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REDUCTION OF WASTE CHROME LEVELS IN TANNERY WASTEWATER: OPTIMIZED DIRECT RECYCLING

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Summary

The chrome tanning process is the most popular tanning method but it results a considerable discharge of chromium to the wastewater. Various processes have been developed to increase the up-take of chromium by the hide with success, but there remains a major chromium discharge to the wastewater.

The wastewater from the tanning process can be reused directly or indirectly but these recycling processes can present problems related to the accumulation of undesirable substances (salts, fat, protein, etc.) and irregularities from batch to batch. The present work is devoted to the development of a direct recycling process that associates a high chromium up-take process with recycling to the pickling bath and then disposal of this bath after pickling. A reduction of the chromium offer to between 4.5% and 5.5% is achieved, against typical values of between 7% and 8%. Good results are obtained for chromium discharge to the wastewater especially when the splitting is done in the lime state where values of chromium about 50 mg/L are obtained.

Introduction

The essential and long established[1] step in leather manufacturing is the tanning process. Tanning with chromium is a process used since the end of the XIX century.[2] In chrome tannage, the cleaned hide material, practically pure collagen, is brought into an acid medium by pickling and then stabilised with complex basic sulphates of trivalent chromium that form crosslinks connecting the carboxyl groups of the collagen polypeptide chains.

In the classical chrome tanning processes the efficiency of chromium utilisation is between 60 and 80%. The process is done in a water medium and is explained in detail by many authors.[2,3,4,5,6,7,8] The process results in a considerable discharge of chromium to the wastewater.

The wastewater from the tanning process can be re-used directly or indirectly. Much work has been done in this area. The direct reuse of the chrome tanning bath is done normally after grading, screening and chemical adjustment; the problem of this recycling process is the accumulation of undesirable substances (salts, fat, protein, etc.) in each cycle, contributing to possible damage to leather quality.[9,10] Indirect reuse of the tanning bath consists basically of three steps: chromium precipitation by alkalis eg. sodium hydroxide, calcium hydroxide, sodium carbonate or magnesium oxide; separation of the chromium hydroxide by sedimentation, filtration or centrifugation; dissolution of the chromium hydroxide and basicity adjustment with sulphuric acid for re-use. The problem of this process is that the chromium liquor quality can change with each batch.[11] Other recycling methods have been developed, namely by ion exchange[9,12] but these methods need development and are expensive when comparing them with the two classical direct and indirect methods.

In this work we suggest a new direct recycling system, which is easy to practice, especially when the splitting is done in the lime state. The system consists of the grading and screening of the tanning bath from the last batch for re-use in the pickling of a new batch. This bath is then drained as wastewater; the tanning of this new batch is done in a new bath by a carefully controlled process with a good chromium up-take.

Materials and Methods

The implementation of this new direct chromium bath recycling idea needs, as a first step, to assure the results of a high chromium up-take tanning process[13] developed previously. A factorial experiment was used to determine the pH, chromium offer, temperature and level of chromium complexing agent.

The hides used were from a lot of Spanish salted hides of 20-25kg from Monteiro Ribas Indústrias (a Portuguese leather company in Porto), we used a pilot drum with capacity for two sides and with speed and temperature control.

Initial high exhaustion tannage

Four trials were done: two with hides split at 4.5mm (*trials A and B*) and two with unsplit hides (*trials F and G*). In each trial, one side was weighed, put in the pilot drum, delimed and bated in the classical way. In the procedure used, the drum was run for 15min with 30% (w/w) water, 6% sodium chloride at 25°C. The specific gravity of the brine was was measured (°Bé); 0.6% (w/w) of formic acid was added with a running time of 15min at 25°C followed by two additions of 0.5% (w/w) of sulphuric acid with a running time of 15min at 25°C for the first addition and 3 or 5hrs (for the split and unsplit hides respectively) running at 25°C for the second addition. The pH was measured and acid penetration controlled with bromocresol green before draining the pickle bath. Under no float conditions we added x% (w/w) of chromium salt and y% (w/w) of sodium acetate with a running time of 1 hour at 30°C. At the basification stage 50% of water was added at 30°C with a

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running time of 30min; addition of z% (w/w) of Plenatol HBE (basifying) with running time of 2 hours at 30°C, 2 hours at 35°C, 2 hours at 40°C, 1 hour at 45°C and 1 hour at 50°C. A blank trial (control) was done following the same procedure, but with chromium, complexant and basifying quantities adjusted to those for an optimised classical process. The liquor pH was measured; the bath was saved for recycling and its chromium content was evaluated. Table I shows the chromium salt, complexant and basifying agent quantities.

TABLE I
Quantities used for the first phase of trials

	Lime split (trials A and B)	Unsplit (trials F and G)	Control
Chromium salt x%	4.7	6	7
Complexant y%	0.5	0.6	0
Basifying agent z%	0.5	0.7	0.8

Next day, the tanned hides were sammed and their chromium contents and pHs were evaluated as per IUC8 and IUC11 norms; the shrinkage temperature and the shrinkage contraction was evaluated according to the SATRA TM17 norm for each trial. The tanned hide pieces were then shaved, dyed, dried and staked, and their roundness and tightness were evaluated at the crust state.

First re-use of waste liquor as pickle

In a second phase of the trials, the tanning bath resulting from the trial B was used for the recycling procedure with split hides at 4.5mm, in the trial C. One side was weighed, put in the pilot drum, delimed and bated as the classical way. Then, the drum run 15min at 25°C with 15% (w/w) of water and 6% of sodium chloride; °Bé was measured; 0,6% (w/w) of formic acid, diluted in 15% (w/w) of the tanning bath from the trial B was added with a running time of 15min at 25°C; one addition of 0.5% (w/w) of sulphuric acid, diluted in 15% (w/w) of the tanning bath from the trial B, with a running time of 15min at 25°C; another addition of 0.5% (w/w) of sulphuric acid, diluted in the rest of the tanning bath from the trial B, with a running time of 3 hours at 25°C; pH was measured, the acid penetration was controlled with bromocresol green and the chromium content of the bath was evaluated; the pickled bath was drained; without bath, addition of x% (w/w) of chromium salt and y% (w/w) of sodium acetate with a running time of 1 hour at 30°C; 50% of water was added at 30°C with a running time of 30min; addition of z% (w/w) of Plenatol HBE (basifying) with running time of 2 hours at 30°C, 2 hours at 35°C, 2 hours at 40°C, 1 hour at 45°C and 1 hour at 50°C; pH was measured; the tanning bath was saved for recycling and its chromium content was evaluated. This procedure was repeated two more times (trials D and E) and is illustrated in Figure 1.

Next day, the tanned hides were sammed and its chromium content and pH was evaluated as the IUC8 and IUC11 norms; the shrinkage temperature and the percent of contraction was evaluated as the SATRA TM17 norm for each trial. Then, the tanned hide pieces were shaved, dyed, dried and staked, and its roundness and tightness were evaluated at the crust state.

In a third phase of the trials, the tanning bath resulting from the trial G was used for the recycling procedure with unsplit hides at 4.5mm, in the trial H. One side was

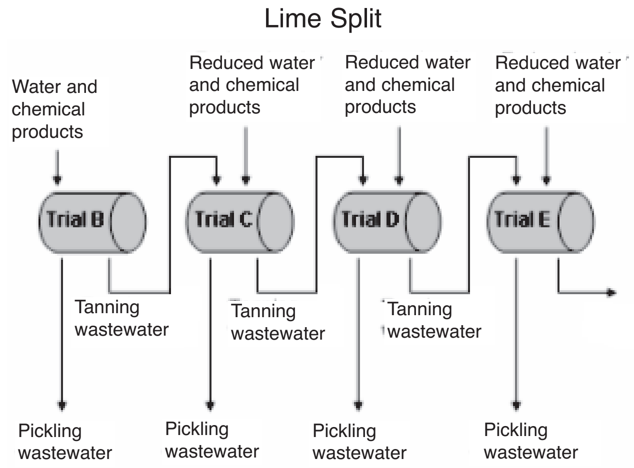

Figure 1. Trial scheme for recycling the tanning bath in the split hide process

weighed, put in the pilot drum, delimed and bated as per the classical way. Then, the drum run 15 min with 15% (w/w) of water, 6% of sodium chloride at 25°C; °Bé was measured; 0,6% (w/w) of formic acid, diluted in 15% (w/w) of the tanning bath from the trial G was added with a running time of 15min at 25°C; one addition of 0.5% (w/w) of sulphuric acid, diluted in 15% (w/w) of the tanning bath from the trial G, with a running time of 15min at 25°C; another addition of 0.5% (w/w) of sulphuric acid, diluted in the rest of the tanning bath from the trial G, with a running time of 5 hours at 25°C; pH was measured, the acid penetration was controlled with bromocresol green and the chromium content of the bath was evaluated; the pickled bath was drained; without bath, addition of x% (w/w) of chromium salt and y% (w/w) of sodium acetate with a running time of 1 hour at 30°C; 50% of water was added at 30°C with a running time of 30min; addition of z% (w/w) of Plenatol HBE (basifying) with running time of 2 hours at 30°C, 2 hours at 35°C, 2 hours at 40°C, 1 hour at 45°C and 1 hour at 50°C; pH was measured; the tanning bath was saved for recycling and its chromium content was evaluated. This procedure was repeated more two times (trials I and J) and is illustrated in Figure 2.

Next day, the tanned hides were sammed and its chromium content and pH was evaluated as the IUC8 and IUC11 norms; the shrinkage temperature and the percent of contraction was evaluated as the Satra TM17 norm for each trial. Then, the tanned hide pieces were shaved, dyed, dried and staked, and its roundness and tightness were evaluated at the crust state.

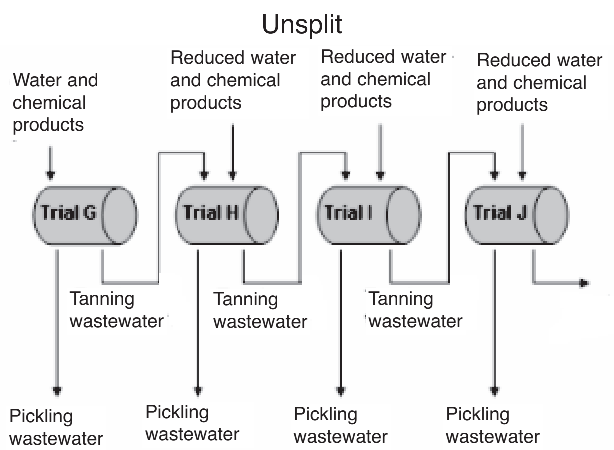

Figure 2. Trial scheme for recycling the tanning bath in the unsplit hide process

TABLE II
Quantities used for the recycling phase of trials

	Lime split (trials C, D, E)	Unsplit (trials H, I, J)
Chromium salt x%	4.5	5.5
Complexant y%	0.5	0.6
Basifying agent z%	0.5	0.7

Results and Discussion

Table III shows the control of the procedure in the first phase of this work with °Bé gravity, pH and chromium content of the respective baths.

TABLE III
Bath control results from the first phase of trials (initial tannages)

	Lime split			Unsplit		
Trial	Control	A	B	Control	F	G
Pickle liquor °Bé	7.5	7.2	7.0	7.0	6.8	7.0
pH (pickling bath)	2.8	2.8	2.9	2.9	2.6	2.9
pH (tanning bath)	3.8	4.1	4.0	3.7	3.8	3.7
Chromium content (mg/l in tanning bath)	1452	632	532	1634	759	850

TABLE IV
Wet-blue tests from the first phase of trials

	Lime split			Unsplit		
Trial	Control	A	B	Control	F	G
pH	3.68	3.80	3.76	3.52	3.61	3.76
Shrinkage temp. (°C)	103	102	101	102	101	101
Contraction (%)	3.5	3.5	4.0	3.0	4.0	3.5
Cr_2O_3 (dry basis %)	4.1	3.4	3.5	3.9	3.5	3.3

The results presented in Table III allow us to prepare a simple material balance which shows that the chromium up-take efficiency for this process is good, between 95% and 97%. Table IV presents the results from the wet-blue tests showing a good performance, although the chromium content is higher for the control trials. At the crust state, the roundness and tightness were very similar for all the trials.

The low chromium concentrations of the waste tanning baths resulting from this process supports the of recycling the waste tan liquor as the pickling bath.

Thus, the proposed process is:

- The tanning bath from the high chromium up-take process is recycled to the pickling of the next batch, after screening.
- At the end of pickling, the used pickle bath is drained to waste with an insignificant chromium content.
- The tanning of the pickled batch then follows in a new bath using the high chromium up-take process. The process is depicted in Figure 3.

This process was used in the second and third phase of trials, as described in Materials and Methods.

The results obtained in this phase of the work for the bath control and for the wet-blue tests are presented in Tables V and VI.

The results shown in the previous tables confirm the validity of the idea to use pickling to promote the chromium sorption process in a hide that, because of its pH, can not yet fix the chromium. The results are very good for the lime split which is easier for the chromium to penetrate. In the crust state, the roundness and tightness were very similar for all the trials in the second and third phase.

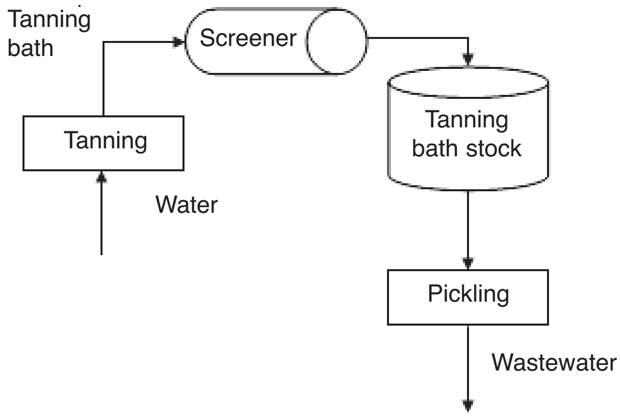

Figure 3. Schematic of the proposed recycling process

TABLE V
Bath control results from the second phase of trials

	Lime split			Unsplit		
Trial	C	D	E	H	I	J
Pickle liquor °Bé	8.2	8.6	8.4	8.5	8.6	8.3
pH (pickling bath)	2.8	2.6	2.9	3.2	2.9	3.2
pH (tanning bath)	3.9	4.0	4.1	3.9	3.9	4.0
Chromium content (mg/l in tanning bath)	55	28	78	304	253	289

TABLE VI
Wet-blue tests from the second phase of trials

	Lime split			Unsplit		
Trial	C	D	E	H	I	J
pH	3.74	3.85	3.72	3.68	3.71	3.73
Shrinkage temp. (°C)	101	102	101	102	101	101
Contraction (%)	3.5	3.0	3.5	4.0	4.5	3.5
Cr_2O_3 (dry basis %)	3.6	3.4	3.4	3.3	3.4	3.3

Conclusions

As was expected, the idea of associating a process of high chromium up-take with direct recycling to the pickling bath - with disposal of the bath after the pickle phase - leads to a great reduction of the chromium lost with the wastewater. The reduction in chromium offer and the impact on the wastewater are represented in Figure 4.

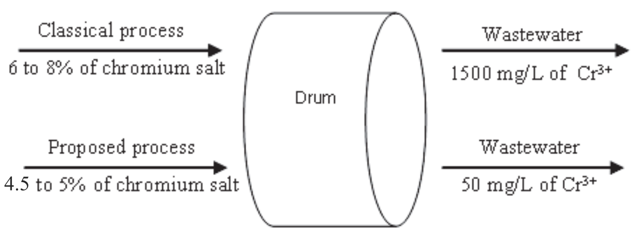

Figure 4. proposed process compared to the classical process

This process is very advantageous when the splitting is done in the lime state. The new procedure is not affected by the drawbacks of other recycling processes because there is no accumulation of salts, fat or protein residues from batch to batch. It will be important to continue the studies in order to improve the chromium up-take in the pickling phase.

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