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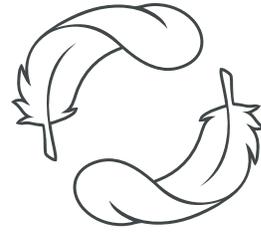
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# C O L D M i l l i n g



## Smooth Leather Milling



# Optimization of Dehairing/Fiber Opening using Ammonium Chloride/Dispase by Response Surface Methodology

by

Chao Tang,<sup>1</sup> Hui Liu,<sup>1</sup> Yadi Hu,<sup>1</sup> Fang Wang,<sup>1\*</sup> Keyong Tang<sup>1\*</sup> and Jide Zhong<sup>2</sup>

<sup>1</sup>Henan International Joint Laboratory of Biomass Resources and Materials, School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

<sup>2</sup>Henan Prosper Skins & Leather Enterprise Co., Ltd, Mengzhou 454750, China

## Abstract

A great number of pollutants including sulfides, suspended solids, and ammonia nitrogen compounds are generated by dehairing and fiber opening with the traditional use of sodium sulfide, calcium hydroxide, and ammonium salt. In this work, ammonium chloride (NH<sub>4</sub>Cl)/dispase system was used for the dehairing and fiber opening as an alternative of sodium sulfide/lime system to simplify the beamhouse operations, as well as to ease environmental pollution. It was found that the removing effect of interfibrillar substance is highly related to the factors such as enzyme catalysis time, temperature and the salt usage. Therefore, the mathematical models of enzyme activity, protein content, polysaccharide content and hydroxyproline content were established by response surface methodology (RSM) with the enzyme catalysis time, temperature and the salt usage as independent variables. It was found that the dehairing/fiber opening effect is the best with 2 % NH<sub>4</sub>Cl (base on hide weight) at 32.5°C for 15h, and only 3.5 h is needed for dehairing. This work might provide a reference for green leather making with enzymes.

## Introduction

Leather making is generally divided into three sections of beamhouse, tanning and finishing.<sup>1</sup> In the beamhouse, the hair and non-collagen components are removed, with the collagen fiber opened for the subsequent tanning. The quality and performance of the resultant leathers are determined by the beamhouse to some degree. Especially, dehairing and liming in beamhouse play an important role in removing the non-collagen ingredients in hides/skins such as soluble protein, elastin and proteoglycan to open the collagen fiber bundles.<sup>2</sup> However, 60%~70% of the total pollution load of the leather industry is produced by dehairing and liming due to the excessive use of lime, sulfide and other chemicals.<sup>3</sup> Among them, 40% of the sulfide does not participate in the reaction, which is directly discharged, resulting in the pollution of sulfide. The sulfide in the wastewater can be easily converted into the toxic gas of H<sub>2</sub>S.<sup>4-6</sup> In addition, the discharged wastewater containing high concentrations of sulfide might contaminate the rivers or land, and destroy plants and organisms. Therefore, great effort has been done

to remove or recover the sulfide from wastewater containing lime, in order to find effective ways to reduce pollution.

Nowadays, new liming materials such as enzymes have been developed to replace the traditional materials, which have been studied in the dehairing and fiber opening because of the high efficiency, environmental friendliness, low dosage and good specificity. Saravanabhavan et al. used complex enzymes as an alternative of chemical reagents in leather making to reduce environmental pollution.<sup>7</sup> Madhumathi et al. explored the influence of pH, substrate concentration and temperature on enzyme activity.<sup>8</sup> Xu et al. used enzymes for enzymatic dehairing and dispersing collagen fiber bundles, and used silica to adsorb and fix chromium ions.<sup>2</sup> Although some works have been done in the production of leather with enzymes, many problems are still faced in the application of enzymes, such as the shortages of high cost, which limits in the commercial applications. As a result, enzymes are usually used as assistant reagents for dehairing and fiber opening, with sulfide and calcium hydroxide the main reagents. In addition, although proteolytic enzymes could attack the proteoglycans of the hair roots, the collagen in the grain layer may be partially destroyed, resulting in poor quality and poor appearance of the final leather, which should account for the seldom applications in industrial scale. Therefore, how to improve the efficiency of enzyme dehairing and opening efficiency of collagen fiber bundles is critical for the quality of leather and green leather manufacturing.

The response surface methodology (RSM) is an effective mathematical and statistical method to design experiments, build models and search for optimal conditions because less time and resources are needed with easier operation and higher dependability.<sup>9, 10</sup> Zhang et al. investigated different ions in assisting neutral protease for interfibrillar substance removal and collagen fiber bundle opening, and found that NH<sub>4</sub>Cl was more effective and eco-friendly.<sup>11</sup> However, there is no study about the effect of NH<sub>4</sub>Cl concentration on the dehairing and collagen fiber opening of cowhide. In order to determine the variable range of Box-Behnken design (BBD), the classic one-time variable method was used to study the effects of NH<sub>4</sub>Cl concentration, processing time, and processing temperature on the dehairing and collagen fiber opening effect of cowhide. The regression model was established by using the BBD method. Through

\* Corresponding author email: cattwm@zzu.edu.cn; kytangzzu@hotmail.com  
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the combination of experiment and RSM simulation, the influence of variables on the process of dehairing of cowhide and collagen fiber opening was studied and analyzed. The results of optimization for dehairing and fiber opening were compared with those of traditional process, which might provide useful information for more efficient application of  $\text{NH}_4\text{Cl}$ /dispase to reduce environmental pollution and improve the quality of leather. In this work, the dehairing effect of cowhides is highly dependent on dehairing time, temperature and salt concentration by the study of control variables. In order to improve the dehairing and fiber opening effects of enzyme, the application condition of enzyme was studied and optimized by response surface methodology (RSM).

## Materials and Methods

### Materials

$\text{NH}_4\text{Cl}$  (ACS pure) and sodium sulfide were purchased from Fengchuan Chemical Reagent Technology Co., Ltd, Tianjin, China. Silver nitrate (AR pure) were from Aladdin Reagent Co. Ltd., Shanghai, China. Wet salted cowhides were from Henan Prosper Skins & Leather Enterprise Co., Ltd, Henan, China. Dispase (neutral protease, extracted from *Bacillus subtilis* by liquid fermentation) and tannin were from Macklin Reagent Co., Ltd., Shanghai, China. Verhoeff's Van Gieson (EVG) dye liquor was provided from Wuhan Servicebio Technology Co., Ltd., Wuhan, China. Distilled water was used in this study.

### The treatment of cowhide

A whole wet salted cowhide was cut into five pieces (from head to tail), and one with uniform thickness was put in the drum for washing and soaking. The water was changed every four hours until no precipitate appeared after silver nitrate solution was dropped into the water, meaning that the salt in the hides was completely removed.<sup>12</sup>

The chosen cowhide was cut into 50 mm × 30 mm pieces. In order to investigate the relationship between the  $\text{NH}_4\text{Cl}$  concentration and the dispersion of collagen fiber, seven pieces of cowhide were put in 20 mL salt/enzyme solution with 0.8 wt % dispase and 0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 wt %  $\text{NH}_4\text{Cl}$ , respectively, followed by vibration for 5 h. In order to investigate the relationship between the duration and degree of collagen fiber opening, six pieces of cowhide were processed with 1 wt %  $\text{NH}_4\text{Cl}$  and 0.8 wt % dispase at 30°C for 5 h, 10 h, 15 h, 20 h, 25 h, and 30 h, respectively. Finally, the effect of temperature was respectively studied at various temperature of 20, 25, 30, 35, 40, 45, and 50°C, with the 0.8 wt % dispase and 1 wt %  $\text{NH}_4\text{Cl}$ .

### EVG staining

The dehaired cowhide samples were embedded by paraffin and cut into slices of 5 mm thickness by a tissue slicer (Shanghai Leica Instrument Co., Ltd., RM2016). After being de-waxed in xylene

and ethanol solutions, the slices were stained with EVG (Elastin van Gieson) solution for 5 minutes and then rinsed with water. To improve the differentiation, the slices were re-dyed and sealed with neutral gum. The samples were observed by a digital slice scanning system (Pannoramic 250/ MIDI, Hungary).

### Analysis of SEM

The cowhide samples after dispase/ $\text{NH}_4\text{Cl}$  process were dried by vacuum freeze drier (Ningbo Xinzhi Biotechnology Co., Ltd., SCIENTZ-18ND) and then cut into pieces of 4 × 4 millimeter. The surfaces of cowhide samples were sprayed with gold powder for more than 1 min. The pores of cowhide surface were observed by focused ion beam scanning electron microscopy (SEM, S4800, Hitachi, Japan) at 10 kV.

### Tanning

The leather samples treated with traditional method or with dispase/ $\text{NH}_4\text{Cl}$  system were soaked in 7 wt % sodium chloride solution with 100 wt % water for 1 hour, then the 4 wt % sulfuric acid which were diluted 10 times were added. After 4 hours, with no float, the sodium thiosulfate was added to be uniformly distributed on the surface of leather sample by vibration (200r/min) for 30 minutes. Water at 300wt% was added at 30°C, and 5 wt %, 10 wt %, 10 wt %, and 10 wt % tannin were used each day. The leather samples were washed in 200wt% water and air-dried at 28°C for 48 hours.

### Establishment of RSM model for collagen fiber opening

RSM is a technique that combines specific mathematical and statistical methods. Since response values and variables are correlated with each other, in order to investigate the relationship between responses and variables, a series of experiments can be designed and the experimental results can be used as responses. So RSM models can be established and variables can be optimized.<sup>9</sup>

The advantage of BBD Design in Design Expert software (version 8.0.6) is that each factor has only three levels, which could greatly reduce the experimental workload. Three important parameters including the time (A), the temperature (B), and the  $\text{NH}_4\text{Cl}$  concentration (C) were analyzed through this method, as shown in Table I. According to this method, 17 experiments can be designed to analyze the interaction between three important

**Table I**  
**Design factor range and levels (coded)**

Independent variable	Units	Coded levels		
		-1	0	+1
Concentration	wt%	0	1	2
Temperature	°C	25	32.5	40
Time	h	5	15	25

influencing parameters,<sup>13</sup> with actual value to each responses shown in Table II.

Analysis of variance was used to determine the influence of factors on experimental results, and the responses obtained by each experiment form response surfaces and contour lines, so that the predicted responses can be visualized more intuitively. The response function for predicting optimal conditions was expressed according to equation (1). The value of  $R^2$  (determination coefficient) was used to evaluate the fitness of the model and the F test was used to check the significance of the model equation. The higher F value means the more accurate model equation.

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^n \beta_{ii} x_i^2 + \sum_{i=1}^n \sum_{j=1}^n \beta_{ij} x_i x_j + \dots + e \quad (1)$$

Where  $Y$  is the result of the dispase activity, proteoglycan concentration, protein concentration, or tensile strength of 17 experiments,  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$ , and  $\beta_{ij}$  are intercept, linear coefficient, quadratic coefficient, and interaction coefficients, respectively,  $n$  is the number of independent variables,  $X$  is the independent factors, and  $e$  is the random error.<sup>14</sup> Response surfaces and contour plots were obtained while variable of the second-order polynomial model was constant.<sup>15</sup>

## Results and Discussion

### Effect of $\text{NH}_4\text{Cl}$ concentration, time, and temperature on collagen fiber opening

$\text{NH}_4\text{Cl}$  is an ionic compound, soluble in water to form the ions of  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$  and  $\text{H}^+$ . The flexibility of dispase can be increased by the interaction with  $\text{NH}_4\text{Cl}$ . The ammonium ion will combine with the negatively charged group of the enzyme to improve the bonding ability of enzyme with substrate and increase the activity of the enzyme. The ionic bonds of interfibrillar substance among the collagen fibers should be destroyed by the strong ionic electrostatic attraction of salt solution, resulting in the hydrolysis of proteoglycan (interfibrillar substance). Therefore, the concentration of  $\text{NH}_4\text{Cl}$  is very important to cooperate with dispase for the dehairing of the

cowhide and the opening of collagen fiber. As shown in Figure 1, the activity of dispase increases with the increase of the  $\text{NH}_4\text{Cl}$  concentration until 1.5 wt % because of the salting-in effect of protein to improve the flexibility of the enzyme, while the effect of salting-out might be carried out with the increase of concentration of  $\text{NH}_4\text{Cl}$ . As shown in Figure 1(C), the protein concentration increased and then decreased with the increase of concentration of  $\text{NH}_4\text{Cl}$  due to the change tendency of enzyme activity, as well as the collagen fiber opening degree and the carbohydrate content in wastewater with same tendency.

As shown in Figure 2, the polysaccharides and elastic fiber in cowhides are gradually reduced with increasing the concentration of  $\text{NH}_4\text{Cl}$  (Figures 2(B) and (C)), while high concentration of  $\text{NH}_4\text{Cl}$  is not good for hydrolyzing the polysaccharides and elastic fiber, probably because of the salting-out of enzyme (Figure 2(E)). The enzyme with different concentrations of  $\text{NH}_4\text{Cl}$  was used for dehairing and collagen fiber bundle opening, with the SEM results shown in Figure 3(A, B, C). The pores in the cowhides surface become clearer and clearer with increasing the  $\text{NH}_4\text{Cl}$  concentration, with the pores hydrolyzed at the  $\text{NH}_4\text{Cl}$  concentration of about 2%. The SEM results of leather tanned with tannins were shown in Figure 3 (a, b, c), where the pores on the cowhides surface became clearer with the  $\text{NH}_4\text{Cl}$  concentration increased to 1%.

The effect of temperature on the cowhide dehairing/collagen fiber opening was investigated, with the results shown in Figure 4. The enzyme activity increases with the increase of temperature from 20°C to 50°C, which was probably because of the increase in the thermal movement and permeation of ammonium ions with the increase of temperature, further improving the flexibility of the enzyme to expedite the hydrolysis of glycoproteins and proteoglycans in cowhide.

The effect of time on the depilation/collagen fiber opening was investigated, with the results shown in Figure 5. The tendency of tensile strength of the tanned leather is slightly decreased with the increase of time because of the excessive hydrolysis of collagen fiber with the long time soaking in  $\text{NH}_4\text{Cl}$ /dispase solution.

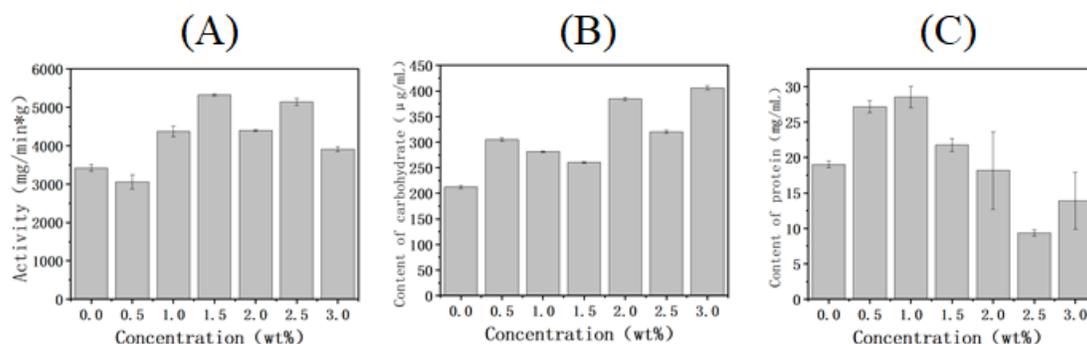


Figure 1. Effect of  $\text{NH}_4\text{Cl}$  concentration on the activity of dispase (A), content of carbohydrate (B) and content of protein (C).

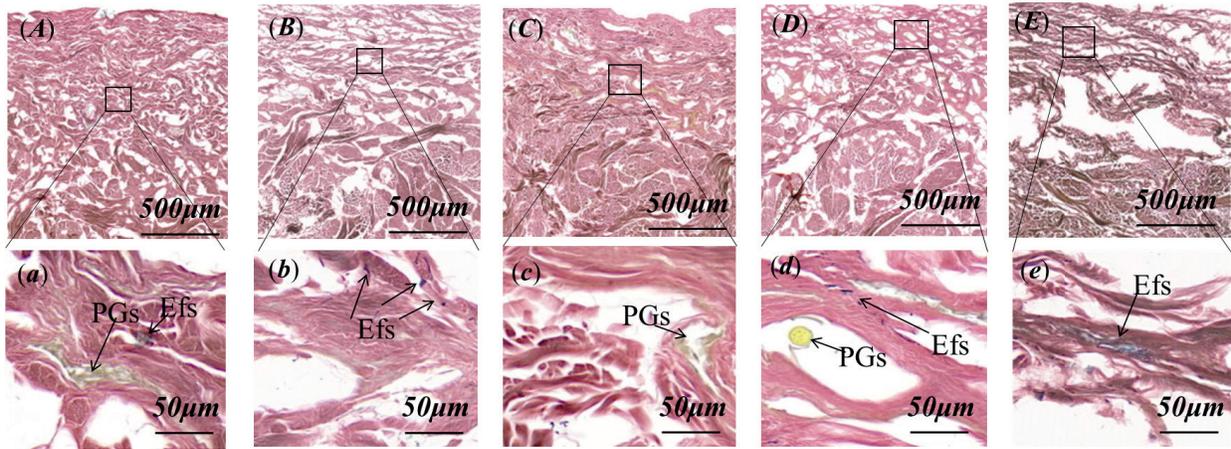


Figure 2. The cross-section images of cowhide processed with 0.8wt% disperse in different concentrations of  $\text{NH}_4\text{Cl}$  by EVG staining: (A) 0%, (B) 1%, (C) 2%, (D) 3%, (E) 4%.

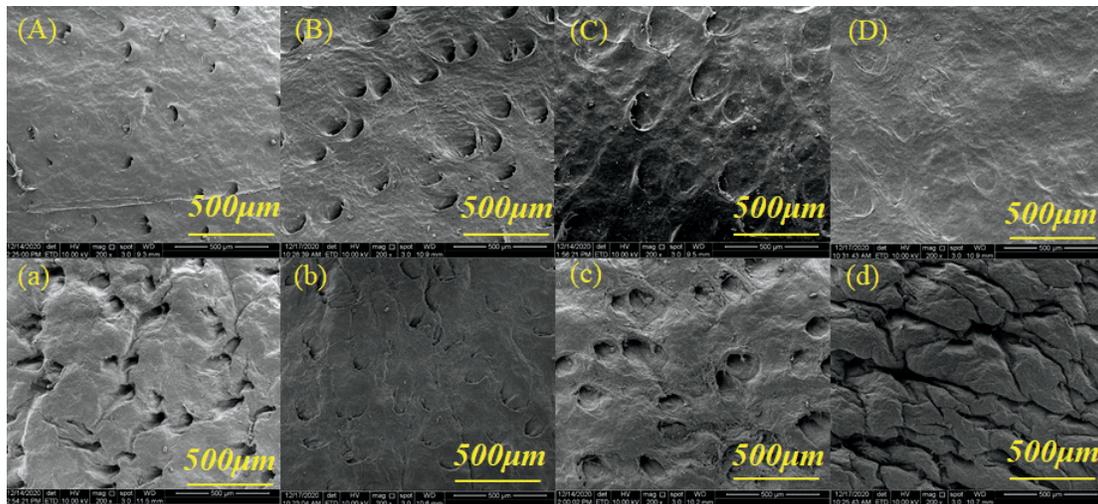


Figure 3. SEM images of surface of samples before ((A) 0%, (B) 1%, (C) 2%, (D) 3%) and after ((a) 0%, (b) 1%, (c) 2%, (d) 3%) tanning.\*

\*The usage of disperse was 0.8 wt % and the percentage was the concentrations of  $\text{NH}_4\text{Cl}$

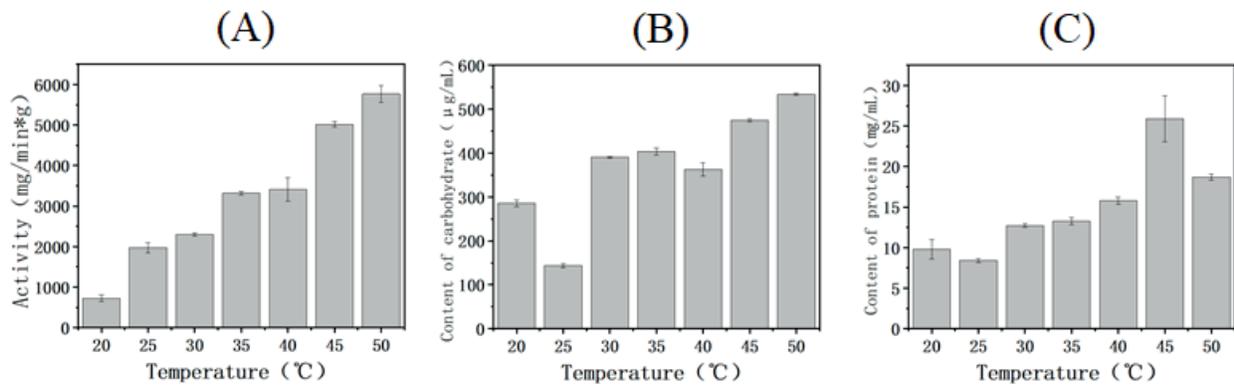


Figure 4. Effect of temperature on the activity of disperse (A), content of carbohydrate in  $\text{NH}_4\text{Cl}$ /disperse solution (B), content of protein in  $\text{NH}_4\text{Cl}$ /disperse solution (C).

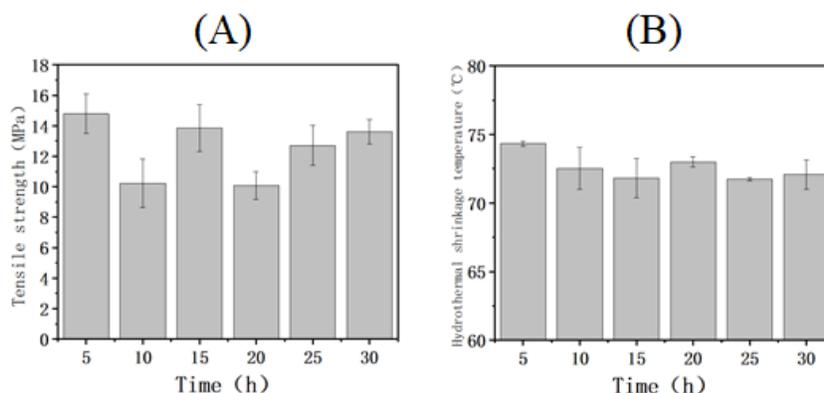


Figure 5. Effect of time on the tensile strength (A), hydrothermal shrinkage temperature (B) of tanned leather.

### RSM modelling

In the RSM model, the independent variables were converted into coded variables (Table I). In RSM, natural variables were converted into coded variables, these coded variables were defined as dimensionless, which had a mean value of zero, and had the same spread or standard deviation.<sup>13</sup> The results of the dispase activity (Y), proteoglycan concentration (G), protein concentration (H), and tensile strength (K) of 17 experiments were shown in Table II. The response values and independent variables were analyzed by regression of Box-Behnken and a quadratic regression model was proposed.

Corresponding coefficients of multiple determination in the ANOVA of each response for evaluating the effect of dehairing/collagen fiber opening, with the detailed results were shown in Table IV. A maximum value for each model was obtained from ten

regression coefficients (Intercept, A, B, C, AB, AC, BC, A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup>) of the model (Table IV). In general, a fitted response surface may produce poor or misleading results unless the model exhibits an adequate fit during the exploring and optimizing proceeding,<sup>13</sup> which makes the checking of model adequacy essential (Table V). A plot of experimental and theoretical values indicated a normal fit ( $R \geq 0.83$ ,  $p < 0.05$ ) for enzyme activity, content of protein, and tensile strength of tanned leather. A high proportion of variability was explained by the RSM models for evaluating the effect of dehairing/collagen fiber opening. The regression models were significant ( $p < 0.02$  or  $p < 0.05$ ) for activity of dispase, content of protein and tensile strength of tanned leather, with general satisfactory coefficient of determination ( $R^2$ ) varying from 0.83 to 0.86, and there is a high correlation between the predicted values and the actual values, as shown in Figure 6. Moreover, coefficient of variation (CV) describes

Table II  
Experimental results of RSM Box-Behnken design

Run	Time h	Temperature °C	NH <sub>4</sub> Cl concentration wt%	Activity Y mg/min*g	Content of carbohydrate G µg/mL	Content of protein H mg/mL	Tensile strength K MPa
1	15.00	32.50	1.00	1319.19	15.03	22.98	23.22
2	25.00	32.50	0.00	1056.16	14.14	25.92	22.58
3	5.00	25.00	1.00	1275.08	9.13	13.09	24.29
4	15.00	40.00	0.00	843.06	15.35	30.57	17.80
5	15.00	32.50	1.00	1282.00	11.61	20.11	17.61
6	25.00	40.00	1.00	706.04	9.27	28.63	24.51
7	25.00	25.00	1.00	913.64	7.50	22.16	16.55
8	15.00	40.00	2.00	906.85	20.36	29.96	20.52
9	25.00	32.50	2.00	1754.70	17.22	26.05	15.30
10	5.00	40.00	1.00	1338.04	18.51	20.50	14.74
11	15.00	32.50	1.00	1150.32	11.47	23.70	18.54
12	15.00	32.50	1.00	1208.73	10.22	20.46	22.00
13	5.00	32.50	2.00	1961.57	11.03	19.72	19.38
14	15.00	25.00	2.00	965.34	8.13	18.31	15.02
15	15.00	25.00	0.00	856.12	9.76	19.09	18.2
16	5.00	32.50	0.00	1221.79	9.44	18.08	15.02
17	15.00	32.50	1.00	1127.65	12.77	25.85	20.37

the extent of the dispersed data. The CV for each response value was within the acceptable range (0%~30%). Since CV is a measure expressing standard deviation, the smaller value of CV means that the model has better reproducibility. In general, a high CV indicates that the variation in the mean value is high and does not satisfactorily develop an adequate response model.<sup>13</sup>

An ANOVA of independent variables in Table III indicated that the concentration of  $\text{NH}_4\text{Cl}$  is the most significant ( $p < 0.02$  or  $p$

$< 0.05$ ) factor affecting the enzyme activity and tensile strength of all response values. The model suggested that the temperature significantly affects the contents of carbohydrate and protein (Table IV). Thus,  $\text{NH}_4\text{Cl}$  concentration and temperature contribute significantly to the response. On the other hand, the processing time has little effect on responses. By considering the regression coefficients obtained from independent and dependent variables,  $\text{NH}_4\text{Cl}$  concentration and temperature might be the most important factors significantly affecting the quality of the resultant leather.

**Table III**  
ANOVA results for response surface quadratic model

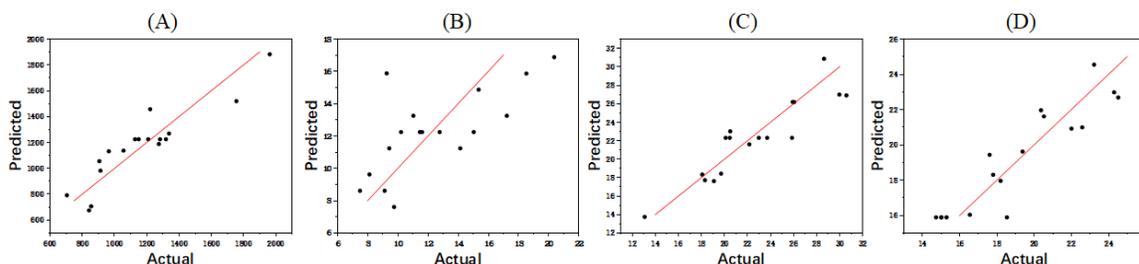
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Status
Model-activity	1.383E+006	9	1.537E+005	3.90	0.0433	significant
A-time (h)	2.332E+005	1	2.332E+005	5.91	0.0453	
B-temperature (°C)	5842.26	1	5842.26	0.15	0.7118	
C-concentration (%)	3.245E+005	1	3.245E+005	8.23	0.0241	
Model-Content of carbohydrate	113.01	3	37.67	4.21	0.0275	significant
A-time (h)	5.000E-005	1	5.000E-005	5.590E-006	0.9981	
B-temperature (°C)	104.91	1	104.91	11.73	0.0045	
C-concentration (%)	8.10	1	8.10	0.91	0.3586	
Model- Content of protein	294.25	3	98.08	21.30	< 0.0001	significant
A-time (h)	123.01	1	123.01	26.71	0.0002	
B-temperature (°C)	171.22	1	171.22	37.18	< 0.0001	
C-concentration (%)	0.018	1	0.018	3.920E-003	0.9510	
Model-tensile strength	141.58	9	15.73	5.08	0.0217	significant
A-time (h)	3.24	1	3.24	1.05	0.3403	
B-temperature (°C)	0.19	1	0.19	0.060	0.8136	
C-concentration (%)	7.70	1	7.70	2.49	0.1587	

**Table IV**  
Regression coefficients of predicted quadratic polynomial models for the activity of dispase, content of carbohydrate and content of protein of  $\text{NH}_4\text{Cl}$ /dispase solution, and tensile strength of tanned leather

Coefficient	Activity of dispase Y mg/min*g	Content of carbohydrate G $\mu$ g/mL	Content of protein H mg/mL	Tensile strength K MPa
Intercept	1217.58	12.41	22.66	15.90
A-time(h)	-170.74	2.500E-003	3.92	-0.64
B-temperature (°C)	-27.02	3.62	4.63	0.15
C-concentration (%)	201.42	1.01	0.047	0.98
AB	-67.64			-1.14
AC	-10.31			0.10
BC	-11.36			-0.81
A^2	223.17			4.95
B^2	-382.55			1.77
C^2	57.81			0.31
R-Squared	0.8336	0.4929	0.8309	0.8672
C.V. %	16.98	24.10	9.47	9.16

**Table V**  
ANOVA results for response surface quadratic model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Status
<b>Activity of dispase mg/min*g</b>						
Residual	2.762E+005	7	39450.56			
Lack of Fit	2.490E+005	3	82996.58	12.22	0.0175	significant
Pure Error	27164.16	4	6791.04			
Cor Total	1.659E+006	16				
<b>Content of carbohydrate <math>\mu</math> g/mL</b>						
Residual	116.28	13	8.94			
Lack of Fit	103.15	9	11.46	3.49	0.1205	not significant
Pure Error	13.13	4	3.28			
Cor Total	229.29	16				
<b>Content of protein mg/mL</b>						
Residual	59.86	13	4.60			
Lack of Fit	37.17	9	4.13	0.73	0.6831	not significant
Pure Error	22.69	4	5.67			
Cor Total	354.11	16				
<b>Tensile strength MPa</b>						
Residual	21.67	7	3.10			
Lack of Fit	18.25	3	6.08	7.11	0.0442	significant
Pure Error	3.42	4	0.86			
Cor Total	163.26	16				



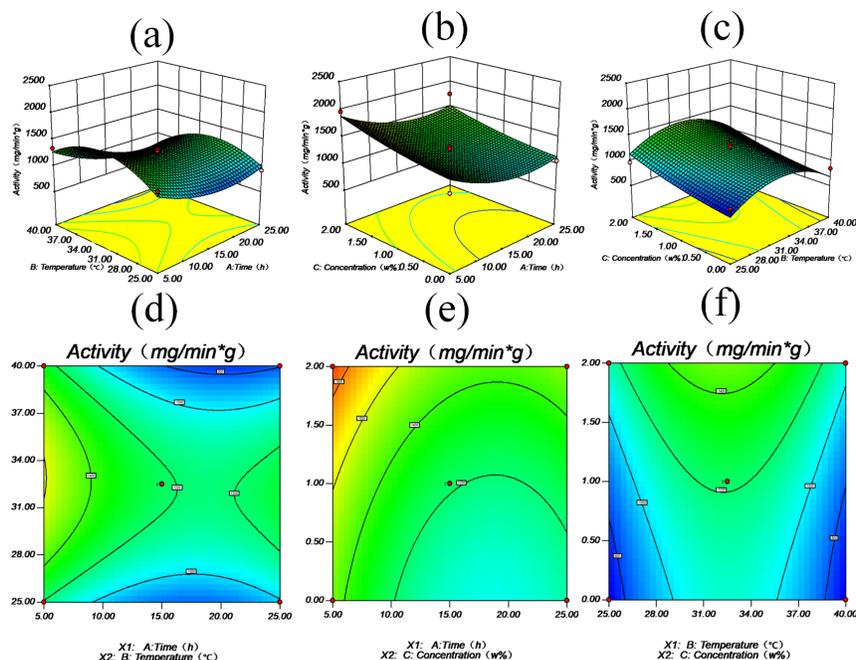
**Figure 6.** Comparison of predicted and experimental responses of RSM results: (A) activity of dispase, (B) content of carbohydrate, (C) content of protein, (D) tensile strength of tanned leather.

### Analysis of response surfaces

As shown in Figures 7~10, three-dimensional (3D) response surface and two-dimensional (2D) contour plots were used to explain the effects of time, temperature and  $\text{NH}_4\text{Cl}$  concentration on the dispase activity, content of carbohydrate, content of protein, and tensile strength, respectively. Figure 7 (a) ~ (c) showed the effects of temperature,  $\text{NH}_4\text{Cl}$  concentration and time on the enzyme activity. Dispase activity decreases with increasing the time, while dispase activity firstly increases with the temperature increasing until  $32^\circ\text{C}$ , and then decreases. As the concentration of  $\text{NH}_4\text{Cl}$  increases, the activity of the dispase increases. The two-dimensional contour map has greater density and greater influence. In Figure 7 (d), compared with the process temperature, the contour density of the process temperature is greater. The process temperature greatly affects the

dispase activity. In addition, from Figure 7 (e) (f), we know that the contour density of the  $\text{NH}_4\text{Cl}$  concentration is greater than the process time and process temperature. Therefore, the  $\text{NH}_4\text{Cl}$  concentration has a greater influence on the dispase activity than the process time.

By the use of  $\text{NH}_4\text{Cl}$ /dispase system, the collagen fiber bundles could be opened. The increase of the gap between the fiber bundles is accompanied with the disappearing of the proteoglycan in them. With increasing the temperature, the concentration of proteoglycan of the solution firstly increases to reach a maximum at  $32^\circ\text{C}$ . As the  $\text{NH}_4\text{Cl}$  concentration increases, the polysaccharide concentration increases too. The concentration of proteoglycan in the solution does not increase significantly with increasing treatment time,



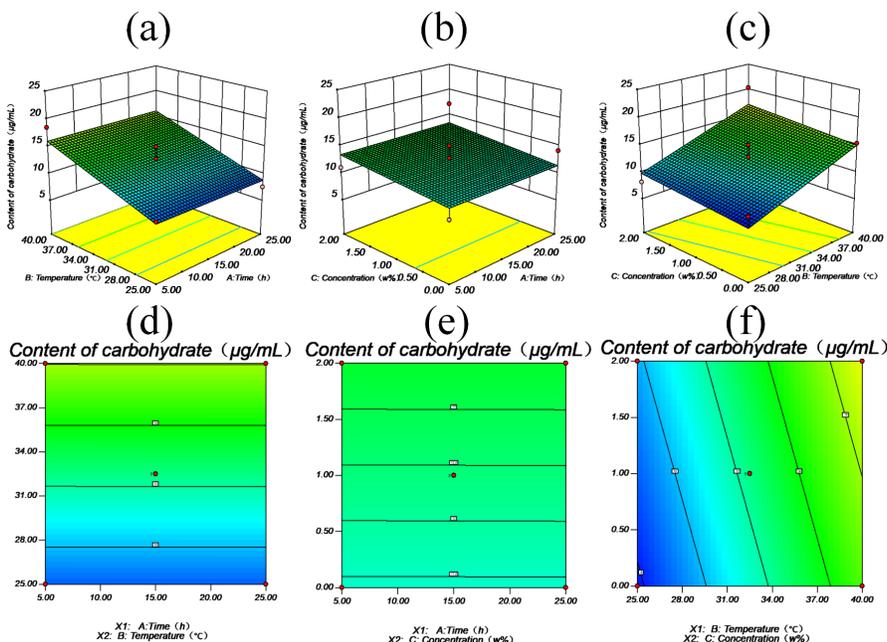
**Figure 7.** Three-dimensional response plots and two-dimensional contour plots showing (a) (d) the effect of time (x1), temperature (x2), and their mutual interaction on dispase activity (Y); (b) (e) the effect of time (x1),  $\text{NH}_4\text{Cl}$  concentration (x2) and their mutual interaction on Y; (c) (f) the effect of temperature (x1),  $\text{NH}_4\text{Cl}$  concentration (x2) and their mutual interaction on Y.

probably because of the reaction and adhesion between the groups of polysaccharides and the collagen fiber after the polysaccharide being shed.

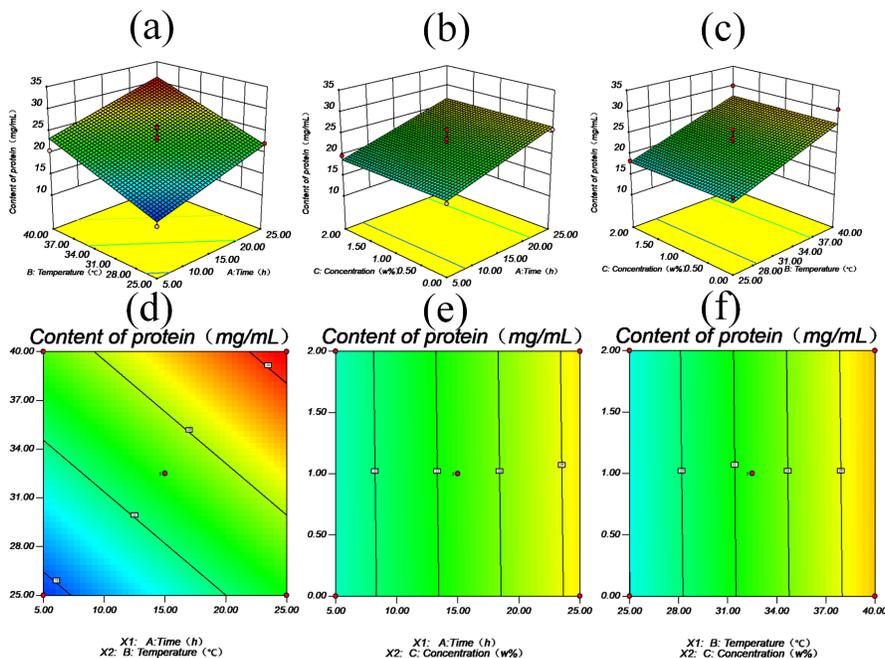
In Figure 8 (d), compared with the treatment time, the contour density of the treatment temperature is greater. So, the treatment temperature has a greater impact on the proteoglycan removal. Besides, in Figure 8 (e), the contour density of the  $\text{NH}_4\text{Cl}$  concentration is greater than the treatment time. Therefore, the

$\text{NH}_4\text{Cl}$  concentration has a greater influence on the shedding of proteoglycans than the treatment time.

There is glycoprotein among the collagen fiber bundles in hides. The shedding of glycoproteins might increase the fiber bundle gaps. At the same time, dispase will also decompose the surface of collagen to increase the protein concentration in the solution. In Figure 9 (a), with the temperature increasing, the protein concentration of the solution increases. The protein concentration



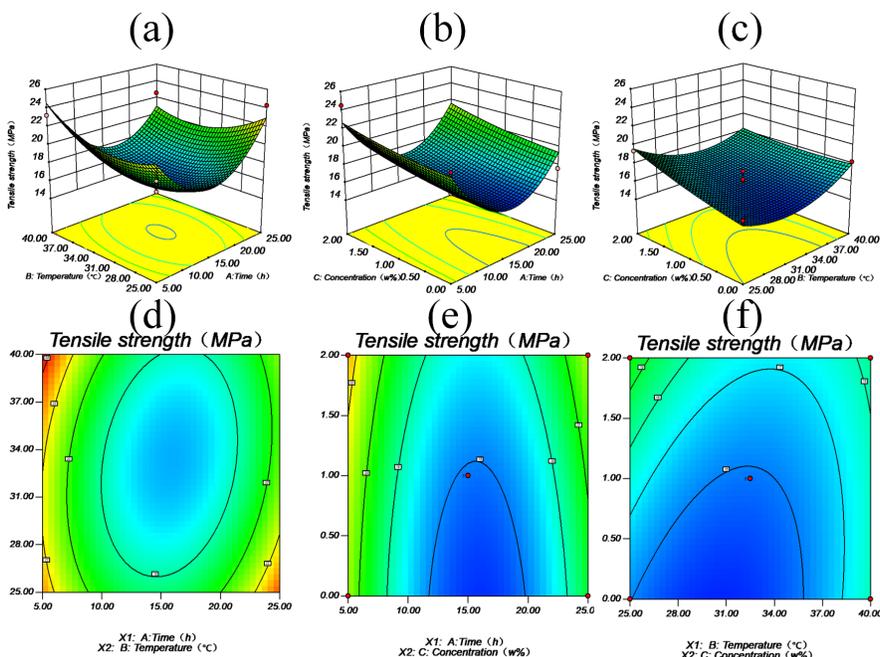
**Figure 8.** Three-dimensional response plots and two-dimensional contour plots showing (a) (d) the effect of time (x1), temperature (x2), and their mutual interaction on content of carbohydrate (G); (b) (e) the effect of time (x1),  $\text{NH}_4\text{Cl}$  concentration (x2) and their mutual interaction on Y; (c) (f) the effect of temperature (x1),  $\text{NH}_4\text{Cl}$  concentration (x2) and their mutual interaction on G.



**Figure 9.** Three-dimensional response plots and two-dimensional contour plots showing (a) (d) the effect of time (x1), temperature (x2), and their mutual interaction on content of protein (H); (b) (e) the effect of time (x1), NH<sub>4</sub>Cl concentration (x2) and their mutual interaction on Y; (c) (f) the effect of temperature (x1), NH<sub>4</sub>Cl concentration (x2) and their mutual interaction on H.

of the solution is not significantly increased with increasing treatment time. In Figure 9(b) and Figure 9(c), with increasing the concentration of NH<sub>4</sub>Cl, the concentration of protein in the solution increases slightly. As shown in Figure 9(d), Figure 9(e), and Figure 9(f), the contour of temperature is larger than the contour density of NH<sub>4</sub>Cl concentration and treatment time. Therefore, the influence of temperature on the shedding of glycoprotein is greater than the NH<sub>4</sub>Cl concentration and process time.

The dispersion effect of collagen fiber will affect the tanning effect. With increasing the gaps between the collagen fiber bundles, more possibility for the cross-linking between collagen fiber and tannin is provided, resulting in better tanning effect. In Figure 10 (a), with increasing the temperature and treatment time, the tensile strength of the tanned leather firstly decreases and then increases, which should be because of the larger gap between collagen fiber became larger and higher degree of dispersion. After 15h, the degree of dispersion increases. The



**Figure 10.** Three-dimensional response plots and two-dimensional contour plots showing (a) (d) the effect of time (x1), temperature (x2), and their mutual interaction on tensile strength (K); (b) (e) the effect of time (x1), NH<sub>4</sub>Cl concentration (x2) and their mutual interaction on Y; (c) (f) the effect of temperature (x1), NH<sub>4</sub>Cl concentration (x2) and their mutual interaction on K.

**Table VI**  
**Pollution loads in waste-water by different processes (unit: kg/t of raw hide)**

		Process(kg/t)			Total(kg/t)
		Dehairing	Fiber opening		
			Reliming	Deliming	
C	COD	1.51±0.11	1.05±0.20	0.29±0.42	2.85±0.53
	NH <sub>3</sub> -N			0.35±0.10	0.35±0.10
	Cl <sup>-</sup>	6.33±0.22	0.85±0.11	4.72±0.13	11.90±0.40
	TS	35.75±0.00	8.30±0.00	7.45±0.00	51.50±0.00
NH <sub>4</sub> Cl/D	COD		0.37±0.10		0.37±0.10
	NH <sub>3</sub> -N		0.20±0.10		0.20±0.10
	Cl <sup>-</sup>		6.77±0.02		6.77±0.02
	TS		18.40±0.00		18.40±0.00

(Note:D:disperse)

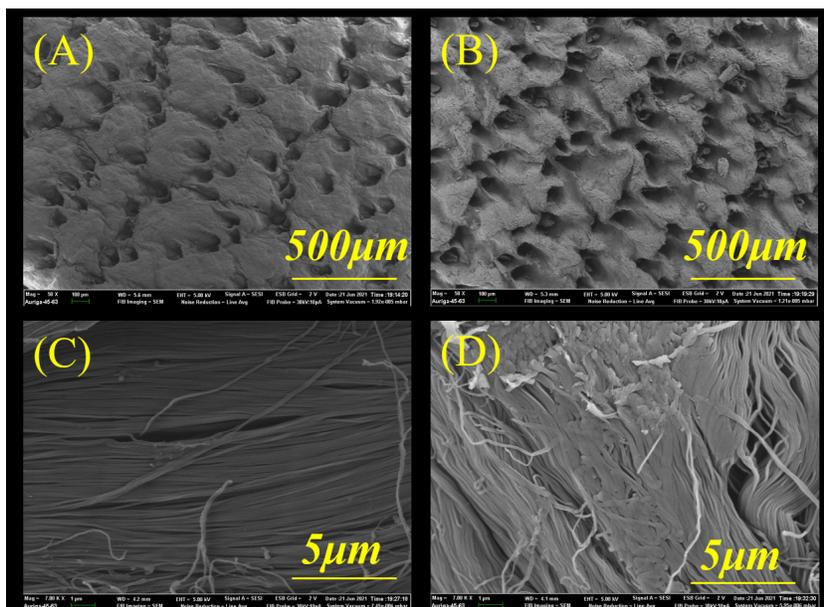
increase of the cross-linking degree of collagen fiber by tannins leads to an increased tensile strength. In Figure 10 (b) and Figure 10 (c), as the NH<sub>4</sub>Cl concentration increased, the tensile strength increased. In Figure 10 (d), the contour of temperature is greater than the contour density of the treatment time, and the contour of the concentration is greater than the contour density of temperature, which means that the NH<sub>4</sub>Cl concentration has a greater influence on fiber opening.

#### Determination of optimization conditions

By analyzing the influence of NH<sub>4</sub>Cl concentration, temperature and treatment time on the fiber opening effect of collagen fiber, it was found that the fiber opening effect of collagen fiber increases with increasing the concentration of NH<sub>4</sub>Cl. Considering economic benefits and environmental issues, the optimal NH<sub>4</sub>Cl concentration was determined at about 1 wt %. With increasing the temperature

**Table VII**  
**Physical properties and hydrothermal shrinkage temperature of tanned leathers by different processes**

Sample	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus (MPa)	Hydrothermal shrinkage temperature (°C)
C	10.3±0.5	29.3±3.0	0.3±0.1	71.6±0.2
NH <sub>4</sub> Cl/D	13.1±1.1	30.9±4.9	0.5±0.1	71.4±0.3



**Figure 11.** SEM images of the surface of tanned leathers in the predicted optimized condition from NH<sub>4</sub>Cl/disperse (A) and traditional (B) Cross-section SEM images of tanned leather from NH<sub>4</sub>Cl/disperse (C) and traditional (D) processes.

and time, both the enzyme activity and the dispersibility of collagen fiber were significantly increased. However, denaturation of collagen fiber and hydrothermal shrinkage will take place at high temperature. Therefore, the optimized temperature was determined to be 32°C. With increasing the treatment time, the dispersibility of collagen fiber increases. Since enzymes might decompose the protein on the cowhide surface, 15 h is the optimal processing time for fiber opening of collagen fiber.

#### Comparison of the tanned leathers obtained in optimized conditions and by traditional process

The optimized conditions were obtained through response surface analysis and compared with the traditional process. As shown in Table VI, the chemical oxygen demand (COD), ammonia nitrogen (NH<sub>3</sub>-N), chloride ion (Cl<sup>-</sup>), and the total solids (TS) of traditional process were significantly higher than those by the optimized NH<sub>4</sub>Cl/diapse process, because of the use of sodium sulfide and calcium hydroxide, which caused serious suspended solids and pollution of sulfide and ammonia nitrogen. In addition, the NH<sub>4</sub>Cl/diapse system has a good selective catalytic effect on the proteoglycans and elastin in the cowhide.

As shown in Table VII, the tensile strength, elongation at break, and elastic modulus of the samples by the optimized NH<sub>4</sub>Cl/diapse dehairing and collagen fiber bundles opening is higher than those by the traditional process, with comparable hydrothermal shrinkage temperature of the tanned leather to the traditional one. Because Na<sub>2</sub>S/Ca(OH)<sub>2</sub> system is used in the traditional dehairing and liming process, the swelling of the rawhide is reached by the breakage of the hydrogen bonds to loosen the collagen fiber structure, resulting in the decrease in tensile strength, elongation at break and modulus of elasticity of the tanned leather. The NH<sub>4</sub>Cl/diapse system might promote the hydrolysis of proteoglycan and elastin to open the collagen fiber bundles with no obvious swelling and more reactive sites for tanning were provided, which was helpful to increase the tensile strength, elongation at break and elasticity modulus of the resultant leathers.

The collagen fiber bundles opening of the sample processed with the optimized NH<sub>4</sub>Cl/diapse method was compared with that by the traditional method. The SEM image of the surface of the sample after tanning was shown in Figure 11 (a) (b), where the pores on the grain by NH<sub>4</sub>Cl/diapse were more uniform. The SEM image of the longitudinal section after tannin tanning was shown in Figure 11(c) (d), indicating better collagen fiber bundle opening by the NH<sub>4</sub>Cl/diapse system, which was conducive to the subsequent process of leather.

## Conclusions

The response surface methodology was used to directly analyze the influence of various factors on the process of dehairing and collagen fiber bundle opening. In the NH<sub>4</sub>Cl/diapse system, the dehairing effect of cowhide is highly dependent on time, temperature and salt concentration. The dehairing and collagen fiber bundle opening conditions optimized by the response surface methodology are 1 wt % NH<sub>4</sub>Cl at 32°C 0.8 wt % diapse solution for 15 h. The physical properties of the tanned leather by the optimized NH<sub>4</sub>Cl/diapse system are superior to those by the traditional dehairing method, with the tensile strength increased by 27.18%, elongation at break increased by 5.46%, and elastic modulus increased by 66.67%. The thermal properties of the tanned leather by the optimized NH<sub>4</sub>Cl/diapse system are similar to those by the traditional dehairing process. The environmental benefit of the optimized NH<sub>4</sub>Cl/diapse system is better than that of the traditional one. The chemical oxygen demand (COD), ammonia nitrogen (NH<sub>3</sub>-N), chlorine ion (Cl<sup>-</sup>) and total solid (TS) are reduced by 87.02 %, 42.86 %, 43.11 % and 64.27 % respectively. These results indicate that the reasonable use of NH<sub>4</sub>Cl can be achieved. By the study, theoretical basis and experimental support might be provided to reduce the environmental pollution as well as improve the dehairing efficiency with comparable or increased leather quality.

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# Effect of Pickling Materials on Leather Quality from a Hide Surface Charge Perspective

by

Tianqi Yang,<sup>1</sup> Yunhang Zeng,<sup>1\*</sup> Qingyong Sun,<sup>2,3</sup> Chao Lei<sup>2</sup> and Bi Shi<sup>1,2</sup>

<sup>1</sup>National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu 610065, China

<sup>2</sup>Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu 610065, China

<sup>3</sup>Sichuan Decision New Material Technology Co, Ltd, Deyang 618000, China

## Abstract

Salt-free pickling technology has recently received increased attention because it produces much lower salt pollution than the conventional pickling technology using formic acid, sulfuric acid, and sodium chloride. However, the existing salt-free pickling materials, for instance, aromatic sulfonic acids (ASAs), lead to reduced leather quality and the reason behind this phenomenon is unclear. In this study, we explored how ASAs affect the properties of tanned leather. Results showed that typical ASAs, such as 5-sulfosalicylic acid, 1,5-naphthalenedisulfonic acid, and 2-naphthalenesulfonic acid, penetrated cattle hide more slowly compared with formic and sulfuric acids because of their large molecular weight and strong intermolecular interactions with hide collagen. ASAs decreased the positive charge of the pickled hide via interactions with their sulfonic acid groups, resulting in the increased adsorption rate of chrome tanning agent to the hide surface. Rapid tanning agent adsorption could impede the deep penetration and uniform distribution of the agent in the ASA-pickled hide. Thus, the properties of wet blues and crust leathers pickled with ASAs are inferior to those of wet blue and crust leather pickled using conventional pickling materials. Our results indicate that a strongly positive charge of the pickled hide is vital to obtaining high-quality leather and provide insights into salt-free pickling materials from a hide surface charge perspective.

## Introduction

Tanning is an important leather-making procedure because it converts hides/skins into leathers with good resistance to acids, alkalis, microbes and heat.<sup>1,2</sup> The most popular tannage is chrome tannage.<sup>3</sup> Pickling is performed prior to chrome tanning to enhance the penetration of the chrome tanning agent into the hide and obtain high-quality leather.<sup>4</sup> The pickling procedure reduces the float pH to 2.8–3.0 by using formic and sulfuric acids to inhibit the hydrolysis of chrome complexes and achieve small-sized chrome tanning agent that could easily penetrate hide.<sup>5</sup> However, a large amount of sodium chloride (6%–7% of the limed hide weight) is needed in the pickling procedure to prevent the hide collagen from acid swelling.<sup>6</sup> Indeed, tanneries around the world use approximately 300,000 tons of salt each year for pickling

and generate massive amounts of high-salinity wastewater, which is harmful to the environment.<sup>7</sup> Thus, pickling effluents with high salinity are a serious challenge in the leather industry.<sup>8</sup>

Salt-free pickling materials, such as sulfosalicylic acid,<sup>9,10</sup> phenol sulfonic acid,<sup>11</sup> naphthalene sulfonic acid,<sup>9,11</sup> and naphthol sulfonic acid,<sup>12</sup> have been developed to reduce the salt pollution generated by the tanning industry. These aromatic sulfonic acids (ASAs) can bind with the side chains of hide collagen via electrostatic interactions and hydrogen bonds (Figures 1[a], 1[b], and 1[c]),<sup>13</sup> thereby avoiding the acid swelling of the hide. ASAs are believed to be suitable replacements for sodium chloride in pickling. Unfortunately, ASAs are not widely used in the leather industry because the comprehensive properties of leather pickled with ASA are inferior to those of conventional leather.<sup>7,11</sup> Why ASA pickling results in leather of relatively low quality remains unclear. Undoubtedly, this knowledge gap hinders further developments in salt-free pickling materials and technologies and undermines efforts to reduce salt pollution in the tanning industry.

Interactions between hide collagen and chemicals, including covalent bonding, coordination, electrostatic interaction, hydrogen bonding, van der Waals interaction, and hydrophobic interaction, affect the penetration and fixation of chemicals in hide/leather.<sup>14–16</sup> Because long-range electrostatic interaction is a major factor influencing the penetration of leather chemicals, this type of interaction has gained extensive attention in leather manufacturing.<sup>17–19</sup> Good penetration and uniform distribution of chrome tanning agent in hide is essential to obtaining high-quality leather. The chrome tanning agent tends to coordinate with the carboxyl group of collagen side chains, which allows the easy binding of the chrome tanning agent but impedes its penetration into the hide.<sup>20–21</sup> The hide collagen is positively charged at a pickling pH of approximately 3, and electrostatic repulsion between hide collagen and the chrome tanning agent could help slow down their surface binding.<sup>7</sup> That is to say, electrostatic repulsion plays an important role in ensuring the penetration depth of chrome tanning agent. ASAs have sulfonic acid groups that can combine with the amino groups of hide collagen and reduce the positive charge of pickled hide,<sup>6</sup> thereby inhibiting the deep penetration and uniform distribution of chrome tanning

\*Corresponding author e-mail: zengyunhang@scu.edu.cn

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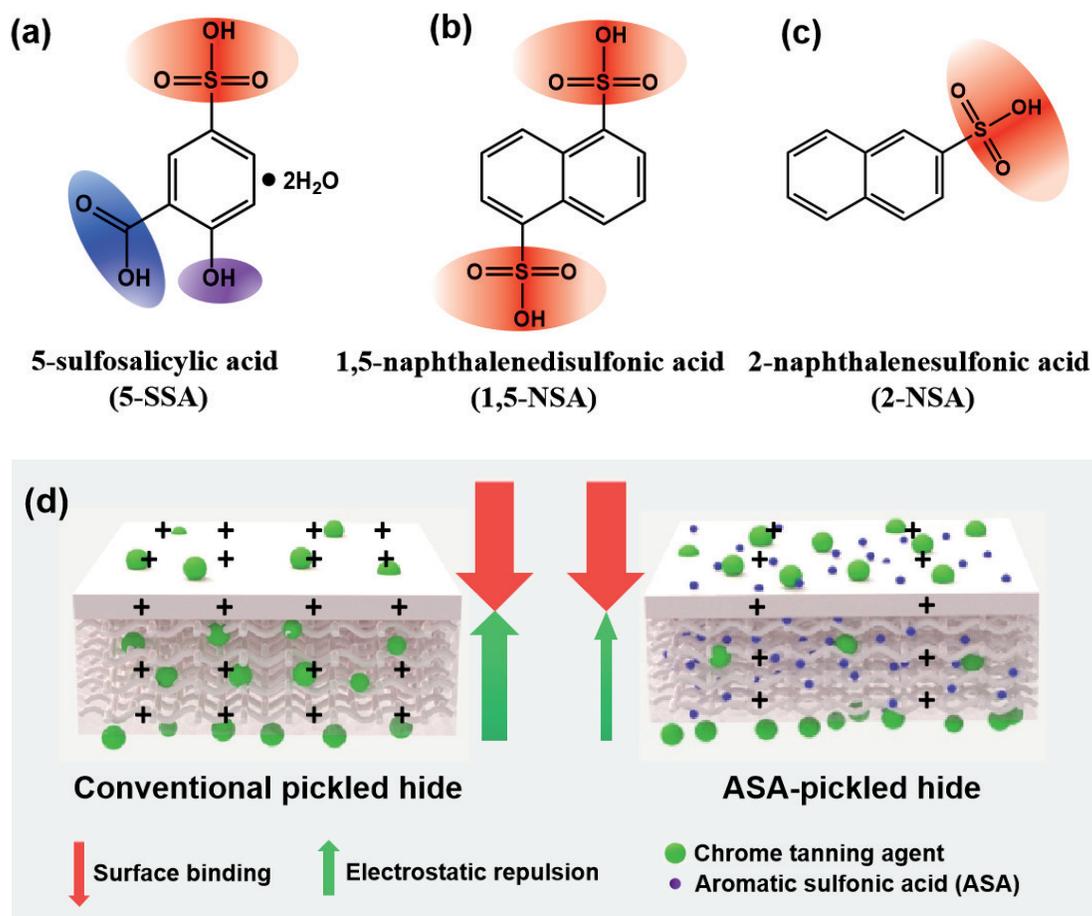


Figure 1. (a-c) Structures of aromatic sulfonic acids. (d) Schematic diagram of effect of the surface charge of pickled hide on chrome penetration.

agent (Figure 1[d]). This mechanism may explain why ASA pickling reduces the quality of leather.

In the present study, conventional pickling materials (i.e., formic and sulfuric acids, and sodium chloride) and typical salt-free pickling materials, such as 5-sulfosalicylic acid (5-SSA), 1,5-naphthalenedisulfonic acid (1,5-NSA), and 2-naphthalenesulfonic acid (2-NSA), were used to pickle cattle hides. The pickling and chrome tanning performance of the materials and the properties of the crust leather were then compared. The effects of the pickling materials on the surface charge of the pickled hides, as well as penetration and uptake of the chrome tanning agent, were further analyzed to explain how pickling materials affect leather quality and provide new insights into pickling materials.

## Experimental

### Materials

Limed cattle hide with a thickness of 2.2 mm was prepared by conventional presoaking, soaking, liming, and splitting. Analytical grade sodium chloride, concentrated sulfuric acid, and formic

acid were purchased from Chron Chemicals Co., Ltd. (Chengdu, China). 5-SSA, 1,5-NSA, and 2-NSA were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Chrome tanning agent ( $\text{Cr}_2\text{O}_3$  content, 25%; basicity, 33%) was provided by Brother Chemical Co., Ltd. (Haining, China). All other chemicals used for leather processing were of commercial grade, while those used for analyses were of analytical grade.

### Pickling experiments

Four limed hides, each weighing approximately 2 kg, were delimed, bated, and washed as shown in Table I. Number 1 bated hide (control) was treated with 7% sodium chloride for 10 min and then pickled with 0.6% formic acid and 0.6% sulfuric acid. Numbers 2, 3, and 4 bated hides were treated with 3% sodium chloride for 10 min and then pickled with 1.4% 5-SSA, 1.2% 1,5-NSA, and 1.0% 2-NSA, respectively. The required final pH of the pickling float (i.e., 2.8) determined the dosages of sulfuric acid, 5-SSA, 1,5-NSA, and 2-NSA used for pickling. After pickling, the four hides were chrome-tanned, as shown in Table I, and then retanned, dyed, and fatliquored according to conventional procedures for crust leathers.

**Table I**  
Pickling and chrome tanning processes

Procedure		Temperature (°C)	Chemical	Dosage (%) <sup>a</sup>	Remark
Pickling	Control	22	water	50	Run 10 min.
			sodium chloride	7	
			formic acid	0.6	Run 30 min.
			sulfuric acid	0.2	Run 20 min.
			sulfuric acid	0.2	Run 20 min.
			sulfuric acid	0.2	Run 20 min; pH 2.8; run 120 min; still overnight. Next day, run 30 min.
	Experimental	22	water	50	Run 10 min.
			sodium chloride	3	
			5-SSA/1,5-NSA /2-NSA	1.4/1.2/1.0	Run 90 min; pH 2.8; run 120 min; still overnight. Next day, run 30 min.
Chrome tanning	22	Chrome powder	3	Run 240 min.	
		Sodium acetate	1	Run 30 min.	
		Sodium hydrogen carbonate	0.2	Run 20 min.	
		Sodium hydrogen carbonate	0.2	Run 20 min; pH 4.0; run 60 min.	
	40	Water	150	Run 120 min; still overnight. Next day, run 30 min.	

Horse up for 48 h, sammy, and shave for a thickness of 1.0 mm.

<sup>a</sup>Percentage of chemicals is based on weight of limed hide.

### Analyses of pickling performance

The pickled hides were cut 5, 10, 20, 30, 40, 60, 90, 120, and 180 min after the addition of formic acid, 5-SSA, 1,5-NSA, and 2-NSA. The hide incisions were checked with methyl red indicator and then observed using a stereo microscope (M205C, Leica, Germany) to determine the penetration depth of the acid. The penetration rate of the acid into the pickled hide was calculated using Formula (1).

$$\text{Penetration rate (\%)} = \frac{T_r}{T} \times 100\% \quad (1)$$

where  $T_r$  is the thickness of red stained part of the pickled hide, and  $T$  is the total thickness of the pickled hide.

The zeta potentials of pickled hides at pH ranging from 3 to 7 were determined using a zeta potential analyzer (Mütek SZP-10, BTG, Germany) according to the method reported in the literature.<sup>22</sup> The zeta potentials of 5-SSA, 1,5-NSA, and 2-NSA aqueous solutions were also measured using a zeta potential analyzer (Nano Brook Omni, Brookhaven, USA) after equilibration at 25 °C for 3 min. Based on

their dosages used for the pickling experiments, the concentrations of 5-SSA, 1,5-NSA, and 2-NSA solutions were 1.4, 1.2, and 1.0 g/L, respectively.

The shrinkage temperature ( $T_s$ ) of the pickled hides was measured using a digital leather shrinkage temperature instrument (MSW-YD4, Shaanxi University of Science and Technology, China). The pickled hides were lyophilized using a vacuum freeze dryer (LGJ-30F, XinYi, China), after which their pore structures were analyzed using a mercury intrusion porosimeter (AutoPore IV 9500, Micromeritics, USA) as described in the literature.<sup>23</sup>

### Analyses of chrome tanning performance

The four hides were sampled 5, 10, 20, 30, 40, 60, 90, 120, 180, and 240 min after the addition of chrome powder. The samples were divided into three layers, including the upper, middle, and lower layers, by using a freezing microtome (CM1950, Leica, Germany) and then dried at 100°C for 8 h. A total of 0.5 g of dried sample was digested with a mixture of 5 mL of nitric acid and 5 mL of H<sub>2</sub>O<sub>2</sub> solution

(30wt%) by using a microwave digestion instrument (Multiwave 3000, Anton Paar, Austria). The concentration of chrome in the digestion solution was determined by inductively coupled plasma-atomic emission spectrometry (Optima 8000DV, PerkinElmer, USA). The chrome content of the hide was calculated using Formula (2).

$$\text{Chrome content (\%)} = \frac{c \times V \times 152}{104 \times w} \quad (2)$$

where  $c$  is the chrome concentration of the digestion solution (mg/L),  $V$  is the volume of the digestion solution (L),  $w$  is the dry weight of the hide (mg), 152 is the molar mass of  $\text{Cr}_2\text{O}_3$  (g/mol), and 104 is the molar mass of Cr in  $\text{Cr}_2\text{O}_3$  (g/mol).

The  $T_s$  and pore structure of wet blue were analyzed as described previously. The cross section of lyophilized wet blue was observed using a scanning electron microscope (SEM, Phenom Pro, Phenom, The Netherlands). The surface of wet blue was also directly observed using a stereo microscope. Color parameters were recorded using a colorimeter (CR-13, Konica Minolta, Japan) by testing 10 different points in each sample. The color difference ( $\Delta E$ ) was calculated using Formula (3).

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (3)$$

where  $L$  is the brightness and describes the color in the range from black to white,  $a$  is the red/green value, and  $b$  is the yellow/blue value.

#### Determination of the physical properties of crust leather

The crust leathers were sampled and conditioned at 20°C and 65% relative humidity for 24 h (ISO 2418:2002). Their physical properties, such as softness, tensile strength, tear strength, and bursting strength, were then measured according to the standards ISO 17235:2015, ISO 3376:2011, ISO 3377-2:2002, and ISO 3379:2015, respectively.

## Results and Discussion

### Penetration of various acids into hide

The penetration of traditional pickling materials (formic and sulfuric acids) and typical ASAs (5-SSA, 1,5-NSA, and 2-NSA) into the hides was compared by detecting color changes in the pickled hides after treatment with methyl red. The hide micrographs observed by stereo microscopy (Figure 2(a)) and the penetration rates of acids into the hide (Figure 2(b)) show that the pickling materials are all transferred slowly into the cattle hide. The inorganic acids completely penetrated the hide within 120 min, whereas the ASAs required more time to penetrate the hide fully. This finding may be explained by the fact that acid radical ions with negative charges are prone to bind electrostatically to the hide surface, which features positive charges (the pI of delimed hide is above 6, and the pH of pickling float is below 3), thus exerting a negative effect on the penetration of acids into the inner layers of the hide. Compared with formic and sulfuric acids, ASAs penetrated the hides more slowly because they have large molecular weights and could form strong intermolecular forces, such as hydrogen bonds, hydrophobic interactions and van der Waals force, with the collagen.<sup>7</sup>

### Surface charge properties of hides pickled with various acids

The surface charge of pickled hide greatly affects the penetration, distribution, and fixation of tanning agents in the leather matrix.<sup>20,24</sup> Therefore, the effect of the pickling materials on the surface charge of pickled hide was evaluated. As shown in Figure 3(a), the zeta potentials of the three ASA solutions are below zero in the pH range of 3–7 and decrease with increasing pH, which means the three ASAs have negative charges during pickling. Figure 3(b) shows that the pI values of the ASA-pickled hides are lower than that of the control pickled hide, likely because sulfonic acid groups in the ASAs can combine with the amino groups of hide collagen. The zeta potentials

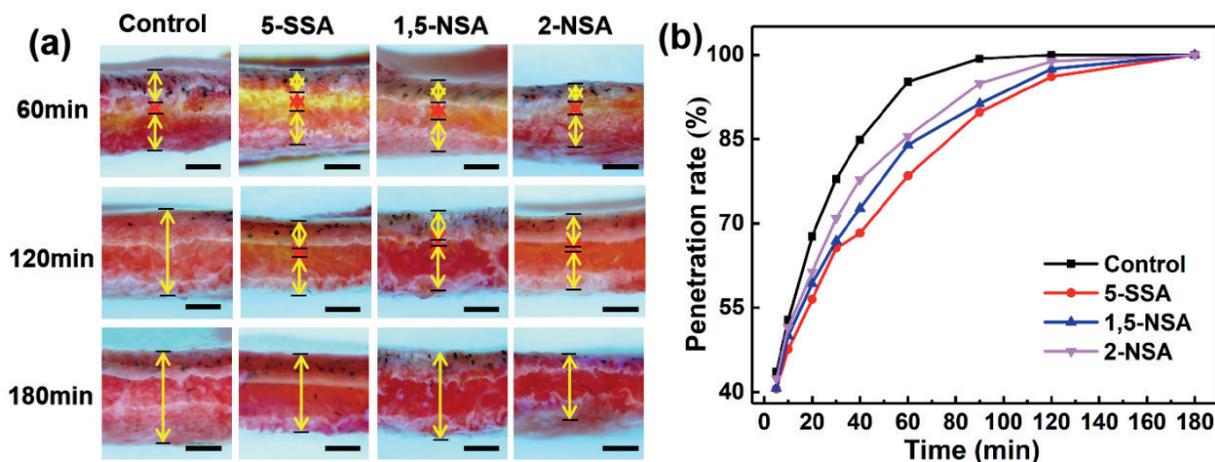


Figure 2. (a) Micrographs of vertical sections of different pickled hides (scale bar, 1 mm). (b) Penetration rates of different acids into the hides over time.

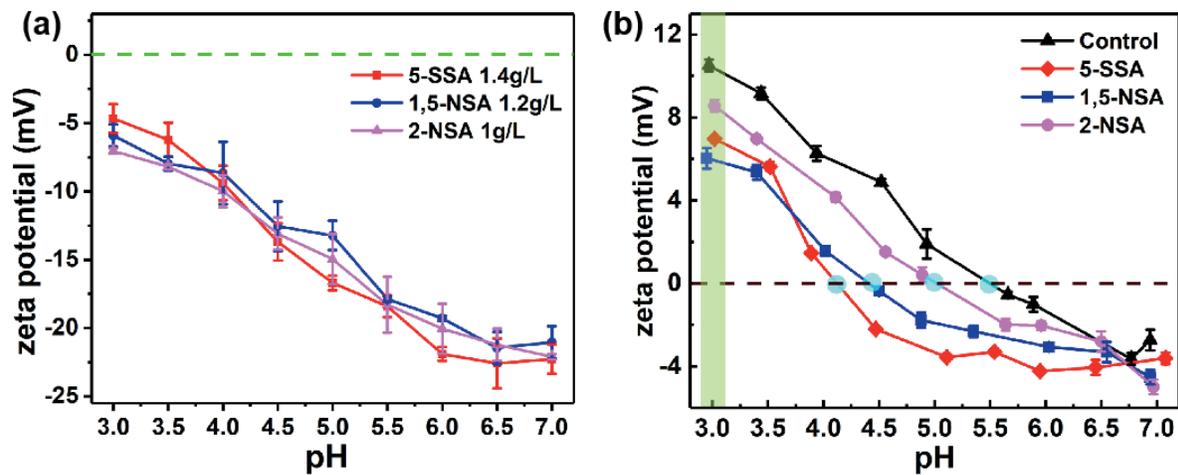


Figure 3. (a) Zeta potentials of 5-SSA, 1,5-NSA, and 2-NSA aqueous solutions. (b) Zeta potentials of different pickled hides.

of the experimental pickled hides at pH 3 were also lower than that of the control hide because of the introduction of sulfonic acid groups to the hide collagen. However, as mentioned in the Introduction, such interaction may not be beneficial to the penetration of chrome tanning agent.

#### Hydrothermal stability and fiber dispersion of hides pickled with various acids

The effects of the pickling materials on the hydrothermal stability and fiber dispersion of pickled hide were evaluated by measuring the  $T_s$  and pore size distribution of the hides. The data in Figure 4 show that the  $T_s$ , porosity, and percentage of small pores (sizes ranging from 0  $\mu\text{m}$  to 5  $\mu\text{m}$ ) of the experimental pickled hides are slightly higher than those of the control hide. These results indicate that the hydrothermal stability and fiber dispersion degree of the ASA-pickled hides are greater than those of the control hide, which is related to the weak tanning property of ASAs.<sup>25</sup> Among the hide specimens, the 5-SSA-pickled hide had the greatest  $T_s$  and fiber

dispersion because 5-SSA bears hydroxyl and carboxyl groups, which can form more hydrogen bonds with hide collagen compared with 1,5-NSA and 2-NSA.

#### Effect of pickling materials on chrome tanning performance

##### Penetration and uptake of the chrome tanning agent

The penetration and uptake of chrome tanning agent in different pickled hides were evaluated by analyzing the adsorption kinetics of the chrome to hide. In the initial stage of chrome tanning (within 60 min), the adsorption of chrome to the four pickled hides occurred quickly and in a similar manner (Figures 5(a)–5(d)). As chrome tanning progressed, adsorption equilibrium was achieved within approximately 120 min. The adsorption kinetic data were further analyzed using the pseudo-first-order (4) and the pseudo-second-order (5) kinetic models as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \quad (5)$$

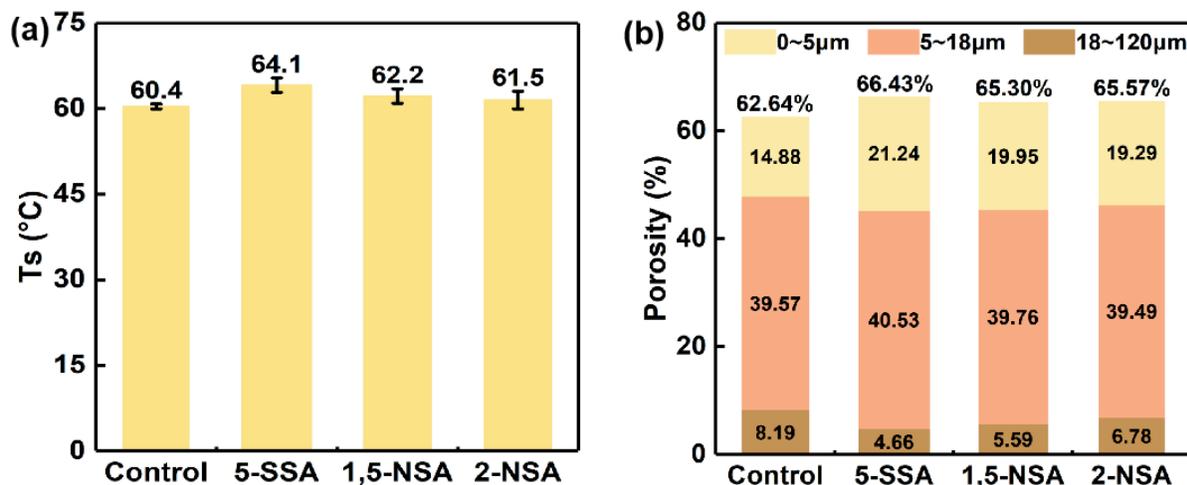


Figure 4. (a) Shrinkage temperatures of the pickled hides. (b) Pore size distributions of the pickled hides.

where  $q_t$  and  $q_e$  are the amounts of chrome adsorbed (mg/g) onto the hides at  $t$  min and equilibrium, respectively, and  $k_1$  and  $k_2$  are the pseudo-first-order ( $\text{min}^{-1}$ ) and the pseudo-second-order ( $\text{g}/(\text{mg}\cdot\text{min})$ ) rate constants, respectively.<sup>26</sup>

Table II compares the pseudo-first-order and pseudo-second-order kinetic parameters of the hides for chrome adsorption. The correlation coefficients ( $R^2$ ) obtained from the pseudo-second-order kinetic model were consistently higher than 0.99. Moreover, the adsorption amounts at equilibrium calculated by the pseudo-second-order kinetic model were much closer to those determined from the experiments (Error < 6%) than those calculated by the pseudo-first-order kinetic model (Error > 24%). These results indicate that the adsorption of chrome to the four pickled hides

follows pseudo-second-order kinetics rather than pseudo-first-order kinetics. Moreover, the adsorption of the chrome tanning agent to hide was controlled by chemisorption.<sup>27</sup> The higher rate constants ( $k$ ) in the experimental groups compared with that in the control group indicate that the experimental pickled hides have more rapid adsorption rates for chrome than the control pickled hide.<sup>28</sup> This finding should be attributed to the less positive charge and the lower resistance to chrome bonding of the ASA-pickled hides.

The data in Figure 5(f) show that the amount of chrome adsorbed by the control pickled hide is higher than those adsorbed by the ASA-pickled hides. In particular, the chrome tanning agent is distributed more evenly in the control hide than in the experimental hides, likely because the rapid adsorption of chrome to the experimental

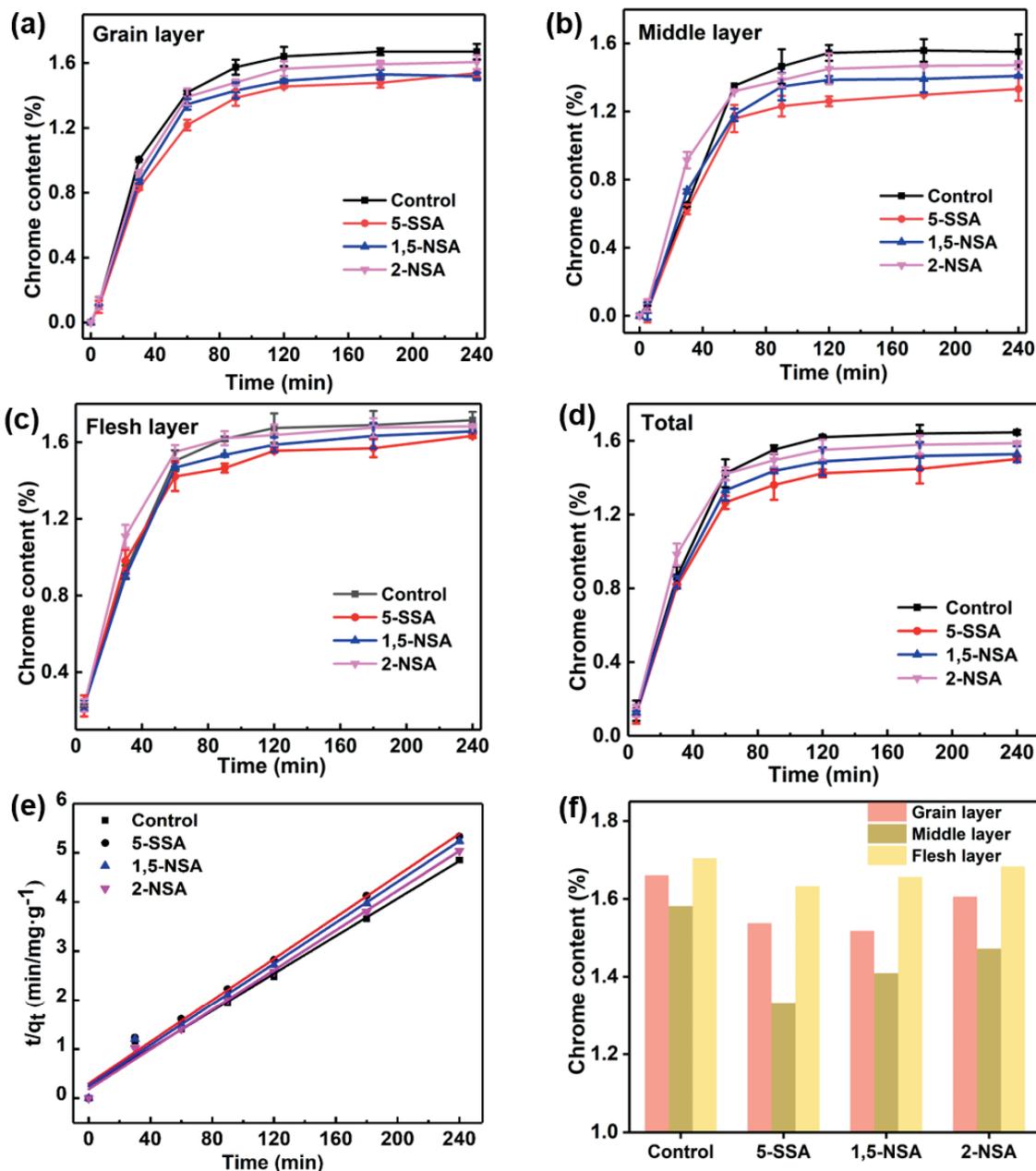


Figure 5. (a-d) Chrome contents of the grain (a), middle (b), flesh (c), and total (d) layers of wet blue. (e) Adsorption kinetics of chrome to hide fitted using the pseudo-second-order kinetic model. (f) Chrome distributions of wet blue.

**Table II**  
Pseudo-first-order and pseudo-second-order kinetic parameters for chrome adsorption

Group	$q_e \text{ exp}$ (mg/g)	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
		$k_1$ (min <sup>-1</sup> )	$R^2$	$q_e \text{ cal}$ (mg/g)	Error (%)	$k_2$ (g/ mg·min)	$R^2$	$q_e \text{ cal}$ (mg/g)	Error (%)
Control	49.47	0.02567	0.9720	37.13	24.94	0.00147	0.9984	52.33	-5.78
5-SSA	45.03	0.01679	0.9440	28.55	36.60	0.00151	0.9906	47.17	-4.75
1,5-NSA	45.84	0.02278	0.9749	31.99	30.21	0.00172	0.9909	48.12	-4.97
2-NSA	47.61	0.02675	0.9864	34.39	27.77	0.00163	0.9951	49.46	-3.89

$q_e \text{ exp}$ : determined by experiments.

$q_e \text{ cal}$ : calculated by the pseudo-first-order or the pseudo-second-order kinetic model.

Error (%) =  $(q_e \text{ exp} - q_e \text{ cal})/q_e \text{ exp} \times 100$ .

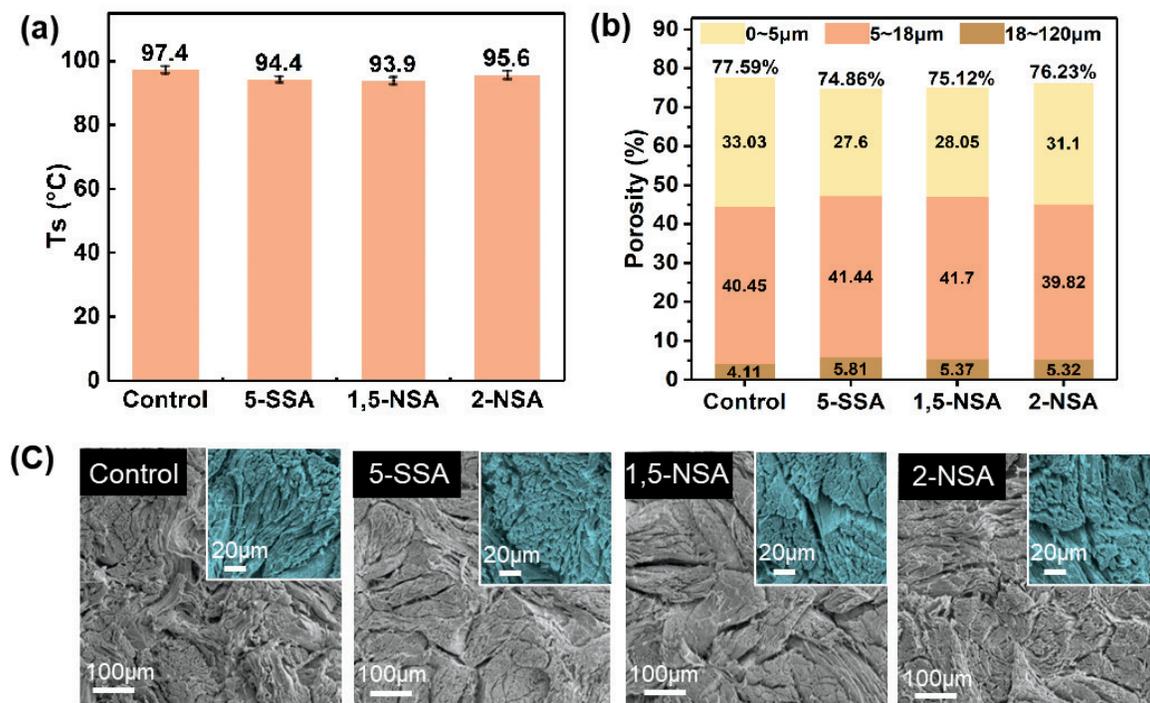
$R^2$ : correlation coefficient.

hide surface impedes its deeper penetration. By contrast, the chrome tanning agent slowly binds to the control hide surface, thereby facilitating the uniform distribution of the tanning agent. These experimental results validate our hypothesis shown in Figure 1.

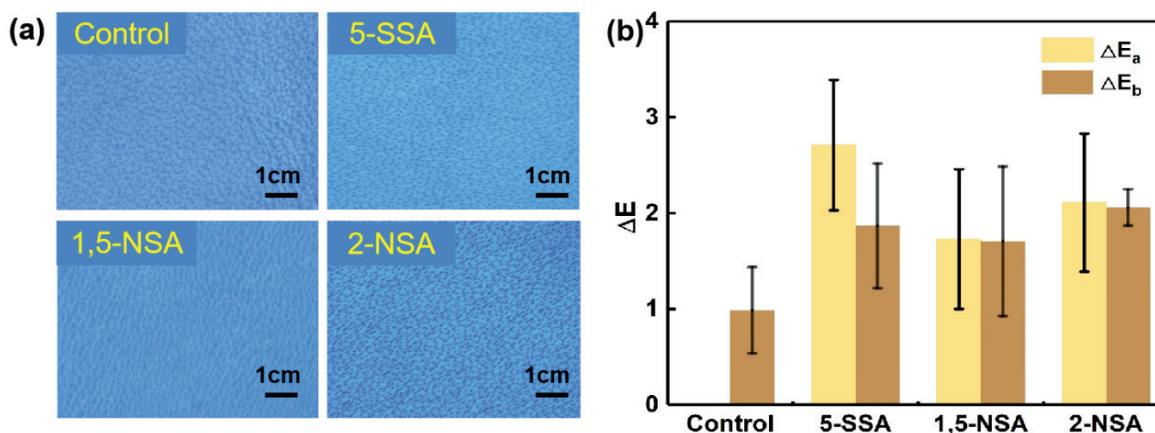
#### Hydrothermal stability, fiber dispersion, and color of wet blues

Figure 6(a) shows that the  $T_s$  of the control wet blue is higher than those of the experimental wet blues. Figures 6(b) and 6(c) show that the collagen fibers of the control wet blue are more disperse than those of the experimental groups. These findings are mainly attributed to the deeper penetration and higher uptake of chrome tanning agent in the control pickled hide, which features more

positive surface charges than the experimental hides. As shown in Figure 7(a), the control wet blue is lake blue, while the experimental wet blues, especially the wet blue pickled with 5-SSA, are teal. The color difference among the hides was obvious when observed with the naked eye. In addition, the wet blue pickled with 2-NSA has a rougher grain surface compared with the other wet blues because of the strong astringency of 2-NSA. A larger  $\Delta E_a$  means a greater color difference between the control and experimental wet blues.<sup>29</sup> The  $\Delta E_a$  values of the three experimental wet blues showed the order 5-SSA > 2-NSA > 1,5-NSA (Figure 7(b)), which is consistent with the results in Figure 7(a). The color uniformity of the wet blues was evaluated by calculating their  $\Delta E_b$ . The results show that the control



**Figure 6.** (a) Shrinkage temperatures of wet blues. (b) Pore size distributions of wet blues. (c) SEM images of cross sections of the wet blues.



**Figure 7.** (a) Colors of different wet blue surfaces. (b)  $\Delta E$  values of different wet blue surfaces.  $\Delta E_a$  reflects the color difference between the control and experimental wet blues. Here, the control wet blue is used as the calibration board.  $\Delta E_b$  reflects the color difference among various points in a single wet blue. Here, one of the points on the wet blue was used as the calibration board.

wet blue has a smaller  $\Delta E_b$  than the experimental wet blues, thereby indicating that the color of the former is more uniform than that of the latter (Figure 7(b)). These results are closely correlated with the adsorption/bonding rate of the chrome tanning agent to the hide surface.

#### Effect of pickling materials on the physical properties of crust leathers

The physical properties of the control and experimental crust leathers, such as their softness, tensile strength, tear strength, and bursting strength, were determined and compared in Table III. The physical properties of the control crust leather were better than those of the experimental leathers mainly because the extensive and uniform distribution of chrome in the control wet blue could promote the penetration and fixation of post-tanning agents and fatliquors. These results suggest that a strongly positive charge of the pickled hide is important to obtain high-quality wet blue and crust leather. Developing salt-free pickling materials with fewer anionic groups or pretreating salt-free pickled hides with cationic oil may help improve the performance of salt-free pickling agents.

#### Conclusion

In the pickling pH range 2.8–3.0, the ASA-pickled hides had fewer positive charges than the conventional pickled hide because the sulfonic acid groups of ASAs are introduced to the hide collagen. This phenomenon resulted in the increased adsorption/bonding rate of the chrome tanning agent to the ASA-pickled hide surface. Therefore, the penetration depth and distribution uniformity of chrome in the ASA-pickled hide were inferior to those in the conventionally pickled hide. These findings could explain why the properties of wet blue and crust leather pickled with ASA are poorer than those of conventional wet blue and crust leather. The results suggest that the influence of salt-free pickling on the surface charge of hide should be seriously considered in future work.

#### Acknowledgements

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**Table III**  
Physical properties of crust leathers

Group	Softness (mm)	Tensile strength (N/mm <sup>2</sup> )	Tear strength (N/mm)	Bursting strength (N/mm)
Control	7.38 ± 0.45	14.12 ± 1.20	14.13 ± 1.69	730.21 ± 8.42
5-SSA	6.86 ± 0.74	13.08 ± 0.98	11.12 ± 2.52	613.98 ± 9.34
1,5-NSA	7.11 ± 0.33	12.44 ± 2.02	12.08 ± 1.88	622.79 ± 9.55
2-NSA	7.39 ± 1.01	14.13 ± 2.45	13.44 ± 2.22	685.03 ± 14.62

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# Synthesis of a Waterborne Melamine Resin and its Retanning Behaviors Investigation

by

Ning Guo-qiang,<sup>a</sup> Zhou Ji-bo,<sup>a</sup> Liao Xue-pin,<sup>a,b\*</sup> and Shi Bi<sup>a,b</sup>

<sup>a</sup>Department of Biomass and Leather Engineering, Sichuan University, Chengdu 610065

<sup>b</sup>National Engineering Research Center of Clean Technology in Leather Industry, Chengdu 610065

## Abstract

Recently, the application of waterborne melamine resin (WMR) is greatly increasing in the leather industry because of its convenient operation, but it often suffers from poor storage stability. Here, two waterborne melamine resin retanning agents (WMRs) with high storage stability were prepared using melamine, glutaraldehyde and collagen hydrolysates (CHs) as raw materials at different mole ratios. FTIR, <sup>13</sup>C-NMR and XPS were used to characterize the chemical structure of synthesized resins, and their retanning behaviors for wet blue and wet white leather were fully investigated. The particle sizes of WMR<sub>1</sub> and WMR<sub>2</sub> were 28.73 nm and 8.78 nm, and their zeta potentials were 4.0 and 4.5, respectively. The introduction of CHs provided not only good water solubility but also amphoteric properties to synthesized resins, thereby resulting in high absorption of retanning and fatliquoring agents. Moreover, the retanning application investigation of WMRs manifested good storage stability and excellent overall performance, which are comparable with commercial retanning agents. This work showed that glutaraldehyde and CH could be used as starting materials in the synthesis of environmentally friendly WMR.

## Introduction

Melamine-formaldehyde resin (MR) is an important retanning agent applied in the leather industry.<sup>1</sup> It is cost effective, and it shows good thickening effects when being used as a retanning agent. Recently, waterborne melamine resin (WMR) has been widely applied because of its convenient operation. However, its further application is limited because of several issues, including formaldehyde release and poor storage stability.<sup>2</sup> Although many studies have been performed in the past few years to decrease formaldehyde release in WMR, its unstable storage remains a common problem that needs effective solutions.<sup>3-7</sup>

Considering its practical relevance, several strategies have been tried to improve the storage stability of WMR. Chemically, its poor storage is due to the presence of high amounts of active methylol

groups, which will be further polymerized to large molecules and precipitated out.<sup>8,9</sup> Therefore, the common and effective approach is introducing a functional monomer to partially block some reactive groups. Methanol is usually used to react with formaldehyde and methylol melamine, which would prevent the polycondensation of methylol groups, thereby enhancing the storage stability of the final product. In addition, caprolactam and benzoguanamine are used to partly replace melamine and reduce the number of methylol groups.<sup>10,11</sup> However, although these methods can improve the storage stability of WMR, they may cause unfavorable effects to the performance of final products. In addition, sulfonation is considered as an effective way to improve the storage stability of WMR. Bisulfite can react with methylol groups, and it favors the generation of a linear polymer chain, thereby resulting in good water solubility. However, this approach may confer excessive negative charges to WMR and finally decrease the absorptance of anionic fatliquoring agents. With the development of the leather industry, a new WMR with high storage stability and good retanning performances is necessary.

Collagen hydrolysates (CHs) contain many polar groups such as amino, hydroxyl and carboxyl, and these groups result in good water solubility.<sup>12</sup> Considering that the synthesis of WMR primarily involves the reaction between the aldehyde groups of formaldehyde and the amino groups of melamine, CHs can participate in the preparation of WMR. Consequently, the polar groups in CHs can be attached to the chains of WMR, and its water solubility can be largely improved. Moreover, CHs are originated from the waste disposal of the leather industry, and they should have natural affinity with collagen fiber. These specific features can not only improve the absorption but also confer an amphoteric property to WMR.

In this paper, two WMR (noted as WMR<sub>1</sub> and WMR<sub>2</sub>) without free formaldehyde were synthesized using melamine, glutaraldehyde and CHs as raw materials at different mole ratios. The structure and retanning performances of WMRs were fully investigated.

\*Corresponding author email: xpliao@scu.edu.cn

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## Materials and Methods

### Materials

Analytical grade chemicals, including melamine, glutaraldehyde and triethanolamine, were all purchased from the Chengdu Kelong Reagent Chemical Factory, China. CHs (Mw≈6000) were provided by Yunnan Luliang Heping Technology Co. Ltd., China. Wet blue leather (cow hide) was obtained from a local tannery and shaved to 1.1 mm for retanning experiments. Wet white leather with 1.5 mm thickness was prepared by hydroxyl-carboxylate-Zr complex tanned cow hide. Specially, wet white leather has a higher isoelectric point than wet blue leather.

### Preparation of WMRs

The preparation process of WMRs is shown in Figure 1. Before reaction, CHs were dissolved in distilled water to obtain 50 wt% aqueous solutions. The pH value of glutaraldehyde and CH was adjusted to 8.3 using triethanolamine. Then, a defined amount of melamine was added into a 500 mL three-necked glass flask equipped with a magnetic stirrer. Subsequently, glutaraldehyde solution was added to the above mentioned mixture and stirred at 65°C for 1 h to prepare the intermediates (MG). Finally, MG was added dropwise into the CH solution, and the reaction was continued for further 60 min to obtain WMRs. For the preparation of WMRs, different molar ratios of glutaraldehyde to CH were used to obtain products with different crosslinking degrees, namely, WMR<sub>1</sub> (1:3 molar ratio) and WMR<sub>2</sub> (1:6 molar ratio).

### Characterization of WMRs

#### UV absorption spectral analysis

UV-vis absorption spectra were obtained using a spectrophotometer (Mapada UV-1800PC) with a scanning wavelength from 200 nm to 400 nm.

#### Nuclear magnetic resonance (NMR) analysis

<sup>13</sup>C-NMR spectra of melamine and MG were recorded using a Bruker AV II 400MHz NMR spectrometer (Bruker, Germany). The MG powder after lyophilization was dissolved in DMSO-D6 (30 mg/mL). Chemical shifts were reported in parts per million (ppm) and referenced to an internal TMS standard for NMR shift control at 39.5 ppm.

#### Fourier transform infrared (FTIR) spectroscopy analysis

FTIR spectra were recorded using an FTIR spectrometer (Thermo Fisher Scientific, USA). The synthesized products were completely lyophilized using an LGJ-30F freezer dryer (XinYi, China). The powdered samples were pressed into a spectroscopic quality KBr pellet (1:200). The scanning range was 4000–400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> with 32 scans, and the spectra were presented as transmittance against wavenumber.

#### X-ray photoelectron spectroscopy (XPS) analysis

XPS elemental surface analysis was performed using an X-ray photoelectron spectrometer (Thermo Fisher Nexsa, USA) with a monochromator Al Kα X-ray source (1486.6 eV).

#### Storage stability

The storage stabilities of obtained resins were evaluated by recording the states of solutions at 25°C during storage.

#### Particle size and zeta potential determination

Mean particle size and zeta potential (ζ) of WMR<sub>1</sub> and WMR<sub>2</sub> were determined using NanoBrook Omni (Brookhaven, USA). Moreover, the particle size and zeta potential of DP (amphoteric, collagen hydrolysates [CHs] contained, liquid), MRS (amphoteric, MR, liquid) and MRA (anionic, MR, solid powder) commercial retanning agents were tested for comparison.

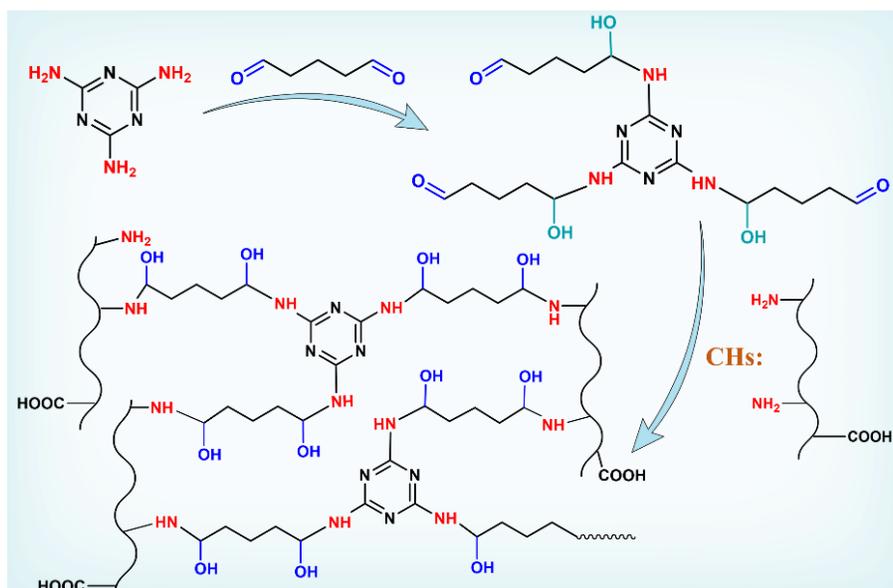


Figure 1. Synthesis of WMRs.

**Table I**  
Retanning processes of wet blue leather

Process	Chemicals	%	Duration (min)	Remarks
Rewetting	Water	400		
	Degreasing agent	0.3	60	Drain
Washing	Water	400	10	Drain
Neutralization	Water	200		
	Sodium formate	2	30	
	Sodium bicarbonate	0.4	10	
	Sodium bicarbonate	0.4	60	pH≈5.5, Drain
Washing	Water	400	10	Drain
Retanning	Water	100	10	
	WMR <sub>1</sub> /WMR <sub>2</sub> /DP/MRS/MRA	8	90	Drain
Washing	Water	400	10	Drain
Fatliquoring	Hot water	100		
	Synthetic fatliquor	10	60	
	Formic acid	1.5	30	pH=3.8–4.0
Washing	Water	400	10	Drain, the leather was hooked to dry and staked

Note: based on wet white weight (w/w)

**Table II**  
Retanning processes of wet white leather

Process	Chemicals	%	Duration (min)	Remarks
Rewetting	Water	400		
	Formic acid	0.3		
	Degreasing agent	0.5	40	Drain
Washing	Water	400	10	Drain
Neutralization	Water	200		
	Neutralization tannin	3		
	Sodium formate	2	30	
	Sodium bicarbonate	0.6*3	15*3+60	pH≈6, Drain
Washing	Water	400	10	Drain
Retanning	Water	100		
	Synthetic tanning agent	10	90	Drain
	Water	100		
	WMR <sub>1</sub> /WMR <sub>2</sub> /MRS/DP/MRA	10	90	Drain
Washing	Water	400	10	Drain
Fatliquoring	Hot water	100		
	Synthetic fatliquor	10	60	
	Formic acid	1.5	30	pH=3.8–4.0
Washing	Water	400	10	Drain, the leather was hooked to dry and staked

Note: based on wet white weight (w/w)

### Retanning performances

The retanning performances of WMR<sub>1</sub> and WMR<sub>2</sub> were determined, and the three commercial MR agents, namely, DP, MRS and MRA, were also tested as control samples. The wet blue leather and wet white leather were cut into halves through the backbone. The retanning processes are summarized in Table I and Table II.

### Absorption

Absorption of retanned leather on retanning agents and fatliquors were measured on the basis of total organic carbon (TOC, Elementar, Germany) and calculated as follows:

$$\text{Absorption rates} = \frac{TOC_0 - TOC_1}{TOC_0}$$

where  $TOC_0$  and  $TOC_1$  were the initial TOC value and the TOC value after a particular process, respectively.

### Physical and mechanical characteristics of leather

All samples were conditioned at  $25^\circ\text{C} \pm 2^\circ\text{C}$  and  $65\% \pm 2\%$  relative humidity for at least 48 h before testing. The mechanical strength, including tensile strength, elongation, percentage elongation at break and tear strength were measured using a universal testing machine (GOTECH, China) based on ISO 3376:2020 and ISO 3377-2:2016 approaches.<sup>13,14</sup>

## Results and Discussion

### <sup>13</sup>C-NMR spectroscopy analysis

The molecular structures of melamine and MG were verified by <sup>13</sup>C-NMR spectroscopy. The results are shown in Figure 2(a). The only peak in the spectrum of melamine was assigned to the triazine ring of melamine.<sup>15</sup> The spectrum of MG can be divided into three parts. The 160–170 ppm region was assigned to the triazine ring of melamine, and the region between 50 and 80 ppm was attributed to the carbon atoms in hydroxymethyl groups produced by the reaction between the -NH<sub>2</sub> group of melamine and the -CHO group of glutaraldehyde. The appearance of these peaks indicated

the successful reaction between melamine and glutaraldehyde.<sup>16</sup> In addition, the signal located at 206.64 ppm was assigned to the carbon atom that attributed to the aldehyde groups of unreacted glutaraldehyde.<sup>17</sup> This peak indicated the presence of the residing aldehyde group and provided the foundation for subsequent reaction with CHs.

### UV absorption spectra

The UV-vis absorption spectra of CH, WMR<sub>1</sub> and WMR<sub>2</sub> are shown in Figure 2(b) to confirm the reaction between MG and CHs. Compared with CHs, a new peak was observed in WMR<sub>1</sub> and WMR<sub>2</sub>. This peak was assigned to the Schiff base originated from the reaction between the amino groups of CHs and the aldehyde groups in MG, indicating the successful reaction between MG and CHs.<sup>18</sup> Considering the results of <sup>13</sup>C-NMR and UV-vis absorption spectral analysis, we can easily conclude that melamine and CHs were successfully connected by glutaraldehyde.

### FTIR spectroscopy analysis of MCH

FTIR spectra of melamine, MG, WMR<sub>1</sub> and WMR<sub>2</sub> are shown in Figure 2(c). In the FTIR spectrum of melamine, the peak around 815 cm<sup>-1</sup> was attributed to the bending vibration of the triazine ring, and the strong peak at 1026 cm<sup>-1</sup> was assigned to -NH<sub>2</sub> swinging vibrations.<sup>19</sup> Moreover, the characteristic peaks in melamine at 3468 and 3415 cm<sup>-1</sup> corresponded to the asymmetric stretching vibrations of the -NH<sub>2</sub> group of melamine.<sup>20</sup> However, in the spectrum of MG, these two peaks were replaced by a broad peak at 3393 cm<sup>-1</sup>, which attributed to the tensile vibration of -OH, demonstrating the successful reaction between glutaraldehyde and melamine. Moreover, the peaks located at 2946 and 2869 cm<sup>-1</sup> of MG were assigned to the antisymmetric and symmetric vibrations of glutaraldehyde methylene, respectively, thereby reinforcing the successful reaction between glutaraldehyde and melamine. Notably, the bending vibration of C=O was observed at 1558 cm<sup>-1</sup>, indicating the presence of residue aldehyde groups.<sup>21</sup> As for WMR<sub>1</sub> and WMR<sub>2</sub>, the peaks at 1648 and 1539 cm<sup>-1</sup> were primarily assigned to amide I and amide II bands, respectively.<sup>22</sup> These bands aroused primarily

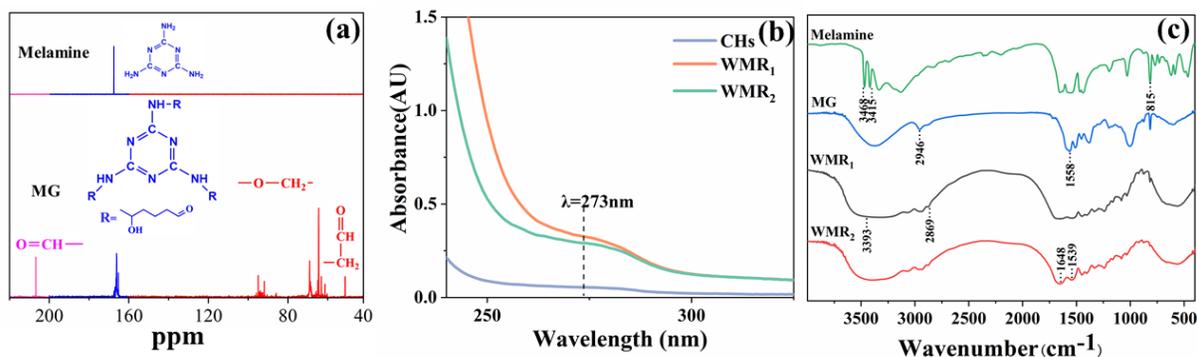


Figure 2. Characterization of WMRs: (a) <sup>13</sup>C-NMR of melamine and MG, (b) UV-vis absorption spectra of CHs, WMR<sub>1</sub> and WMR<sub>2</sub>, (c) FTIR spectra of melamine, WMR<sub>1</sub> and WMR<sub>2</sub>.

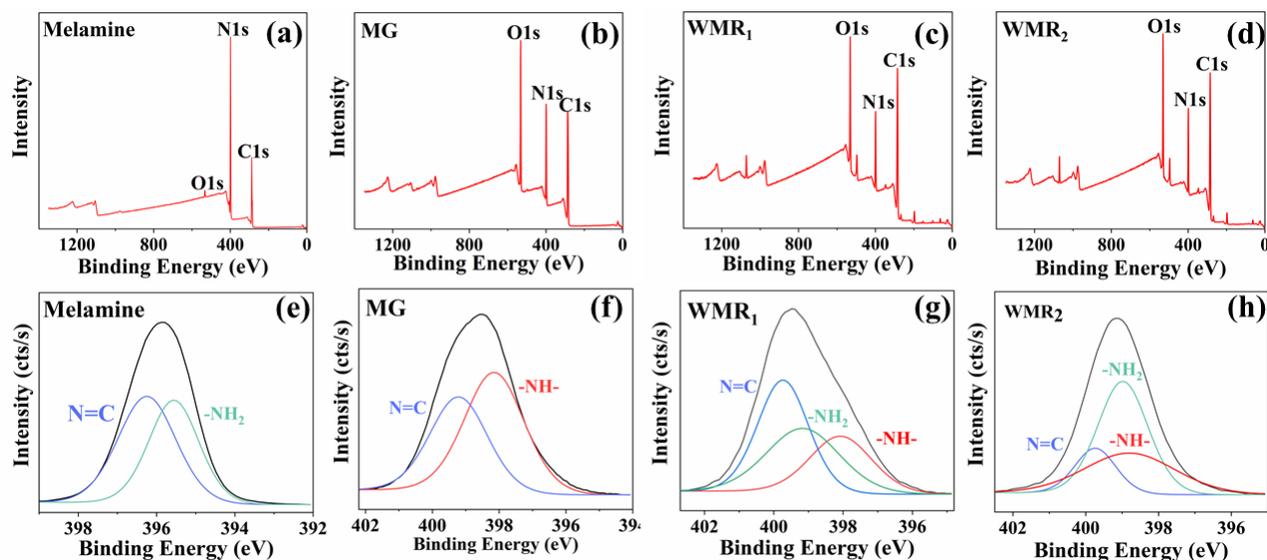


Figure 3. XPS spectra of melamine, MG, WMR<sub>1</sub> and WMR<sub>2</sub>.

by the reaction between aldehyde groups of MG and amine groups of CHs, indicating the successful reaction between MG and CHs.<sup>23</sup> The results of FTIR determination indicated that WMR<sub>1</sub> and WMR<sub>2</sub> were synthesized successfully as expected.

#### XPS analysis

XPS analysis of melamine, MG, WMR<sub>1</sub> and WMR<sub>2</sub> was performed, and the bulk concentration of these elements is displayed in Figures 3(a)–(d). For melamine, C1s and N1s peaks were observed at 248.8 and 395.9 eV, respectively. However, MG showed an increasing intensity of O1s and a decreasing intensity of N1s, indicating the formation of covalent bonds because of the reaction between melamine and glutaraldehyde.<sup>24</sup> The XPS curve fitting data for N1s of melamine, MG, WMR<sub>1</sub> and WMR<sub>2</sub> are presented in Figures 3(e)–(h). A new peak assigned to the -NH<sub>2</sub> group was observed in WMR<sub>1</sub>, which may be attributed to the residue amino groups of CHs, indicating the successful introduction of CHs.<sup>25</sup> Compared with WMR<sub>1</sub>, WMR<sub>2</sub> showed an increasing intensity of peaks for -NH<sub>2</sub>. This result was in accordance with the increasing dosage of CHs in the synthesis of WMR<sub>2</sub>. XPS analysis clearly revealed the successful reaction among melamine, glutaraldehyde and CHs.

#### Storage stability

The storage stability of WMR<sub>1</sub> and WMR<sub>2</sub> was compared with MG (Figure 4). MG, WMR<sub>1</sub> and WMR<sub>2</sub> were all obtained initially as a transparent solution. However, white precipitation was observed in the solution of MG after 1 day, whereas WMR<sub>1</sub> and WMR<sub>2</sub> still exhibited a clear and transparent solution even after 75 days. This result indicated the excellent storage stability of WMR<sub>1</sub> and WMR<sub>2</sub> and demonstrated that the introduction of CHs can improve the stability of WMRs.

#### Particle size and zeta potential

As shown in Figure 5(a), the average particle sizes of WMR<sub>1</sub> and WMR<sub>2</sub> were 28.73 and 8.78 nm, respectively, which were larger than that of two commercial melamine retanning agents, namely, DP (5.78 nm) and MRS (2.92 nm), but smaller than MRA (46.87 nm). These five retanning agents showed small average particle sizes, which could improve their penetration in leather.

The zeta potential of WMR<sub>1</sub>, WMR<sub>2</sub>, MRS and DP at different pH is shown in Figure 5(b). WMR<sub>1</sub>, WMR<sub>2</sub>, MRS and DP were both amphoteric electrolytes with isoelectric points at 4.0, 4.5, 4.0 and 3.2, respectively. However, MRA was an anionic retanning agent. WMR<sub>2</sub> exhibited a higher isoelectric point than WMR<sub>1</sub> because WMR<sub>2</sub> conducted a high usage of CHs. Commonly, electrostatic interaction plays an important role in leather making. The increase of positive charge may pose positive effect on the absorption of subsequent

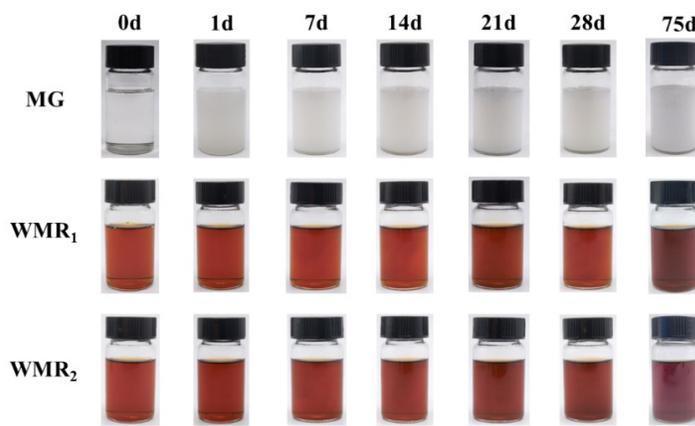


Figure 4. Storage stability of WMRs.

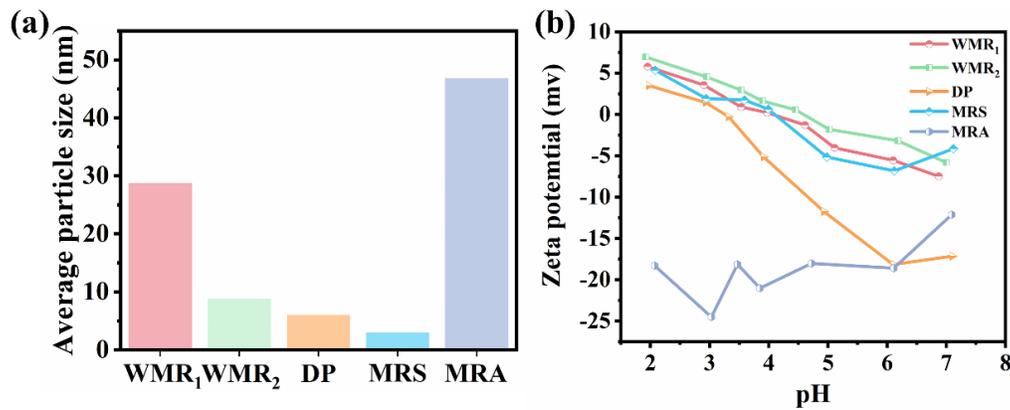


Figure 5. (a) Average particle size of different retanning agents. (b) Zeta potential of retanning agents at different pH.

anionic materials. Therefore, the high isoelectric points of WMR<sub>1</sub> and WMR<sub>2</sub> may improve the absorption of subsequent anionic fatliquoring agents and dyestuffs.<sup>26</sup>

### Retanning performances of WMRs

#### Absorption

The absorption of different retanning agents and fatliquors are shown in Figure 6. Leather making is the balance between permeation and combination. Particle size and electrostatic interaction can affect the permeation and combination of chemical substances, thereby playing an important role in leather making.<sup>27</sup> As shown in Figure 6a, the absorption of all retanning agents in the retanning process of wet white leather were higher than that of wet blue leather in the same operation, which can attribute to the higher positive charge of wet white leather. MRA, an anionic retanning agent, seems to have been absorbed easily by wet white leather or wet blue leather when it applied in the retanning operation. But in fact, MRA is only partly dissolved in water, leading to the false appearance of absorption. In case of MRS, its absorption is the lowest due to its higher isoelectric point. These facts suggested that the leather with higher positive charge is favorable for the absorption of retanning agents with relative more negative charge. In addition, WMR<sub>1</sub> showed a lower isoelectric point than WMR<sub>2</sub>, but it exhibited higher absorption. This result may be ascribed to the low particle size of WMR<sub>2</sub>, which is unfavorable for its combination with leather.

For the subsequent anionic fatliquors, it can be observed that the absorption of wet blue leather is higher than wet white leather due to the binding sites of wet white leather was more consumed at retanning operation, as shown in Figure 6b. This fact indicated that the retanning and fatliquoring operations should be considered together for the purpose of manufacturing good leather. In general, an amphoteric material with a high isoelectric point is favorable for the combination of subsequent anionic fatliquors. Consequently, WMR<sub>1</sub> and WMR<sub>2</sub> obtain higher results than MRS. In case of DP, its absorption is comparable with WMRs even its isoelectric point is lower than WMRs. This result may be attributed to the high affinity of CHs with collagen fibers. The collagen-based filler usually has good compatibility with collagen fibers, thereby resulting in high absorbance of retanning agents. Moreover, as shown in Figure 6(b), WMR<sub>1</sub> obtained the highest absorbance of fatliquor (91.03%), which was in accordance with the absorption of retanning agents. The high isoelectric point of WMR<sub>1</sub> is favorable for the absorption and fixation of anionic fatliquors.

### Physical and mechanical characteristics of leather

The physical and mechanical characteristics, including tensile strength, elongation and tear strength, are all significant indicators of the durability evaluation of leather samples.<sup>28</sup> The leather samples retanned by different retanning agents are shown in Figure 7. In general, the tensile strength and tear strength of retanned wet

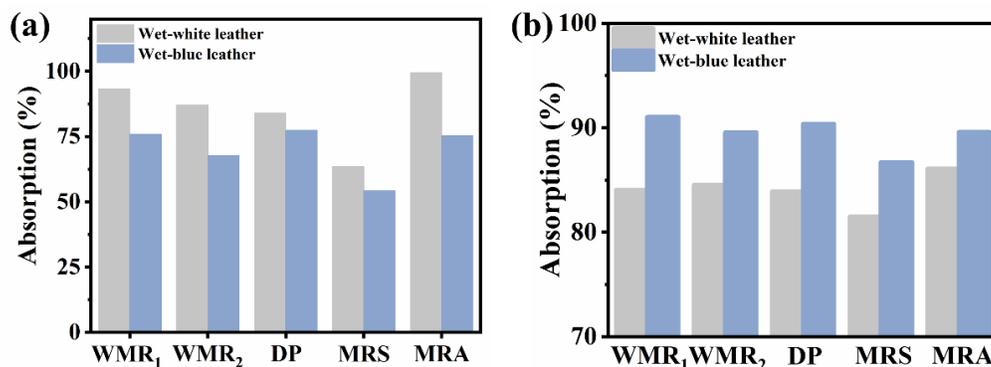


Figure 6. Absorption of retanned leather on retanning agents (a) and fatliquors (b).

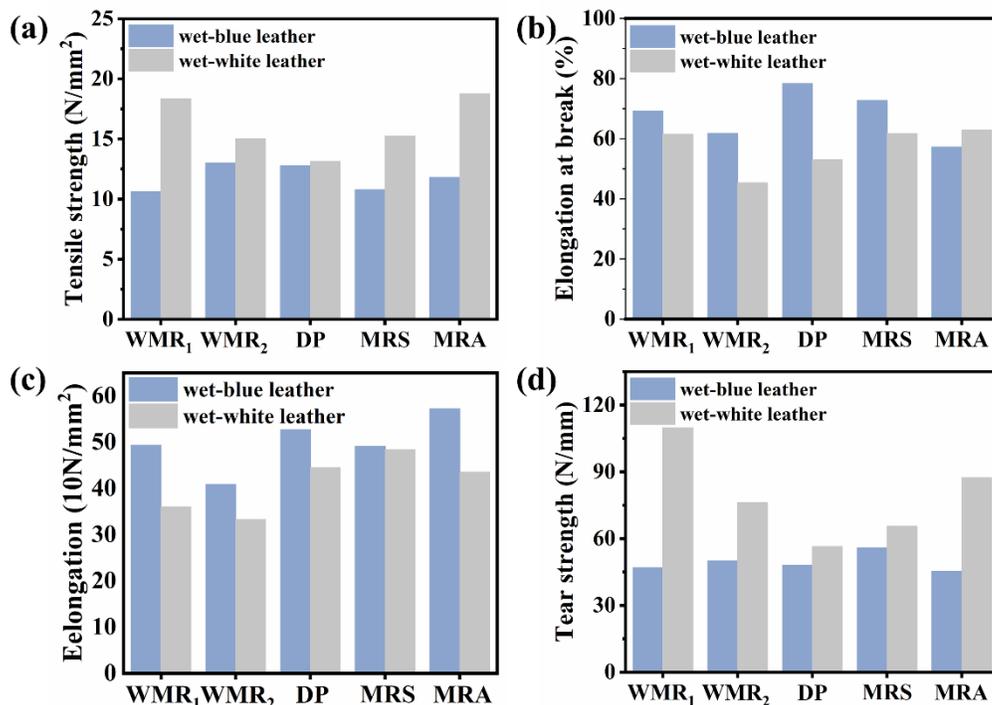


Figure 7. Physical and mechanical properties of leather retanned by DP, MRS, WMR<sub>1</sub> and WMR<sub>2</sub>. (a) tensile strength, (b) elongation at break, (c) elongation and (d) tear strength.

white leather were higher than that of wet blue leather (Figure 7a,d), meanwhile the elongation and elongation at break were opposite (Figure 7b,c). These facts were similar with the common retanned wet white and white blue leather. The retanning effects of WMR<sub>1</sub> and WMR<sub>2</sub> were comparable with other retanning agents, but they are more convenience at application due to they are in liquid state. Specially, WMR<sub>1</sub> greatly increased the tensile strength of wet white leather, as shown in Figure 7d, probably due to its higher absorption, as shown in Figure 6a.

## Conclusions

In this study, glutaraldehyde was conducted as a crosslinking agent to react with melamine and CHs to prepare WMRs used as retanning agents. Melamine was bonded with CHs by glutaraldehyde through the reaction between aldehydes and amino groups. Using this approach, the polar groups in CHs were attached to the chains of WMRs, and their storage stability was largely improved. Further investigation on the experimental indicated that the physical and mechanical properties of leather samples retanned by WMRs were comparable and/or even better than commercial controls. The introduction of CHs provided not only good storage stability but also amphoteric character and collagen fiber affinity to WMRs, thereby resulting in excellent retanning performances.

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# Melamine Ethoxylates as Novel Formaldehyde Free Replacements of Resin Re-Tanning Agents

by  
Jochen Ammenn\*

## Abstract

Melamine urea formaldehyde condensates or resin re-tanning agents are commonly used in the leather industry. They give rise to homogeneous filling, are easily and widely applicable, but generally contribute to free formaldehyde, measurable in emission or extraction methods. Many projects to resolve this issue have been carried out. The weakness of the resin re-tanning is the reversibility of the bond formation between formaldehyde and two amino groups. The formaldehyde forms a methylene group after condensation with two amino groups and releases water. This methylene group can be hydrolyzed under acidic conditions to release formaldehyde again, reversing the synthesis.

Melamine ethoxylates were found to be a formaldehyde free, stable, and easily applicable alternative. Besides the fact that they are made without formaldehyde, it proved to be possible to incorporate renewable components into their synthesis, giving rise to an even more sustainable product. Another sustainable aspect of this chemistry is the delivery of the potential product as a concentrated liquid versus most resin re-tanning agents being placed into the market as spray dried powders, consuming significant amounts of energy in the process.

Melamine ethoxylates show advantages in application on leather in comparison with classical resin re-tanning agents. An insight into the scope of application will be given, showing that melamine ethoxylates can be considered a formaldehyde free replacement for resin re-tanning agents.

## Introduction

Within the leather making process the re-tanning step has the role to determine main leather article properties like fullness, softness, grain tightness, fastness properties, and tear strength. Major classes of synthetic re-tanning agents are phenol formaldehyde condensates and melamine urea formaldehyde condensates. Depending on the chemistry, rest monomeric phenol, formaldehyde, bisphenol S and bisphenol F can be a problem with the phenol formaldehyde condensates,<sup>1</sup> also known as syntans. Besides melamine urea formaldehyde, urea formaldehyde condensates are also applied as re-tanning agents, both commonly referred to as resins. Melamine urea formaldehyde and urea formaldehyde condensates have similar

properties on leather and face the same problem: slow release of formaldehyde. This process will be closely described.

Melamine ethoxylates were developed as an alternative to melamine urea formaldehyde condensates, resolving this problem by avoiding the use of formaldehyde. In their formulation other sustainable aspects were incorporated, like partially renewable components and moving away from the energy consuming spray drying process. Application results on a widespread of leather articles and details about fastness properties will be given.

## Experimental

Chemicals were of reagent grade and obtained from commercial sources without further purification. Dynamic viscosity was determined according to DIN 51550.

Synthesis of the melamine ethoxylates were carried out in steel autoclaves connected to a vacuum pump and an ethylene oxide storage steel cylinder, positioned on a balance. A typical example was carried out like this: 24 g of melamine were dissolved in 24 g glycerin in a 300 mL steel autoclave and warmed to 160°C under stirring. To this solution 192 g ethylene oxide were dosed within 6 hours. The reaction was allowed to proceed at this temperature for 3 hours, until the pressure became constant. The pressure was released and a vacuum of 15 mbar was applied to the autoclave to remove volatile components. 235 g of a yellow liquid with low viscosity (935 mPa-s) was obtained.

Re-tanning was carried out with wet blue, obtained from the treatment of pickled pelt with 6-8% chromium sulfate. In a typical example, 100 g of wet blue of southern German origin with a thickness of 1.7 mm was treated in a 3.5 L tanning drum with 100 g water, 1.2 g sodium formiate and 0.3 g sodium bicarbonate and the drum was turned for 90 minutes. The resulting float had a pH of 4.5. Eight grams of the retanning agent referring to active material were added and turning of the drum was continued for 90 minutes. The float was discharged and the leather washed with 200 g water.

Subsequently, the leathers were treated with one percent of a standard brown dye and with two percent of a standard fat liquor in 200 g water for 90 minutes, before the float was acidified with 0.7 g 85% concentrated formic acid and the drums were turned for 20

\*Corresponding author email: jochen.ammenn@stahl.com

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minutes. The float was discharged and the leathers were dried via hang drying over night without vacuum at room temperature and stacked. The comparison was run with a standard melamine urea formaldehyde resin or a polyethylene glycol, subjected to the same procedure.

To evaluate the role of melamine ethoxylates in leather articles, the amount of melamine ethoxylates was reduced in the recipe and other products were added to the re-tanning float, like phenolic or sulfone syntans, polyacrylic re-tanning agents, vegetable tanning agents like Mimosa or Tara, or water proofing agents. Products and amounts depending upon need in the article.

The lightfastness and heat ageing properties were determined via Xeno test in a Suntester according to DIN EN ISO 105-B06.

The softness can be quantified according to DIN EN ISO 17235, or via haptics. Grain tightness and fullness were evaluated via haptics.

The free formaldehyde can be measured after derivatization with dinitrophenylhydrazine in solution after extraction of leather according to ISO 17226.

## Results and Discussion

### Melamine Urea Formaldehyde Condensates

Urea formaldehyde condensates were discovered in 1884.<sup>2</sup> Since the 1930's, urea formaldehyde condensates were used as impregnating resins in the production of chipboards. This helped to make the wood industry far more sustainable, since the huge amounts of waste in sawing of trees could be converted to chipboards, which is a good example for how chemistry can help to convert waste into value. Later, melamine formaldehyde condensates and melamine urea formaldehyde were developed, giving additional characteristics to chipboards like fire resistance properties.

Melamine formaldehyde condensates were first applied on leather in 1942 as tanning agents in the form of a formaldehyde releaser.<sup>3</sup>

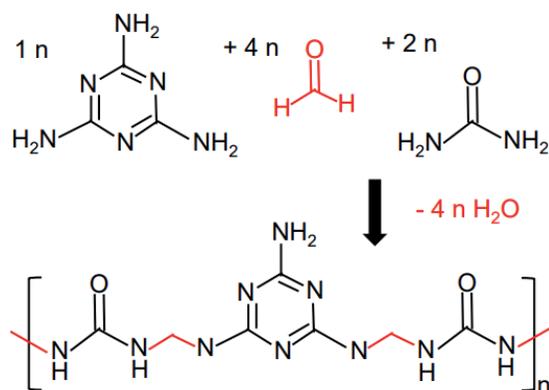


Figure 1. Synthesis of melamine urea formaldehyde condensates

For application as re-tanning agents in leather the water solubility had to be improved. This issue was the same for melamine urea formaldehyde, and urea formaldehyde condensates. This work will focus on melamine urea formaldehyde condensates, keeping in mind that problems of these similar chemistries and approaches to resolve these problems are parallel.

Melamine urea formaldehyde condensates are generally made under moderate basic or acidic conditions in water.<sup>4</sup> The formula of the reaction can be seen in Figure 1. The chain length, reflected in the number "n", is dependent mainly on the amount of formaldehyde, but also on other reaction conditions such as time and temperature. The bonds deriving from formaldehyde are marked in red in the product.

The issue of improving water solubility could be resolved by adding sulfites to the condensation.<sup>5</sup> The sulfite condenses with amino methylol (-CH<sub>2</sub>OH) groups, deriving from an excess of formaldehyde submitted to the poly condensation. The methylol group, by reacting with the sulfite, releases water and forms a sulfonic acid group attached to the poly condensate via a methylene group. The resulting structure is depicted in Figure 2.

In a basic pH-range the newly formed methylene bridges between two amino group deriving from formaldehyde are quite stable.

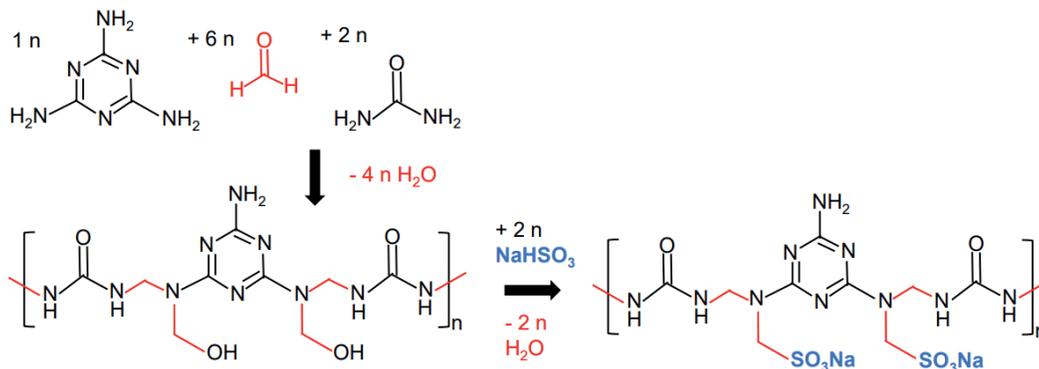


Figure 2. Water soluble melamine urea formaldehyde condensates

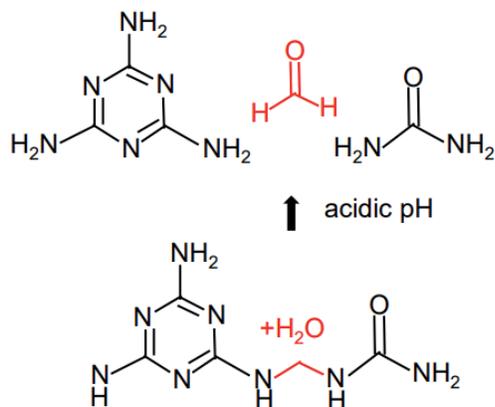


Figure 3. Hydrolysis of a melamine urea formaldehyde condensate

The re-tanning process is commonly carried out in floats at acidic pH ranging from pH = 3 to pH = 6. In this pH range the melamine urea formaldehyde condensates are not stable and slowly begin to hydrolyze the methylene, bridging two amino functionalities and releasing formaldehyde. This problem is inherent to this class of chemistry and requires both acidity and presence of water. The speed of hydrolysis is increased by lowering the pH, increasing the amount of acid, or increasing the temperature.<sup>6</sup> The hydrolysis is depicted in Figure 3.

The release of formaldehyde can be quantified in emission or extraction assays. In the emission test according to UNI EN 27587 a flow nitrogen is blown through a test tube with the pure product as powder product or liquid product. Emitted formaldehyde is carried with the nitrogen flow and directed into a cartridge, where the formaldehyde is derivatized. The derivatized formaldehyde can be washed from the cartridge and quantified via High Pressure Liquid Chromatography (HPLC). This method is pH neutral. The pH of the test sample will not change during the test. If the melamine urea formaldehyde condensate is adjusted to a basic or neutral pH, low values of formaldehyde will be obtained with this method.

In the extraction assay UNI EN 17226 leathers samples can be analyzed for formaldehyde. The leathers are cut into pieces, extracted with warm water for a defined time. The resulting aqueous solution is derivatized under acidic condition and the derivatized solution is submitted to High Pressure Liquid Chromatography for quantification. Due to the acidic pH in solution, the melamine urea formaldehyde condensates are prone to partial hydrolysis. The acidity

originates from strong acids like phosphoric acid, commonly used to establish the reaction conditions for derivatization with 2,4-dinitro-phenyl-hydrazins<sup>7</sup> and frequently present in derivatization product formulations. Consequently, higher values of formaldehyde will be obtained with this method for leathers made with melamine urea formaldehyde condensates.

From an application view in the leather industry the melamine urea formaldehyde condensates give rise to homogeneous filling, medium softness without compromising on grain tightness, if used in re-tanning.

### Melamine Ethoxylates

Various attempts have been made in the past to overcome the formaldehyde release from melamine urea formaldehyde condensates. We developed melamine ethoxylates as a potential alternative to melamine urea formaldehyde condensates and urea formaldehyde condensates. One of the first decisions to make within the project was to decide on the chemicals to use. Choices were gaseous ethylene oxide or liquid ethylene carbonate, with a clear favor for ethylene oxide for sustainability reasons: in a reaction with ethylene carbonate, one equivalent of carbon dioxide would be released. The first hurdle resulting from that decision was to enable the solid and quite unreactive melamine to react with gaseous ethylene oxide. This issue could be resolved by dissolving the melamine in a solvent. To again comply with sustainable principles, we decided for a renewable solvent and identified glycerin out of a screening. The solvent will remain in the final product and can help to augment the penetration of the polymer. Glycerin is widely available for instance from the production of biodiesel. We then screened the reaction conditions of the ethoxylation.<sup>8</sup>

The minimum requirement for a successful reaction was the complete reaction of the melamine to achieve a final product without toxic components, since melamine bears the hazardous label H361f, meaning it was proven to have an impact on fertility of rodents. The resulting melamine ethoxylate is a liquid with low viscosity that contains no water. It is readily soluble in water and could be easily applied on leather. The synthesis of melamine ethoxylates is depicted in Figure 4.

The screening to identify optimized ethoxylation conditions for melamine is summarized in table I:

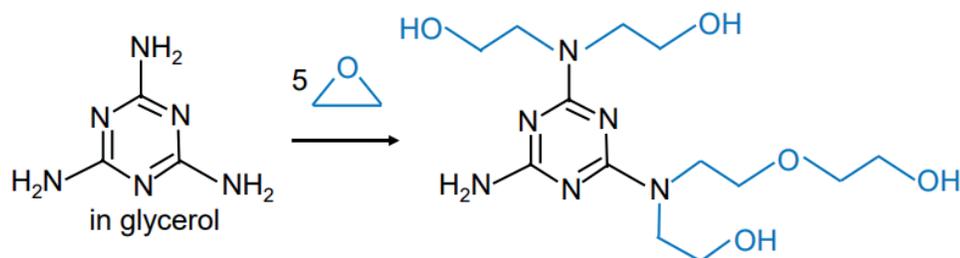


Figure 4. Synthesis of a melamine ethoxylate

**Table I**

Screening results of the re-tanning of bovine wet blue of different melamine ethoxylates against a standard melamine urea formaldehyde condensate and polyethylene glycol:

+ = better; 0 = similar; - = worse

Product	Number of ethylene oxide equivalents / 1 equivalent of melamine	Leather properties compared to standard melamine urea formaldehyde	Leather properties compared to polyethylene glycol (PEG)
Melamine Ethoxylate 3 EO	3	-	+
Melamine Ethoxylate 5 EO	5	0	+
Melamine Ethoxylate 7 EO	7	-	+
Melamine Ethoxylate 10 EO	10	-	0

As can be seen in Table I, with a minimum of three equivalents of ethylene oxide per one equivalent of melamine we were able to see a re-tanning effect compared to a leather re-tanned with polyethylene glycol. With five equivalents ethylene oxide we observed on optimum that did not improve raising the equivalents ethylene oxide to seven or more, if compared to a melamine urea formaldehyde resin. From ten equivalents ethylene oxide and onwards, we still saw a re-tanning effect. However, this effect could also be achieved by re-tanning with polyethylene glycol (PEG). Polyethylene glycols are made from pure ethylene oxide, are widely available and show only a weak re-tanning effect. Goal of our effort was to obtain superior re-tanning results compared to polyethylene glycol and similar effects to the standard melamine urea formaldehyde condensate. This was achieved with the sample deriving from five equivalents ethylene oxide. We scaled

this composition up and tested the resulting pilot batch in further application tests.

As depicted in Table II, leathers made with the pilot batch of the melamine ethoxylate performed better in fastness properties than leathers made with a standard melamine urea formaldehyde condensate. Lightfastness and heat ageing properties were determined according to DIN EN ISO 105-B06. Concerning filling properties, similar results were observed for both chemistries, while softness properties on leather was better with the melamine ethoxylate. Huge advantage on the side of the melamine ethoxylate is low free formaldehyde measured according to ISO 17226. The analysis on wet blue revealed free formaldehyde in the same range as after re-tanning with the melamine ethoxylate (< 10 ppm).

**Table II**

Re-tanning of bovine wet blue with the optimized melamine ethoxylate against a standard melamine urea formaldehyde condensate

+ = better; 0 = similar; - = worse

	Pilot batch melamine ethoxylate	Standard melamine urea formaldehyde condensate
Lightfastness	+	0
Heatfastness	+	0
Color strength	+	0
Filling	0	0
Softness	+	0
Grain tightness	0	0
Free Formaldehyde: ISO 17226	< 10 ppm (wet blue: < 10 ppm)	67 ppm (wet blue: < 10 ppm)

Table III

Results of re-tanning of bovine wet blue or wet white with melamine ethoxylates in a mixed recipe compared to a melamine urea formaldehyde condensate in the mixed recipe

+ = better; 0 = similar; - = worse

	Shoe upper based on wet blue	Shoe water-proof based on wet blue	Boot Nappa based on wet blue	Automotive based on wet blue	Upholstery based on wet blue	Automotive based on wet white
<b>Other re-tanning agents</b>	Phenolic syntan, Mimosa, Polyacrylic	Sulfone syntan waterproof agent	Phenolic syntan, Mimosa, Polyacrylic	Sulfone syntan, Tara	Phenolic syntan, Tara	Sulfone syntan, Tara
<b>Color strength</b>	+	+	+	+	+	+
<b>Filling</b>	-	-	-	-	-	-
<b>Softness</b>	0	0	+	+	+	0
<b>Grain tightness</b>	0	0	0	0	0	0

Two sets of six different leather articles were made with re-tanning recipes typical for these articles. In one set of leather articles the optimized melamine ethoxylate was used, in the other set same amount of a standard melamine urea formaldehyde condensate was applied. Differences between the two sets were noted in Table III; a "0" indicates same performance for both chemistries. Other re-tanning components required to make these leather articles are listed in the upper part of Table III. The melamine ethoxylate gave superior results in color strength in the leather articles, compared to leathers made with a standard melamine urea formaldehyde condensate. Three leather articles resulting from re-tanning with melamine ethoxylate showed superior softness. Observed fullness was less pronounced for all leather articles made with the melamine ethoxylate. Grain tightness on leather was similar for both chemistries.

An example of the color strength advantage of the melamine ethoxylate is shown in Figure 5. The same amount of melamine ethoxylate gives rise to darker shades than a standard melamine urea formaldehyde resin, reducing bleaching.

## Conclusions

The melamine ethoxylate is a liquid product with low viscosity that contains no water. It can readily be diluted with water. This is a sustainable advantage over classical melamine urea formaldehyde condensates, which are made in water and are mostly subjected to spray drying, affording huge amounts of energy to obtain a concentrated product. Another aspect of improved sustainability is the glycerin inside the product, giving rise to partially renewable

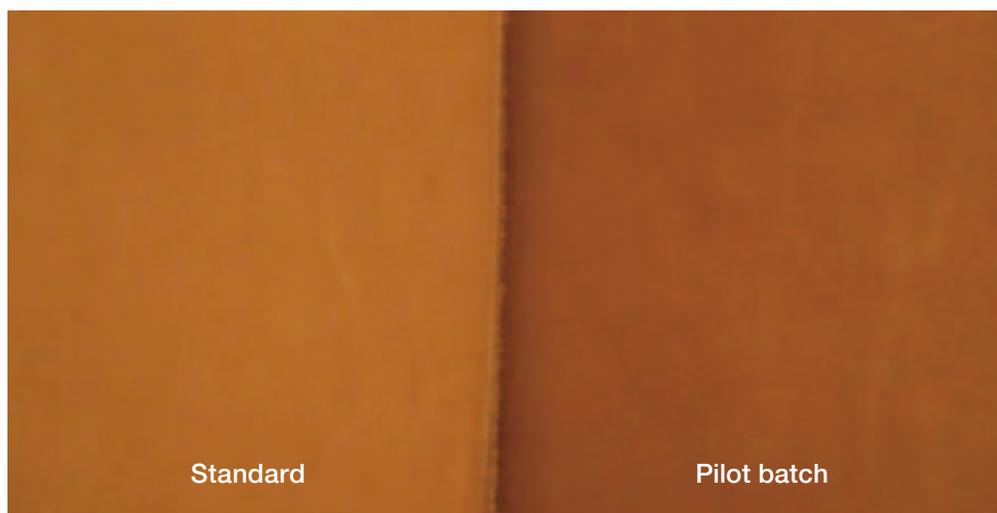


Figure 5. Re-tanning example of a standard melamine urea formaldehyde resin (Standard, left) compared to the pilot batch of melamine ethoxylate

starting materials, in contrast to entirely oil-based melamine urea formaldehyde condensates. In performance on leather, the melamine ethoxylate gave superior results in color strength as well as in light fastness compared to a standard melamine urea formaldehyde condensate and partially better softness, while maintaining the grain tightness.

Overall, we identified melamine ethoxylates as a sustainable alternative to melamine urea formaldehyde condensates, resolving the issue of free formaldehyde.

### Acknowledgements

I wish to express my gratefulness to my collaboration partner Andreas Kunst (BASF, Ludwigshafen, Germany).

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# A Research on the use of Aluminum Sulphate in Parchment Production and its Effects on Ageing and Color

by

Nilgün Kayahan Kolan and Eser Eke Bayramođlu\*

Ege University, Faculty of Engineering, Department of Leather Engineering,  
35100 Bornova-İZMİR – TÜRKİYE

## Abstract

In this study, different proportions (2.5%, 5% and 10%) of Aluminum sulfate were used as tanning agents during parchment production. The research was carried out on goat skin and also there were no usage of any tanning agents as control groups. Finished leathers have been exposed to ageing conditions. Before and after ageing color measurements on all finished leathers have been conducted with Konica Minolta CM-3600d brand spectrophotometer. The impacts of the aluminum sulfate utilized in the research on light fastness were also inspected by using an ATLAS-XENOTEST ALPHA+ test instrument. Visible whitening on the color of parchment was observed when tanning process with aluminum sulphate was performed.

## Introduction

Parchment is a material invented to write on. It is a material that made from skin of certain animals such as lamb and goat. Firstly, the hair is removed from the skin by liming, then it is cleaned by washing and dried by stretching and rubbing. The importance

in carrying and transcription of information made parchment a milestone in science and art history.<sup>1</sup>

It is known that citizens of Pergamum were the first community to invent and use parchment. This is supported by historical documents. Moreover, it is indicated that, the name parchment is coming from Pergamum.<sup>2,3</sup> The story of invention of parchment in Pergamum lies within outgrown Pergamum library. The Egyptians, who were owners of the Alexandria Library, became so jealous about the Pergamum library that they put a ban on sending papyrus to Pergamum. Thus, citizens of Pergamum invented parchment and developed it.<sup>1</sup>

Actually, İsmail Araç is the last tanner (88 years old) who produces parchment in a traditional method in Türkiye. İsmail Araç trained two apprentices (Demet Sağlam Tokbay and Nesrin Ermiş) who become masters through Ahi-order traditional ceremony. The Ahi-order ceremony is performed according to its original style and traditionally symbolized after 107 years and attracted quite a lot of attention (Figure 1). Important endeavors of Journalist Lütfü Dağtaş and Mehmet Gönenç, mayor of Bergama, who are architects of this ceremony, can be traced in the book they published and offered as a cultural service.<sup>2</sup>



**Figure 1.** Traditional Ahi ceremony held in Bergama on 2017  
(Photo: Prof. Dr. Eser Eke Bayramođlu)

\*Corresponding author email: eser.eke@ege.edu.tr, eserekebay@gmail.com

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Parchment was manufactured in this research by applying aluminum sulfate to the pelts with various ratios and light-fastness is examined. Moreover, color values of specimens of Parchment manufactured with different methods were measured before ageing process and after 24 hours and 96 hours of ageing processes. According to data obtained and with the use of aluminum sulfate, visible bleaching and temporal variations on light-fastness were determined.

## Material and Method

### Material

Domestic goat skin, aluminum sulfate, ammonium sulfate,  $\text{CaCO}_3$  and  $\text{Na}_2\text{S}$  were used for the process.

### Method

Skins, while they were treated according to Parchment treatment formula, the following stages were processed after liming:

- 1st group is washed after liming and left for drying by stretching.
- 2nd group's lime is eliminated after liming process, it is processed by acids and enzymes, pH 3 is decreased and they are tanned with 2.5% of aluminum sulfate for 12 hours and they are washed and left for drying.
- 3rd group's lime is eliminated after liming process, it is processed by acids and enzymes, pH 3 is decreased and they are tanned with 5% of aluminum sulfate for 12 hours and they are washed and left for drying.
- 4th group's lime is eliminated after liming process, it is processed by acids and enzymes, pH 3 is decreased and they are tanned with 10% of aluminum sulfate for 12 hours and they are washed and left for drying.

Dried parchments were taken from the drying bench, scraped and the sides cleaned. Light-fastness test of specimens of Parchment obtained was done according to EN ISO 105-B02 method whereas Color Measurement Test was done with Konica Minolta CM-3600d model spectrophotometer (In-House Method).

### Light-Fastness Test

Light-fastness Test was done according to EN ISO 105 B02 Normal: 2002. Discoloring on leathers' colors and leathers' surfaces were observed during the time due environmental impacts. This formation was accelerated with Light-fastness Test and results were obtained.<sup>4</sup>

Test samples were cut and prepared with 1 cm × 4 cm dimensions. Samples prepared were properly placed on panels. Test selected

was started according to specialties, after panels were placed by an expert in the ATLAS Xenotest Alpha+ model machine. Samples were treated for 72 hours. Samples taken out from the machine were measured using grey and blue scales and fastness degrees determined.

### Ageing Test – Color Change Test

Manufactured Leathers – Light-fastness Test was done according to International Standard ISO 17228 ULTCS/IUF 412, concerning Ageing Test and Color Change Test.<sup>5</sup>

Samples of 15 × 15 dimensions were cut from all leather samples for this test. Ageing Test was done in three different ways. These standards are respectively the following: the first one was solely ageing with heat, the second one was ageing with heat and humidity and the third one was ageing with heat and humidity cycles on different degrees. In this standard, extended general purpose ageing method, 96 hours, 50°C and 90% humidity was applied.

Colors of samples were measured before starting the ageing test with Konica Minolta CM-3600d model spheroidal spectrophotometer. Measurements were processed according to CIE Lab color system. Second Minolta color measurement was done after having applied first standard of ageing test and impacts of ageing were observed. Leather samples were again exposed to ageing process and color was again measured on Minolta. Increase of "L" value indicates an augmentation of brightness and whiteness whereas a decrease of "L" value indicates a diminution of brightness and whiteness. Color measurements were done on different points of 4 different leather samples and mean value of values measured were considered. Only "L" values elaborated, for dyestuff was not used in this research.

### Statistical Analyses

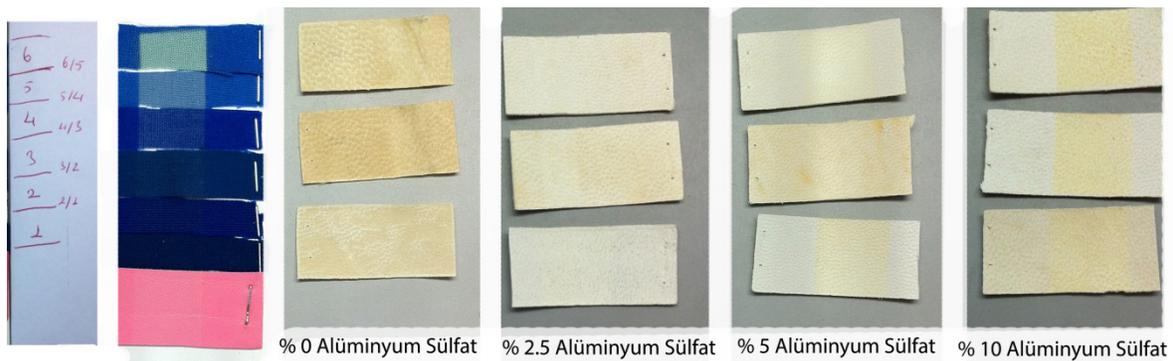
Data obtained from color measurement done after the Ageing Test was analyzed with Wilcoxon Signed Ranks Test and Kruskal Wallis Test. Statistical difference before and after the Ageing Test was considered. Besides, color changes observed on the leather with application in different rates of aluminum sulfate to the leather was analyzed with Kruskal Wallis Test.<sup>6</sup>

## Results and Discussion

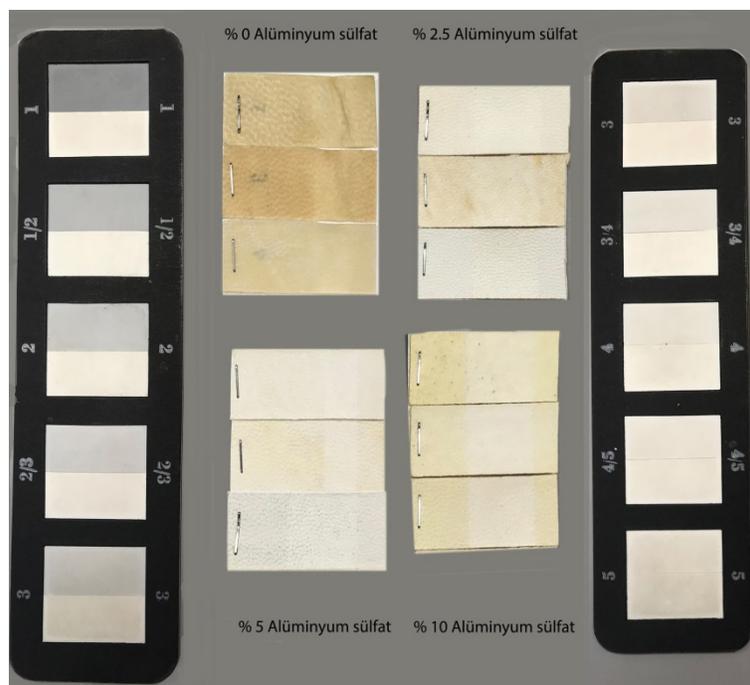
Whereas a visible whiteness occurs on leathers tanned with aluminum sulfate, a slight decrease was determined when light-fastness is considered. This difference was not observed among groups which included aluminum sulfate. Results of both grey scale and blue scale are coherent among them (Table I).

**Table I**  
Light fastness results of the parchments

	Groups	Grey scale	Blue scale
0% Aluminum sulfate	Control 1	4	2/1
	Control 2	4	2/1
	Control 3	5	1
2.5% Aluminum sulfate	4. Parchment	4	2
	5. Parchment	3	3/2
	6. Parchment	4/5	2/1
5% Aluminum sulfate	7. Parchment	4/5	3/2
	8. Parchment	4/5	2
	9. Parchment	3/4	4
10% Aluminum sulfate	10. Parchment	3/4	4
	11. Parchment	5	4
	12. Parchment	4/5	4/3



**Figure 3.** Comparison on blue scale of Light-Fastness Test results.



**Figure 4.** Comparison on grey scale of Light-fastness Test results.

### Ageing Test – Color Change Test Results

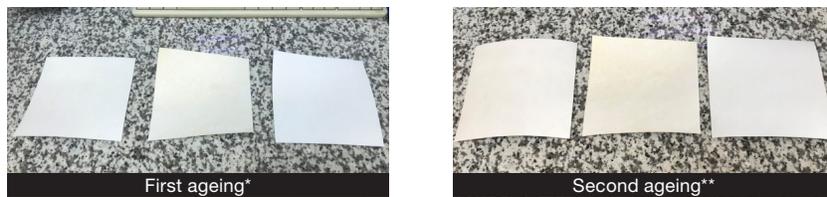
**Table II**  
Color Change Test Results by Minolta

	Groups	First Measurement	Second Measurement (after the first ageing: 50°C, 90% humidity, 24 hours)	Third Measurement (after the second ageing: 50°C, 90% humidity, 96 hours)
0% Aluminum sulfate	Control 1	72.35	70.37	70.70
	Control 2	70.47	68.97	69.22
	Control 3	78.95	77.36	77.56
2.5% Aluminum sulfate	4. Parchment	91.36	90.90	90.36
	5. Parchment	90.07	89.39	89.48
	6. Parchment	92.01	91.8	91.55
5% Aluminum sulfate	7. Parchment	92.89	92.58	92.16
	8. Parchment	89.62	88.62	88.46
	9. Parchment	91.68	91.33	91.01
10% Aluminum sulfate	10. Parchment	92.31	91.83	91.81
	11. Parchment	92.74	92.50	93.37
	12. Parchment	85.53	88.03	88.37

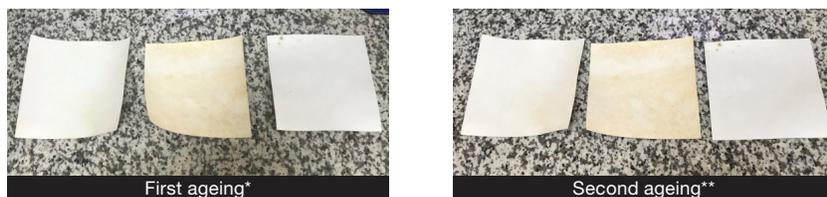
State of specimens of Parchment before and after ageing is observed on figures.



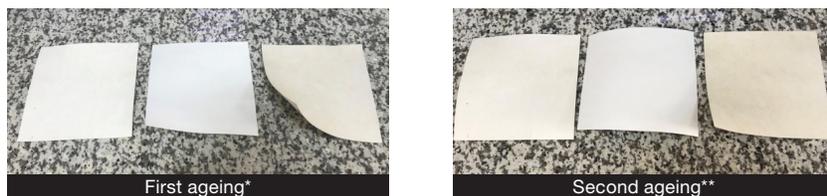
**Figure 5.** Control 0% Aluminum sulfate



**Figure 6.** 2.5% Aluminum sulfate



**Figure 7.** 5% Aluminum sulfate



**Figure 8.** 10% Aluminum sulfate

\*First ageing: Second Measurement (after the first ageing: 50°C, 90% humidity, 24 hours)

\*\*Second ageing: Third Measurement (after the second ageing: 50°C, 90% humidity, 96 hours)

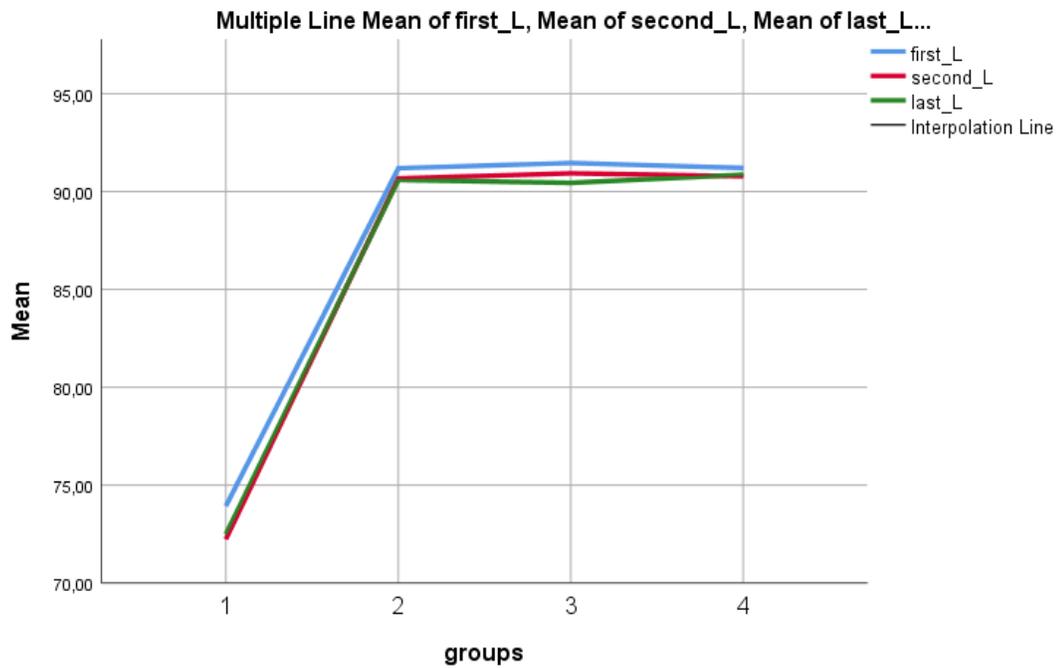


Figure 9. Statistical diagram graph of the color changing before and after ageing

Discoloration on leather surface, color changes and deterioration on physical forms occurred after the Ageing test (Figures 5, 6, 7 and 8)

Statistically significant difference among values read before ageing and after the first ageing was determined ( $p < 0.05$ ); however, no statistical difference was found between the second ageing and the first ageing ( $P > 0.05$ ). Besides, whereas there exists a significant difference ( $p < 0.05$ ) between the Kruskal Wallis Test and the Control Group, in other words parchments which do not include aluminum sulfate and leathers tanned with aluminum sulfate, no significant difference was determined among groups concerning leathers tanned with different rates of Aluminum sulfate ( $P > 0.05$ ).

### Conclusion

Discoloration and color changes with close rates occurred on all leather groups; however, whereas physical deformation is much more in the control group, we have observed that it is lesser on leather samples treated with Aluminum sulfate. Close results are obtained on physical tests applied on leathers tanned in different groups, in terms of leathers treated with 2.5%, 5% and 10% rates. To conclude, we can say that a physical difference occurred between the control group and parchments tanned with Aluminum sulfate but the use in different rates of aluminum sulfate did not generate

quite a difference in itself. Significant bleach on the parchment is determined with the use of aluminum sulfate.

### Acknowledgement

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# Stahl's innovations driven by sustainability

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With the rise of both electric and self-driving, cars are becoming quieter and anti-squeak and rattle materials are becoming increasingly important. At the same time, improved anti-stain performance is required, because of the current trend for pale-colored car seats. Therefore, we have developed Stay Clean. This low-VOC coating technology protects pale-colored leather and vinyl surfaces against common stains, such as dye from jeans, spilled coffee and dirt. Our solution also makes surfaces low-squeak, which is a great asset as global research has shown that a squeaking car interior is one of the biggest annoyances among car owners. Another trend in car interior is the popularity of matt surfaces. Therefore, we have developed PolyMatte®. This non-squeaking solution provides a luxurious feel to the finished article in combination with flexibility and scratch and abrasion resistance. Our portfolio contains many products, varying from beamhouse products, tanning systems to finishes,

duller concentrates, crosslinkers and thickeners to leveling agents, defoamers, colorants and hand modifiers. Our most sustainable option is Green PolyMatte®, which is based on rapeseed oil (20%) instead of crude oil-derived intermediates. If you would like to know what our Stahl solutions for automotive can do for your business, please visit [www.stahl.com](http://www.stahl.com) or contact us at: [alexander.campbell@us.stahl.com](mailto:alexander.campbell@us.stahl.com).

If it can be imagined, it can be created



Stay Clean



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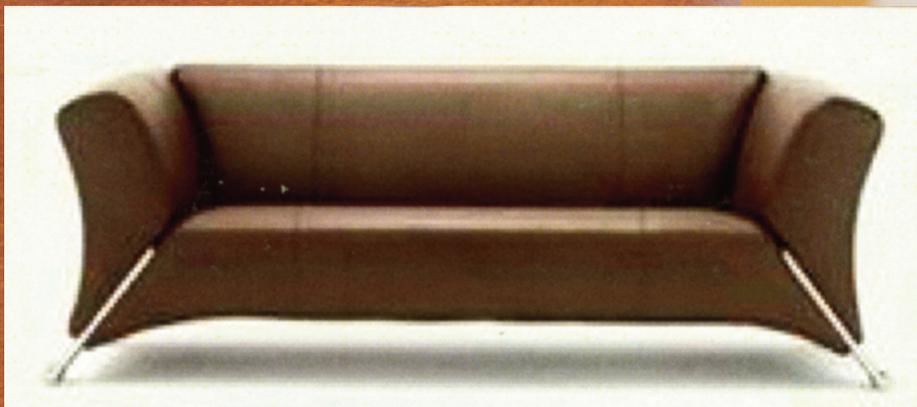
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## Obituary

**Thomas R. Bley** 59, Lincolnton, North Carolina (formerly of Fremont and Derry, New Hampshire), passed into the arms of his maker on March 24, 2022, after a lengthy illness. Following in his family's footsteps, Tom proudly represented the 3rd generation in the leather industry and often stated it was "in my blood". He was widely known for being veracious in his work ethics. When faced with a tough question or situation, his stoic German traits of wisdom and thoroughness were his strong suit. Prior to his illness, Tom was employed by Stahl USA as Sr. Technical Sales Advisor for NAFTA Leather accounts. Prior to that he worked for Tannin Corp., BASF Corp., Corium Leather & Supatco. He started his apprenticeship and worked his way up to assistant finisher at Hoyt and Worthen Tanning Corp.



Tom enjoyed working on and repairing small engines. In all the years, only one weed whacker earned a ride to the dump. His favorite pastimes were fishing, hunting, skiing, pushing his luck as an occasional lumberjack and his leather recliner (yes, he

handpicked the leather). He loved living out in the woods of North Carolina, surrounded by wildlife. Occasionally, someone would be the recipient of the latest photo of "Blacky", our resident snake, or perhaps an oversized cutout of Big Foot in the woods.

Tom developed a love of live musicals and intimate singer/songwriter concerts. He was known to swipe a poster or two off the venue wall and have it autographed. One of his highlights was a trip to NYC, sitting front row center, for the Carol King play "Beautiful". Dislikes? Besides heights, he hated surprises, even if they weren't his, and felt it was his duty to inform the recipient beforehand.

Known to his close friends as "Big T", his genuine smile, infectious laughter, and his appreciation of a good joke, always insured a great time. Apologies go out to friends and coworkers who put up with his ear-piercing whistling. After all, those factory buildings had excellent acoustics.

Tom's soul has taken flight but will linger in the lives of those he loved: Wife Dorothy "Dodo" Dixon; brother and childhood partner in mischief, Michael Bley; sisters Iris Bley-LaFlamme, Regine Bley and Monika Sullivan; parents Ernst and Renate Bley; extended family, friends and his beloved dogs Ellie and Boomer.

A Celebration of Life will be held at a later date.

## Lifelines

**Chao Tang** received his Bachelor's degree in 2019 from Henan University of Science and Technology, majored in Materials Chemistry, and now, he is a Master's degree student in Zhengzhou University, majoring in Biomass Resources and Engineering. His research is focused on leather chemicals and clean leather making.

**Hui Liu** received his PhD degree in 2020 from School of Materials Science and Engineering at Zhengzhou University, China. His research is focused on the mechanism and application of simplified clean and ecological leather with biological enzyme.

**Yadi Hu** is a PhD candidate of School of Materials Science and Engineering at Zhengzhou University, majored in the materials physics and chemistry. Her research is focused on the degradation mechanism of modern and historical leathers under the effect of storage environmental conditions.

**Fang Wang** graduated from Zhengzhou University with a Bachelor degree in 1991, majoring in Chemistry. She has been working in School of Materials Science and Engineering at Zhengzhou University since 1993, and she is now a senior engineer, with the research field of leather structure and properties.

**Keyong Tang** received his PhD degree in 1998 from Sichuan University, Chengdu, China. He has been working in Zhengzhou University since 1990, and he is now a professor in the School of Materials Science and Engineering, Zhengzhou University. His research interests include the structure and properties of leather and collagen, leather chemicals, and clean leather making. He has published more than 100 papers, co-authored 4 books and edited 1 book in the field of leather chemistry and engineering.

**Jide Zhong** was graduated from Shaanxi University of Science and Technology with a Bachelor's degree in 1990, majored in Leather Chemistry and Engineering. He has been working in Henan Prosper Skins & Leather Enterprise Co., Ltd, since 1998. He is now a senior engineer and the Technical Director in Henan Prosper Skins & Leather Enterprise Co., Ltd.

**Tianqi Yang** received her Bachelor's degree in Light Chemical Engineering from Qilu University of Technology in 2019. Now she is pursuing her Master's degree in Light Industry Technology and Engineering at Sichuan University. Her current research focuses on the clean leather production.

**Yunhang Zeng**, see *JALCA* 115, 270, 2020

**Qingyong Sun** received his Bachelor's degree in Light Chemical Engineering from Sichuan University in 2009, and his Master's degree in Biomass Chemistry and Engineering from Sichuan University in 2012. Now he is pursuing his Ph.D degree in Leather Chemistry and Engineering at Sichuan University. His current research focuses on synthesis and application of amphiphilic polymer.

**Chao Lei** received his Bachelor's degree in Light Chemical Engineering from Qilu University of Technology in 2017, and his Master's degree in Leather Chemistry and Engineering from Sichuan University in 2020. Now he is pursuing his Ph.D. degree in Light Industry Technology and Engineering at Sichuan University. His current research focuses on collagen fiber-reinforced polymer composites.

**Bi Shi**, see *JALCA* 99, 220, 2004

**Ning Guo-qiang**: postgraduate, Sichuan University, Biomass chemistry and engineering, Chengdu, China. E-mail: ningggq@stu.scu.edu.cn.

**Zhou Ji-bo**: Ph.D Candidate, Sichuan University, Biomass chemistry and engineering, Chengdu, China. E-mail: zt1812431172@gmail.com.

**Liao Xue-pin**: professor, Sichuan University, Chengdu, China. E-mail: xpliao@scu.edu.cn, major in clean technology of leather manufacture and green leather chemicals.

**Shi Bi**: professor, Sichuan University, Chengdu, China. E-mail: shibi@scu.edu.cn, major in clean technology of leather manufacture, green leather chemicals and tannins chemistry.

**Jochen Ammenn**: Studied chemistry at the University of Goettingen, Germany, subsequent Ph.D there in the field of natural product synthesis. Project leader in medicinal chemistry for Eli Lilly in Hamburg, Germany. Group leader in medicinal chemistry for the European Molecular Biology lab in Heidelberg, Germany. Joined BASF in 2009: production support for poly condensates and R&D Wet End for the leather department. Since 2018 with Stahl; same role as before with BASF. Presentations at all IULTCS conferences since 2009. Presentation at ALCA meeting 2014 and 2016.

**Nilgün Kayahan Kolan** completed her primary and secondary education in İzmir Reşat Nuri Güntekin Primary School and her high school education in Sıdıka Rodop.

After graduating from the Department of Handicrafts at Akdeniz University in 2004, she completed her undergraduate education in Mimar Sinan Fine Arts University, in the main branch of Traditional Turkish Arts, Carpet-Kilim and Old Fabric Patterns, in 2011.

After completing her undergraduate education, she got Pedagogical Formation from Dokuz Eylül University and worked as an expert tutor at İzmir Public Education Centers between 2012-2016.

In 2019, she completed her master's degree, Leather Engineering at Ege University Institute of Science.

**Eser Eke Bayramoğlu** is the world's first female leather professor in the field of leather. She is working as full Professor at Ege University, Faculty of Engineering, Department of Leather Engineering.

Currently instructs in leather microbiology, hazardous fungi during leather production, leather production practice, microorganism control for the leather industry, leather crafts, finishing materials and techniques, leather handicrafts and marketing. She has relevant skills and rich experience on the research of leather making technology and new product development from green chemicals. She also gives lectures about leather technology abroad. Twenty-four awards have been won since 1993 including 17 publication awards. She created microbiology laboratory in her department. She also worked with her graduate student, as an official consultant, for establishing a cosmetic company, Flamel Chemistry, which is producing keratin from waste hair and wool.

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