A Rationalized Leather Process for Wet-end: Pre-tanning－Integrated Post-tanning System

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Abstract: The conventional leather process is related to huge consumption of water, chemicals and time. To alleviate these problems, a new process for tanning and post-tanning was developed. In this process, bated pelt was directly pre-tanned with a melamine resin. Then, the pre-tanned pelts were split and shaved. As for post-tanning, several operations including, chroming, retanning, dying and fatliquoring were effectively integrated in the same one bath: a moderate quantity of dyes and fatliquors were employed firstly; then a chrome agent was added into the same bath; when the chromium absorbed almost completely, the bath pH was raised and the retanning and filling materials were added; at last, some fatliquors were employed to obtain the high oil content leather. Comprehensive analysis of leather properties, environmental and economic benefits were carried out for the conventional and the experimental process. The results indicate that the functional properties of the experimental leathers had no significant difference to the leathers from conventional process, but there is a considerable reduction in cost of leather production in the modified process. Furthermore, the new process results in remarkable reduction in pollution parameters such as BOD load, COD load, TSS and chroma by 55.04%, 58.04%, 39.42%, and 90%, respectively. Also, the consumptions for water and chemicals were reduced by 42.73% and 40.29%, respectively.
Key words: leather-making; clean technology; tanning; post-tanning; environmental benefits

1 Introduction

Conventional chroming process generally involves in pickling, chroming and basifying, and there are several defects existing in the process[1,2]: ⑴8-10% salt and 1.0-1.2% sulfuric acid were used in pickling, which results in higher contents of chlorides, sulfates and chemical oxygen demand (COD) in the effluent. ⑵The uptake of chromium in conventional chroming is lower (70-80％), a considerable amount of chromium left in the effluent may result in environmental problems[3]. ⑶ A great deal of chrome containing solid wastes such as splittings and shavings are produced, which is certainly difficult to be degraded and harmful on the environment if discharged directly.

Conventional post-tanning process involves in a variety of operations comprising rehydration, rechroming, basification, neutralization, washing, retanning, filling, washing, dying, fatliquoring, fixing and washing. Post-tanning processes hold a pH range of 3.8-6.5. A large amount of water and chemicals are consumed in post-tanning processes. Usually, only about 60-80% chemical is absorbed in the post-tanning. The residual chemicals are drained with wastewater, which cause seriously environmental pollution. According to information available[4], the post-tanning account for about 50％ of COD of tannery effluent. Additionally, the water consumption should not be belittled because of so many washings existing in the conventional process, the post-tanning occupies about 40-45％ water usage in leather manufacture[5].

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The conventional tanning and post-tanning process holds a large amount of water usage because of numerous operations followed with several washings. So, a question is posed: will the water consumption be reduced significantly if several operations are integrated in the same bath? Also, a conventional process subjects the skin to wider pH variations, which results in a net increase in TSS, COD, chlorides and sulfates in the effluent and also impairing the surface properties of the skin matrix[6]. So, another question is: if the variations of pH in the process are limited, will the pollution loads in effluent be lowered, and then will the physical strengths of final leather be improved?

Due to the considerations on the questions mentioned above, recently, the rationalization of tanning and post-tanning processes was studied and a optimized leather process was developed, that is the Pre-tanning－Integrated Post-tanning System(Fig.1). In this work, the entire process has been changed to achieve water and chemicals saving and emission reduction as well as better quality of leather production. Spent liquors from all the unit operation were mixed to analyze for pollutants. Then the accounts of chemicals and water consumption have been carried out for both the conventional and the experimental processes. Also, the physical and chemical characteristics as well as hand and visual evaluation have been carried out for leathers with the both processes. At last, the environmental and economic auditing has also been conducted for the experimental process.

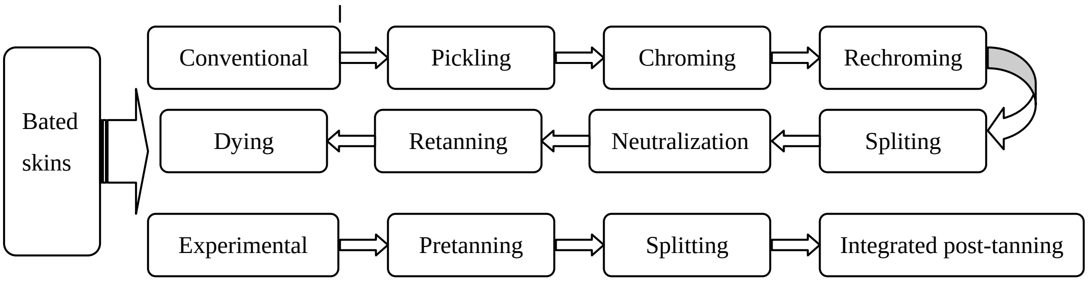

Fig. 1 Flow chart for conventional and experimental processes

2 Experimental

2.1 Materials

Wet salted pigskins were treated from soaking to bating as usual. The bated pelts were cut along the backbone line, left parts for the conventional process, and right parts for the experimental ones.

The pre-tanning agent was a kind of low-polymerized melamine resin (effective constituent is about 40-50%). The chemicals employed in the experiment are of commercial grade, the chemicals used for analytical technique are of reagent grade. Several main chemicals used for control and experimental processes are described as follow: the Basyntan AN (Retanning agent), Relugan GTW (Glutaraldehyde) and Lipoderm A1 (Fatliquor) are provided by BASF Ltd; the fatliquors such as PELASTOL 94S and PROVOL BA are provided by Zschimmer&Schwarz Ltd; the retanning agent ART-1 come from the Chinese Academic of Science (Chengdu); the pickle-less chrome agent C-2000 come from Xinhui Ltd (Guangdong).

2.2 Experimental and Conventional Leather Process

Experimental and conventional processes are provided as Tab.1 and Tab.2 respectively.

As Tab. 1 showing, bated pelts were directly pre-tanned with melamine resin. The bated pelts were of high pH value (6.8-7.0) and most active groups of collage were exposed. Hence, the reactivity of pre-tannage could be fully reflected. Then, the pre-tanned pelts were split and shaved. Since there was no chromium existed in the splittings and shavings, the wastes could be treated and reused more easily.

Furthermore, a moderate quantity of dyes and fatliquors were employed. Negative charge is dominant in the skin because of no chromium in pre-processing, therefore the electronegative dyes and fatliquors may penetrate smoothly into the collage fibers. Also, a pickle-less chrome agent was added into the same bath, neither chromium deposition nor course grain was caused. Meanwhile, the pH value of bath and inner skins was decreased to 3.2-3.6 with the adding of the tanning agent[7], this pH condition helped the syntans, dyestuffs and fatliquors permeated into collage matrix to aggregate and combine additionally. When chromium absorbed almost completely, the bath pH was increased by adding sodium bicarbonate, then the retanning and filling materials were added in the bath. At last, some fatliquors could be employed if high oil content leathers were needed.

Tab. 1 Experimental process (E)

Process	+	%	Chemicals	T(℃)	Time(min)	Remarks
Pre-tanning		100	Water	40		The final pH should be 6.1-6.3
	+	10	Malamine resin		6×60	O/N, run for 0.5 hour
The leathers were piled for 24 h, then split and shaved to a uniform thickness (1.1-1.2mm), and weighted.						
Rehydration		200	Water	25	120	
Integrated		80	Water	25		
Post-tanning	+	1.2	Acid black dye NBK			
	+	1.5	Aluminium chloride	40	40	
	+	2.0	Basyntan AN		30	
	+	2.0	Lipoderm A1		60	
	+	6.0	C-2000		120	
	+	1.0	Relugan GTW		60	
	+	2.0	ART-1		60	
	+	1.5	Sodium bicarbonate		30	pH5.0-5.5
		100	Water			
	+	2.0	Lipoderm A1	58	60	
		3.0	PELASTOL 94S			
		3.0	PROVOL BA			
	+	0.5	Formic acid		20	pH4.0
Washing		200	Water	25	10	

2.3 Appearance and Hand Evaluation of Leathers

Crust leathers from the conventional as well as the experimental process were assessed for softness, fullness, grain smoothness, surface color and general appearance by hand and visual examination.

2.4 Physical Testing of Leathers

Samples for various physical tests from the experimental and the conventional crust leathers were obtained as IUP method[8]. Physical properties such as tensile strength, tear strength, grain crack strength and rubbing fastness were examined as the standard procedure[9].

2.5 Chromium and Oil Content and Shrinkage Temperature of Crust Leathers

Samples from the experimental and control leathers were split into three average layers, respectively. The chromium content of each layer was estimated as potassium chlorate standard procedure[9], and the oil content as methylene dichloride extraction standard procedure[9]. Samples were initially analyzed for moisture content[10] and the final results were expressed on dry weight basis of leather. The shrinkage temperature of the leather was measured using the Hg Shrinkage Temperature Tester. The uniformity of chromium and oil distribution in the leathers was calculated as following formula:

$$\text{Uniformity}(\%)=\frac{2\times Cr_2O_3 \text{ in Middle layer}}{Cr_2O_3 \text{ in Grain layer} + Cr_2O_3 \text{ in Flesh layer}}\times 100\%$$

Tab. 2 Conventional process (C) for control

Process	+	%	Chemicals	T(℃)	Time(min)	Remarks
Pickling		100	Water	22		pH 2.5-3.0.
	+	8.0	Sodium chloride		5	O/N, run for 0.5 hour
	+	0.5	Formic acid		20	
	+	1.2	Sulphuric acid		120	
Chrome tanning		50	Water	38	2×60	50% pickling bath was drained.
	+	0.5	Cationic oil		20	
	+	8.0	Basic chromium sulphate			
		1.0	Sodium acetate		120	
Basification		1.2	Sodium bicarbonate			pH3.8-4.0
The leathers were piled for 24 h, then split and shaved to a uniform thickness (1.1-1.2mm), and weighted.						
Rehydration	+	200	Water	25	120	
Rechroming		150	Water	38		
	+	3.0	Basic chromium sulphate		120	
	+	3.0	Relugan GTW		60	
Washing			Water		5	Twice
Neutralization		150	Water	34		
	+	1.0	Ammonium bicarbonate		60	
		1.0	Sodium acetate			
	+	3.0	ART-1		60	
		3.0	Basyntan AN			pH5.5-5.8
Dyeing and Fatliquoring		200	Water	55		
	+	3.0	Acid black dye NBK		60	
	+	4.0	Lipoderm A1		60	
		3.0	PELLASTOL 94S			
		4.0	PROVOL BA			
Fixing		0.5	Formic acid	25	20	pH4.0
Washing		200	Water	25	10	

2.6 Analysis of Chromium in Spent Liquor

Chromium liquor collected from the conventional tanning was analyzed for chromium content as the H_2O_2 standard procedure[11]. The liquor was pre-treated by 1mol/L NaOH and 3% H_2O_2 to decrease the influence of the residual dyestuff and retanning agent, then, analyzed as the H_2O_2 standard procedure [12].

2.7 Analysis of Composite Waste Liquors

Composite liquors from the conventional and experimental processes were collected from all unit processes except from soaking to bating. The pollution indicators such as COD, BOD, TSS and Chroma were examined after 15 hours as the standard procedure [11]. From this, COD load and BOD load were calculated, the calculation formula is provided as follow:

$$\text{Pollution load (mg/kg raw skins)} = \frac{\text{Test value (mg/L)} \times \text{Volume of effluent (L)}}{\text{Weight of raw skins(kg)}}$$

3 Results and discussion

3.1 The pH Variations

The pH behavior of unit process in the experimental and the conventional leather production is presented in Fig.2. It is evident that the experimental process possess a narrow pH range and small variation frequency of pH compared to the conventional process, this is due to the presence of several acid-basification reaction in the traditional processing[6]. By contrast, the new process holds a narrow pH variation between two successive processing which may be helpful for the properties of final leathers.

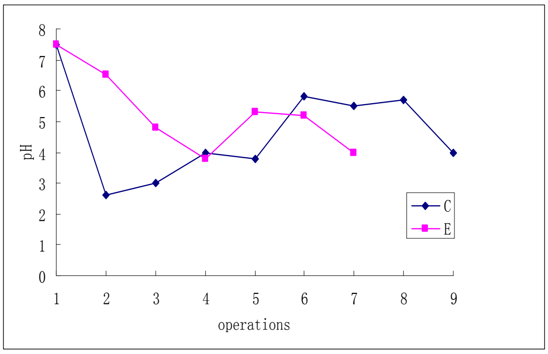

Fig. 2 The pH variations of unit operations in the conventional[c] and the experimental process[e]

c: 1 Bating, 2 Pickling, 3 Chroming, 4 Basification, 5 Rechroming, 6 Neutralization, 7 Dying, 8 Fatliquoring, 9 Fixing; e: 1 Bating, 2 Pretanning, 3 Dying(Fixing), 4 Chroming, 5 Neutralization, 6 Fatliquoring, 7 Acidification.

3.2 Physical Characteristics and Hand Evaluation

Tab. 3 Several properties of crust leathers from the two processes

Process	Ts(℃)		Changes of Thickness (%)		Changes of Area (%)
	Pretanned skin	Crust leather	Belly	Back and Butt	
C	-	114.3	17.63	17.04	-6.75
E	87.5	107.5	42.26	26.34	-9.01

The Ts of pre-tanned pelts are increased evidently in the new process and meets the requirements of the hydrothermal stability for splitting (Tab.3). In addition, the thicknesses of experimental sample are increased much more than the controls, especially in the belly area, this is helpful for the evenness of leathers and the area of splits.

The average ratings of visual and hand performance for the leathers were evaluated by three experienced tanners (Fig.3). The experimental leathers exhibit better fullness compared to the contrasts due to the better filling of the melamine resin. Others properties such as softness, grain smoothness, and surface color are comparable with that of the conventional process, or even better. The general appearance of the experimental leathers was similar to the control.

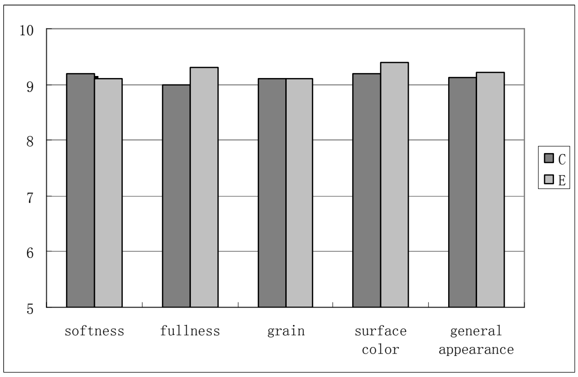

Fig. 3 Properties of the leathers

Tab.4 shows the strength properties of the leathers, such as tensile, tear and grain crack strength. It can be seen that the experimental leathers possessed varying degrees improvement in tensile, tear and grain crack strength by 4.89%, 19.07% and 39.39%, respectively. The reason may be that pickling was avoided in the modified chroming and the collagen was not damaged by salts and strong acids, so little collagen was hydrolyzed in the experimental process compared to the control.

Tab. 4 Physical strength data of conventional and experimental leathers

Sample	Tear strength (N/mm^2)		Tensile strength (N/mm^2)		Elongation at break（10N）%		Rubbing fastness		Grain crack strength (kgF/cm^2)
	Parallel	Vertical	Parallel	Vertical	Parallel	Vertical	Dry	Wet	
C	68.61	55.32	28.16	18.09	64.35	82.34	4.5	4.5	29.40
E	74.28	55.72	28.43	26.63	70.16	75.34	4.5	4	40.98

3.3 Chemical Characteristics

Tab.5 shows the uptake of chromium was improved remarkably in the experimental compared to the control. The chrome complex bound not only with collagen, but also with the melamine resin that had been linked to collagen through one end, which caused many cross-links between chromium and collagen. The shrinkage temperature of the leathers from the modified process was higher than 100℃, which meets the requirements for shoe upper. This indicates that 6% chrome agent offer is sufficient for leather in the new process.

Tab. 5 Comparison of leathers from the conventional and the experimental process

Sample	Chromium usage（%）	Ts(℃)	Uptake of chromium (%)	Chromium content of effluent (g/L)	Moisture content (%)
C	11	114.0	82.48	1.54	18.38
E	6	107.5	96.21	0.15	18.59

Tab. 6 Distribution of chromium and oil content in leathers

Sample		Grain	Middle	Flesh	Average	Uniformity(%)
Oil(%)	C	7.21	5.90	7.11	6.74	58.35
	E	8.20	6.04	7.01	7.08	56.84
Cr_2O_3(%)	C	3.99	3.27	4.37	3.88	78.23
	E	3.74	3.52	4.12	3.79	89.57

Tab.6 shows that the leather with the new process exhibits a uniform chromium distribution along the entire cross section. The reason may be that pelts were previously treated by melamine resin, which increased the porosity of skin matrix, and promoted the permeation of chromium. Also, the leather from modified process enjoyed higher amount of oil compared to the conventional leather in the middle layer as well as average level.

3.4 Environmental Benefits

Tab. 7 Analysis of composite effluents

Process	COD		BOD		TSS(mg/L)	Chroma	Volume of effluent(L)
	Value(mg/L)	Load	Value(mg/L)	Load			
C	5643.75	51.21	285	2.58	312	200	33.8
E	5132.05	21.49	278	1.16	189	20	15.6

The composite effluents were collected from all the unit process after bating. The impact of the composite liquors on environment are evaluated by four pollution parameters such as BOD, COD, TSS and Chroma, a direct comparison of the observed BOD and COD values may not give proper results. Hence, theses values have been converted into emission loads, see Tab.7. It can be seen that the modified process possess an evident reduction in BOD load, COD load, TSS and chroma by 55.40%, 58.04%, 39.42%, and 90%, respectively. Also, the amount of composite liquor is decreased by 53.84%. So the potential of the new process for reducing water consumption is remarkable, which is important to the developing of leather industry.

3.5 Economic Benefits

The technical feasibility as well as cost effectiveness is generally required on commercialization of any newly developed process in the industry. So, the input of the chemicals has been monitored for the conventional and the experimental process. The observed values have been calculated for processing 1 metric ton of pigskins. The total amount of chemicals consumed in the conventional and the experimental processes is 489 and 292 kg, respectively. That is to say, the new process possesses a reduction in total chemical consumption by 41% compared to the control.

For the time-consuming, the new process is 27.6 hours, which is 14.9 hours less than the conventional process. So, the process is able to improve the production efficiency and lower the energy consumption in leather manufacture.

4 Conclusions

In this work, a modified process has been developed for clean leather manufacture. The leathers obtained with the experimental process hold comparable or superior functional properties than that of leathers from the conventional process. Also, there is a considerable reduction in the cost of leather production in the modified process. Most importantly, the new process results in remarkable reduction in pollution parameters such as BOD load, COD load, TSS and Chroma by 55.04%, 58.04%, 39.42%, and 90%, respectively. Also, the consumptions for water and chemicals were reduced by 42.73% and 40.29%, respectively. This is a significance achievement on current circumstance.

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