A Cleaner Chrome-Free Tanning Regime: Sulfonated Urea-Phenol-Formaldehyde Condensed Polymer and Ferrous Sulfate Tanning

by

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Abstract

The potential of iron as a tanning agent has been known for a long time, but commercial exploitation has been limited because of concerns over loss of strength and darkening of color with time. To overcome these drawbacks, a combination tannage using ferrous sulfate and phenol-condensed polymers is proposed. Trials indicate that a combination tannage using sulfonated urea-phenol-aldehyde- condensed polymer (Sul.) after ferrous sulfate (Fe(II)) treatment produces favorable results. Shrinkage temperatures of up to 90°C were observed, with tensile strength of 238.3 kg/cm^2, tear strength of 73.3 kg/cm, and elongation at break of 62.1%. The Sul.-Fe(II) tanned leather was lighter in color compared to iron tanned leather, and neither a darkening of color or a reduction in strength upon ageing was observed. The combination tanning system also has demonstrable environmental benefits compared to basic chromium sulfate (BCS)-Fe(II) tanning systems. The Sul.-Fe(II) combined system helps to reduce chemical oxygen demand (COD), and total solids (TS) content. Through experiments it is evident that COD, TS loads are reduced by 37.59% and 36.35%, respectively for Fe(II)-Sul. method compared to Fe(II) method. So Fe(II)-Sul. regime developed not only has advantages in reducing pollution loads but also seems to be techno-economically viable.

Resumen

El poder del hierro como agente curtiente es conocido desde hace mucho tiempo, pero su explotación comercial ha sido limitada debido a la preocupación por la pérdida de resistencia y el oscurecimiento del color con el paso del tiempo. Para superar estos inconvenientes, un curtido combinado con sulfato ferroso y polímeros fenolicos-condensados se propone. Los ensayos indican que un curtido combinado con polímeros sulfonados de condensación de fenol-urea-aldehído (Sul) luego del tratamiento con sulfato ferroso (Fe (II)) produce resultados favorables. Se observó temperatura de contracción hasta 90°C, con resistencia a la tracción de 238.3 kg/cm^2, resistencia a la rotura de 73,3 kg/cm, y alargamiento a la rotura de 62,1%. El cuero curtido con la combinación Sul.-Fe (II) demostró ser color más claro en comparación con el cuero curtido solo al hierro; ni oscurecimiento del color, ni una reducción en la tenacidad con el envejecimiento se han observado. El sistema de combinación de curtido también ha demostrado beneficios ambientales en comparación con los sistemas de curtido del sulfato básico de cromo (SBC)-Fe (II). El sistema combinado de Sul.-Fe (II) ayuda a reducir la demanda química de oxígeno (DQO) y el contenido de sólidos totales (ST). A través de experimentos, es evidente que el DQO y las cargas de ST se reducen en un 37,59% y 36,35%, respectivamente, para la combinación de Fe (II)-Sul comparado con el método de Fe (II) . Por lo tanto el desarrollo de Fe (II)-Sul no sólo tiene ventajas en la reducción de las cargas contaminantes, sino también parece ser tecno-económicamente viable.

Introduction

The leather industry is concerned about environmental toxicology and requirements for the safe disposal of process waste.[1] The tanning process stabilizes hide or skin against wet heat, enzymatic attack and thermo-mechanical stress. These properties can be obtained by treatment with mineral tanning agents including the basic salts of chromium, aluminum, and zirconium as well as organic tanning agents such as vegetable tannins and aldehydes.[2] Although these methods are effective and inexpensive, there are difficulties associated with the toxicity of the reagents and disposal problems associated with process waste,[3] consequentially much research is focused on clean tanning systems. There is considerable interest in using iron as a tanning material because of its low cost and low toxicity. The general application of single iron tannage has been limited because of the associated loss of strength and darkening of the color

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Mention of product trade names in solely to facilitate experimental reproduction by others.

upon ageing.[4,5] This has been attributed to the redox behavior of the metal ion.[6,7] It is proposed that combination of iron with a reducing agent would prevent the oxidation of Fe(II) to Fe(III). Our previous research indicated that some phenol-condensed polymers can manufacture light colored leather and can also have a synergistic effect with Fe(II) which can result in high shrinkage temperatures (Ts). The advantages of prepared phenol-condensed polymers include low toxicity, a low recommended treatment level, no bioaccumulation and a consequent reduced risk to both human health and environment. The influences of different phenol-condensed polymers (Fig. 1) and ferrous sulfate (Fe(II)) combination tannages have been explored.[8] The results indicate that a sulfonated urea-phenol-aldehyde (Sul.)-Fe(II) combination tanning system can produce leathers with 90°C shrinkage temperatures and light coloration.[9]

This paper examines the potential for tanning applications of a Sul.-Fe(II) combination system. The development of a new Sul.-Fe(II) tanning system and its performance under a range of tanning conditions are presented, and the physical chemical characteristics, the effect of ageing and the environmental impact of the tanning system are described.

EXPERIMENTAL

Materials
All chemicals used for the experimental work were commercial grade. The Ferrous sulfate (Fe(II)) was of laboratory grade, and the sulfonated urea-phenol-aldehyde condensed polymer (Sul.) was prepared by the National Engineering Laboratory for Clean Technology Leather Manufacture. All the fat liquors came from the Lianfeng Chemical and Trade Co. Ltd. Pickled goatskins were used for the tanning trials.

Preparation of Sul.
The following is the preparation of Sul.; firstly, 1.0 mol urea, 1.0 mol phenol, 2.8 mol formaldehyde and 12.0 mol distilled water were added to the same flask. After 3 hours at 85°C, 0.5 mol sulfate is added, and the temperature raised 98°C, reaction time is 2 hours. Finally, the product obtained will have a yellow color and a pH of 7.8.

Tanning trials
The pickled goatskins (at pH 2.8) were used for both the control and the experimental garment leather tanning systems. Three pickled skins were cut in half, and one half was used for each trial. The trials used Fe(II)-Sul combination tanning, and chrome (BCS) tanned and iron (Fe(II)) control tanned leathers were obtained using the following procedures.

After the skins were treated, they were piled and allowed to age overnight. Then the shrinkage temperatures of all samples were measured using a standard shrinkage tester.

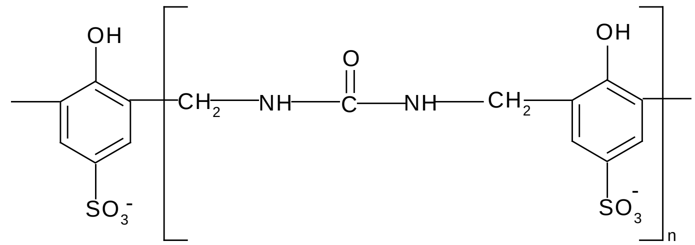

Figure 1. Molecular structure of sul.

Determination of shrinkage temperature
The shrinkage temperature, which is a measurement of hydrothermal stability of leather, was determined using a Theis Shrinkage Meter.[10]

Analysis of strength characteristics
Samples of standard dimensions for various physical tests were obtained according to the IULTCS method.[1] The leather specimens were conditioned at 80±4°C for a period of 48 h. The physical properties such as tensile strength, % elongation at break, and tear strength were then investigated.[12] Each value reported is an average of three experiments with a standard deviation of ± 1. In order to determine the effects of ageing on strength properties of the leather, samples of leather after fatliquoring, produced with all different treatment conditions, were aged for three and six months under the natural light and were then tested for strength according to the IUP method.[13]

Spent tan liquor analysis
The spent tan liquors for both the combination tanning systems and the control experiments were collected and analyzed for Chemical Oxygen Demand (COD) and total solids (TS) by conventional analytical methods.[14,15,16]

RESULTS AND DISCUSSION

Physical Testing Analysis and Hand Evaluation of Leathers
The Ts and physical testing data for samples tanned with Fe(II)-Sul., Fe(II) and BCS are given in Tables 1 and 2. It is clear that 3% FeSO4, 3% Sul and 2% Sodium tartrate results in a Ts of 90°C after fat liquoring and the single FeSO4 tanning system gives a Ts of 88°C after fat liquoring. The two values are close to one another but are significant less than for BCS (115°C). The performance of the samples was assessed by evaluating certain physical properties including strength and organoleptic characteristics. It is evident that Fe(II)-Sul. tanned leathers have higher values for tear strength and % elongation at break than those of Fe(II), BCS regimes. For tensile strength, the value for Fe(II)-Sul. are lower than that of BCS, but it is higher than that of Fe(II).

SUL.-Fe(II) COMBINATION TANNING PROCESS

Tanning			
Pickled liquor	50%		Check pH 2.8~3.0
Sul.	3 %	60 min	
$FeSO_4$(as FeO)	3%	60 min	Check penetration
Sodium tartrate	2%	30 min	
Water	50%	10 min	
Sodium bicarbonate	1.0~2.0%		
Water	15%	(3×10 min) +2 hrs	Check pH
Fat liquoring**			
Water	100%		The fat liquors are emulsified with hot water at 60°C 1:20 dilution*
Lecithin Fatliqouring Agent (QUIMIDERM LC)	3%		
Non-ionic Fatliqouring Agent (QUIMIDERM NP-2)	3%		
Phosphoester Fatliquoring Agent(QUIMIDERM OLN-P)	4%	60 min	
Retanning			
Amino Resin (LANXESS R-83)	3%	30 min	
Melamine Resin (LANXESS GR)	3%	30 min	
Melamine Resin (LANXESS R-12)	3%	30 min	
Fixing			
Formic acid	2%		
Water	20%	(3×10 min) +30 min	
Washing			
Water	200%	10 min	
Drain			Pile over night

*1:10 dilution and given in 3 aliquots at 10 min intervals;
**Generally, the post tanning process for garment leather manufacture is neutralizing the leather to a pH of 5.0-5.2.
The post tanning process was carried out without neutralization because the pH of the Fe(II)-Sul tanned leather was 5.3-5.5.

The measurements taken after ageing are shown in Table 3. All the strength characteristics were better for the Fe(II)-Sul combination tanning when compared to the control Fe(II). The properties of the leather made from Fe(II)-Sul combination tanning were much better than control Fe(II) tanned leather in terms of softness, grain smoothness, feel and color (which was lighter). The tear strength was higher than that of the control BCS tanning. After ageing, it can been seen that there was no significant decrease in physical strength characteristics of the Fe(II)-Sul combination tanned material. It is also clear that after ageing there was significant reduction in strength characteristics for control Fe(II) tanning. Examining the data in Table 3 reveals no significant differences have been found between the characteristics of the Fe(II)-Sul. and BCS tanning systems stored after three and six months. It is well known that Fe(II) salts have a easy tendency to oxidize to Fe(III), which can darken the color of the leather. In our research the yellow brown for Fe(II) tanning system tended to become darker brown after aging, while the yellow kept stable for Fe(II)-Sul. regime.

Spent tan liquor analysis

The spent tan liquor was collected and analyzed for COD and TS by conventional analytical methods (see Table 4). An estimate of the impact of COD and TS on the environment requires the calculation of the emission load. Emission loads were calculated by multiplying COD/TS (mg/L) by volume of composite effluent (L) per ton of raw skins processed. It is evident the COD, TS loads are reduced by 37.59% and 36.35%, respectively for Fe(II)-Sul. method compared to Fe(II) method. Especially the reduction of TS by 19.63% for Fe(II)-Sul. method compared to BCS method is a significant

CONTROL Fe(II) TANNING PROCESS

Tanning			
Pickled liquor	50%		Check pH 2.8–3.0
$FeSO_4$ (as FeO)	6%	60 min	Check penetration
Sodium tartrate	2%	30 min	
water	50%	20 min	
Sodium formate	1%		
Sodium bicarbonate	1%		
water	10%		Check pH 3.8-4.0
Neutralization			
water	100		
Sodium formate	1		
Sodium bicarbonate	1		
Washing			
Water	100		
Fat liquoring			
water	100%		The fat liquors are emulsified with hot water at 60°C 1:20 dilution
Lecithin Fatliqouring Agent (QUIMIDERM LC)	3%		
Non-ionic Fatliqouring Agent (QUIMIDERM NP-2)	3%		
Phosphoester Fatliquoring Agent (QUIMIDERM OLN-P)	4%	60 min	
Retanning			
Amino Resin(LANXESS R-83)	3%	30 min	
Melamine Resin(LANXESS GR)	3%	30 min	
Melamine Resin(LANXESS R-12)	3%	30 min	
Fixing			
Formic acid	2%		
Water	20%	(3×10 min) +30 min	
Washing			
Water	200%	10 min	
Drain			Pile over night

achievement in avoiding pollution. It can be seen from Table 4 that the COD values were higher than that of the control BCS and Fe(II) tanning systems, this was caused by the presence of Sul. However, the TS of the Fe(II)-Sul. tanning system was lower, and within accepted industry standards. The comparative environmental impacts of leather prepared with the different methods revealed that the Fe(II)- Sul. combined tanning system resulted in lower environmental impacts than leather made via the other methods. When Sul. was prepared phenol and formaldehyde were introduced, so the values of phenol and formaldehyde for Fe(II)-Sul. system in the spent tan liquor were determined. The results indicated that phenol and formaldehyde concentrations were quite low, therefore probably not significantly influence the technical and economical value of Fe(II)-Sul.regime.

Techno-economic feasibility

The composite costs for control and experimental leather processing of 1000 kg raw hide are provided in Table 5. The water cost in experimental processes is reduced by about 10%, 25% compared to Fe(II), BCS tanning systems, respectively. And the consumption of sodium bicarbonate by the Fe(II)-Sul is cut 53.33%, 20% compared to control processes, because the process of Fe(II)-Sul tanning does not require a

CONTROL BCS TANNING PROCESS

Tanning			
Pickled liquor	50%		Check pH 2.8~3.0
BCS (basic chrome sulfate as Cr_2O_3)	8%	60 min	Check penetration
Water	50%	10 min	
Sodium formate	1 %		
Sodium bicarbonate	1 %		
Water	10%		
Neutralization			
Water	100		
Sodium formate	1		
Sodium bicarbonate	1		
Washing			
water	100		
Fat liquoring			
water	100%		The fat liquors are emulsified with hot water at 60°C 1:20 dilution
Lecithin Fatliqouring Agent (QUIMIDERM LC)	3%		
Non-ionic Fatliqouring Agent (QUIMIDERM NP-2)	3%		
Phosphoester Fatliquoring Agent (QUIMIDERM OLN-P)	4%	60 min	
Retanning			
Amino Resin (LANXESS R-83)	3%	30 min	
Melamine Resin (LANXESS GR)	3%	30 min	
Melamine Resin (LANXESS R-12)	3%	30 min	
Fixing			
Formic acid	2%		
Water	20%	3×10 min +30 min	
Washing			
Water	200%	10 min	
Drain			Pile over night

neutralization stage which can save sodium bicarbonate, greatly. To allow sufficient penetration, the process time required for Fe(II)-Sul and Fe(II) was longer than for BCS, which used more power. However, this does not affect the economic feasibility of the Fe(II)-Sul, because the other process benefits offset this additional cost. Another advantage of using this system is a discernable reduction in environmental impact, as measured by COD and TS. Overall, there will be a net reduction in the total cost of leather production by Fe(II)-Sul regime.

Any new process must be commercially feasible as well as achieving required quality standards to attract market interest. Products based Fe(II)-Sul combination tanning have being widely used in the tanneries both in the north and south of China, making about 200 kg of products per day. Our novel Fe(II)-Sul tanning regime is being used by Tengyue Ltd. Co. in Hebei, and Ningbo Shunfan Leather Production Company in Zhejiang since February 2005. Production for the two companies amounts to a total of 1,000 sheepskins every day.

CONCLUSIONS

A new Fe(II)-Sul combination tanning system has been studied, and shown to produce leathers with a shrinkage

TABLE I

Ts of different tanning systems

Tanning system	Before fat liquoring Ts/°C	After fat liquoring Ts/°C
Fe(II)-Sul	93±0.5	90±0.5
Fe(II)	90±1.0	88±1.0
BCS	118±0.5	115±1.0

±refers to standard deviation of the measured values.

TABLE II

Evolution of physico-chemical characteristics for leathers after fatliquoring

Tanning system	Tensile strength (kg/cm^2)	Tear strength (kg/cm)	% Elongation at break	Organoleptic properties
Fe(II)-Sul	238.3±	73.3±	62.1±	Yellow, soft body
Fe(II)	218.5±	55.6±	61.3±	Yellow-brown, stiff
BCS	288.7±	63.7±	62.3±	Blue, soft, fine

TABLE III

Physical strength of fatliquored leathers after ageing three and six months

Tanning system	Tensile strength(kg/cm^2)		Tear strength(kg/cm)		% Elongation at break		Organoleptic properties	
	3 months	6 months	3 months	6 months	3 months	6 months	3 months	6 months
Fe(II)-Sul	236.2±3.6	233.7±2.8	70.4±2.8	70.2±2.0	58.3±4.1	58.0±3.1	Yellow, soft body	Yellow, soft body
Fe(II)	206.1±3.5	182.1±3.1	55.7±3.2	49.6±2.3	53.7±2.8	49.8±4.0	Black, stiff	Black, stiff
BCS	287.9±2.5	280.0±2.0	62.2±3.4	62.1±2.7	60.5±2.6	60.1±2.9	Blue, soft, fine	Blue, soft, fine

TABLE IV

Composite liquor analysis for spent liquor

Tanning system	COD (ppm)	TS (ppm)	Phenol (ppm)	Formaldehyde (ppm)	Emission load(kg/ton of raw hide processed)			
					COD (g/L)	TS (g/L)	Phenol (mg/L)	Formaldehyde (mg/L)
Fe(II)-Sul	3213	35,630	10.60	9.41	180.6	56.9	0.99	0.63
Fe(II)	2913	51,231			289.4	89.4		
BCS	2800	47,812			190.3	70.8		

TABLE V

The consumption of different tanning regime (processing capacity: 1000kg of pelts)

Items	Fe(II)-Sul regime	Fe(II)	BCS
Water/L	2000	2200	2500
Sodium bicarbonate/kg	15	23	18
Time/min	400	400	375
Power/(kWh)	120	200	188

temperature of 90°C. The leathers obtained were lighter in color when compared to a control Fe(II) tanning system. After ageing, the leathers tanned with the Fe(II)-Sul combination system did not darken in color and or show reductions in strength. The Fe(II)-Sul combination tanning system also exhibits environmental benefits in terms of reduced TS and COD values when compared to single Fe(II) and BCS tanning systems.

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