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ //123.2/76.8/1.2.

pH(10%): 1.64

Isoelectric Range: 3.10 - 4.30

Solids %: 30.8

The aldehyde functional polymers followed the general procedure with methacrolein (MAc) providing the aldehyde. The preferred procedure with all weights in grams was:

Monomer Composition: MAA/MAc//92.3/7.7

Initiator Mix: Distilled Water/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ //54.0/16.8.

Reaction Vessel Content: Distilled Water/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ //127.0/1.2.

Neutralization Mix: Distilled Water/NaOH//61.0/7.2

pH(10%): 4.69

Solids %: 33.4

One sample was made with acrylic acid (AA) in place of MAA.

Monomer Composition: AA/MAc//111.0/6.0

Initiator Mix: Distilled Water/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ //54.0/16.8.

Reaction Vessel Content: Distilled Water/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ //127.0/1.2.

Neutralization Mix: Distilled Water/NaOH//61.0/7.2

pH(10%): 4.78

Solids %: 31.4

### B. Tanning Tests.

All tanning tests were carried out in small, clear plastic drums with approximately 2000 gram capacity. Basis white weights for the tests averaged about 450 grams with pickle

floats of 50%.

For tanning with the polyampholytes it was necessary to start with lime stock then bate, delime and pickle with salt and sulfuric acid to a pH of 1.8-2.0 to prevent precipitation of the polymer and allow it to penetrate. Penetration was followed by staining a fresh cut with methylene blue. With lime split grains penetration was achieved in one to two hours. For full thickness lime stock penetration was achieved in two to three hours. At this time 10% sodium bicarbonate was added in increments over a period of 30-60 minutes to bring the liquor pH up to 4.0-4.2, well within the isoelectric ranges, in order to insolubilize the polyampholyte and, hopefully, improve the stability of the tannage. A sample was taken for shrinkage temperature. A crosslinking reagent was added, and drumming continued for one to two hours. A sample was taken for shrinkage temperature, and the stock stored in the float for several days at ambient temperature after which another shrinkage temperature was taken.

For tanning studies with the aldehyde function polymers

lime stock was bated, delimed and pickled with a buffered acetic acid mixture to achieve a liquor pH of 4.5-5.0. The stock was drummed until 100% penetration by the methylene blue test, and then the liquor pH was adjusted with 10% formic acid to 4.0-4.2. After a sample for shrinkage temperature was taken, a crosslinker was added and drumming continued for two hours. A sample for shrink temperature was taken, and the stock stored in the float at ambient temperature for several days after which a second sample for shrinkage temperature was taken.

### C. Retanning Tests

Large pieces (~1000 g.) of lime split grain were bated, pickled and tanned with the polyampholyte in one test and aldehyde functional polymer in another. After aging they were wrung and retanned in separate drums. An upholstery weight blue stock shaved to 1.2 mm was also run as a control. The formulation typical of an automotive upholstery retannage is shown in Table I.

After this retannage, another was run, but with a minimum

TABLE I  
Retannage for Automotive and Furniture Upholstery Leathers

Operation	Products	T°C	Quantity %	Time (min)	Controls	Remarks
Wash/Drain	Water	40	200	15		Closed Door
Prefatliquor	Water	40	100			
	Fatliquor A		3.0			4/1 w water
Drain/Wash/Drain	Aux. syntan A		2.0			Mix with
	NaHCO <sub>3</sub>		0.5	30	pH 5.5	
	Resin syntan		2.0	30		Add dry
	Water	50	300	10		Closed Door
	Water	50	75			
Retan	Glutaraldehyde B		2.0	15		1/4 w water
	Fatliquor A		6.0	30		1/4 w water
	Tara		4.0			Mix with
	Phenolic syntan		4.0	20		w water to mix
	Brown dye G		4.0			mix with
	Black dye R		4.0	60		
	Aux syntan B		2.0	20		1/4 w water
	Formic acid		1.0	20		pH 4.6
	Formic acid		1.5	30		pH 3.6
	Formic acid		1.5	30		
Drain/Wash/Drain	Water	55	300	10		Closed door
Drain/Wash/Drain	Water	55	300	10		Closed Door
Fatliquor	Water	55	100			
	Fatliquor A		5.0	30		1/4 in water
	Aux syntan C		1.0	30		
Drain/Wash/Drain	Water	55	300	10		Closed door

Horse 72 hours, wring, stretch toggle by hand, dry at ambient temperature 48 hours, wet back, mull overnight, stake and air off. Leathers were not dry milled, but placed in a Constant Temperature Room (CTR) (23°C, 50% RH) for conditioning prior to testing.

of fatliquor and retanning agents but with the same level of dye to check dye fixation and bleeding. This was simply a wash and drain twice, float, add 4% each of Brown dye G and Black dye R, run 30 minutes, acidify with formic acid to pH 3.1, check dye exhaustion, neutralize with sodium bicarbonate to pH 3.5, add 5% Fatliquor A and 1% of Auxilliary syntan C, run 30 minutes, DWD, haul and horse, wring, stretch toggle, wet back, mull, stake, air off, condition in the CTR.

#### D. Test Methods

1.  $T_s$  - Modified Theis procedure.<sup>23</sup>
2. pH (10) - Product diluted ten parts per hundred with distilled water and pH measured.
3. Isoelectric range - Product diluted one part per hundred with distilled water and titrated with 0.1 N sodium hydroxide with stirring. pH of the solution was continuously monitored and recorded at first cloud formation and at first clarification. The pH difference is reported as the isoelectric range.
4. Tensile properties by ASTM D 2209.

### RESULTS AND DISCUSSION

#### A. Tanning Tests

The first tests were with the polyampholyte-(MAA/DMAEMA/EA/HEMA//72/13/10/5). They were designed to determine the effect of the level of copolymer used as well as to

study the effect of added crosslinking agents. The data are shown in Table II. Here the most significant information is that the copolymer without cross linking gives a much lower  $T_s$  (56) than was expected (>70) for an all methacrylate copolymer so that crosslinking would have to increase the  $T_s$  much more to achieve an acceptable value. None-the-less, the addition of crosslinking agents with only a short aging time did increase the  $T_s$  considerably, although it is not clear which crosslinker is better. Glutaraldehyde A was used so the samples with this crosslinker did yellow considerably. For further studies the MAA content of the copolymer was increased by decreasing DMAEMA and eliminating EA.

The second series was to evaluate the revised polyampholyte composition (MAA/DMAEMA/HEMA//81/9/10) crosslinked with oxazolidine and two aldehyde containing copolymers(MAA/MAC//93/7) and (AA/MAC//111/7) each with diethylenetriamine, (DETA) which with pendent amine groups could react with the aldehyde groups of the tanning agent. The data in Table III show that the higher percent of MAA in the polyampholyte did not improve the  $T_s$  before crosslinker addition, but the addition of oxazolidine with ample time for reaction to occur produced a  $T_s$  well in the range for automotive upholstery leather. Covington reported in his work<sup>20</sup> a similar need to allow enough time for the crosslinking reaction to take place at an ambient temperature, because he, like we, could not raise and control the temperature well enough to speed up the

TABLE II

#### Studies with Polyampholyte (Hydroxyl functionality)

% Solids on Pickled Weight	%, Crosslinker	$T_s$ deg C.	
		Before xlinker	After xlinker
10	5, Glutaraldehyde	56	70*
10	5, Oxazolidine	56	68*
20	10, glutaraldehyde	61	78**
20	10, Oxazolidine	56	61**

\*Overnight in Liquor    \*\*3 hours in Liquor

TABLE III

#### Copolymer Effect on $T_s$

Type Functionality	p-(MAA/DMAEMA/HEMA) Hydroxyl	p-(MAA/MAC) Aldehyde	p-(AA/MAC) Aldehyde
% Solids on DPW	10	10	10
$T_s$ before Xlinker	55	64	61
%, Xlinker	5, Oxazolidine	2, DETA	2, DETA
$T_s$ after 2 hours	61	65	61
$T_s$ After 10 days	84	68	61

TABLE IV  
Crossinker Studies with Both Systems

Polymer	Polyampholyte	Polyampholyte	p-MAA/MAC	p-MAA/MAC
% Solids on DPW	20	20	20	20
Xlinker	Glutaraldehyde B	Oxazolidine	DETA	Oxazolidine
% on DPW	5	5	2	5
Time aged	3 Days	3 Days	3 Days	3 Days
$T_s$	86	74	76	84

TABLE V  
Properties of Retanned Leathers

	Control Blue Stock	Polyampholyte	p-MAA/MAC
$T_s$ deg. C	>90	80	80
Thickness mm	1.59	2.46	1.64
Young's Modulus, psi	2865	3585	4262
Strain at Break, %	37.7	39.2	38.6
Stress at Break, psi	966	1742	3011

crosslinking reaction rate. From these data we can conclude that DETA does not effect sufficient reaction with the aldehyde containing polymers to be very effective in increasing the  $T_s$ . What is interesting to note is that the  $T_s$  achieved with the MAA based copolymer was only slightly better than that with the AA counterpart, an indication that the aldehyde functionality was interacting with the amine groups of collagen in a manner similar to that of glutaraldehyde. This observation is worth following up to determine whether this effect would improve the properties imparted by acrylic acid based syntans.

The third series was run to establish the cross linking agent for each copolymer to give the greatest increase in  $T_s$ . Glutaraldehyde B was compared to oxazolidine for the hydroxyl system while DETA was compared to oxazolidine for the aldehyde system. The data in Table IV show that the glutaraldehyde gave a considerably higher  $T_s$  than oxazolidine for the polyampholyte while oxazolidine is the choice for the aldehyde system. These two copolymer compositions were prepared in larger quantities to provide tanned stock so that after retanning there would be sufficient material to measure some physical properties.

#### B. Retanning Tests

The upholstery leather retannage formulation was run on the grain split of blue stock shaved to 1.2-1.4 mm as a control side by side with the two experimental tannages prepared from lime split grains. We did not have the equipment to shave these pieces, and an attempt to split them was not successful. The retannage formulation is shown in the

experimental section. Dye penetration was complete for all leathers, but exhaustion was better for the chrome control. When washing after dyeing bleeding was slight for the chrome control, but moderate for both of the experimental systems. When dry, the chrome leather was a dark brown while the experimental leathers were black. Because we were looking for better dyeing with the polyampholyte, and did not observe this, we wondered whether the anionic materials added ahead of the dye blocked the effect we were looking for. For this reason, we prepared leathers using a simplified retannage with dye added before a nominal amount of fat liquor and syntan. Both tannages showed good dye exhaustion, good penetration, and good fixation based on the very small amount of dye removed on washing. The color was black on both leathers without significant difference. It may be that the oxazolidine used to crosslink the aldehyde containing tanning agent introduced some cationic functionality which aided dyeing, but this would have to be confirmed by preparing leathers with a more neutral crosslinking system than oxazolidine.

Table V shows the properties measured with the retanned leathers. All three leathers have about the same elongation at break, while the experimental leathers have higher tensile strengths, which might be related to the fact they were not shaved and could have a higher ratio of corium to grain layer. The higher Young's moduli of the experimental tannages means they have greater resistance to stretching, which correlates with their slightly firmer handle as compared to the chrome tanned control. Since all methacrylate copolymers tend to be fairly hard, we believe the inclusion of a small amount of acrylate monomer in the copolymers

would improve hand without a significant loss in other critical properties.

### CONCLUSIONS

The results reported here are sufficient to conclude that leathers tanned with low molecular weight methacrylic acid copolymers with functional comonomers and then followed by reaction with known crosslinking agents and followed by retanning do have the shrinkage temperature and physical properties suitable for automotive and furniture upholstery leathers. It would seem reasonable that retan formulations more suited to these acrylic copolymer tannages will need to be developed with attention paid to fatliquors and dyes..

While we were not able to continue this work, should any other research group follow it up, we would recommend that any additional studies include the following:

1. Concentrate on copolymers and post tanning chemicals rather than on polyampholytes.
2. Determine if acrolein could replace methacrolein while introducing enough "acrylate" effect to have a softening effect on the leather.
3. Identify other functional monomers and crosslinking agents which could be of benefit.
4. Optimize levels of functional monomers in the copolymer for maximizing Ts.
5. Determine whether acrylate monomers incorporated in the copolymer can improve leather hand and reduce the levels of fat liquors required
6. Conduct retanning studies to provide guidelines for use of these new tanning agents and perhaps even improve Ts to levels closer to 100 degrees C.

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### PROPRIETARY CHEMICALS

The mention of these proprietary chemicals in our manuscript does not constitute an endorsement by the U.S. Department of Agriculture.

Chemical	Trade Name
Fatliquor A	Eureka 950R
Auxilliary Syntan A	Tanigan PAK N
Resin Syntan	Relugan R-7
Glutaraldehyd A	Relugan G-50
Glutaraldehyd B	Relugan GTW
Oxazolidine	Paramel 373
Phenolic Syntan	Basyntan DLE
Auxilliary Syntan B	Atlastan AR
Auxilliary Syntan C	Tamol NNOL
Brown G Dye	Sandoderm Brown G
Black R Dye	Sandoderm Black R

### CONVENTION DISCUSSION

*Prasad Inaganti, Howes Leather Corporation - Between polymethacrylate and polyacrylic acid, my understanding is that polymethacrylate has better tanning properties. Now when you introduce the aldehyde functionality into poly-methacrylate, does it really improve the tanning relative to polyacrylic acid?*

I think that part of the reasons that we did not get as high a shrink temperature with these copolymers as we might have expected in the first place is because you are diluting them by putting even 10% of a comonomer into the system. You are diluting the amount of carboxylate, if you will, or carboxyl group that is in the chain which probably is the main source of getting tanning through hydrogen bonding. I think that has been studied before and demonstrated to be the major role in tanning. Polymethacrylate is like a rigid rod. It is a spiral. I should have some of Anton's polymer examples such as paper clips to show you. It is a rigid rod, a spiral, with the monomers extending out from this chain so that they are available for reaction. We purposely stuck to methacrylates for the functional monomers to make sure that they would stick out and be available for reaction.

*David Rabinowich, Jos. Lowenstein & Sons - Chrome chloride tanning will only give you 80 °C. You don't have any of the ionic double sulfates. So 80 °C is what you would get with chrome chloride.*

It is right in the ballpark. Thank you.